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General, Physical, and Inorganic Chemistry.

General features of disruptive discharge for obtaining instantaneous spectrograms. H. Nagaoka, D. Nukiyama, and T. Futagami (Proc. Imp. Acad. Tokyo, 1927, 3, 499—502; cf. A., 1927, 1117).—Photographs of the disruptive discharge between metallic electrodes placed in contact show clouds of vapour round the electrodes. The tracks of luminous particles radiate outwards and terminate in dots, the loss in continuity being due to oxidation. Forking is often observed in the tracks, indicating that the particles break up into smaller units. Instantaneous spectrograms show that most lines appear at the first moment as emission, reversal increasing later on, since the vaporisation process is not completed at once. Photographs and spectrograms have been obtained which yield information as to the state of the vapour. Emission depends to some extent on the phase of the electric oscillations; most lines, however, appear at the maximum of the field. Multiple emission of some lines occurs during a half oscillation. R. A. Morton.

Light excitation [of metallic spectra] by means of the metastable state in atoms of noble gases. F. Paschen (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1927, 207—213).—Under certain conditions in a discharge tube, atoms of the rare gases exist in a metastable condition for a relatively long period (10^{-2} sec.). By means of collisions, they can give up energy corresponding with the following voltages: helium $19{\cdot}72_7$, neon 16·6, argon 11·5. When the discharge tube contains a small proportion of foreign atoms, liberated by heat or electrical sputtering from aluminium, magnesium, zinc, or cadmium, the spectra of these metals are excited by collisions between atoms of metal and metastable rare gas atoms. In the negative glow, neutral atoms are excited, and a considerable number of simple, positively-charged ions of the metallic foreign substance also make their appearance spectroscopically manifest; thus, in addition to arc lines, all the terms of the first spark spectrum are excited provided that they exceed T, where $T=T_0^+-E$, T_0^+ being the deepest term of the first spark spectrum of the metal and E the excitation voltage of the rare gas. In the positive glow, more neutral atoms are excited than in the negative glow. In a side tube, branching from near the positive column, it was possible to detect metastable neon atoms (by absorption of the 6402 Å. neon line) at a distance of 2 cm. from the positive light. In this region of the tube, neutral atoms of metal vapour alone undergo excitation. Only such terms in the first spark spectrum as are greater than T' make their appearance, T' being defined by $T'=T_0+T_0^+-E$, T_0 being the fundamental term of the arc spectrum. Excitation therefore seems to be due to collisions, and the emission is much more intense than in experiments using electronic impacts. The interpretation is fully substantiated by the experimental data.

R. A. Morton.

Electrodeless ring discharge in hydrogen. G. Herzberg (Ann. Physik, 1927, [iv], 84, 553—564).—The discharge produced by placing a bulb containing hydrogen inside a solenoid carrying damped wave-trains of unspecified voltage and frequency has been examined spectroscopically. In the pressure range 0·05—26 mm., three types of bright luminous rings are observed. When the containing bulb is of quartz, a persistent fluorescence is induced in the walls of the bulb by the discharge, which is found to emit, in addition to the hydrogen spectrum, the silicon lines 4131/28 and 3906 Å. R. W. Lunt.

Spectrum of electrodeless ring discharge in hydrogen. G. Herzberg (Ann. Physik, 1927, [iv], 84, 565—604; cf. preceding abstract).—The spectroscopic data obtained are reviewed at great length. The inner blue ring emits 23 terms of a very pure Balmer series; by reducing the catalytic effect of the walls of the containing vessel the first 18 terms can be obtained without a trace of fine structure. The purity of the Balmer series so obtained has enabled a direct determination to be made of the series limit. The relative intensities of the lines H_α, H_β, H_γ, H_δ, H_ϵ have been found to be 1·00, 0·95, 0·40, 0·14, and 0·15 respectively. R. W. Lunt.

Fine structure of Balmer lines. G. Hansen (Ann. Physik, 1927, [iv], 84, 688).—Statements criticising Hilger's Lummer–Gehrcke plates appearing in a communication of the author (*ibid.*, 1925, 78, 558) are withdrawn. R. W. Lunt.

Spectrum of carbon arcs in air at high current densities. J. W. Ryde (Proc. Roy. Soc., 1927, A, 117, 164—182).—The degree of excitation provided by carbon arcs cored with metallic salts at high current densities is found to be intermediate between the ordinary arc, in which only the C I line 2478 Å. appears with any intensity, and Merton and Johnson's discharge tubes (cf. A., 1925, ii, 723), in which the two C II doublets at about 3920 and 2837 Å. appear strongly. If the current through such a cored carbon arc is increased, a bright central core develops in the arc stream soon after the limiting current density for ordinary arcs is exceeded. In this core are developed

the spectra of C I, N I, O I, together with the Balmer series and the strongest lines of the red spectrum of argon. Several marked differences in the relative intensities of the C I and N I lines are found compared with those obtained by the discharge tube methods. In addition to the N I line spectrum, the first negative nitrogen bands also appear in the arc stream. Fifty-three new lines have been found, and are attributed to C I, N I, and O I. Five of these complete the N I quadruplet system multiplet $4P-P'$, and two others belong to the $5^4P-P'$ multiplet. Many of the N I and O I lines show considerable broadening and large displacements to the red, amounting in some cases to more than 2 Å. These effects are correlated with the series classifications. The Swan bands are strongly excited close to and inside the positive carbon, but do not appear at all in the arc stream under normal conditions. They show up faintly when a jet of hydrogen is directed on the arc, and very brilliantly when the hydrogen is replaced by coal gas. No lines were observed which could be attributed to helium, even when the arc was run at 250 amp., contrary to the report by Bell and Bassett (Science, 1922, 56, 512). The seven lines they attributed to helium are really some of the stronger C I, N I, and O I lines, together with the unidentified pair at 4392 and 4385 Å.
L. L. Bircumshaw.

Infra-red radiation of nitrogen. A. H. Poetker (Physical Rev., 1927, [ii], 30, 812—824).—The first positive group of nitrogen bands has been extended to the region of 1·5 μ. The broad radiation maxima corresponding with the 0, +1, and +2 sequences have been analysed into individual bands. The wave-lengths, wave-numbers, and intensities of the principal infra-red lines of the nitrogen spectrum in the ranges 8936·60—7531·06 and 10498·4—8941·7 Å. are tabulated. Birge's assignment of vibration quantum numbers is modified. The oxygen triplet at 9265 Å. has been resolved, the wave-lengths being 9265·67, 9262·61, 9260·31 Å.
A. A. Eldridge.

Density necessary to produce the nebulium spectrum. C. T. Elvey (Nature, 1928, **121**, 12).—It is not known whether a nebular spectrum can be produced when the density of a mixture of oxygen and nitrogen becomes sufficiently low; from astrophysical observations, however, and certain assumptions, it is computed that the mean density at which the nebular spectrum appears is $1{\cdot}8\times10^{-17}$ g./c.c.
A. A. Eldridge.

Spectrum of doubly-ionised oxygen (O III). A. Fowler (Proc. Roy. Soc., 1928, **A**, **117**, 317—330).—The spectrum of doubly-ionised oxygen, obtained by using suitably strong discharges in vacuum tubes, has been examined in the region extending from the red to 2228 Å. in the ultra-violet. The lines were distinguished from those of O II by the method of comparing the intensities of the lines under the action of different discharges. More than 300 lines are catalogued, of which about one half have been classified by the author and others. The assigned term values are based on a sequence of three singlet D terms, the deepest term being of the type $^3P_0$. By adopting Bowen's suggestion that the two well-known green lines in the spectra of gaseous nebulæ may represent the irregular combinations $2p^3P_2-2p^1D_2$, $2p^3P_1-2p^1D_2$ of O III (A., 1927, 997), the value 444,661 is obtained for the deepest term $2p^3P_0$. The corresponding ionisation potential of O III is 54·88 volts. The spectrum, as was to be expected, is in general similar to that of N II, and the terms so far determined are in full accordance with Hund's theory. A modified, and more generally applicable, system of notation is suggested. L. L. Bircumshaw.

Spectrum of fluorine (F I). II. H. Dingle (Proc. Roy. Soc., 1928, **A**, **117**, 407—416; cf. A., 1927, 1).—The previous observations have now been extended farther into the infra-red, and a number of new lines observed. The wave-lengths of 16 lines in the region 7600—8400 Å. have been measured. The additional data have enabled the spectrum to be analysed more thoroughly than was previously possible, and a more complete correlation has been established with the terms to be expected on the Heisenberg–Hund theory. It is shown that de Bruin's scheme (A., 1927, 490) cannot be accepted. The observations of Bowen in the extreme ultra-violet (A., 1927, 285) have led to a slight modification of the analysis previously proposed, the interval 250, proposed by de Bruin for a ^2P term, being adopted as a ^2D interval, and the ^2P term with a separation of 533 being rejected. An ionisation potential of approximately 18·6 volts is indicated. Relative term-values of F I, based on the two metastable states of the core, have been deduced. L. L. Bircumshaw.

Reversal of neon lines excited at radio-frequency. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1927, **3**, 496—498).—The reversal of neon lines has already been studied for light excited at 50 cycles (A., 1927, 705), and experiments have now been carried out at 10^6 cycles. The length of the luminous column in the capillary tube was capable of ready adjustment, and it was found that the reversal varied in different parts of the tube. In one position the amount of reversal was the same at 50 cycles as at 10^6 cycles, whilst in another position the amount was much smaller at high cycles. The results may depend on the occurrence of metastable neon. R. A. Morton.

Spectra of phosphorus for different degrees of ionisation. G. Déjardin (Compt. rend., 1927, **185**, 1453—1454).—The variations observed with an electrodeless discharge have enabled the spectra characteristic of different degrees of ionisation of the phosphorus atom to be separated (cf. Millikan and Bowen, A., 1925, ii, 610; Saltmarsh, *ibid.*, 724). The presence of new rays in the ultra-violet region below 2700 Å. is recorded. J. Grant.

Spark spectra of chlorine. L. Bloch and E. Bloch (Ann. Physique, 1927, [x], **8**, 397—423).—Using an electrodeless discharge tube containing sodium chloride, a large number of chlorine lines have been photographed and classified in accordance with methods already applied to the arc and spark spectra of bromine (A., 1927, 802). The oscillatory discharge allows the lines to be classified as belonging to Cl II and Cl III. Arc lines Cl I corresponding with the spectrum of the neutral atom are observed only very feebly, if at all, in the condensed discharge. No spark spectra of orders higher than the second (Cl III) are recorded in the photographs. A table is given summarising the present position with regard to the spectrum of chlorine. R. A. MORTON.

Spark spectra of chlorine and of bromine in the Schumann region. G. VAUDET (Compt. rend., 1927, **185**, 1270—1272).—The method of Bloch (A., 1926, 329) has been used to determine the spark spectra of chlorine and of bromine between 2250 and 1300 Å. Lists of rays and their intensities are given, rays common to both elements being due to impurities (cf. Turner, A., 1926, 1071). J. GRANT.

Shifts and reversals in fuse-spectra. A. C. MENZIES (Proc. Roy. Soc., 1927, **A**, **117**, 88—100).—An account is given of the spectra obtained when wires are suddenly short-circuited so as to carry currents of upwards of 100 amp. The material of the wire is thus vaporised, and the light from the momentary arc is photographed by the spectrograph through the metallic vapour. The method is simple and convenient. For copper, five, possibly six, new terms have been deduced, leading to the allocation of 32 new lines. All those lines which are reversed have final orbits 1^2S_1, $^2D_2$, or $^2D_3$. Lines have a tendency to shift as the current increases, and it is found that the shifted lines having high-level initial terms which are moved to the red come from initial states belonging to (core+s) configurations, whilst those shifted to the violet have initial terms belonging to (core+d) configurations. Measurements made with zinc agreed, on the whole, with those for copper. For iron, the magnitude of the shift depends on the greatness of the term and the electron configuration to which it belongs. Lines the initial terms of which have structure d^6s, s, or d^7, s, will suffer a large shift to the red in the high current arc, and it is predicted that for lines which shift to the violet, the initial terms involved will have structures d^6s, d, and d^7, d.

L. L. BIRCUMSHAW.

Arc spectrum of germanium. C. RICHTER (Naturwiss., 1927, **15**, 266).—The existence of five terms with frequency differences 557·11, 852·81, 5715·33, and 9242·38 is demonstrated.

A. A. ELDRIDGE

Spectra of gallium, germanium, and indium. R. J. LANG (Physical Rev., 1927, [ii], **30**, 762—769).—The vacuum-spark spectra of gallium, germanium, and indium were photographed in the ultra-violet. The series spectra of Ga III and Ge IV, already investigated by Carroll, have been re-measured, new lines are included, and term values have been recalculated. The series spectra of Ga II, Ge III, and In II are also tabulated. A. A. ELDRIDGE.

Regularities in the spark spectrum of silver. K. MAJUMDAR (Nature, 1927, **120**, 918).—The deepest $^3D_3$ term has a value of about 138,000, corresponding with an ionisation potential of about 17 volts, the consecutive differences being 1577 ($^3D_3-{}^3D_2$), 2999 ($^3D_2-{}^3D_1$), and 2306 ($^3D_1-{}^1D_1$).

The arc spectrum of silver is a purely doublet spectrum. The ionisation potential of Ag^+ is about 22 volts. A. A. ELDRIDGE.

Secondary electron emission from tungsten. H. E. KREFFT (Ann. Physik, 1927, [iv], **84**, 639—673).—The ratio of the number of secondary electrons emitted from a gas-free tungsten surface at temperatures up to 1480° Abs. to the number of incident electrons has been determined as a function of the energy of the incident electrons in the range 0—700 volts. The ratio shows a maximum at 15·3 volts, a minimum at 20 volts, and 18 inflexions in the range above 25 volts. These inflexions agree well with the data for critical excitation potentials for soft X-radiation given by Richardson and Chalkin.

R. W. LUNT.

Spectrum of mercury in the far ultra-violet. G. DÉJARDIN (Ann. Physique, 1927, [x], **8**, 424—465).—The arc and spark spectra of mercury in the region 2700—1850 Å. have been studied in detail, using as light sources an electrodeless discharge, a condensed spark between copper and mercury electrodes, a three-electrode tube, and an argon-filled quartz mercury-vapour lamp. A large number of new lines are recorded, and these, together with those already known, have been classified into four groups corresponding with different stages of excitation. The first corresponds with the arc spectrum Hg I, and the others, E_1, E_2, E_3, very probably correspond with the spark spectra Hg II, Hg III, and Hg IV. The arc spectrum obtained with the electrodeless discharge is characterised by the development of secondary triplet series and by the appearance of certain combinations forbidden by the selection principle. The variations in wave-length of certain arc lines observed in the condensed discharge are discussed. The electrodeless discharge shows a line at 2269·92 ± 0·05 Å. which may correspond with $1S-2p_1$. The E_1 group of lines supports Carroll's schematic classification (A., 1926, 214), and the 1941·52 Å. line is regarded as the less refrangible component of the first principal doublet of Hg II. The ionisation potential of Hg^+ is 19 volts, in agreement with Carroll's value for the highest spectral term. Earlier work (A., 1924, ii, 709) on the excitation of spark lines by electronic impact is confirmed and extended to the far ultra-violet. The Hg II spectrum can be divided into two sub-groups. R. A. MORTON.

Spectroscopy of the mercury spark produced in a sustained circuit oscillating at high frequency. J. ROSSIGNOL (Compt. rend., 1927, **185**, 1273—1274).—The spectral modifications of the spark produced between an amalgamated copper electrode and a drop of mercury in an oscillating circuit sustained by a three-electrode valve have been studied in relation to variations of the frequency (wave-lengths 2·40—4300 metres). Arc spectra were normally obtained at 3 metres, but at low frequencies (84 metres) first-order spark rays appeared owing to an increase in the self-induction of the circuit. Second-order spark rays appeared at 140 metres, whilst at 200 metres spark rays of Hg^+ (2947·1 and 2916·3 Å.) were obtained. Above this, no further changes were observed. The rays 3914·4, 3027·5, 2534·8, and 2482·1 Å. were produced only at frequencies of about 10^8, and the resonance ray (2536·5 Å.) was always reversed. J. GRANT.

Post-arc conductivity and metastable states in mercury. M. L. Pool (Physical Rev., 1927, [ii], 30, 848—863).—Post-arc conductivity, ascribed to residual positive ions and electrons, has been observed for 0·1 sec. after a mercury arc has been switched off. The critical restriking potential, previously attributed to the existence of long-lived metastable atoms, is accounted for by the distorted electrical fields which are set up as a result of electron diffusion.

A. A. Eldridge.

Quantum rotation of the mercury atom. R. G. Loyarte (Physikal. Z., 1927, 28, 904—908).—It has been shown that a number of excitation potentials of mercury can be reproduced by adding 1·4 or multiples thereof to the voltages corresponding with known lines or terms in the arc series (cf. A., 1927, 602). Six excitation potentials discovered by Jarvis (A., 1927, 1119) appear to correspond with 1·4, 2·80, 4·20, and with voltages obtained by subtracting 1·4 or 2·8 from known potentials. It is assumed that the constant difference is to be ascribed to a quantised atomic rotation. By considering 23 lines, extending from the extreme red to the vacuum region, it is shown that all of these can be accounted for by $\Delta\nu$, $2\Delta\nu$, $4\Delta\nu$, and known arc terms to or from which $\Delta\nu$, $2\Delta\nu$, or $3\Delta\nu$ has been added or subtracted. The mean value of $\Delta\nu$, calculated from the spectroscopic data, is 11,316 cm.$^{-1}$, corresponding with 1·390 volts. It would appear that the energy corresponding with an electron jump is in part absorbed in increasing the rotational energy of the atom by one or more quanta, and in part is used up as emission of a light quantum of a certain frequency. R. A. Morton.

Density of the vapour in the mercury arc and the relative intensities of the radiated spectral lines, with special reference to the forbidden line 2270. B. Venkatesachar (Proc. Roy. Soc., 1927, A, 117, 11—29).—The effect of changing the density of the vapour in a mercury arc (other conditions of excitation being kept unaltered) on the relative and absolute intensities of the radiated lines has been studied within the pressure range 20—0·1 mm. The effect of lowering the vapour density on the series lines (including the intercombination lines) is to increase the absolute intensities of all lines below $m=5$ and to diminish those of all lines above $m=6$. A theory is developed to account for this, based on the assumption that inelastic collisions between excited atoms in lower energy levels and thermally energetic normal atoms form the chief source of the radiators of the higher members. The supply from this source to the radiators of the lower members of a series is regarded as negligible. The forbidden line 2270 behaves like the earlier members of the series lines, and increases in intensity on lowering the density of the vapour, even with current densities of the order of 3 amp. per cm.$^{-2}$ In one set of photometric measurements, the line 4916 showed the greatest intensity change on lowering the vapour density ($I_2/I_1=1{\cdot}40$), followed by the lines 5769 and 5790 ($I_2/I_1=1{\cdot}30$), whilst the smallest increase ($I_2/I_1=1{\cdot}15$) was shown by the lines 5461, 4358, and 4047. These results are consistent with the view that the dimensions of the orbits of the valency electron increase in passing from the state 2^3S_1 to the state 3^1S_0.

Using an arc with a large dead space, it was found that, on raising the pressure by the introduction of air, higher members of series lines were developed. On pumping out the air, higher members beyond $m=11$ disappeared entirely, whilst the forbidden line 2270 and the spark line 2262 became conspicuous. If the density of the vapour is reduced by cooling the arc, many of the spark lines which are excited in the mercury arc are greatly reduced in intensity, whilst others either remain unchanged or gain in intensity. To the second class belong lines the radiators of which are excited atoms in lower energy levels. It is suggested that the lines 2847·8 and 2260·4, which occur in this group, form the first pair of a subordinate series in the spectrum of Hg^+, 1942·5 and 1642·5, according to Carroll, forming the first pair of the principal series. L. L. Bircumshaw.

Line spectrum of mercury in absorption. Occurrence of the forbidden line 2270 $1^1S_0-1^3P_2$. (Lord) Rayleigh (Proc. Roy. Soc., 1927, A, 117, 294—299; cf. A., 1927, 496, 607).—An arrangement is described by means of which the forbidden mercury line 2270 can be observed as a sharp absorption line in the unexcited vapour. As a source of light, first the continuous hydrogen spectrum was used, then the continuous spectrum accompanying the cadmium spark. It is necessary to employ a high spectroscopic resolving power and the largest possible mass of mercury. The breadth of the line is estimated as roughly 0·08 Å. The breadth of the resonance line 2537 in saturated air at atmospheric pressure is several times as great as that of the forbidden line in pure mercury vapour at atmospheric pressure, and the total radiation absorbed is also several times as great. The forbidden line requires about 10^7 times as much mercury to bring it into evidence as the resonance line. No trace was found of the other forbidden line 2656, and from this it appears that, under equal energy density of incident radiation, a transition from the normal to the 1^3P_0 state has less probability than one to the 1^3P_2 state.

L. L. Bircumshaw.

Fine structure of some mercury lines. W. H. McCurdy (Proc. Nat. Acad. Sci., 1927, 13, 701—703).—A correction of the fine structure of the lines 3650 and 2967 Å. as given by Nagaoka, Sugiura, and Mishima (A., 1924, ii, 798). W. E. Downey.

Variation of intensity ratios of optically excited spectrum lines with the intensity of the exciting light. E. A. Baker (Nature, 1927, 120, 917—918; cf. Wood, A., 1927, 1117).—Experiments on photographic action give results similar to those obtained by Wood for mercury vapour, and place the photographic action among the phenomena of phosphorescence. A. A. Eldridge.

Strength of anomalous dispersion in the non-luminous vapour of thallium and cadmium. W. Kuhn (Kgl. Danske Videnskab. Selsk. math.-physik. Medd., 1926, 7, No. 12, 3—87; Chem. Zentr., 1927, i, 2511).—An expression is given for the longitudinal magnetic double refraction for any anomalous Zeeman effect, and data for the anomalous magnetic rotation-dispersion in non-luminous vapours are recorded as follows: thallium, 3776 Å. ($2p_2-2s$), 0·08; 2768 Å. ($2p_2-3d_2$), 0·20; cadmium, 3261 Å. ($1S_2-2p_2$), $1·9\times10^{-3}$; 2288 Å. ($1S-2P$), 1·20. Thallium lines originating from the $2p_1$ state were also observed. Absolute *f*-values for these and for lines not directly observable were obtained by using the intensity rule for multiplets. A. A. Eldridge.

X-Ray *K* absorption in elements tungsten (74) to uranium (92), and *K* screening numbers. J. E. Mack and J. M. Cork (Physical Rev., 1927, [ii], **30**, 741—746).—New values are recorded for the *K* absorption edges of tungsten, osmium, iridium, platinum, gold, mercury, thallium, lead, bismuth, thorium, and uranium. An attempt to determine Sommerfeld's screening numbers for the *K* shell has led to the conclusion that Sommerfeld's "relativity correction" does not account for all the curvature of the lines in the Moseley diagram. A. A. Eldridge.

***M*-Series *X*-ray absorption spectra of osmium, iridium, and platinum.** R. A. Rogers (Physical Rev., 1927, [ii], **30**, 747—754).—The absorption spectra of osmium, iridium, and platinum were investigated from 3·5 to 7 Å., and the following discontinuities (Å.) observed: osmium 6·194 (M_1), 5·975 (M_2), 5·027 (M_3), 4·412 (M_4), 4·037 (M_5); iridium 5·961 (M_1), 5·754 (M_2), 4·851 (M_3), 4·270 (M_4); platinum 5·736 (M_1), 5·541 (M_2), 4·674 (M_3), 3·738 (M_5). Values of $(\nu/R)^{\frac{1}{2}}$ are not in complete agreement with those computed by Bohr and Coster and by Sommerfeld. A. A. Eldridge.

Law of absorption of *X*-rays by matter. P. Villard (Compt. rend., 1927, **185**, 1415—1419).—Deviations from the law of Bragg and Peirce (A., 1914, ii, 792) have been studied in terms of the variation with λ of the constant *C*, where $\tau/\rho=C\lambda^3$, the ratio τ/ρ being the partial coefficient of true absorption of *X*-rays by matter (fluorescence), as distinct from that of simple diffusion. For wave-lengths of the order of 0·1 Å., *C* passes through a maximum often 40% higher than the constant value it assumes for the longer wave-lengths, and diminishes rapidly for the shorter wave-lengths. The results are explainable by atomic resonance, the exponent 3 in the Bragg and Peirce law being accepted, although the law itself refers only to limiting cases and involves a coefficient which is not constant, but is dependent on resonance phenomena. J. Grant.

Azimuthal distribution of *X*-rays scattered in an ideal gas. H. Mark and K. Schocken (Naturwiss., 1927, **15**, 139—140; Chem. Zentr., 1927, i, 2391—2392).—Experiments with carbon dioxide and argon show that for constant azimuth the intensities are proportional to the gas pressure. For large angles, the atom factor appears to depress the increase in the total intensity. A. A. Eldridge.

Experimental tests of theories of the absorption of *X*-rays. F. K. Richtmyer (Physical Rev., 1927, [ii], **30**, 755—761).—Experimental values of $R_L{}^K$, the ratio of the magnitude of the true absorption coefficient on the short wave-length side of, but infinitely near to, the *K* absorption discontinuity to that on the other side, accord best with Kramers' theory, whereas the absolute magnitude of the absorption discontinuity is given by de Broglie's theory. In the wave-length range $\lambda_K/2<\lambda<\lambda_K$ the absorption coefficients of tin are a linear function of λ^3. A. A. Eldridge.

Absorption of *X*-rays in various elements. F. K. Richtmyer (Nature, 1927, **120**, 915—916).—The experimental results referred to by Jonsson (A., 1927, 1118) appear to be in conflict with theory. If $\delta_K=E_K/E_{L1}$, the relative numbers of *K*- and *L*-photo-electrons must be independent of the relative numbers of *K*- and *L*-electrons in the atom. A. A. Eldridge.

Zeeman effect of the symmetrical top according to wave mechanics. E. U. Condon (Physical Rev., 1927, [ii], **30**, 781—784).—Theoretical. A. A. Eldridge.

Intensities in the Stark effect of helium. II. J. M. Dewey (Physical Rev., 1927, [ii], **30**, 770—780; cf. A., 1927, 180).—The helium atom is regarded as a perturbed hydrogen-like atom, and calculations based on the quantum theory of perturbations are made of the new lines appearing in the Stark effect. The results, although of the correct order of magnitude, deviate considerably from the experimental values. The deviations may be partly due to differences in the number of atoms excited to different states of almost the same energy. A. A. Eldridge.

Application of quantum mechanics to the Stark effect in helium. J. S. Foster (Proc. Roy. Soc., 1927, A, **117**, 137—163).—The perturbation theory of quantum mechanics has been applied to the Stark effect in the arc spectra of helium. By means of the theory, the displacements and intensities of the lines emitted by the perturbed system can be calculated without the aid of further information regarding the nature of the inner field, apart from the term values of the unperturbed atom. The first order displacements, calculated for a number of field strengths for Stark components of the eight-line groups $2P-4Q$, $2P-5Q$, $2S-4Q$, $2S-5Q$, and the corresponding orthohelium lines (considered as singlets), are in good agreement with the observations. The ultimate disposition of the components at extremely high fields has been calculated. In very high fields the group patterns for parhelium and orthohelium are nearly identical. The theoretical intensities of the components have been calculated in fields of 10, 40, and 100 kilovolts/cm., and are in agreement with the qualitative observations. In particular, the theory accounts satisfactorily for the observed disappearance of numerous components when the displacement is equal to that of the $2P-nP$ line at zero field. New measurements are recorded of displacements of helium components in fields of 100 and 83 kilovolts/cm., and Lo Surdo photographs of the groups 4922, 4026, and 3965 Å. in high fields are reproduced for the first time. L. L. Bircumshaw.

Thermodynamics, wave-theory, and Compton effect. C. V. Raman (Nature, 1927, **120**, 950—951).—Objections to Compton's explanation of the nature of the Compton effect are summarised, and the author's views, which are being presented and developed elsewhere, are indicated.
A. A. Eldridge.

Photo-electric conductivity of sulphur. B. Kurrelmeyer (Physical Rev., 1927, [ii], 30, 893—910).—The current produced in sulphur by a given illumination is directly proportional to the applied field from 20 to 15,000 volts/cm. and to the intensity of illumination. No evidence of secondary current was found. On illumination of the crystal, the current reaches its full value rapidly (probably less than 10^{-4} sec.); when the illumination is removed, the current immediately falls almost to zero, a small residual current being due to the motion of positive ions. The initial value, as well as the subsequent shape, of the current–time curve depends on the previous history of the crystal. The curve showing the current per unit of incident energy as a function of the wave-length has a maximum at 470 mμ. The optical absorption curve is unusual, having a point of inflexion near 570 mμ, but asymptotic after 650 mμ. Since substances in which the primary ionisation takes place in the pure crystal material have $n>2$, and the substances having $n>2$ investigated by Gudden and Pohl possessed photoconductivity, the variation of the current in sulphur (where $n_a=1{\cdot}93$, $n_\beta=2{\cdot}00$, and $n_\gamma=2{\cdot}19$ for 768 mμ) with crystal orientation was investigated. The currents in different directions are equal in absolute magnitude, but exhibit a unipolarity along the direction of the acute bisector of the optic axes, with components along other directions. It is suggested that sulphur has a polar axis, if not crystallographically, then at least due to atomic asymmetries. A. A. Eldridge.

Relation between the secondary electron emission from nickel and tungsten and temperature. H. Nukiyama and H. Horikawa (Tech. Repts. Tôhoku Imp. Univ., 1927, 7, 49—56).—The secondary electron emission–temperature curve for nickel has discontinuities in the regions 350—400° and 780—890°. With tungsten, the apparent secondary electron emission remains approximately constant until temperatures at which the primary emission occurs are attained; thereafter it apparently tends to increase with temperature. The temperature relations in this region are, however, somewhat uncertain. The critical potentials of tungsten are 10, 16, 18, 26, 29, 41, 46, and 77·5 volts (cf. Petry, A., 1926, 989). J. S. Carter.

Chemical action of electrons of moderate velocity on temper films. G. Tammann and G. Veszi (Z. anorg. Chem., 1927, 168, 41—45).—The chemical action of electrons having a velocity of 100—150 volts on very thin films of various metallic oxides and halides has been investigated by observation of the colour changes of the film as its thickness alters. The method is much more accurate than that of measuring the change of pressure as gas is evolved; *e.g.*, a change of thickness of 10 μμ, which is easily recognised by the change of colour, corresponds in the case of the reduction of cuprous oxide with an evolution of only 3×10^{-3} mm.^{3} of oxygen per mm.^{2} of surface. The results show that films possessing metallic conductance, *i.e.*, which are transparent to electrons, are unaltered by bombardment with electrons of moderate velocity, whereas those which conduct electrolytically are reduced to metal. H. F. Gillbe.

Diffraction of electrons by a crystal of nickel. C. Davisson and L. H. Germer (Physical Rev., 1927, [ii], 30, 705—740).—A detailed account of the experimental basis of results already published (A., 1927, 492). A. A. Eldridge.

Recoil electrons from aluminium. A. A. Bless (Physical Rev., 1927, [ii], 30, 871—877).—The values obtained for ν/R (where ν is the frequency of a quantum having the same energy, and R is Rydberg's constant) for electrons ejected from aluminium by the scattering of X-rays of wave-length 0·48 and 0·712 Å., respectively, were 190 and 84·1, in agreement with Compton's, but not Wilson's theory of scattering. A. A. Eldridge.

Excitation of polarised light by electron impact. II. Mercury. H. W. B. Skinner and E. T. S. Appleyard (Proc. Roy. Soc., 1927, A, 117, 224—244; cf. Skinner, A., 1926, 1074).—A continuation of previous work (*loc. cit.*). The percentage polarisations of the individual spectral lines are measured by the methods of photographic photometry, the velocity of the exciting electron stream being varied from 9 to 200 volts. The lines are polarised in various ways; some are polarised positively (*i.e.*, with the electric vector parallel to the electron stream), and some negatively, whilst the lines 4078 and 4108 Å. show no appreciable polarisation. The polarised lines show a characteristic variation of the polarisation with the velocity of the electron stream, the most striking feature being a steep increase in the polarisation with increasing voltage for low velocities, and a subsequent maximum for a velocity corresponding with a few volts above the excitation point. For high velocities there is in most cases a definite reversal of the sign of polarisation. It is shown that the various polarisation effects may be interpreted to give information about the dynamics of the collision process in which an atom is excited by electron impact. L. L. Bircumshaw.

Dark space in high-frequency discharges. S. Smith (Nature, 1927, 121, 91).

Smallest carriers of electricity in gases. L. B. Loeb (Ann. Physik, 1927, [iv], 84, 689—696).—The criticisms of Schilling (A., 1927, 708) on the author's data for the mobility of ions in air are repudiated at length, and Schilling's experimental values are adversely criticised. R. W. Lunt.

Mobility of ions in gases. M. Laporte (Ann. Physique, 1927, [x], 8, 466—554).—In a gas, ions of the same sign exhibit either identical or different mobilities. The alternatives correspond with either a unique constitution for any ion of a given sign, or a series of ions formed from more or less complex aggregates of neutral atoms round the charged centre. Hitherto, no conclusive decision between the two alternatives has been possible. A method analogous in principle to Fizeau's method for determining the velocity of light has been adapted to the problem. The ions are drawn by an electric field across gaps inserted in parallel rotating plates. In all the gases investigated the variations in mobility exceed the experimental error. The apparatus allows the proportions of ions of different mobilities to be determined, so that distribution curves showing mobility against number of ions can be obtained. In dry air the positive ions show mobilities varying between 0·82 and 2·02, with a maximum at 1·27, whilst the negative ions vary between 1·32 and 3·30, maximum at 2·16 (cm./sec. per volt/cm.). The addition of moisture effects an acceleration of the positive ions and a retardation of the negative ions, the maxima being at 1·47 and 1·79 in air saturated with water vapour. Busse has, however, shown that in perfectly dry air both ions have a mobility of 15 (A., 1926, 1074; 1927, 4). The distribution curves for dry oxygen and nitrogen are the same for the positive ions as for air, but a discrepancy is found for the negative ions, and it is shown that the negative ions in air must be oxygen ions, a result in harmony with the great electronegative affinity of oxygen. The influence of electronic affinity is still more marked with argon, since the distribution curves for negative ions in this gas depend essentially on the degree of purity. Highly purified argon shows a large proportion of very mobile ions which are probably due to free electrons. Indeed, the saturation current in perfectly pure argon can be realised with voltages about 1/50 of those necessary in air. The chemical nature of a gas, and therefore the external electronic configuration of its atoms, is thus of fundamental importance in determining the formation of multimolecular ions.

Many theories postulate an electrostatic polarisation of neutral molecules, by which it would follow that the electrons should exhibit identical behaviour in oxygen, nitrogen, and argon. This consequence is contrary to experience. The work of Busse makes clear the importance of water vapour in the formation of complex ions; the results probably mean that the most active affinity factors are suppressed by complete desiccation. The ions are described as aggregates $M^+ + nH_2O + pM$, in which n and p are variable and sometimes fairly high numbers.

R. A. Morton.

Absorption of potassium ions in various gases. F. M. Durbin (Physical Rev., 1927, [ii], 30, 844—847).—The loss by scattering, retardation, or neutralisation suffered by a beam of positive potassium ions, accelerated by 8·5—350 volts, in passing through air, hydrogen, nitrogen, helium, oxygen, or argon has been measured. Curves show the effect of pressure in helium and nitrogen, and the ratio of the mean free path for absorption to its kinetic theory value as a function of the velocity of the ions; oxygen is most, and helium least, effective in weakening the rays.

A. A. Eldridge.

Magneto-chemistry of vanadium. N. Perrakis (J. Phys. Radium, 1927, [vi], 8, 473—480).—An amplification of work previously published (A., 1927, 288, 717, 805).

J. S. Carter.

Relative intensities of positive rays from the isotopes of lithium. J. L. Hundley (Physical Rev., 1927, [ii], 30, 864—870).—Using Dempster's method of positive-ray analysis, the relative intensities of positive rays from the isotopes of lithium for lithium silicate, lithium aluminate, lithium phosphate and iron oxide, and spodumene were determined for various temperatures. The ratio Li^7/Li^6 decreases with rise of temperature; Li^6 has a greater work function than Li^7.

A. A. Eldridge.

At. wt. and packing effect. S. Meyer (Naturwiss., 1927, 15, 623—625; Chem. Zentr., 1927, ii, 1230—1231).—The atomic nuclei of elements of which the at. wts. are integral multiples of 4 are not necessarily composed of helium nuclei as such. The energy necessary for the disintegration of a helium nucleus must be greater than that available from radium-C' α-particles. Where it has been found possible to liberate protons, these must have been present in the nucleus in an isolated condition, possibly as constituents of "proton shells." The deviations from integers of the at. wts. of the first 24 elements (except aluminium) are positive, and thereafter negative; all elements with negative deviation have odd valency. The at. wts. of the isotopes of elements of even number are nearly always even.

A. A. Eldridge.

Average energy of disintegration of radium-*E*. C. D. Ellis and W. A. Wooster (Proc. Roy Soc., 1927, A, 117, 109—123).—A direct experimental test has been made to decide between the alternative theories as to the mechanism of the β-ray type of disintegration. For the purpose of testing whether, in a β-ray body, every atom gives out the same energy on disintegration, the β-ray emission from radium-*E* has been analysed by means of a magnetic field and the intensity of the rays of various energies determined by means of an ionisation chamber. A curve is plotted, showing the distribution of energy among the disintegration electrons when they have escaped from the parent atoms, and from this it is deduced that the average energy per disintegration of the emitted particles is 400,000 volts to within 15%. The average energy of disintegration has also been determined by measuring the heating effect of the β-rays, a source of radium-*E* being enclosed in a calorimeter the walls of which are thick enough completely to absorb the β-radiation. The fact that the value obtained by this method, 350,000±40,000 volts, agrees with that estimated from the distribution curve proves definitely that the disintegration electrons must be emitted from the nucleus with varying energies. If the alternative hypothesis, that the energy of disintegration is a characteristic constant of the atom, were correct, then the heating experiment would have given a value close to 1,000,000 volts, *i.e.*, 2·8 times the actual experimental figure.

L. L. Bircumshaw.

Atomic groupings [of radioelements]. (Mlle.) C. Chamié (Compt. rend., 1927, 185, 1277—1279).—Atomic groupings of radioelements (A., 1927, 605) have been obtained using a solution of polonium in ammonia, large volumes of water, and cedar-wood oil. The phenomenon is independent of the introduction of silver into mercury activated by polonium, and also of the time of exposure and water-vapour content of the emanation used in the activation of mica. Each group contains on the average 10^6—10^8 atoms of polonium, and the photographs indicate normally a star-shaped structure in which the radial lines correspond with the paths of α-particles.

J. Grant.

Elasticity of the collisions of α-particles with hydrogen nuclei. P. M. S. Blackett and E. P.

Hudson (Proc. Roy. Soc., 1927, A, **117**, 124—130).—Collisions in which the α-particle and proton approach extremely closely to each other, making forked tracks of narrow angle, are very suitable for accurate study. Two photographs of this type have been measured with considerable accuracy, and it is found that the collisions are elastic within the limits of experimental error. The probable errors of measurement are discussed. L. L. Bircumshaw.

Formation of sulphur trioxide under the action of α-particles. J. E. Maisin (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, i, 172—177).—The oxidation of sulphur dioxide by oxygen in presence of radon has been followed manometrically. No evidence for the existence of persulphuric anhydride was obtained, sulphur trioxide being apparently the principal reaction product. The ratio of the number of molecules disappearing from the gaseous phase to the number of pairs of ions produced is about 1·5. Assuming the simple reaction $2SO_2+O_2=2SO_3$, this result indicates that each pair of ions produces one molecule of sulphur trioxide. J. S. Carter.

Powers of retardation of atoms relative to α-particles. S. Rosenblum (Compt. rend., 1927, **185**, 1275—1277).—The ratio A_1X_2/A_2X_1 defines the retarding power of an atom relative to α-particles, where A and X refer to the superficial densities and the atomic weights, respectively, of two elements producing the same loss of relative velocity. Gold is taken as the standard of comparison, and X may be substituted by the constant K of the author's equation (A., 1927, 1120). It is then shown for a number of elements that the expression $N/(N+4)^{\frac{1}{2}}$ measures the retarding power of an element in terms of its atomic number (N). The electronic absorption of energy decreases when N increases, and the α-particles liberate most energy when in collision with loosely-held electrons. J. Grant.

γ-Ray emission and the law of radioactive transformation. J. C. Jacobsen (Nature, 1927, **120**, 874—876).—In the author's method of determining the period of transformation of radium-C' (A., 1924, ii, 142), the number of α-particles was found to decrease approximately exponentially with increasing distance from the source, whereas Barton's curve (A., 1927, 86), obtained with a differently constructed apparatus, rose from zero to a maximum position, and then fell. The origin of the disagreement is discussed, and Barton's curve is considered to be free from error. Such a curve is obtained when the γ- and α-transformations are assumed to take place according to an exponential law, the constants λ_γ and λ_α being suitably adjusted. These constants appear to be of the same order of magnitude; if they are considered to be equal, and the velocity of the recoil atoms is taken as 2×10^5 cm. per sec., λ_γ is 10^5 sec.$^{-1}$, the recoil due to the emission of the γ-rays being disregarded. A. A. Eldridge.

Measurement of penetrating radiation. K. Büttner (Naturwiss., 1927, **15**, 158—160; Chem. Zentr., 1927, i, 2391).—Absorption measurements were made under various conditions.

A. A. Eldridge.

Pleochroic haloes and the age of the earth. F. Lotze.—See this vol., 150.

Limits of the periodic system. A. von Antropoff (Z. Elektrochem., 1927, **33**, 475—476; cf. Meyer, A., 1927, 710).—Polemical.

Limits of the periodic system. E. Meyer (Z. Elektrochem., 1927, **33**, 476; cf. preceding abstract).—A reply to Antropoff. H. J. T. Ellingham.

Quantum theory of molecules. M. Born and R. Oppenheimer (Ann. Physik, 1927, [iv], **84**, 457—484).—Mathematical. R. W. Lunt.

Diameters of atoms and ions. A. Ferrari (Nuovo Cim., 1927, **4**, 39—47; Chem. Zentr., 1927, i, 2626).—Using Goldschmidt's values of atomic radii, the "absolute densities" of certain ions have been calculated. In particular sub-groups of the periodic classification, the values generally increase with increasing at. wt., and are greater for the right than for the left sub-groups. Magnesium belongs in this respect to the right sub-group. Fluorine and oxygen have higher densities than have the homologues immediately following. Increasing the charge of positive ions greatly increases the density.

A. A. Eldridge.

Effective cross-section of gas molecules in chemical kinetics. G. Kornfeld (Z. physikal. Chem., 1927, **131**, 97—104).—It has been shown by Nordheim (A., 1926, 654) that in the transfer of energy by collisions between atoms and molecules there must be an effective cross-section for these which is appreciably greater than that determined from elastic collision. This variable effective cross-section must be important in certain groups of chemical reactions where it is not a question of double decomposition between molecules, but of energy transfer from one to another. This is the case, for instance, in sensitised reactions in which the energy necessary for the reaction, which is greater than the available thermal energy, is supplied by foreign molecules. Even in purely thermal reactions, the variable effective cross-section may be all-important, *e.g.*, in unimolecular reactions, or, in fact, whenever the continuance of the reaction is dependent on the supply or removal of energy by collision. Finally, catalytic reactions which depend on the action of a trace of foreign substance may be included. In the case of the catalytic influence of a trace of water vapour on the combination of chlorine and hydrogen, the lower limiting value of the effective radius of the water molecule has been calculated from the available data to be at least thirty times that calculated from the kinetic theory of gases.

M. S. Burr.

Structure of the Swan bands. J. D. Shea (Physical Rev., 1927, [ii], **30**, 825—843).—Theoretical. A detailed quantum analysis is based on published data. The moment of inertia of the Swan band carrier for infinitely small vibration is $15{\cdot}84\times10^{-40}$ g. cm.^{2} for the initial state in the emission process, and $17{\cdot}03\times10^{-40}$ g. cm.^{2} for the final state. Johnson's suggestion that the Swan bands may be due to acetylene is criticised, and a compound C—C or, if possible, C^-—C^- is suggested as carrier.

A. A. Eldridge.

Ultra-violet band system of carbon monosulphide and its relation to those of carbon monoxide (the "4th positive" bands) and silicon monoxide. W. Jevons (Proc. Roy. Soc., 1928, A, **117**, 351—375; cf. Martin, *ibid.*, 1913, 89, 127).—A quantum analysis has been made of the band-heads in the system discovered by Martin (*loc. cit.*) in the region 2837—2436 Å. in the tube discharge through carbon disulphide vapour and in the carbon arc fed with sulphur. An examination of Martin's spectrograms leads to a Deslandres scheme for the band-heads and to the assignment of the vibrational quantum numbers n', n''. The bands are probably of the simplest type, with single R, Q, and P branches. From a study of the variation of the interval between the two heads of each double-headed band with n' and n'', the two heads are ascribed to the R and Q branches, respectively, the less refrangible Q head being the less intense. The bands of the progression $n'=1$ are abnormal, their R heads being less intense than their Q heads, and the separations of the two heads of each band being abnormally large. Moreover, the distance of the $n'=1$ vibrational level in the initial state from the $n'=0$ level is abnormally large compared with that indicated by the spacing of the other n' levels. Similar anomalies have been found by Birge (cf. A., 1927, 184) for the final state of the CO Ångström system, which is also the initial state of the CO 4th positive system. Several points of similarity between the latter and the CS system are discussed. It is shown that the ultra-violet systems of SiO and CS both resemble the 4th positive system of CO, in that (*a*) the bands of all three systems show degradation to the red, and (*b*) the ratio of the system-origin to the resonance line of the comparable atom is approximately the same for each system. The three systems are therefore ascribed to the electronic transition $1^1P \rightarrow 1^1S$, where 1^1S is the normal state and 1^1P the second excited state of the molecule. There is an even closer resemblance between the CO and SiO systems than between the CO and CS systems as regards (*a*) the ratio of system-origin to comparable atomic line, (*b*) the proportional increase of vibrational frequency, and (*c*) the intensity distribution and proportional decrease of moment of inertia in the transition $1^1P \rightarrow 1^1S$.
L. L. Bircumshaw.

Radiation from explosions of carbon monoxide and oxygen to which hydrogen has been added. W. E. Garner and F. Roffey (Nature, 1928, **121**, 56—57).—The radiation from an explosion of an equimolecular mixture of carbon monoxide and oxygen falls sharply when 0·07% of hydrogen is present, and continues to fall slowly when the percentage of hydrogen is gradually increased to 2%. The effect is not due to absorption in front of the explosion wave, and is probably not due to the absorption by water vapour formed in the wave-front.
A. A. Eldridge.

Shape of the carbon dioxide molecule. K. L. Wolf (Z. physikal. Chem., 1927, **131**, 90—96).—Theoretical. The shape of the carbon dioxide molecule is discussed on the basis of the existing data for molecular heat, infra-red absorption, and dielectric constant, the last being determined experimentally or deduced from dispersion data. The evidence is in favour of a molecule in which the atoms are arranged symmetrically in a straight line (cf. Eucken, A., 1926, 882; Barker, A., 1922, ii, 805).
M. S. Burr.

Electronic states and band spectrum structure in diatomic molecules. VI. Theory of intensity relations for case *b* doublet states. Interpretation of CH bands, 3900, 4300 Å. R. S. Mulliken (Physical Rev., 1927, [ii], 30, 785—811; cf. A., 1927, 607, 916).—Theoretical intensity equations are obtained for all possible branches in transitions between doublet electronic states falling under Hund's case *b*, and a revised notation is proposed. The energy differences between F_1 and F_2 terms (s parallel or antiparallel to j_k) are considered qualitatively for a series of cases between *a* and *b*, for normal and inverted doublets. The structure and intensity relations of the CH band at 4300 Å. agree with the theoretical for a case *b* $^2D \rightarrow {}^2P$ transition; for the 3900 Å. band, agreement with theory is equally good for a case *b* $^2S \rightarrow {}^2P$ transition. Initial term values for both bands are given. It is considered likely that the ^2P, ^2D, and ^2S levels of CH are derived respectively from the three lowest states, ^2P, ^1D, and ^1S of carbon.
A. A. Eldridge.

Continuous absorption of light in potassium vapour. R. W. Ditchburn (Proc. Roy. Soc., 1928, A, **117**, 486—508).—A spectrophotometric method is described for measuring relative absorption coefficients of a vapour for different wave-lengths without keeping the vapour pressure absolutely constant. Results are given for potassium over the range 4000—2200 Å. and under widely different experimental conditions. The total experimental error is nearly all photographic and is about 2—3%. The main features of the results are explicable on the view that the measured absorption is the sum of that due to the potassium molecule and that due to the atom. The changes in the experimental curves caused by changes of the vapour pressure of potassium, the pressure of the filling gas, and the temperature are indicated, and the results are discussed in connexion with the theory of atomic and molecular absorption. An attempt has been made to separate the atomic and molecular absorptions on the assumption that the molecular absorption is directly proportional to the molecular concentration and the atomic absorption to the atomic concentration, but it is found that in general these assumptions are not justified, and a satisfactory quantitative separation is not possible. The fact that the amount of atomic absorption appears to be much less than that expected may possibly be due to the partial or total re-emission of the absorbed radiation. An experiment in which continuous absorption produces line fluorescence is described, and is explained by assuming that the molecule is ionised into one neutral atom, one ionised atom, and one electron. The heat of dissociation of the potassium molecule is derived from the absorption curves and used to calculate the degree of association in potassium vapour under different conditions of temperature and vapour pressure.
L. L. Bircumshaw.

Relative intensity of the principal doublet (*H*, *K*) and of the diffuse doublet (*X*) in the

spectrum of the calcium chromosphere. C. Davidson (Month. Not. Roy. Astr. Soc., 1927, **88**, 30—33).—A series of photographs with varying exposures of the chromospheric spectrum in the neighbourhood of these lines has been obtained by focussing an image of the sun tangential to the slit of the spectrograph. After correcting for the superimposed continuous spectrum from Planck's formula, for T=5000°, it was found that the intensity of the line, 8542 Å., of the diffuse doublet is somewhat greater than that of K_1 at a level between 1000 and 2000 kilometres above the photosphere. At heights above 4000 kilometres, X rapidly ceased to be recorded. The results, although incomplete, are therefore in agreement with Milne's prediction, derived from a consideration of the mechanics of the ionised calcium atom, that the infra-red lines (X) should be more intense than H, K at low levels, whilst at high levels they should be fainter. G. A. Elliott.

Spectrophotometric observations on the growth of oxide films on iron, nickel, and copper. F. H. Constable (Proc. Roy. Soc., 1928, **A, 117**, 376—387; cf. A., 1927, 930).—The growth of oxide films has been studied on thin films of iron, nickel, and copper supported on china clay rods and on massive rods of these metals, comparative spectrophotometric observations being made of the character of the reflected light at frequent intervals during the oxidation. The colour sequence shown during the oxidation of the reduced metals brightens considerably during activation, owing to the increase in the reflecting power of the metallic films. Experiments on the oxidation of a copper rod composed of surfaces of burnished, sand-papered, and electrolytically deposited metal showed that the composite nature of the reflected light was practically independent of the irregular nature of the surface, only its intensity being altered. The brightness of the colour sequences varied in the same way as the brightness of the metal surface on which they were formed. The colour sequence on copper shows the red colours much more strongly than the blue, due partly to the strong reflexion of red light by metallic copper. On nickel no reds are observed, their place being taken by brown, and the blue colours are strongly accentuated. This effect is ascribed to the strong specific absorption of nickelous oxide. The colours on iron are normal, but after the first blue the sequence is distorted by the strong specific absorption of the oxide film, the dispersion of the oxide, and the tendency of the oxide to form a detached coating over the surface. The thicknesses of homogeneous films of a given colour have been calculated from the experimental data, using Kundt's values for the refractive indices and Cauchy's formula. The tables are used, with observations of the rate of formation of the colours, to show that from 300° to 500° the velocity of oxidation decreases in the order copper, iron, nickel.

L. L. Bircumshaw.

Displacement of absorption bands of organic dyes, dissolved in different alcohols with constant and varying concentrations of dye. L. Hirschler (Biochem. Z., 1927, **190**, 411—423).—Very few dyes were found which, when dissolved in a homologous series of alcohols, did not show displacement of the absorption bands in passing up the series, the shift being in most cases towards the red. With most dyes showing this displacement, there occurs, with change of medium, an asymmetric change of the width of the bands. The far greater displacement of the bands obtained by varying the concentration of the dye is explained as an asymmetric change in the width of the bands.

P. W. Clutterbuck.

Spectrum of CaSrS-samarium mixed phosphors. M. Travniček (Ann. Physik, 1927, [iv], **84**, 823—839).—The phosphorescent system $[Ca_mSr_n]S$–Sm+LiF has been investigated. The calcium phosphor shows a sharp red emission line at 6058·6 Å., whilst the strontium phosphor has a corresponding line at 6036·8. Using this emission as a criterion, it is found that the transition through mixtures of calcium and strontium is perfectly continuous, as is to be expected if the phosphorescence centre is a definite compound. Each component of the phosphor exercises some effect on the emission. In exactly the same way, the X-ray investigation shows the lattice constant to vary continuously. The crystalline nature of the sulphide diluent is of great importance in determining emission from the phosphor, since lattice constant and frequency vary in the same sense.

Freshly-prepared mixed phosphors are unstable, showing ageing phenomena. Striking differences are recorded between fresh and one-year-old magnesium sulphate–, barium sulphate–, and magnesium oxide–samarium phosphors both in respect of wave-length and intensity of the emission bands. The interpretation of the results is discussed.

R. A. Morton.

Dielectric constants of four electrolytes as given by the Carman electrometer method. C. C. Schmidt (Physical Rev., 1927, [ii], **30**, 925—930).—Curves showing the relation between the dielectric constant and concentration of aqueous solutions of sodium chloride (up to 0·018N) and potassium chloride (up to 0·01N) exhibit a minimum, and corresponding curves for barium chloride (up to 0·024N) and copper sulphate (up to 0·028N) exhibit two minima. In all cases the dielectric constant reaches a value greater than that of water (cf. Walden, Ulich, and Werner, A., 1925, ii, 512, 773).

A. A. Eldridge.

Arrangement of the electrometer method for measuring the dielectric constants of electrolytes. A. P. Carman and C. C. Schmidt (Physical Rev., 1927, [ii], **30**, 922—924).—An adaptation of Carman's method (A., 1924, ii, 809) is described.

A. A. Eldridge.

Dielectric constants of aqueous solutions of electrolytes. H. Zahn (Physikal. Z., 1927, **28**, 916—918).—Polemical. The investigations of Hellman and Zahn (A., 1926, 778; 1927, 7) are not consistent with results obtained by Pechhold (A., 1927, 919) and show much better agreement with the work of Skancke and Schreiner (A., 1927, 932). Pechhold found that the curves showing dielectric constant plotted against temperature all exhibited a minimum. It is claimed that only a few electrolytes really show this minimum and that Pechhold's results are vitiated by the employment of too low a frequency. Fürth contests the criticism in a discussion.

R. A. Morton.

Dielectric constants of ammonia, phosphine, and arsine. H. E. Watson (Proc. Roy. Soc., 1927, A, **117**, 43—62).—A detailed description is given of the apparatus and method used for obtaining absolute values of dielectric constants. All possible sources of constant error were explored. Determinations were made at high frequency, the change in capacity with pressure of a condenser containing gas being compensated by a variable condenser in series so as to keep the frequency of the system constant. An exact setting was obtained by the method of beats with a second oscillating system. Measurements of the dielectric constants of ammonia, phosphine, and arsine were made at approximately −47°, 16°, and 100°, and at three frequencies, and the variation of dielectric constant with pressure was also examined. The following mean values of $(\varepsilon-1)\times10^5$ at 1 atm. and at −47°, 16°, and 100°, respectively, were obtained: ammonia, 1099, 659, 406; phosphine, 337·3, 238·1, 168·7; arsine, 251·0, 191·6, 146. From these, the value of BN in Debye's equation, $\varepsilon-1=N(A+B/T)$ was calculated, and finally μ, the electric moment. The absolute values found for ammonia are considerably higher than those obtained by Jona (A., 1919, ii, 130), but the value calculated for μ is approximately the same in each case. Ammonia and phosphine conform approximately with Debye's formula, whilst for arsine the value of B is substantially zero, so that this gas is similar to the permanent gases so far as its dielectric constant is concerned. μ is much smaller for phosphine than for ammonia and smallest for arsine.

L. L. Bircumshaw.

Molecular volumes of liquids at their b. p. A. E. Arbusov (Z. physikal. Chem., 1927, **131**, 49—60).—An apparatus for the determination of the density of a liquid at its b. p. is described. Using the most recent at. wt. data, the molecular volumes of the following liquids at the b. p. have been determined: methyl, ethyl, propyl, *iso*propyl, and *iso*butyl alcohols, *iso*butyl iodide, chloroform, and benzene. The results are in good agreement with the best data of earlier investigators; they make it possible also to explain some of the errors in the older determinations.

M. S. Burr.

Atomic volume relations in certain isomorphous series. A. F. Hallimond (Min. Mag., 1927, **21**, 277—284).—The molecular volumes of several series of salts of potassium, rubidium, and cæsium are tabulated, and it is shown that the ratio of the differences (Cs—K)/(Rb—K) is a constant. Also for the chlorides, bromides, and iodides of the alkalis and the alkaline earths the ratio of the differences in molecular volumes (I—Cl)/(Br—Cl) is a constant. From these data are calculated the atomic volumes of the metals and the volumes of the acid radicals, showing that the volume of any one metal varies in its different salts. The general conclusions reached are (1) that in any two isomorphous salt-series formed from the same eutropic elements the volume of an element in one series bears to its volume in the other series a ratio which is the same for all members of the group, and (2) that the eutropic replacement of one element by another of different volume does not alter the volume of the rest of the molecule.

L. J. Spencer.

Specific volumes of low-melting picrates. P. Walden, H. Ulich, and E. J. Birr (Z. physikal. Chem., 1927, **130**, 495—515).—The appropriate technique for the determination of the true specific volume of low-melting solids at temperatures below 220° is described with the preparation and purification of the following ammonium picrates: ethyl-, propyl-, *n*-butyl-, *iso*butyl-, *n*-amyl-, *iso*amyl-, *n*-heptyl-, dimethyl-, methylethyl-, diethyl-, dipropyl-, di*iso*amyl-, triethyl-, tripropyl-, tri*iso*propyl-, dimethyldipropyl-, triethylpropyl-, diethyldipropyl-, methyltripropyl-, ethyltripropyl-, tetrapropyl-, and tetra*iso*amyl-. It is shown that for these substances the true specific volume, φ, is more accurately represented by the expression $\varphi_\theta=\varphi_0(1+\alpha\theta)$, where θ is the temperature, than by Mendeleev's formula. It is also shown that for the picrates of primary, secondary, and tertiary amines the molecular volume at 150°, V, is related to the number of carbon atoms in the ammonium group, N, by $V=157+18{\cdot}8N$; for quaternary ammonium bases the equation $V=152+18{\cdot}4N$ applies.

R. W. Lunt.

Volumes and the homologue characteristic. I. and II. F. Wratschko (Pharm. Presse, 1927, **32**, 6—9, 73—76; Chem. Zentr., 1927, i, 2791—2792).—I. The homologue characteristic R applicable to a particular aliphatic series applies also to series with a benzene, naphthalene, or anthracene ring. Each increase of two hydrogen atoms depresses the value of R by 10 units; each ring depresses it by 30 units. The formula $R=3M/d_4^0-16n=73+10C-5H-30A$ (where C, H, and A, respectively, are the numbers of carbon atoms, hydrogen atoms, and rings) is given.

II. Phenylethyl-, but not *s*-trimethylphenyl-, 1-methyl-4-*iso*propylphenyl-, *p*-tolyl-, *p*-xylyl-, or *p*-*iso*propylphenyl-acetylene or phenylallylene, is a normal homologue of phenylacetylene. Penta- and hexa-alkylbenzenes are dicyclic.

A. A. Eldridge.

Change in the refractive index of air when an electric glow discharge is passing through it. J. B. Seth (Nature, 1927, **120**, 880).—The change, which is local, and maximal at a pressure of 25 mm., was studied by observing the shift in the interference fringes obtained by Jamin's plates.

A. A. Eldridge.

Periodic anomalies in the properties of long-chain compounds. W. B. Lee (Trans. Faraday Soc., 1927, 23, 630—640).—From an examination of the available data relating to molecular rotatory power, static friction, density, heat of crystallisation, packing density of unimolecular films, viscosity, toxicity, esterification constants of acids, double refraction, X-ray spacings, b. p., capillary activity, dielectric constant, and many other properties, it is found that a well-defined irregularity is evident in certain series of long-chain compounds on the addition of the fifteenth carbon atom to the chain, although a departure from the normal behaviour may begin at the fourteenth. Similar, but less pronounced, irregularities may also be frequently observed at the fifth and tenth carbon atoms. This applies to certain optically active carbinols, as well as to normal fatty acids and their salts. To account for these anomalous properties in homologous series, it is suggested that the carbon atoms are disposed in space in the form of a spiral or helix, in such a way as to cause a periodicity in those properties of the molecule which ultimately depend on residual affinity. This conception, therefore, requires that polarity should influence molecular rotatory power, a view which is supported by the experiments of Rule and Smith (A., 1925, ii, 1120). The model suggested does not agree with that deduced from *X*-ray analysis, which applies, however, only to the solid state. It is possible that, in solution or in the molten state, rotation of the carbon atoms and their linkings may take place to produce the open-pentagonal type of structure required. On this hypothesis the increments in molecular volume for each CH_2 group added to the chain should become non-alternating with respect to odd and even members of a series above the m. p. A certain amount of evidence confirms this conclusion. M. S. Burr.

Rectilinear diameter of ethylene. E. Mathias, C. A. Crommelin, and H. G. Watts (Compt. rend., 1927, **185**, 1240—1242).—The deviations of ethylene from the law of rectilinear diameter are of the order of about 1% and are of the same nature as observed for argon and carbon dioxide, *i.e.*, the diameter is slightly concave for temperatures near the critical point and slightly convex for lower temperatures. The angular coefficient of the diameter is −0·00061277, and the critical coefficient 3·524. J. Grant.

Experimental test of Maxwell's distribution law. J. A. Eldridge (Physical Rev., 1927, [ii], **30**, 931—935).—Measurements of the velocity distribution of molecules in cadmium vapour give results which agree, within the experimental error, with Maxwell's law. A. A. Eldridge.

Rotating-crystal *X*-ray photographs. G. Greenwood (Min. Mag., 1927, **21**, 258—271).—An outline is given of the rotating-crystal *X*-ray method, and it is shown how the constants of the crystal are related to the distances between the "layer-lines" and the spaces between the spots. The method is applied to the examination of the tetragonal crystals of tetramethylammonium iodide and tetraethylammonium iodide. The former has the cell dimensions $a=8{\cdot}05$, $c=5{\cdot}75$ Å., containing two molecules of NMe_4I, and the space-group probably V_d^3 (not holohedral as given by Vegard in 1917). The latter is scalenohedral V_d^5 with $a=12{\cdot}29$, $c=6{\cdot}82$ Å., containing four molecules of NEt_4I. L. J. Spencer.

Difficulties in the quantitative determination of the scattering power of atoms for incident *X*-rays. J. M. Bijvoet (Chem. Weekblad, 1927, **24**, 574—579).—A discussion of the relative advantages of the single-crystal and crystal-powder methods of measuring scattering power. S. I. Levy.

Grating spectrograph for *X*-rays of long wave-length. J. Thibaud (J. Phys. Radium, 1927, [vi], **8**, 447—450).—A vacuum spectrograph involving a diffraction grating with tangential incidence and suitable for the spectroscopic examination of *X*-rays of long wave-length is described. The theory of such an instrument has already been given (A., 1927, 286). Data previously recorded (*ibid.*, 803) are discussed in greater detail. J. S. Carter.

Radiograph of a crystal having the face-centred cubic lattice. M. Majima and S. Togino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 75—78).—Laue photographs with *X*-rays incident at various angles on an aluminium crystal are reproduced. The orientation of the axis of any crystal having a face-centred cubic lattice can then be determined by a comparison of its radiograph with these photographs. A more accurate result is obtained, however, if various crystal faces are identified in the radiograph under examination by means of the standard photograph, and the orientation of the axis is determined from these by calculation. R. Cuthill.

Relation of the surface of crystals to their mass and volume. C. Hrynakovski (Arb. Komm. Math. Naturwiss. Posen, 1925, *A*, 2, 1—27; Chem. Zentr., 1927, i, 2626—2627).—The relative rapidity of growth of single planes in an individual crystal is a function of its mass, although this rule is valid only for a particular stage of growth. The quotient of the actual and hypothetical (spherical) surfaces is constant for each crystal; the value falls (1·593—1·229) with increasing symmetry in the triclinic, monoclinic, and regular systems. In twinning and overgrowth higher values are obtained. The quotient of the actual surface and mass or volume becomes disproportionately smaller with increase in the latter. A. A. Eldridge.

Crystal lattice of lithium nitride, Li_3N. R. Brill (Z. Krist., 1927, **65**, 94—99; Chem. Zentr., 1927, i, 2629—2630).—There are four molecules in the elementary cell; the space-group appears to be T^4, that of ammonia, so that the two molecules are analogous. A. A. Eldridge.

***X*-Ray study of magnesium oxychloride cement.** T. Maeda.—See B., 1928, 54.

Alkylamine alums, and other substitutions in ammonium aluminium sulphate. K. Spangenberg (Fortschr. Min. Kryst. Pet., 1927, **11**, 344—347; Chem. Zentr., 1927, i, 2630).—A discussion of the lattice structure of the alums and their derivatives. A. A. Eldridge.

Analysis of mixed crystals and alloys. A. Erdal (Z. Krist., 1927, **65**, 69—82; Chem. Zentr., 1927, i, 2707).—In the system potassium bromide–ammonium bromide true mixed crystals of the sodium chloride type are formed when 0—40% of ammonium bromide is present. Vegard's additivity rule is valid. Ammonium bromide has a $6{\cdot}87\times10^{-8}$ cm. In the system copper–silver true mixed crystals are formed only when the components are nearly pure. A. A. Eldridge.

***X*-Ray examination of iron nonacarbonyl, $Fe_2(CO)_9$.** R. Brill (Z. Krist., 1927, **65**, 85—93; Chem. Zentr., 1927, i, 2629).—The crystals are hexagonal, a 11·08, b 6·45, c 15·8 Å., with four molecules in the elementary cell. A. A. Eldridge.

Crystal structures of two intermetallic compounds [of copper with magnesium and with aluminium]. J. B. Friauf (J. Amer. Chem. Soc., 1927, **49**, 3107—3114).—The structures of the compounds Cu_2Mg and $CuAl_2$ were calculated from Laue, rotation, and powder photographs. The former compound has a unit cube of edge 6·99 Å. containing 8 molecules. The structure is derived from the space-group O_h^7 (Wyckoff's notation), the atoms having the same arrangement as the metal atoms in spinel (Bragg, Phil. Mag., 1915, [vi], **30**, 305). The unit cell of $CuAl_2$ is tetragonal, with $a=6·04$ Å. and $c=4·86$ Å., and contains 4 molecules (cf. Jette, Phragmén, and Westgren, B., 1924, 299). The atomic arrangement may be derived from the D_{4h}^{18} and other space-groups. S. K. Tweedy.

Crystallography of double nitrates of neodymium and praseodymium. R. B. Ellestad and F. A. Gray (Z. Krist., 1927, **65**, 140—141; Chem. Zentr., 1927, i, 2797).—The double nitrates, $2R(NO_3)_3,3M(NO_3)_2,24H_2O$, scalenohedral trigonal, hygroscopic, have the following values of c/a: neodymium–zinc 1·569, –nickel 1·579, –magnesium 1·576, –manganese 1·580, –cobalt 1·584; praseodymium–zinc 1·584, –nickel 1·576, –cobalt 1·567, –manganese 1·565, –magnesium 1·562. Etch-figures on the (111) faces form equilateral triangles. A. A. Eldridge.

***X*-Ray and electrical investigation of the system palladium–hydrogen.** J. O. Linde and G. Borelius (Ann. Physik, 1927, [iv], **84**, 747—774).—The lattice constant of pure palladium is given by $a=3·888+4·6\times10^{-5}(t-20)$ Å. Using a modified Debye method, the lattice constants of palladium in an atmosphere of hydrogen have been determined at 100°, 150°, and 200° over the pressure range 0·1—4 atm. The results are consistent with two phases: (i) hydrogen dissolved in palladium, lattice constant 3·888—3·92 Å., concentration of hydrogen below $c=0·5H/Pd$; (ii) palladium hydride Pd_2H, lattice constant 3·978. Two forms of palladium hydride Pd_2H probably exist. Under certain conditions, a third phase appears which is a continuation of the first phase, *i.e.*, it is a hydrogen solution with the concentration greater than $c=0·5H/Pd$.

When palladium is made the cathode in the electrolysis of, *e.g.*, sulphuric acid, the amount of hydrogen absorbed will vary with current density, time, and temperature. A number of palladium samples so treated have been studied by the Seeman–Bohlin method. As the hydrogen content increases, the system shows two phases at first, followed by a phase exhibiting a lattice constant of 4·034, which rises to 4·07 Å. with supersaturation. The relation between lattice constant and hydrogen concentration is approximately linear. The resistance of the palladium–hydrogen system increases regularly up to a concentration $c=0·75H/Pd$, and then decreases, the fall being very marked from $c=0·85$ onwards; whence it is concluded that the compound PdH has a relatively small resistance. From the pressure–concentration diagram it is concluded that the system is best envisaged as a metallic mixed-crystal system with the components Pd and PdH. R. A. Morton.

Notation of mercurammonium salts. M. François (Ann. Chim., 1927, [x], **8**, 341—362).—The theories of Rammelsberg (A., 1889, 347) and of Pesci (A., 1890, 1211; 1891, 268) concerning the structures of complex mercurammonium salts are criticised mainly in view of the author's work (A., 1899, ii, 657; 1900, ii, 208; 1906, i, 484). If in a system composed of one to four ammonium groups two hydrogen atoms are replaced by a mercury atom, it is possible to formulate all complex salts containing one to eight atoms of mercury, the majority of which are known. The additive compounds of mercuric halides and ammonia should be formulated as for other metallic salts, and not as dimercurammonium ammonium iodides; thus the instability of the compound obtained by passing ammonia over red mercuric iodide points to the formula $HgI_2,2NH_3$ and not $Hg_2NI,3NH_4I$ (Pesci, *loc. cit.*). H. Burton.

Lattice constant of thallous iodide. T. Barth (Z. physikal. Chem., 1927, **131**, 105—106; cf. A., 1926, 896).—By comparison with sodium chloride, the lattice constant of thallous iodide has been corrected to 4·198±0·002 Å. If the value of the exponent n (*loc. cit.*) be taken as 8, the corrected values for mixed crystals of thallous bromide and iodide are in agreement with the lattice theory of Grimm and Herzfeld (Z. Physik, 1923, **16**, 79). M. S. Burr.

Crystal structure of linneite, polydymite, and sychnodymite. G. Menzer (Fortschr. Min. Kryst. Pet., 1927, **11**, 315—316; Chem. Zentr., 1927, i, 2639).—Linneite is face-centred cubic, with edge of unit cube, containing 8 molecules of Co_3S_4, 9·398±0·007 Å., space-group probably O_h^7. Polydymite, $(Ni,Fe,Co)_4S_5$, has a 9·405±0·007 Å., and sychnodymite, $(Co,Cu,Ni)_4S_5$, has a 9·434±0·007 Å. Polydymite and sychnodymite are not considered to be essentially distinct from linneite. A. A. Eldridge.

Crystal structure of berzelianite. W. Hartwig (Fortschr. Min. Kryst. Pet., 1927, **11**, 307—308; Chem. Zentr., 1927, i, 2639).—Berzelianite, Cu_2Se, is face-centred cubic, the structure being probably that of fluorite with the atom positions: Se (0, 0, 0), Cu $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$; edge of unit cube containing 4 molecules, 5·731±0·008 Å. Natural berzelianite contains small quantities of silver and sulphur. A. A. Eldridge.

Crystal structure of the chondrodite series. W. H. Taylor and J. West (Proc. Roy. Soc., 1928, A, **117**, 517—532).—A qualitative *X*-ray examination by the rotating-crystal method and by the ionisation spectrometer has been made of crystals of chondrodite, humite, and clinohumite. The chondrodite group is of interest since it supplies a good example of morphotropy, the c/a or c/b ratio changing in a simple, progressive manner with additions of the molecule Mg_2SiO_4 (olivine) on passing through the series, whilst the a/b ratio remains unchanged. Furthermore, all three crystals are based on the hexagonal form of the two possible close-packed arrangements of oxygen atoms, and the Mg_2SiO_4 portion of the crystals is found to possess the olivine structure. The dimensions of the unit cells, including that of olivine, are as follows (the crystallographic *b* axis is taken as the *a* axis and *vice versa*, and *c′* denotes the thickness of the unit cell perpendicular to the *c* face): chondrodite (2 molecules in the unit cell, space-group probably C_{2h}^5, possibly C_{2h}^4), $a=4{\cdot}733$, $b=10{\cdot}27$, $c=7{\cdot}87$, $c'=5\times1{\cdot}488$ Å., $\alpha=109°\ 2'$; humite (4 molecules in the unit cell, space-group V_h^{16}), $a=4{\cdot}738$, $b=10{\cdot}23$, $c=20{\cdot}86$, $c'=14\times1{\cdot}490$ Å.; clinohumite (2 molecules in the unit cell, space-group probably C_{2h}^5, possibly C_{2h}^4), $a=4{\cdot}745$, $b=10{\cdot}27$, $c=13{\cdot}68$, $c'=9\times1{\cdot}492$ Å., $\alpha=100°\ 50'$; olivine (4 molecules in the unit cell, space-group V_h^{16}), $a=4{\cdot}755$, $b=10{\cdot}21$, $c=5{\cdot}98$, $c'=4\times1{\cdot}495$ Å. From an examination of the *X*-ray rotation photographs, it appears that the crystals of the chondrodite series consist of alternate layers, parallel to the *c* face, of $Mg(OH)_2$ and Mg_2SiO_4, based on an arrangement of oxygen atoms and OH-groups in hexagonal close packing. The oxygen atoms appear to determine the dimensional relations of the unit cell, whilst the magnesium and silicon atoms control the pattern and thus the cell symmetry. The $Mg(OH)_2$ layer has the same thickness in each crystal, but that of the olivine layer (measured perpendicular to the *c* face) has the ratio of 2 : 3 : 4 in chondrodite, humite, and clinohumite, respectively. The layers of olivine structure in humite, unlike those in chondrodite and clinohumite, are bisected by reflexion planes parallel to the *c* face. This causes alternate layers of $Mg(OH)_2$ in humite to be mirror images of each other, and explains the orthorhombic symmetry of the crystal.

L. L. Bircumshaw.

Crystallography of sucrose. G. Vavrinecz (Z. Krist., 1927, **64**, 543; Chem. Zentr., 1927, i, 2406).—New determinations give the ratios $a:b:c=1{\cdot}2518:1:0{\cdot}89458$; $\beta=102°\ 55{\cdot}24'$.

A. A. Eldridge.

Crystal form of carbamide nitrate. A. Hestermann (Z. Biol., 1927, **86**, 561—568).—Crystallographic data are cited from which it is concluded that carbamide belongs to the monoclinic system.

E. A. Lunt.

Crystallography of some simple benzene derivatives. W. A. Caspari (Phil. Mag., 1927, [vii], **4**, 1276—1285).—The lattice dimensions of crystals of the phenylenediamines and aminophenols are recorded. R. Cuthill.

New kinds of mixed crystals. VI. D. Balarev [with R. Kaischev and G. Kratschev] (Z. anorg. Chem., 1927, **168**, 154—162; cf. this vol., 7).—When barium sulphate is precipitated in presence of increasing amounts of alkali metal chlorides or potassium nitrate, the amount of alkali salt included in the precipitate first increases to a maximum, at which the crystalline form of the precipitate changes, then falls again, these results being in agreement with Grimm's observations on the inclusion of potassium permanganate (A., 1924, ii, 828). On the author's theory, the maximum corresponds with the point at which the foreign salt adsorbed on the exterior of the sulphate crystals commences to influence their porosity. In support of this view, it is further found that the amount of foreign salt in the crystals is, in general, the greater the more water they contain. These facts also lend confirmation to the theory that the occlusion by barium sulphate of various salts of a different crystalline form is a purely mechanical effect, depending on the existence of an internal surface within the sulphate crystals. As a cause of this porosity of the sulphate particles, the existence of two different forms of the salt suggested itself, the transition from one to the other in the solid state increasing the fineness of capillaries already present, and also producing new ones; this was found to be so by experiment. By precipitating barium chloride with sulphuric acid at the b. p. in a solution acidified slightly with hydrochloric acid, or in the cold, a form of barium sulphate is produced having a solubility at 18—20° of 2·3 mg./litre of water, which agrees with the accepted value obtained by the conductivity method. From a solution very strongly acidified with hydrochloric acid, however, a form with a solubility of 3·3 mg. at 18—20° separates, this being in aqueous solution at the ordinary temperature metastable in respect of the other variety, and passing into it either spontaneously or on addition of nuclei or barium chloride solution to its saturated solution. R. Cuthill.

Free energies of solid compounds deduced from their crystal structure: with special reference to calcite and aragonite. J. L. Buchan (Trans. Faraday Soc., 1927, **23**, 672—676).—By considering the simplest lattice, determined from *X*-ray measurements, from which the crystal can be built up, regarding the ions as point charges, and calculating the work required to bring up each ion from an infinite distance to its place in the lattice, the value for the free energy of formation of calcite from Ca^{++} and CO_3^{--} ions is found to be −4060 g.-cal/mol. at 18°, and for aragonite −3680 g.-cal./mol. Hence, at 18°, aragonite is unstable with regard to calcite, and the free energy of transition from aragonite to calcite is −380 g.-cal./mol. (cf. this vol., 133). The value for the free energy of formation of calcite from the elements calcium, carbon, and oxygen has also been calculated and compared with that deduced from thermochemical data. In the same way the free energies of aragonite, ferrous and manganous carbonates, sodium nitrate, ammonium iodide, and sodium chloride have been calculated, and the results tabulated. M. S. Burr.

Evaporation and dissolution phenomena of zinc. G. Aminoff (Z. Krist., 1927, **65**, 23—27; Chem. Zentr., 1927, i, 2707).—Only facets corresponding with the lattice planes (0001), (1011), (1120), and (1010) give goniometer reflexions. The rate of dissolution in sulphuric acid is lowest in the direction of the *c*-axis. A. A. Eldridge.

Magnetic properties of single crystals of nickel. W. Sucksmith, H. H. Potter, and L. Broadway (Proc. Roy. Soc., 1928, **A**, **117**, 471—485).—The crystals were prepared from Mond pellets by slow cooling from the molten liquid contained in a long cylindrical alundum crucible, and the specimens were subsequently ground by hand on a fine oil-stone. Measurements were made of the component of magnetisation parallel to the applied field (I_P) and perpendicular to the field (I_N) in the principal crystal planes, and of the variations of these two vectors on rotating the field in the plane of the disc. The ballistic method employed by Honda and Kaya was used for the measurement of I_P, whilst I_N was determined by Weiss' torsion method. It is shown that the existence of directional properties in the crystal invalidates the use of the torsion method for the measurement of I_P. The magnetisation coincides with the field when the latter is applied along the symmetry axes, the direction of easiest magnetisation being along the trigonal axis. The results are compared with the data for iron obtained by previous investigators. L. L. Bircumshaw.

Magnetic properties of single crystals of nickel. S. Kaya and Y. Masiyama (Nature, 1927, **120**, 951—952).—A record of experiments performed with crystals (7×2·3 cm.) of nickel grown by slowly lowering out of an electric furnace a crucible of the molten metal. A. A. Eldridge.

The metallic state. W. Hume-Rothery (Phil. Mag., 1927, [vii], 4, 1017—1045).—The various theories of the metallic state are discussed critically with special reference to properties other than those of electrical or thermal nature. Only the electron lattice theory of Lindemann (A., 1915, ii, 47) gives a rational picture of the way in which the crystal lattices of metals are built up, and the same theory is in general agreement with the compressibility data and tensile properties. This theory is the only one giving an explanation of the plasticity of metals, which is regarded as due to the relatively great difference in size of the positive ions and negative electrons from which the lattice is built up. Owing to the precessional motion of the elliptical electronic orbits, the zones of repulsion round the metallic ions will vary periodically, and a motion of this type is thought to be the cause of supraconductivity in some metals at the temperatures of liquid helium. This conception is in agreement with the fact that supraconductivity is shown by some metals and not by others. Relations between the inter-atomic distances in metals and salts are pointed out.

W. Hume-Rothery.

Cohesion: a general survey. C. H. Desch (Trans. Faraday Soc., 1927, **24**, 53—64).—A general review of phenomena in connexion with cohesion, summarised under the following headings: (1) relations between tenacities of substances measured by different kinds of tests, (2) elastic limit, (3) failure by fatigue, (4) hardening effect produced by the cold working of metals, (5) dependence of the manner of deformation on the rate of application of stress and the time for which it is applied, (6) nature of the crystal boundaries in metals, and the intercrystalline cement theory, (7) nature of crystal surfaces, (8) adhesion of solders or other materials, thin films of which can unite solid masses, also the adhesion of electrodeposited material, (9) diffusion in solids, (10) nature of cohesion and the application of the equation of van der Waals. W. Hume-Rothery.

Properties of non-metallic elements in relation to their cohesive forces. A. M. Taylor (Trans. Faraday Soc., 1927, **24**, 157—159).—In non-metals the linkings are homopolar and the cohesive force in the solid is due to electrical doublets arising from the deformation of the electronic shells. In polar salts the linkings are heteropolar and the cohesive force is due to the ionic charges plus the above electrical doublets. The doublets are produced under the influence of an electric field of intensity E by deformation of the electronic shells, and their moments may be written $p=\alpha E$, where the constant α may be found by measurement of the atomic refractivity, or from the correction of the Rydberg number in the formulæ for the series spectra. The attractive force between two doublets falls off as the inverse fourth power of the distance, which results in a greater value for the compressibility k than when the inverse square law alone is concerned. Hence, in salts, an increase in α leads to an increase in k, and this is confirmed experimentally for potassium chloride, bromide, and iodide. In non-metals, both α and k are high, and the force F between two doublets may be written $F=cp^2/r^4-\beta/r^n$, which on differentiating and eliminating β from the equilibrium condition ($F=0$, $r=r_0$) leads to $F^1=-cp^2(4-n)/r^5$, the corresponding expression for polar compounds being $F^1=-(er)^2(2-n)/r^5$. The quantity F^1 varies rapidly with r, and more rapidly in non-metals than in polar compounds, indicating that the restoring force on a displaced particle is more anharmonic in the non-metals. In agreement with this, the thermal expansion of non-metals is higher than that of salts. When high values of k are found in non-metallic elements or in polar compounds, it is probable that the units possess considerable electrical moment.

W. Hume-Rothery.

Relation of fatigue to cohesion in metals. H. J. Gough (Trans. Faraday Soc., 1927, **24**, 137—148).—A summary of recent work carried out at the National Physical Laboratory on cyclical stress relations, the nature of deformation by plastic strain slip, the hardening produced by slip, and the manner of the initiation and propagation of fatigue cracks. R. W. Lunt.

Relation of hysteresis to cohesion and fatigue in metals. B. P. Haigh (Trans. Faraday Soc., 1927, **24**, 125—137).—Experiments are described in which metallic rods have been subjected to approximately sine-wave form tensile stresses of frequency 2000 cycles per sec. Annealed ductile metals are characterised by three well-defined sections of the hysteresis–time curve: a brief evolution of heat during not more than 2·5×10⁵ cycles, during which period the hysteresis falls to a low but slowly rising value which constitutes the second stage; in the third stage the hysteresis rapidly increases followed by fracture. Curves typical of a number of metals are discussed. R. W. Lunt.

Plasticity problems in metals. G. Sachs (Trans. Faraday Soc., 1927, **24**, 84—92).—Mathematical analyses of a number of characteristic types of distortion in metals produced by shear are reviewed and discussed with particular reference to cases of industrial importance. R. W. Lunt.

Relation between cohesion and tensile and dielectric strength. A. F. Joffé (Trans. Faraday Soc., 1927, **24**, 65—72).—Experiments are described in which, by avoiding surface cracks, the tensile strength of rock salt is 160 kg./mm.; the value deduced from Born's theory is 200 kg./mm. The discrepancy between the observed values of the dielectric strength of glass, mica, rosin, picein, oil, and benzene and those predicted by theory (approx. 10^8 volts/cm.) has been shown to be non-existent by investigating the dielectric strength of thin sheets of these substances. The accepted values refer to sheets of greater thickness than 5 μ; these low values are attributed to the heat dissipated in the dielectric in an intense field by existing ions and by new ions formed by collision in the relatively long path between the electrodes, since it is known that the dielectric strength diminishes rapidly as the temperature rises. R. W. Lunt.

Mechanical and electrical cohesion and molecular forces. A. Joffé (Physikal. Z., 1927, **28**, 911—916).—Born's electrical theory of the solid state appears to break down in respect of cohesion since rock salt comes apart under a tension of 0·4 kg./mm.², whereas according to the theory 200 kg./mm.² should be required. If a crystal of rock salt is suspended in hot water and its resistance to tension then determined, it is found that the moist crystal can withstand up to 30—160 kg./mm.² without breaking. It is argued that inequalities in the crystal surface tend to disappear as the layers of salt are dissolved and that the high resistance of the perfect crystal is in accordance with theory. Similarly, a globule of salt was subjected to cooling in liquid air and then plunged into hot water or molten lead. The crystal withstood in this way pressures of 25 and 70 kg./mm.² without disintegration.

The resistance of crystals to electrical forces shows that whilst 10×10^7 volts/cm. represents the theoretical voltage, actually only 3×10^5 volts are required for disruption of rock salt. The discrepancy is general and the following factors may operate in causing it: (1) the higher the temperature the greater the tendency to disruption under lower voltages, and as heat may be developed by the current, this factor will tend to lower the disrupting voltage; (ii) excitation of ions by collisions with the ions first formed; (iii) local concentration of the electrical field; (iv) widening of the breach by mechanical effects following the original effect. It is shown that very thin films of dielectrics will actually withstand voltages not much less than those predicted by the electrical theory. R. A. Morton.

Incidence of chemical attraction on cohesion. T. W. Richards (Trans. Faraday Soc., 1927, **24**, 111—120).—Following an historical review it is suggested that mechanical equilibrium in atomic contacts is determined by an expression of the following form: $p+\Pi_0(v_0/v)^m=\Pi_\rho(v_0/v)^n+P_e$, where p is the external pressure, Π_0 the sum of all intrinsic compression effects, Π_ρ the intrinsic distending pressure, $P_e=T\alpha/\beta$ the thermodynamic thermal pressure, where α and β are the coefficients of expansion and compression respectively, v is the volume, and v_0 the volume at some standard state at which Π_0 is defined. It follows that $\beta=1/\Pi_0(n-m)$. In the case of a binary compound the following expression is advanced for $\beta:x/(n-m).[x/\Pi_1+(x-1)/\Pi_2]$, where x is the fraction of each atom subjected to a cohesive pressure Π_1, and $1-x$ the fraction subjected to intense chemical pressure Π_2. This analysis indicates the existence of internal pressures in non-volatile solids of the order of the tensile strength of glass; such values are consistent with the heats of formation and of evaporation of such substances. R. W. Lunt.

Interweaving of crystal gratings. G. von Hevesy and G. Rienäcker (Ann. Physik, 1927, [iv], **84**, 674—688).—The diffusion of silver iodide into cuprous iodide, and *vice versa*, has been investigated at 480°; the process is found to be reversible, the cuprous iodide being uniformly distributed throughout the entire mass after a period of 12 hrs. The velocity of diffusion has been determined from measurements of the conductivity of the diffusing layers. If a layer of cuprous iodide be placed in contact with a layer containing an equivalent amount of silver sulphide, then after 4 days the iodide layer contains 7·8 mol.-% of cuprous iodide and 92·2 mol.-% of silver iodide; the sulphide layer contains 8·2 mol.-% of silver sulphide and 91·8 mol.-% of cuprous sulphide. Approximately the same composition of iodide and sulphide layers is observed if a layer of silver iodide is allowed to diffuse into a layer containing an equivalent amount of cuprous sulphide. These results show that the process is reversible and that a true equilibrium is reached, the crystal grating becoming interwoven.

R. W. Lunt.

Radiate crystallisation. B. Popov (Fortschr. Min. Kryst. Pet., 1927, **11**, 320—321; Chem. Zentr., 1927, i, 2627).—The phenomenon was investigated with malonamide and resorcinol.

A. A. Eldridge.

Temperature factors of *X*-ray reflexion for sodium and chlorine in the rock-salt crystal. I. Waller and R. W. James (Proc. Roy. Soc., 1927, **A**, **117**, 214—223).—Theoretical. If F_1 and F_2 are the average atomic scattering factors, at a given angle, for chlorine and sodium, respectively, at 0° Abs., then the amplitude factor at a temperature T, for spectra where the waves scattered by the chlorine and sodium atoms are in phase, will be $F_1e^{-M_1}+F_2e^{-M_2}$, and for spectra where they are out of phase, $F_1e^{-M_1}-F_2e^{-M_2}$, M_1 and M_2 being functions of T. It is shown that if allowance is made for the different values of M for the two atoms, Waller's theoretical formula for the temperature coefficient (A., 1927, 816) agrees with experiment in the case of rock salt from 86° to 500° Abs. L. L. Bircumshaw.

Focal structure of smectic substances. R. Gibrat (Compt. rend., 1927, **185**, 1491—1492).—Assuming that the forces acting on each element of homogeneous matter of a smectic body are constant in magnitude and direction, and may be represented by a single resultant, the positions of such resultants are given by an ellipse and a hyperbola placed focally to one another. This structure is often seen in practice, *e.g.*, when an isotropic liquid is cooled.

J. Grant.

Salts with low m. p. II, III, and IV. Electrical conductivity, viscosity, and molecular

state of fused picrates. P. Walden, H. Ulich, and E. J. Birr (Z. physikal. Chem., 1927, **131**, 1—48; cf. this vol., 107).—An apparatus is described for the measurement of the electrolytic conductivity of small quantities of fused salts. Measurements of the conductivity of twenty-two alkylammonium picrates, at temperatures between 40° and 220° at intervals of 10°, have been made. At the higher temperatures, the dependence of equivalent conductivity on temperature may be indicated by the formula $\lambda = A(t-\theta)^2$, where A and θ are characteristic constants. With increase in the number of $:CH_2$ groups, but the same degree of substitution, the equivalent conductivity decreases, but the value also depends on the character of the molecule, *e.g.*, *n*-butyl- or *n*-amyl-ammonium picrate has a higher conductivity than the corresponding *iso*-compound. The degree of substitution has also a marked influence. For the same mol. wt., the conductivities of the salts of the primary, secondary, tertiary, and quaternary amines are approximately in the ratio of 1 : 2 : 1·7 : 7. The temperature coefficient of conductivity is $2/(t-\theta)$ or $2\sqrt{A}/\theta$. Thus, at equally reduced temperatures $t-\theta$, all the salts have the same temperature coefficient. The results bear out the observations of Kohlrausch on solutions, and of Biltz on conductors of all kinds (A., 1924, ii, 515), that the conductivity temperature coefficient in all conductors is greater the smaller the conductivity. For the primary and quaternary amines, θ is approximately constant, the mean values being 76·7 and 41·7, respectively. The viscosities of the same picrates have been determined by Poiseuille's method in an apparatus which is described. The fluidity $\varphi = 1/\eta$ may be represented with considerable accuracy by the formula $\varphi = a(t-\delta)^2$, where α and δ are characteristic constants. The mean values for δ in the primary and quaternary groups are 83·7 and 49, respectively, only a little higher than the corresponding values for θ in the conductivity formula. The values of α, however, are very much larger than the values of A for the same salts. With increasing mol. wt., and the same degree of substitution, the viscosity first diminishes and then increases. For the same mol. wt., when the number of $:CH_2$ groups is between 7 and 10, the viscosities of the normal primary, secondary, tertiary, and quaternary amines are approximately in the ratio of 4 : 1·6 : 1·2 : 1. The salts with the greatest fluidity have the smallest temperature coefficient. The molecular state of the fused substituted ammonium picrates is discussed. By comparison of the conductivity data for the fused salts with those for infinitely dilute solutions, it is concluded that the picrates of the quaternary bases are practically completely dissociated, whilst those of the secondary are 50% and of the tertiary and primary 20% dissociated. The effect of increasing size of cation is similar to that in infinitely dilute solution, and may be explained by decreasing mobility of the ion with increasing size, without at the same time any appreciable change in degree of ionisation. In accordance with Bjerrum's conception, a non-ionised molecule is regarded as a pair of ions which, through marked reciprocal deformation, have acquired properties very different from those of the free or associated ions. M. S. Burr.

Theory of electric and magnetic birefringence in liquids. C. V. Raman and K. S. Krishnan (Proc. Roy. Soc., 1927, A, **117**, 1—11).—It has been shown that the Langevin–Born theory of electrical birefringence fails to give the magnitude of the Kerr constant in liquids correctly in terms of the constants of the molecule as determined in the gaseous condition (A., 1927, 397), and a modification of the theory is suggested. According to Langevin and Born, whilst the individual molecule is anisotropic, the polarisable matter present round it is so distributed that the local polarisation field acting on the molecule is independent of its orientation in the field. This assumption cannot be correct in a dense fluid, and it is now suggested that the orientation of the molecule determines the distribution of matter around it, and therefore also the local polarisation field acting on it. When the Langevin–Born theory is modified so as to take into account this "anisotropic" polarisation field, the resulting expression is in better accordance with facts than the original expression. In general, the influence of the anisotropy of the polarisation field is to diminish the magnitude of the Kerr effect to be expected. This is explained as being due to the fact that the longer geometrical dimension of a molecule tends to be also the direction of maximum electrical and optical susceptibility. The distribution of the molecules in a dense fluid therefore tends to be such that their mutual influence is equivalent to an apparent diminution in the anisotropy of the molecules.

L. L. Bircumshaw.

Dispersion of metals in solid salts under the action of an electric current. T. Peczalski (Compt. rend., 1927, **185**, 1588—1591).—An iron tube filled with a salt (potassium, barium, or strontium chloride) and containing a copper rod placed axially, was heated to a temperature below the m. p. of the salt, and the iron and copper portions were then connected to a source of current. Above 300° the conductivity increased rapidly after 1 hr. when the copper was made positive, and copper was detectable in the salt. When the copper was negative the increase was slower and iron was detectable in the salt. The use of aluminium and alumina in place of the copper and the salt, respectively, gave negative results except for an increase in conductivity in the former case when the iron was positive. The results are explainable by emission of ions of the metal, whilst there is also evidence of electrolysis of the salt vapours, with the formation of unstable compounds between the metal and the cations and subsequent deposition of the former in the salt.

J. Grant.

Inductive power in the gaseous state. Cordonnier and Guinchant (Compt. rend., 1927, **185**, 1448—1450).—Measurements for 33 gases of inductive power, K, relative to air, have shown that for mixtures with air or carbon dioxide the dielectric excess, $K-1$, is a linear function of the partial pressure of one of the constituents and that the relation is subject to the same degree of accuracy as Dalton's law. The ratio L/R (L the Lorenz constant, R the molecular refractivity) is an index of chemical constitution. For normal substances it is 1, whilst the substitution of hydrogen by a methyl group increases R by 4·6, although the increase is much greater if the molecule contains an electronegative group. If $L>R$, the value of L is usually greater for the gaseous than for the liquid state at the same temperature. For pairs of isomerides the compound containing an enolic or a replaceable hydrogen atom has the highest inductive power. J. GRANT.

Effect of *X*-rays on the crystallisation of antimony. M. CAMPA (Nuovo Cim., 1927, 4, 28—31; Chem. Zentr., 1927, i, 2630—2631).—Antimony subjected during solidification to moderately hard X-rays has a Hall coefficient 15% smaller than the normal. A. A. ELDRIDGE.

Magnetic analysis. O. VON AUWERS (Physikal. Z., 1927, **28**, 871—882).—A summary of published work in which the advantages of magnetic analysis are stressed. The theoretical basis is discussed together with the relationship between magnetic and mechanical properties. Various types of practical application are instanced. R. A. MORTON.

Thermo-electric effect in single-crystal bismuth. R. W. BOYDSTON (Physical Rev., 1927, [ii], **30**, 911—921).—The thermal *E.M.F.* against constantan of single-crystal bismuth was determined for various orientations, and the thermo-electric power and Peltier heat were computed. The Peltier heat and difference in Thomson coefficients for $\mathrm{Bi}\perp$ against $\mathrm{Bi}\|$ were also computed. Polycrystalline bismuth and zinc give results in accord with Linder's formula. A. A. ELDRIDGE.

Permeability of iron at high frequencies. C. GUTTON and (MLLE.) J. MIHUL (Compt. rend., 1927, **185**, 1197—1198; cf. A., 1927, 614).—The mean magnetic permeabilities for a constant frequency of soft iron and piano wires are constant for small field strengths (up to about 1 gauss) and then increase with the field strength. J. GRANT.

Toluoylenol. S. RÖSCH (Fortschr. Min. Kryst. Pet., 1927, **11**, 327—328; Chem. Zentr., 1927, i, 2641).—Enolic toluoylbenzoylmethane, $C_6H_4Me\cdot C(OH){:}CHBz$ or $C_6H_4Me\cdot CO\cdot CH{:}CPh\cdot OH$ forms rhombic tablets, $a:b:c=3{\cdot}092:1:1{\cdot}166$. The refraction increases from the red to the violet: α 1·635—1·690, β 1·644—1·805, γ 1·932—2·359. The double refraction is very great: $\beta-\alpha$ 0·009—0·015, $\gamma-\alpha$ 0·297—0·669, $\gamma-\beta$ 0·288—0·554. A. A. ELDRIDGE.

Temperature measurements and catalytic wall effects in the glow discharge. R. SEELIGER and H. STRAEHLER (Physikal. Z., 1927, **28**, 894—904).—The temperatures within a discharge tube have been measured by means of inserted thermo-elements and by a manometric device based on the sagging of a thin sheet of mica under pressure. Using pure neon and pure hydrogen, curves have been obtained showing the temperature developed at points from 0 to 15 mm. from the axis of the discharge tube with discharges running under known currents and with defined gas pressures. When the thermo-element was protected from actual contact with the discharge by means of a glass sheath, the results were fundamentally divergent from those obtained with a bare thermo-element. Provided, however, that the outside of the glass sheath was covered with a thin film of metal it was found that the results with the bare thermo-element could be reproduced. Experiments with gases containing traces of impurities showed that the temperatures developed in the discharge tube were consistently higher for the bare thermo-element than for the sheathed element. Pure gases showed little sign of this discrepancy. It is concluded that the results are not due to experimental error, but to a real difference in temperature brought about by the catalysing action of the metallic surface. R. A. MORTON.

Critical temperatures of boron trichloride and silicon tetrachloride. T. W. PARKER and P. L. ROBINSON (J.C.S., 1927, 2977—2981).—The critical temperatures of these substances, purified by vacuum fractionation, were determined by means of an improved form of apparatus. The temperature recorded at the appearance of the meniscus in the cloud during the change from vapour to liquid was taken as the critical temperature. The mean values are 178·8±0·2° for boron trichloride and 233·6±0·2° for silicon tetrachloride. Slightly lower values were, however, obtained by maintaining the substance near the critical temperature for some time, or after heating it at a higher temperature. G. A. ELLIOTT.

Thermal conductivities of certain liquids. G. W. C. KAYE and W. F. HIGGINS (Proc. Roy. Soc., 1928, **A**, **117**, 459—470).—The thermal conductivities of a number of common liquids have been determined by a plate method, over a range of temperatures up to 200° (where feasible). The apparatus consisted of two aluminium blocks, the upper "hot block" containing an electric heating coil and the lower "cold block" being provided with radiating fins. The test liquid was contained in a small trough running round the upper end of the cold block, and formed a layer, about 20 cm.² in area and up to 0·5 mm. thick, between the two blocks. An aluminium guard plate containing a subsidiary heating coil was mounted above the hot block and separated from it by a thin film of air, and by adjusting the current through the subsidiary coil it was arranged that the energy supplied to the main heating coil should be almost all transmitted downwards through the test liquid. Corrections were applied for lateral heat loss from the hot block, heat transferred through the liquid in the trough, and heat lost by evaporation from the liquid in the trough. The following results were obtained for the conductivity at 20° and the temperature coefficient α in the expression $K_t=K_0(1+\alpha t)$, respectively: water, 0·0014, +0·001; glycerol, 0·00068, +0·0005; castor oil, 0·00043, −0·0005; aniline, 0·00041, 0·0000; olive oil, 0·00040, −0·0003; cylinder oil, 0·00036, 0·0004; transformer oil, 0·00032, −0·0006; "B.P." paraffin, 0·00030, −0·0001; paraffin oil, 0·00029, −0·0005. L. L. BIRCUMSHAW.

M. p. of the substituted amides of dibasic acids. C. R. BARNICOAT (J.C.S., 1927, 2926—2929).—The dibasic acids and their amides, anilides, *o*- and *p*-toluidides, and *p*-bromoanilides, up to the

C_{13}-member, have been prepared and their m. p. determined. The successive members of each of these series show alternation in m. p. For the free dibasic acids this alternation is considerably greater than for the corresponding monobasic acids, but it diminishes with increasing mol. wt. With the anilides the alternation appears to exhibit an unusual arrangement in groups of four members, whilst for the toluidides and *p*-bromoanilides it is less marked and more regular. An explanation of these variations on the theory of alternating polarities is put forward. The following new compounds are described: *Dicarboxylamides* of n-*nonane*, m. p. 173°, and n-*decane*, m. p. 189°; *dicarboxyanilides* of n-*nonane*, m. p. 156°, n-*decane*, m. p. 191°, and n-*undecane*, m. p. 158°; o-*toluidides* of *glutaric*, m. p. 222°, *adipic*, m. p. 222°, *pimelic*, m. p. 174°, *suberic*, m. p. 185°, *azelaic*, m. p. 171°, and *sebacic*, m. p. 179°, acids; *dicarboxy*-o-*toluidides* of n-*nonane*, m. p. 164°, n-*decane*, m. p. 164°, and n-*undecane*, m. p. 142°; p-*toluidides* of *glutaric*, m. p. 218°, *adipic*, m. p. 241°, *pimelic*, m. p. 206°, *azelaic*, m. p. 198°, and *sebacic*, 201°, acids; p-*bromoanilides* of *succinic*, m. p. 284°, *glutaric*, m. p. 256°, *adipic*, m. p. 268°, *pimelic*, m. p. 240°, *suberic*, m. p. 248°, *azelaic*, m. p. 225°, and *sebacic*, m. p. 225°, acids; *dicarboxy*-p-*bromoanilides* of n-*nonane*, m. p. 215°, n-*decane*, m. p. 213°, and n-*undecane*, m. p. 202°.

G. A. ELLIOTT.

Glass. I. Transition between the glassy and liquid states in the case of some simple organic compounds. G. S. PARKS and H. M. HUFFMAN (J. Physical Chem., 1927, **31**, 1842—1855).—The specific heats of *n*-propyl alcohol and propylene glycol in the liquid and in the supercooled states have been determined by the method previously described (A., 1925, ii, 491). There is a sharp change in specific heat during the transition between the glassy and the liquid states. The specific heat–temperature curves are similar in form to those of ethyl alcohol (*loc. cit.*) and of glycerol (Gibson and Giauque, A., 1923, ii, 124), the sharp rise in specific heat occurring at higher temperatures as the number of hydroxyl groups in the molecule increases. The specific heat and thermal conductivity in the glassy state are the same as in the crystalline condition, but are different from the values observed for the liquid state. A temperature range, 17° for *n*-propyl alcohol, 30° for propylene glycol, and 40° for glycerol, marks the transition between the glassy and liquid states.

L. S. THEOBALD.

Density of molten magnesium. K. ARNDT and G. PLOETZ (Z. physikal. Chem., 1927, **130**, 184—186).—The density of magnesium, determined by a sinker method in an atmosphere of hydrogen, is found to range from 1·58 to 1·51 over the temperature interval 666—720°. The work of Edwards and Taylor (B., 1923, 608) is in good agreement, and the final values given are 1·601, 1·536, and 1·470 at 650°, 700°, and 750° respectively. L. S. THEOBALD.

Physical properties of some derivatives of *cyclo*hexane. N. N. NAGORNOV and L. A. ROTINJANC (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 162—173; cf. A., 1925, ii, 646).—Results are given of measurements of the vapour pressures at different temperatures, the critical temperatures, the m. p., and the specific volumes from the b. p. to the m. p. for methyl*cyclo*hexane, chloro*cyclo*hexane, and *cyclo*hexanol. For *cyclo*hexane, t_c 281·0°, the vapour pressure is given by $\log P=7{\cdot}01516-1306{\cdot}4/(235{\cdot}24+t)$; $dP/dt=22{\cdot}89$ mm. at the b. p. For methyl*cyclo*hexane, b. p. 100·8°, t_c 301·5°, the specific volume is given by $1{\cdot}27143/(1-0{\cdot}001084t-0{\cdot}000000126t^2-0{\cdot}0000000033t^3)$ and the vapour pressure by $\log P=6{\cdot}50393-1089{\cdot}9/(200{\cdot}0+t)$; $dP/dt=21{\cdot}1$ mm. at the b. p. For chloro*cyclo*hexane, b. p. 142·9°, m. p. −43·9°, t_c 314—325°, the specific volume is expressed by $0{\cdot}98228/(1-0{\cdot}0009564t+0{\cdot}0000001758t^2-0{\cdot}00000000303t^3)$; $\log P=7{\cdot}15895-1619{\cdot}5/(235{\cdot}6+t)$ and $dP/dt=19{\cdot}9$ mm. at the b. p. For *cyclo*hexanol, b. p. 160·6°, t_c 377°, the specific volume is $1{\cdot}05929/\{1-0{\cdot}0007856(t-25)-0{\cdot}000001472(t-25)^2\}$; $\log P=6{\cdot}80369-1199{\cdot}1/(145{\cdot}0+t)$, $dP/dt=22{\cdot}5$ mm. at the b. p. Except for *cyclo*hexanol, which is associated, the values of the ratio between the temperature Abs. and volume is almost constant for these compounds.

Albertosi's formula, $d^{5/3}=A-BT$ (A., 1916, ii, 214), may be converted into the form $V=V_{T=0}/(1-CT^{3/5})$, where V and $V_{T=0}$ are the specific volumes at T° Abs. and 0° respectively, and C is a constant, equal to A/B. In this form, the expression differs from Mendeléev's law for the expansion of liquids principally in the exponent in the denominator. When this law is applied over a wide temperature range at low temperatures, deviations are observed, the magnitudes of these increasing as the temperature is lowered. For liquids obeying Cailletet and Mathias' law of the linear dependency on the temperature of one half of the sum of the densities of liquid and vapour, at temperatures corresponding with low vapour pressures the vapour pressure may be neglected, as it falls within the limits of accuracy of ordinary measurements of liquid density. In such case the law of expansion becomes $d=a-bt$ or $V=V_0/(1-kt)$, which is Mendeléev's law. As the vapour pressures of most organic compounds for pressures up to 100 mm. vary around 0·0004, this law should hold under these conditions, and this is actually confirmed by the data for methyl*cyclo*hexane. If it is assumed that the coefficient k of Mendeléev's formula depends on the temperature and this dependency is expressed by $k=a+bt+ct^2$, the formula becomes $V=V_0/(1+at+bt^2+ct^3)$, which agrees very accurately with the experimental data for any temperature interval nearly to the b. p. T. H. POPE.

Relation of vapour pressure to particle size. S. L. BIGELOW and H. M. TRIMBLE (J. Physical Chem., 1927, **31**, 1798—1816).—Thomson's equation connecting vapour pressure with particle size is critically examined and is considered to have a very restricted range. Microscopical examination of sulphur droplets shows that whenever clear zones appear, as in Ostwald's experiment, the central, growing particle is always crystalline. No measurable distillation occurs when all droplets are kept in the liquid state, at a constant temperature, which is contrary to the requirements of Thomson's equation. Other liquids which wet glass show no distillation at a constant temperature, and it is concluded that such liquids form droplets in equilibrium with a continuous film of the liquid itself on the wetted solid. With mercury, however, large globules were found to increase in size at the expense of the smaller drops, but this distillation ceased at the end of a few days before the complete disappearance of the latter. With iodine, naphthalene, and camphor, such growth could not be detected at a constant temperature, but it could be always observed when slight temperature differences were not eliminated. Distillation between a large and small meniscus in the case of benzene, toluene, ether, or water is too slow to permit the determination of the equilibrium position of the meniscus. The utility of Thomson's equation is questioned. L. S. Theobald.

Equation of state for easily liquefied hydrocarbons. II. Weight of a litre of *n*-butane. M. Beckers (Bull. Soc. chim. Belg., 1927, 36, 559—590).—A repetition of van Bogaert's determination of the weight of a litre of *n*-butane (A., 1927, 719) at 0° and under 710 mm. pressure has given the value 2·5192 g. R. Cuthill.

Change of compressibility with pressure. L. H. Adams (J. Washington Acad. Sci., 1927, 17, 529—533).—The compressibilities, β, of a number of elements and minerals have been determined directly or, when possible, from the change in length produced by pressure, P, the latter method being the more sensitive. When β is plotted against $d\beta/dP$ a curve is obtained from which the order of magnitude of the pressure coefficient of compressibility may be determined if the mean compressibility over a given pressure range is known. Tellurium and the alkali halides do not fall on the curve. J. Grant.

Effect of temperature on the viscosity of air. R. S. Edwards (Proc. Roy. Soc., 1927, **A**, 117, 245—257; cf. Williams, A., 1926, 234; Rankine, *ibid.*, 671).—The measurements were made in order to test Williams' conclusions (*loc. cit.*) respecting the validity of Sutherland's law of the variation of viscosity with temperature. A constant-volume method was used, the bulb containing the air and the capillary tube being surrounded by a vapour jacket to obtain definite temperatures. The following mean values were obtained for $\eta_\theta \times 10^4$ (c.g.s.u.): 1·7846 at 15°, 2·181 at 100°, 2·529 at 184·4°, 2·954 at 302·0°, 3·425 at 444·5°. The ratios of the viscosities, η_θ/η_{15}, show good agreement with the results of previous investigators with the exception of Williams. Sutherland's formula is strictly obeyed over the range considered, and no evidence is found of the breakdown discovered by Williams in the neighbourhood of 300°. The value of 118 is found for Sutherland's constant. L. L. Bircumshaw.

Internal friction in solids. A. L. Kimball and D. E. Lovell (Physical Rev., 1927, [ii], 30, 948—959).—The internal friction constant has been determined for the following materials: rubber, celluloid, tin, maple wood, zinc, glass, aluminium, brass, copper, tungsten, iron, steel, phosphor-bronze, molybdenum, nickel, nickel-steel, and monel metal. Constants for some of these materials and bronze are also calculated from the results of other investigators. A. A. Eldridge.

Method for comparing the times of mixing of two transparent liquids in different proportions, and some experimental results, particularly with gasoline and carbon disulphide. L. E. Dodd (J. Physical Chem., 1927, 31, 1761—1789).—A method of measuring the time of mixing of two or more transparent liquids, in which use is made of the optical effects produced by striæ on a beam of transmitted light, is described. The abrupt disappearance of the striæ makes possible the determination of this time with an accuracy of 3%. The data obtained with gasoline and carbon disulphide are reported and discussed, and results with water and a salt solution indicate the possibility of a wider application of the method. L. S. Theobald.

Refractometry of binary liquid systems. I. and II. V. J. Anosov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 379—404, 455—457; cf. A., 1926, 234).—I. Three types of refractive-index curves are distinguished: (1) for ideal mixtures—a straight line or a curve closely approximating thereto; (2) for systems in which dissociation of the component occurs—a curve convex to the axis of concentration, and (3) for systems with reciprocal chemical action—a curve concave to the concentration axis.

Results are given for six binary liquid systems. For ethyl acetate–stannic chloride and piperidine–allylthiocarbimide in which the components react strongly, chemical combination is characterised by change in direction and by a maximum divergence from additivity. The piperidine–allylthiocarbimide curve exhibits a singular point.

II. The refractive index of mixtures of acetone and chloroform at 13° gives a curve slightly concave to the axis of composition (cf. Zawidzki, A., 1901, ii, 6). The values for the system acetic anhydride–water show a minimum for the composition $C_2H_4O_2$ and a maximum between 60 and 70 mols.-% H_2O, possibly indicating the formation of the compound orthoacetic acid, $CMe(OH)_3$. For benzene–glyceryl trinitrate, the refractive index isotherm at 12·5° exhibits concavity towards the axis of composition, the glyceryl nitrate probably undergoing association. T. H. Pope.

Magnetic susceptibility of binary liquid systems. N. A. Trifonov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 434—435; cf. A., 1926, 234).—The magnetic susceptibility for the system allylthiocarbimide–dimethylaniline is related linearly to the molecular composition. Acetone–carbon disulphide gives a curve convex to the axis of abscissæ, whilst for acetone–chloroform the curve is concave and exhibits a maximum. For strengths of magnetic field 14—17 kilogauss and for temperatures 10—30°, the magnetic susceptibility is independent of both field strength and temperature. T. H. Pope.

Magnetic rotation of the plane of polarisation by binary liquid mixtures. N. A. Trifonov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 436—440).—For the mixtures allylthiocarbimide–dimethylaniline, acetone–carbon disulphide, acetone–chloroform, allylthiocarbimide–piperidine, and acetic anhydride–water, the magnetic rotation curves are symbatic to the viscosity curves. With systems in which the components react with one another, there is considerable deviation of the isotherms from rectilinearity. T. H. Pope.

Certain physical properties of mixtures of solutions of hydrochloric acid with sodium and potassium hydroxides. N. A. Trifonov, K. I. Samarina, V. J. Anosov, and S. I. Tscherbov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 441—442).—The values of the specific gravity, coefficient of viscosity, magnetic rotation, refractive index, and electrical conductivity are given for an approximately 5*N*-hydrochloric acid solution to which gradually increasing amounts of potassium (or sodium) hydroxide solution of similar concentration were added. The curve expressing each property in relation to the composition of the mixed solution consists of two branches meeting at an angle at the point corresponding with neutrality, the deviation from additivity being greatest at this point. T. H. Pope.

Eutectic f.-p. depression in binary mixtures. III. E. Kordes (Z. anorg. Chem., 1927, **168**, 177—188; cf. A., 1927, 1132).—The rule that the relative eutectic depressions of the f. p. of the components of a binary mixture are in the inverse ratio of the concentrations of the components in the eutectic mixture is applicable to many binary mixtures in which compound formation occurs. Divergencies arise, however, if either of the eutectic constituents decomposes on fusion; nevertheless, in such cases, the rule is generally valid if it is assumed that dissociation occurs completely. The hypothesis of partial dissociation will, however, explain the facts equally well in most instances. In a few cases where the eutectic temperature does not obey the rule even if decomposition is assumed to take place, it seems probable that solvate formation occurs. The rule is also applicable to binary systems which in the sense of the phase rule consist of more than two components. R. Cuthill.

Binary azeotropic mixtures of ethyl alcohol with petroleum hydrocarbons. Y. Tanaka and T. Kuwata (J. Fac. Eng. Tokyo, 1927, **17**, 117—126).—A study of the azeotropic mixtures formed by ethyl alcohol and hydrocarbons shows that a simple relation exists between the b. p. of hydrocarbons or the mean b. p. of their mixtures, and the compositions and the mean b. p. of the azeotropic mixtures formed by the hydrocarbons or their mixtures and ethyl alcohol. The relation between the b. p. of hydrocarbons and the weight percentage of ethyl alcohol in azeotropic mixtures can be represented by a straight line corresponding with $W_H=(160-T_H)/1{\cdot}15$ for paraffin and naphthene hydrocarbons and with $W_H=(140-T_H)/0{\cdot}89$ for aromatic hydrocarbons, where W_H is the weight percentage of hydrocarbon in the azeotropic mixture and T_H the b. p. of the hydrocarbon. These results were arrived at from distillation experiments with azeotropic mixtures of ethyl alcohol with the following purified hydrocarbons: *n*-hexane, *cyclo*hexane, *cyclo*hexene, *n*-heptane, methyl*cyclo*hexane, benzene, toluene, and purified commercial gasoline samples of b. p. 117—119°, 129—131°, and 146—150°, respectively. The observed values of the weight percentage of hydrocarbons contained in azeotropic mixtures agree with the calculated values to within ±3%. Hydrocarbons or their mixtures with b. p. below 45° or above 160° cannot form azeotropic mixtures under atmospheric pressure.

The relations between the b. p. of hydrocarbons and azeotropic mixtures are represented by a hyperbolic curve of formula $(T_H-T_{AZ})(81-T_{AZ})=K$, where T_{AZ} is the b. p. of azeotropic mixture and K is a constant equal to about 236 for paraffin and naphthene hydrocarbons, and about 150 for aromatic hydrocarbons. The b. p. of azeotropic mixtures can thus be calculated from the b. p. of the hydrocarbon contained in the azeotropic mixtures to within ±1%.

For commercial gasoline having a wide range of b. p., good agreement is shown between the observed and the calculated values of T_{AZ}. The formulæ given above are equally applicable to hydrocarbon mixtures having a wide range of b. p. provided T_H and T_{AZ} are taken as mean the b. p. of the hydrocarbon mixture and of the azeotropic mixture, respectively. R. A. Pratt.

Azeotropism in binary systems containing an amide. M. Lecat (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, ii, 87—97).—The azeotropic data for binary systems containing acetamide or propionamide are collected and discussed. Empirical formulæ are given for the azeotropic lowering in systems containing hydrocarbons, esters, halogen compounds or ethers, and acetamide. J. S. Carter.

New binary azeotropes. IX. M. Lecat (Ann. Soc. Sci. Bruxelles, 1927, **47**, *B*, i, 149—158).—A further list of binary azeotropic mixtures and non-azeotropic systems is given. J. S. Carter.

Partial vapour pressures of benzene–toluene and benzene–ethylbenzene mixtures. T. Bell and R. Wright (J. Physical Chem., 1927, **31**, 1884—1886).—The partial pressures of the above mixtures have been determined at 20° using the air-current method and analysing the condensed liquid by means of the effect on the f.-p. depression of an added quantity of benzene. Complex formation, if any, occurs only to a slight extent. L. S. Theobald.

Viscosity of fused metals and alloys. I. L. Losana (Notiz. Chim.-Ind., 1927, **2**, 1—4; Chem. Zentr., 1927, i, 2706).—A description of methods. A. A. Eldridge.

Copper–silicon alloys of high copper content. W. Geiss and J. A. M. van Liempt (Z. anorg. Chem., 1927, **168**, 31—32).—The electrical resistance R, the temperature coefficient α of the resistance, and the tensile strength of copper–silicon alloys containing up to 6% Si have been measured between 20° and 100°. $R\alpha$ is approximately constant up to 5% Si; above this limit R increases very rapidly, but the change in α is very small. The rate of corrosion of the alloys in air decreases with increase of silicon content. H. F. Gillbe.

Rate of evaporation of small spheres as a method of determining diffusion coefficients. Diffusion coefficient of iodine. B. Topley and R. Whytlaw-Gray (Phil. Mag., 1927, [vii], 4, 873—

888).—An experimental arrangement is described for measuring the rate of evaporation of freely-suspended spheres of volatile material. It is shown that the diffusion coefficient of the vapour, D, is given by the equation $-dS/dt=8\pi MDp/\rho Rt$, where S is the surface area of the sphere at a time t, M the mol. wt., p the saturation pressure of the vapour, and ρ the density of the sphere. The correction applied for the self-cooling of the sphere is given by $T_2-T_1=pD\lambda/RT_2k$, where k is the specific conductivity of the gas through which diffusion takes place and λ the specific heat of the material. The values of D for iodine measured at 4 temperatures showed good agreement with direct measurements in straight tubes, the mean values being 0·0851, 0·0814, 0·0808, and 0·0767 at 30·05°, 25·05°, 20·00°, and 14·00° respectively. C. J. SMITHELLS.

Reciprocal action between dissolved gases and solvent on the basis of the dependence of gas solubility on temperature. G. TAMMANN (Z. Elektrochem., 1927, **33**, 425—428).—Theoretical. The solubility of gases in water is closely related to the presence of the polymerised molecules, $(H_2O)_6$, and the form of the temperature–solubility curves for the commoner gases, as well as the formation of crystalline hydrates, are discussed in reference to this view. L. S. THEOBALD.

Traube's rule in connexion with hydrotropy. [Influence of salts of alkylbenzenesulphonic acids on the solubility of benzoic and phthalic acids.] H. FREUNDLICH and G. V. SLOTTMAN (Biochem. Z., 1927, **188**, 101—111).—Measurements have been made at 20° of the solubility of benzoic and phthalic acids in water in the presence of varying concentrations of sodium benzenesulphonate, *p*-toluenesulphonate, and *p*-ethylbenzenesulphonate. The ratio of the increase of solubility ΔL to the solubility L_c is a function of the concentration C of the added salt of the form $\lambda_c=\lambda_0c^n$, where $\lambda_c=\Delta L/L_c$ and λ_0 and n are constants specific to the system concerned. The ratio of the concentration of sodium benzenesulphonate to that of sodium *p*-toluenesulphonate, and of sodium *p*-toluenesulphonate to that of sodium *p*-ethylbenzenesulphonate which produce the same increase in solubility of benzoic acid has a mean value of 1·54 throughout the range examined. In the case of phthalic acid this ratio has a mean value of 1·61. These results therefore provide a further illustration of Traube's rule for an homologous series. E. A. LUNT.

Ionic distribution coefficients. E. LARSSON (Svensk Kem. Tidskr., 1927, **39**, 122—130; Chem. Zentr., 1927, ii, 1231—1232).—The solubility of silver acetate, propionate, benzoate, phenylacetate, hydrocinnamate, phenoxyacetate, benzilate, α-naphthoate, and triphenylpropionate in water and alcohol at 25° was determined by titration with thiocyanate; values of $P(A)$ in the equation $P(\mathrm{Ag})+P(A)=2\log l_1/l_2-0{\cdot}4l_1^{1\,3}+4l_2^{1\,3}$, where l_1 and l_2 are the solubilities and $P(\mathrm{Ag})=2{\cdot}1$, are tabulated. The greater the number of benzene rings in the anion, the smaller (in general) is the distribution coefficient; anions containing hydroxyl or carboxyl groups yield larger values. For a monobasic tartaric ion the value 3·8 is computed; for succinic acid 3·0, and for propionic acid 1·6. A. A. ELDRIDGE.

Adsorption. IV. Adsorption by coconut charcoal from binary mixtures of saturated vapours. The systems methyl alcohol–benzene, ethyl alcohol–benzene, *n*-propyl alcohol–benzene, and *n*-butyl alcohol–benzene. F. G. TRYHORN and W. F. WYATT (Trans. Faraday Soc., 1928, **24**, 36—47).—The experimental method was the same as that used for ethyl alcohol–benzene mixtures (A., 1926, 788). A review of the results for the four systems confirms the theory of three-stage adsorption already put forward (*loc. cit.*). The sharpness and extent of the second stage vary greatly from system to system. For the methyl and ethyl alcohol mixtures this stage is usually well defined, but is indistinguishable in the propyl alcohol mixtures. In the butyl alcohol mixtures it becomes more prominent and extensive as the concentration of alcohol in the liquid increases. This tendency towards second-stage masking also occurs in the methyl and ethyl alcohol mixtures, when the initial liquid mixtures are near to those of the minimum b. p., and an explanation is offered which suggests that the replacement of alcohol by benzene molecules (or *vice versa*) in the adsorbate is synchronous with a steady increase in the number of molecules adsorbed. The cause of the replacement is to be found in the tendency of the liquid adsorbate to come into equilibrium with the remaining liquid mixture. As equality of composition is never reached, it is inferred that the selective properties of a charcoal modify the vapour pressures of adsorbed substances in different degrees (cf. Baker, J.C.S., 1927, 949). A quantum mechanism based on energy transfer in the infra-red region is suggested for this effect. L. F. GILBERT.

Selective adsorption [of electrolytes during precipitation]. M. GELOSO and (MLLE.) L. S. LÉVY (Compt. rend., 1928, **186**, 35—37).—The distribution of electrolytes between the solid and liquid phases produced by the precipitation of manganese dioxide from an acid solution containing ferric and cupric sulphates has been studied. The distribution of each electrolyte between the solid and liquid phases does not appear to be modified by the presence of the other electrolyte. J. GRANT.

Adsorption by metallic hydroxides. V. Comparative study of the adsorptive power of iron, aluminium, and chromium hydroxides for acids and alkali. K. C. SEN (J. Physical Chem., 1927, **31**, 1840—1841).—The adsorption of citric, racemic, oxalic, malic, succinic, hippuric, benzoic, and sulphuric acids and of arsenious oxide by chromium hydroxide is much greater than by ferric and aluminium hydroxides. Except for sulphuric acid, ferric hydroxide shows a greater adsorptive power than aluminium hydroxide. L. S. THEOBALD.

Adsorption of acids by filter-paper. II. S. G. MOKRUSCHIN and E. J. KRYLOV (Kolloid-Z., 1927, **43**, 387—389).—On the basis of the theory of electrical adsorption (Mokruschin and Essin, A., 1926, 573) an explanation is given of the fact that for small amounts of adsorption the maximal adsorption is reached at low concentrations. Curves are given for the adsorption of citric, formic, phosphoric, arsenic, acetic, monochloroacetic, and trichloroacetic acids by filter paper. The experimental results are in complete agreement with the formula previously derived (*loc. cit.*). E. S. HEDGES.

Adsorption on dissolved molecules. II. M. S. MARINESCO (J. Chim. phys., 1927, 24, 593—620; cf. A., 1927, 1135).—The viscosities and diffusion coefficients of solutions of certain fluorescein derivatives etc. in water and in various alcohols have been measured. To obtain the diffusion coefficients a microcolorimeter of special design was used. The results are interpreted in terms of Einstein's theory (Z. Elektrochem., 1908, 14, 235—239), and indicate the formation of an adsorbed layer of the solvent on the surface of the large solute molecules. This layer is approximately unimolecular for all the solvents considered, although the degree of adsorption depends to some extent on the electrical properties of the solvent and of the solute. In alkaline solutions of fluorescein a layer of hydroxyl ions may be adsorbed and adsorption of the solvent is then prevented. G. A. ELLIOTT.

Absorption of water by gelatin. D. J. LLOYD and W. B. PLEASS (Biochem. J., 1927, 21, 1352—1367).—Sodium chloride in the presence of hydrochloric acid and up to a concentration of $0{\cdot}01M$ suppresses the swelling of gelatin due to acid; at greater concentrations it causes a coagulation of the acid gelatin. The maximum of acid swelling is at p_H 2·6. In the presence of sodium hydroxide the salt also suppresses the swelling due to the alkali. The salt has no further action even at high concentrations ($2M$). The maximum alkaline swelling is at p_H 9·8. The swelling of gelatin due to acid or alkali increases as an exponential function of the temperature. The point of minimum swelling of ash-free gelatin (isoelectric point) is at p_H 5·0. At this point sodium chloride promotes water absorption, swelling being proportional to the logarithm of the concentration of the salt. At p_H 5 in the absence of salts swelling increases slowly with rising temperature up to 15° or 18°, after which with further rise there is a decrease of swelling at the same p_H. Sodium chloride increases swelling slowly with temperature up to about 18°, after which there is very rapid increase ending at about 20° in complete dissolution of the gelatin. The greater the concentration of sodium chloride present the lower the temperature at which dissolution occurs. At p_H 7 in the absence of salts gelatin shows some swelling due to the alkali present. The addition of sodium chloride up to $0{\cdot}01M$ causes a suppression of swelling; at greater concentrations the salt, as at p_H 5·0, induces a swelling which is in logarithmic ratio to its concentration. At p_H 7 in salt solutions stronger than $0{\cdot}01M$ the effect of temperature on swelling resembles that at p_H 5. When the concentration of sodium chloride is less than $0{\cdot}01M$, or in the absence of salts, the effect of temperature on swelling at p_H 7 is intermediate between its effects in the alkaline and in the isoelectric zones. When gelatin is in solution as electrically-charged particles the effect of adding sodium chloride is mainly electrostatic, but when present in electrically neutral forms the salt acts by adsorption and hydration. The theoretical aspects of swelling are discussed. S. S. ZILVA.

Heat of adsorption of oxygen on charcoal. A. F. H. WARD and E. K. RIDEAL (J.C.S., 1927, 3117—3128).—An apparatus for the determination of the heat of adsorption and the amount of adsorption of oxygen by charcoal is described, and values have been obtained for four different charcoals. The rates of autoxidation have been measured at 40° by the method of Rideal and Wright (A., 1925, ii, 806). The area of methylene-blue adsorption, the ash content, and the true and apparent bulk densities have also been determined. High initial heats of adsorption were observed, due to the existence of patches of more active charcoal surface. The extent of these was measured by the amount of oxygen adsorbed, and was found to be proportional to the rate of autoxidation of the charcoal. From data previously obtained (*loc. cit.*), it is possible to calculate the amount of amyl alcohol necessary to poison the autoxidation of the charcoals considered. This bears a constant ratio to the amount of oxygen adsorbed with the initial high heat of adsorption. The behaviour of one charcoal of high ash content was exceptional and seems to indicate an instability of the carbon surface. M. S. BURR.

Determination of the value of adsorbents. W. BACHMANN and L. MAIER (Z. anorg. Chem., 1927, 168, 61—72).—Determination of the adsorption maximum of an adsorbent does not give complete information as to its value, especially for industrial purposes. Complete sorption and desorption curves are necessary. Such curves may be obtained for silicic acid gels by Gustaver's method with considerable accuracy, and in 1/20th—1/30th of the time usually required. The characteristic hysteresis curves are obtained. H. F. GILLBE.

Absorption of butyric acid on water surfaces. C. R. BURY (Phil. Mag., 1927, [vii], 4, 980—984).—Calculations of the amount of butyric acid absorbed on water surfaces, from measurements of surface tension, have assumed that the activity of the acid is proportional to its concentration. This assumption is unjustified and new calculations using Jones and Bury's values for activity (this vol., 128) are given. Butyric acid forms saturated surface layers at the water–air surface, in which the area occupied by a molecule of acid is independent of concentration over a wide range, but increases slightly with temperature. The area occupied by a molecule at the water–hexane interface is smaller than at the water–air surface, but larger than that occupied by the higher fatty acids and alcohols. There is no evidence of the formation of a saturated surface layer at the water–benzene interface. C. J. SMITHELLS.

Adsorption. XXI. Influence of similarly charged ions on the coagulation of sols of Congo-red, benzopurpurin, and cerium hydroxide. S. GHOSH and N. R. DHAR (Kolloid-Z., 1927, 43, 389—395).—In their behaviour towards coagulation, sols may be divided into two groups, which the authors term "anomalous" and "normal." The anomalous sols require more of a univalent positive ion for coagulation in dilute than in concentrated solution, and the coagulating power of a mixture of electrolytes with ions of different valencies is not additive towards such a sol. Congo-red is an anomalous sol, and cerium hydroxide behaves as a normal sol. Benzopurpurin occupies an intermediate position, since it behaves normally towards mixtures of electrolytes, but gives an anomalous dilution effect.

E. S. Hedges.

Sorption. M. Tarlé (Bull. Chem. Soc. Japan, 1927, 2, 304).—A reply to Sameshima (A., 1927, 1135).

R. Cuthill.

Hydrolytic adsorption and equilibrium displacement. D. Talmud (Kolloid-Z., 1927, 43, 386—387).—When a solution of aluminium sulphate is agitated with activated charcoal, adsorption of sulphuric acid occurs and the excess of aluminium hydroxide remains in colloidal solution. The amount of sulphuric acid adsorbed can be determined by washing out the charcoal with an emulsion of light petroleum in water and then titrating with sodium carbonate. Using a mixed solution containing 0·66% of aluminium sulphate and 4·01% of potassium sulphate, the amount of sulphuric acid adsorbed by charcoal is greater than the sum of the amounts adsorbed from the two solutions separately.

E. S. Hedges.

Adsorption anomalies. Wo. Ostwald (Kolloid-Z., 1927, 43, 268—276).—From a consideration of published data it is shown that adsorption anomalies occur both for very small and very large amounts of the adsorbent. The relative adsorption decreases for small amounts of the adsorbent and has a maximum value for a critical amount of solid phase. When a large excess of the adsorbent is used, the relative adsorption again falls, but later passes through a minimum and begins to rise again. The behaviour is explained as being due to the dispersion of some of the adsorbent, so increasing the surface; with very small amounts of adsorbent, the adsorption causes the coagulation of this dispersed material, corresponding with the fall in the relative adsorption. The anomaly in the region of large amounts of adsorbent is explained as a normal function of the curve connecting x/m with m, where x is the amount of adsorbed material and m the amount of adsorbent.

E. S. Hedges.

Derivation of an adsorption equation from Langmuir's theory of residual valencies. M. N. Chakravarti and N. R. Dhar (Kolloid-Z., 1927, 43, 377—386).—The following adsorption equation is derived: $a/A=(\alpha\mu/K)^{1/n}/[1+(\alpha\mu/K)^{1/n}]$, where α is the adsorption coefficient, μ the number of molecules striking against the surface, a the adsorbed amount, A the maximal adsorption, and n the valency of the adsorbed ions. It follows from the equation that for strong adsorption the degree of adsorption will increase with the valency of the ion, but for slight adsorption the multivalent ions will be adsorbed least. For small concentrations of the adsorbed substance the equation approximates to the ordinary logarithmic equation. The equation shows that the diminution of adsorption by the presence of a foreign substance is the greater the less the substance is adsorbed. This has been established experimentally. The theory is in good agreement with experiments on the adsorption of various electrolytes by manganese dioxide and by the hydroxides of iron, aluminium, and chromium.

E. S. Hedges.

Cohesion in surface films. N. K. Adam (Trans. Faraday Soc., 1927, 24, 149—154).—The nature of the cohesive forces in surface films of long-chain substances on water, aqueous solutions, and hydrochloric acid is discussed. These films are of three types, the condensed type with close-packed, nearly vertically oriented molecules, the gaseous type, in which the molecules are flat in the surface and move independently, and the expanded type, intermediate in area and properties between the first two. The author's previous suggestion (A., 1926, 1002), that, in the expanded type, the molecules have their chains coiled in helices with vertical axis, is rejected because liquid-expanded films have now been found with areas different from the 48 Å.², which was previously considered to be a constant for this type of film, this supposed constancy being the foundation for the helical theory. These films probably contain tilted molecules, but the peculiar properties of each head determine primarily the spacing of the heads, and secondly the tilting of the chains. In the condensed films the rigidity increases with the length of the chain, the temperature of expansion at which the condensed film breaks down being raised about 10° near 0°, and 7° near 60° for each additional carbon atom. The lateral adhesion also depends on the heads and end groups. The attraction of the end group for water is one of the chief factors in determining the stability of a film, the following being a rough classification; (*a*) very weak attraction, no film formed: hydrocarbon, $\cdot CH_2I$, $\cdot CH_2Br$, $\cdot CH_2Cl$; (*b*) weak attraction, films unstable (groups in increasing order of attraction for water): $\cdot CH_2\cdot OMe$, $\cdot C_6H_4\cdot OMe$, $\cdot OAc$; (*c*) strong attraction: $\cdot CH_2\cdot OH$, $\cdot CO_2H$, $\cdot CN$, $\cdot CO\cdot NH_2$, $\cdot CH{:}N\cdot OH$, $\cdot C_6H_4\cdot OH$, $\cdot CH_2Ac$. It is probable that the intermolecular forces in these films are of the same nature as those in the crystals of the substances concerned, and relations between the m. p. are traced in this way.

W. Hume-Rothery.

Effect of the acidity of the support on the structure of unimolecular films. H. Egner and G. Hägg (Phil. Mag., 1927, [vii], 4, 667—670).—The dissociation constants of the fatty acids are all in the region of 10^{-5}, and it has been shown by Adam (A., 1921, ii, 488) that a palmitic acid film on water exhibits a maximum spreading tendency when the p_H of the water is less than 5·5. It is suggested therefore that for films of fatty acid on water the hydrogen-ion concentration at which the spreading is most rapid is numerically equal to the negative logarithm of acid dissociation constants of the fatty acid. The possible application of the principle to the determination of the dissociation constants of sparingly soluble substances is indicated.

A. E. Mitchell.

Electrostatically charged limiting surfaces. R. Auerbach (Kolloid-Z., 1927, 43, 114—131).—The diminution in surface tension of liquids bearing simple electrostatic and double-layer charges has been studied theoretically, and investigated experimentally for water, mercury, acetone, and *iso*butyl alcohol. Under certain definite conditions reproducible negative values for the surface tension were obtained.

The energetics of electrical dispersion are discussed. By means of electrical charges, liquids may be dispersed in air or insulating liquids, resulting, in the latter case, in emulsions of the water-in-oil type, in which the disperse phase carries free charges. It is possible to recover these charges so that the system may be regarded as an "accumulator" for free electrical energy. The evidence for this view is that an electroscope may be discharged or a Geissler tube made to glow from the emulsion. R. A. MORTON.

Surface tension of protein solutions. III. J. H. ST JOHNSTON (Biochem. J., 1927, 21, 1314—1328).—As in the case of gelatin (cf. A., 1925, ii, 659; 1926, 1092) the surface tension of caseinogen and egg-albumin solutions varies with the p_H. There is a maximum at the isoelectric point and secondary maximum at a lower p_H; the minimum corresponds with the maxima of other properties. Neutral salts in low concentration lower the surface tension of the above proteins in acid solution but raise it in a greater concentration. Denaturation of egg-albumin lowers its surface tension. There is a rapid fall at first in the surface tension of freshly made up acid or alkaline solutions of caseinogen, the equilibrium not being reached until nearly 24 hours. The bearing of these results on the Donnan equilibrium is discussed.

S. S. ZILVA.

Permeability of membranes. IV. Variations of transfer numbers with the dried collodion membrane produced by the electric current. L. MICHAELIS and A. A. WEECH (J. Gen. Physiol., 1927, 11, 147—158; cf. A., 1927, 727).—When an electric current is passed through a collodion membrane separating a solution of potassium chloride on the cathode side from a solution of potassium nitrate on the anode side the transfer number for chlorine ions depends on the concentration of potassium chloride, also on the strength of the current and on the previous treatment of the membrane.

W. O. KERMACK.

Permeability of gelatin membranes. R. COLLANDER (Protoplasma, 1927, 3, 213—222).—Although the living protoplasm is much more readily permeable to surface-active, and incidentally lipoid-soluble, substances than to inactive substances, such differences are not observed with membranes of copper ferrocyanide or collodion (A., 1925, ii, 201; 1926, 791). The behaviour of these two classes of substances towards a gelatin membrane has therefore been investigated to ascertain whether a membrane composed of protein substance resembles the living protoplasm in its selective permeability. Such investigations have been carried out by Traube and co-workers (cf. A., 1925, i, 735), but it is claimed that their results are inconclusive since the molecular dimensions of the substances investigated are small compared with the pore dimensions of the gelatin gel. No such criticism can be levelled against the present data, which have reference to thick membranes and to organic substances of high mol. wt. A surface-active and -inactive substance were allowed to diffuse simultaneously through the same membrane, measurements being made with aqueous and methyl-alcoholic solutions. The measurements show that molecular size (as measured by molecular refraction) is the main factor governing the rate of diffusion, the capillary-active or -inactive nature of the substance being relatively unimportant. The differences between the present results and those obtained with the living protoplasm are briefly discussed, and the present data interpreted as supporting the lipoid theory.

J. S. CARTER.

Dialysis. I. Law of decrease in dialysis. II. Course and rate of dialysis as a function of the "specific surface." H. BRINTZINGER (Z. anorg. Chem., 1927, 168, 145—149, 150—153).—I. It is found that if c_0 is the concentration of a diffusible ion or molecule at the commencement of a dialysis, the concentration c_t after a time t is given by the expression $c_t = c_0 e^{-\lambda t}$. Here λ is a constant if the liquid being dialysed is kept well mixed, the specific surface is not too small, the concentration difference of the diffusible ion on the two sides of the membrane is maintained maximal, and considerable temperature variations do not occur. From the above equation, the rate of dialysis at time t may be shown to be given by the relation $d(c_0 - c_t)/dt = \lambda c_t$.

II. For a particular dialysis, λ is directly proportional to the specific surface, from which it may be deduced that the times required to reach a given concentration are inversely proportional to the specific surface, and also to λ. R. CUTHILL.

Filtration phenomena. A. SIMON and W. NETH (Z. anorg. Chem., 1927, 168, 221—254).—Experiments have been made on the rate of filtration of water and aqueous solutions of electrolytes, chiefly acids and bases, through various types of crucible with porous bottom, including Schott crucibles with sintered glass bottoms, Berlin crucibles with porous porcelain plates, Haldenwanger porous porcelain crucibles, and a Neubauer platinum crucible. In filtering with the aid of suction, it is found that as the amount of liquid which has passed through the crucible increases, the rate of filtration, even of pure water, diminishes, gradually at first, then more and more rapidly, until the crucible becomes practically stopped up. The rate at which stoppage is approached is different for different liquids, and in some instances a particular liquid may temporarily promote the subsequent filtration of a different liquid. Hydroxide solutions appear to be particularly effective in blocking up the filter, yet the phenomenon is not entirely ionic, since it is observed with non-electrolytes, such as acetone. With all the liquids examined, it is found that a second filtration following soon after the first occurs at a steady rate, without the crucible becoming choked. If, however, the first filtrate is kept for 20—30 hrs. in a closed vessel, or boiled, on being filtered again it behaves as if it were a fresh unfiltered liquid, so that it cannot be suspended matter in the solutions which retards filtration. Under comparable conditions, the rate of filtration of a freshly-filtered liquid is greater than that of the same liquid unfiltered. When unfiltered water is filtered under hydrostatic pressure without suction, the rate of filtration first rises, then passes through a maximum, and ultimately falls below the initial rate. Using water which has previously been filtered, however, the rate of filtration remains steady at the maximum value, indicating that the fall observed with unfiltered water must be due to the same causes as the phenomenon manifested in filtration by suction, rather than to the separation of air in the pores of the filter, as Zakarias has suggested (A., 1925, ii, 862). The initial rise must be due to the wetting of the capillaries and removal of air, since it is absent when boiled-out water is filtered in a vacuum with a crucible the pores of which have previously been filled with water. In order to arrive at an explanation of the various phenomena observed, attempts were first made to detect electrification of the sintered mass. After water had been filtered through it, it was found to hold a positively-charged silver iodide hydrosol, but to allow a similar sol with a negative charge to pass. Application of a *P.D.* across the mass showed little more than an ordinary electro-osmosis effect. Attempts to detect static charges were also fruitless. No evidence could be obtained of any swelling of the filtering material. It appeared probable that stoppage of the crucible might be brought about by the larger species of water molecules, since the refractive index of water was slightly increased by filtration, but this effect was subsequently found to be due to the removal of dissolved gases. No satisfactory explanation of the above phenomena has therefore been obtained. R. Cuthill.

Relationship between the viscosity of water and the pressure and that of solutions and the concentration. G. Tammann and H. Rabe (Z. anorg. Chem., 1927, **168**, 73—85).—The viscosities of solutions of potassium chloride, bromide, and iodide and of ammonium chloride and nitrate have been determined by the Ostwald viscosimeter at 0°, 10°, 30°, and 75° at concentrations of 1—5*M*. The change of the relative viscosity of the solutions, referred to water as unity at each temperature, has been calculated as a function of the difference ΔK between the internal pressure of the solution and of the solvent; ΔK is interpolated from coincident pressure values of the isobars of water under a pressure ΔK and those of the solutions. The differences between the curves showing the relationship between viscosity η and external pressure yield linear curves for all the potassium salts investigated. The relationship between the viscosity of water at 0° and the pressure p is given with considerable accuracy for the pressure range 0—2000 atm. by the equation $\eta=1-0{\cdot}1349\times10^{-3}p+0{\cdot}5778\times10^{-7}p^2$. For the potassium halide and nitrate solutions the equation $\eta=1-0{\cdot}1349\times10^{-3}\Delta K+0{\cdot}5778\times10^{-7}\Delta K^2+\sigma_\eta\,.\,\Delta K$ is valid, η being the viscosity of the solution and σ_η a constant characteristic of the salt. Similar equations hold at higher temperatures.

The variation with pressure of the interionic friction in a solution is similar to, but not identical with, that of the viscosity, the constant σ_η being different. Further, the influence of temperature on the viscosity is greater than that on the interionic friction. H. F. Gillbe.

Preparation of colloidal sulphur by means of hydrazine. Wo. Ostwald and I. Egger (Kolloid-Z., 1927, **43**, 353—355).—Stable sols of sulphur can be prepared by the action of hydrazine hydrate on sulphur and then dispersing in hot water, or by pouring the sulphur–hydrazine solution into water and then dialysing. E. S. Hedges.

Kinetic studies on the formation of starch paste. I. Formation of starch paste in the cold. Wo. Ostwald and G. Frenkel (Kolloid-Z., 1927, **43**, 296—312).—A study has been made of the formation of paste from starch suspensions under the influence of various added substances, and of the effect of varying the concentration, temperature, moisture, and previous treatment. The substances which facilitate the change are sodium, potassium, and ammonium thiocyanates, sodium and potassium hydroxides, hydrochloric acid, sodium salicylate, and carbamide. The viscosity curve of the process is S-shaped, like that of the setting of plaster of Paris. The experimental curves can be divided into three groups, according to the portion of the S-shaped curve which can be realised. The addition agent becomes effective at a certain critical concentration and has a large "concentration coefficient." The concentration of the starch suspension and the temperature are also of great influence on the velocity of formation of paste. Different velocities were found for different kinds of starch, and thus this effect can serve as a means for the characterisation of starch.
E. S. Hedges.

Aqueous extracts of seeds as agents in the preparation of silver sols. E. V. Miller and R. P. Hibbard (Plant Physiol., 1926, **1**, 409—413).—Stable, negatively-charged silver sols are obtained by adding 2 drops of 0·1*N*-silver nitrate solution to the filtered aqueous extracts of various seeds. The reduction, which is probably due to proteins, with sugar as stabiliser, is accelerated by exposure to sunlight, although over-exposure precipitates the silver.
Chemical Abstracts.

Colours of colloidal silver, especially on flocculation. E. Wiegel (Koll.-Chem. Beih., 1927, **25**, 176—230).—The colour of colloidal solutions is discussed with particular reference to the many colours which are characteristic of silver sols. Using *p*-hydroxyphenylglycine as a reducing agent, silver sols having a variety of colours can be produced. Comparison of the colour of such unprotected sols with that of sols prepared in presence of gelatin shows that the colour is in no way due to the relations between the gelatin and silver in the colloidal particle. The particles are anisotropic, giving rise to a stream-double refraction. Unpurified silver sols prepared by Carey Lea's method using dextrin undergo a colour change on keeping for some months, the colour in transmitted light changing from yellow to orange, purplish-red, violet, and then blue. It is shown that this change is due to a slow coagulation of the colloidal silver, and the velocity of the change depends on the electrolyte content of the sol. With progressive coagulation there occurs a displacement of the absorption maximum in the region of greater wave-lengths and a broadening of the absorption band. When the coagulated silver is dried, a product is formed the colour of which is complementary to the colour of the sol in transmitted light. The stream-dichroism observed in the silver sols on slow coagulation shows that the particles are anisotropic, and comparison of the experimentally obtained extinction curve with theoretical curves leads to the conclusion that the particles are leaf-like. The anisotropy becomes stronger with increasing age of the sol. Experiments were also carried out on Carey Lea's silver sols prepared by the citrate method. It was observed that the flocculating power of bivalent cations is about 100 times that of univalent cations. In sols prepared both by the dextrin method and also by the citrate method, flocculation by bivalent cations is accompanied by the normal colour sequence: yellow, red, violet, blue; but with univalent cations an anomalous colour sequence is observed: yellow, yellowish-green, dark green, blue. These anomalous colours appear to be mixed and are probably due to partial flocculation. Addition of a small amount of silver nitrate to an old, reddish-violet, slightly alkaline silver sol produces a colour change to green. This is due to the adsorption of silver oxide by the silver particles, because the same effect can be produced by direct addition of a silver oxide sol, and also the reddish-violet colour returns after addition of ammonia or sodium thiosulphate. The particles of the green sols are negatively charged. The light absorption of the two components of the particles is not additive. The dextrin silver sols, especially those having an orange colour, are sensitive to light. The most effective rays are the blue and violet, flocculation taking place in a few seconds. E. S. Hedges.

[Refractive] indices of colloidal solutions. A. Boutaric and [Mlle.] G. Perreau (Rev. gén. Colloïd., 1927, 5, 658—662).—An illustration of the applicability of an interferential refractometer to the study of colloidal solutions. The difference between the refractive index of a sol and that of the intermicellar liquid obtained by dialysis increases linearly with the concentration of the sol. In presence of electrolytes the refractive index of a sol remains constant until actual precipitation commences. Adsorption during sedimentation may be followed refractometrically.

J. S. Carter.

Emulsions with refraction colours. I. D. Bhalla, S. S. Bhatnagar, and N. A. Yajnik (Kolloid-Z., 1927, 43, 366—377).—The authors describe experiments on the formation of emulsions with refraction colours in which the influence of the volume of both phases, the nature and concentration of the emulsifier, and the temperature has been studied. Stable gels of a gelatin solution in glycerol were prepared, showing refraction colours. Two types of coloured emulsions can be distinguished: (*a*) those which on rise of temperature undergo a colour change from blue, through green, to yellow, (*b*) those which undergo the reverse colour change. The view put forward by Holmes and Cameron (A., 1922, ii, 269) that such a coloured emulsion requires equality of refractive indices of the two phases but a difference in optical dispersion, has been established experimentally. E. S. Hedges.

Viscosimetry of colloidal systems. Wo. Ostwald (Kolloid-Z., 1927, 43, 190—209).—Consideration of data published elsewhere shows that similar results are obtained for the structure viscosity effect when different forms of apparatus are used. The agreement between the results obtained with the Couette apparatus and the capillary viscosimeter is at variance with accepted views. The author attempts an explanation. E. S. Hedges.

Viscosity anomalies of sols in the Couette apparatus. Wo. Ostwald (Kolloid-Z., 1927, 43, 210—214).—Anomalies are shown by the sols of gelatin and starch in the Couette apparatus, which are not met with when the capillary viscosimeter is used. It is claimed that the non-reproducibility of the anomalies in the capillary viscosimeter is not at variance with the author's experiments, which indeed show that the observed results are due to the special construction of the Couette apparatus. In the case of the gelatin sol the effect is due to the adsorption of the colloid on the inner cylinder, so increasing the roughness of the wall. In the case of the starch sol the anomaly is explained by the destruction of the structure of the sol in carrying out the measurement by the Couette method. E. S. Hedges.

Structure and formation of colloidal particles. H. Freundlich (Trans. Faraday Soc., 1927, 23, 614—623).—The application of *X*-ray measurements to the determination of the state of aggregation and the crystalline form of colloidal particles, and the various optical methods for determining their shape, with special reference to the use of the azimuth diaphragm, are discussed. An account of the different possible structures of colloidal particles, the factors influencing their formation, and the changes which they undergo after formation, is also given.

M. S. Burr.

Sols with structure-viscosity. I. Viscosimetry of ammonium oleate sols. II. Structure-turbulence of sols of cotton-yellow and mercury sulphosalicylate. Wo. Ostwald, R. Auerbach, and J. Feldmann (Kolloid-Z., 1927, 43, 155—181, 181—187).—I. An account is given of very extensive measurements of the viscosity of ammonium oleate sols, using many different forms of apparatus. The reproducibility of the results compares favourably with that obtained with other sols, *e.g.*, gelatin. The viscosity curves obtained for ammonium oleate sols are compared with those for gelatin sols; on the whole, there is no essential dissimilarity. The behaviour of sols of ammonium oleate as regards turbulence and structure viscosity depends on the concentration of the sol, structure-viscosity becoming more prominent in the more concentrated sols. Mechanical treatment reduces the viscosity for high and medium velocities. Heating at 65° destroys completely the usual viscosity relations of ammonium oleate sols. These results are discussed from a theoretical point of view. The measurements carried out by means of the capillary viscosimeter confirm those obtained by Hatschek and Jane (A., 1926, 240), using the Couette apparatus.

II. The structure-turbulence anomaly shown by the viscosity of ammonium oleate sols (preceding abstract) is found also in sols of cotton-yellow (whether purified or containing salts) and in gels of mercury sulphosalicylate. The effects are obtained using either the Couette apparatus or capillary viscosimeters of various types. Cotton-yellow sols containing sodium sulphate at various concentrations develop structure-turbulence, which disappears again at higher concentrations. There is a maximum viscosity at about 1·3%. Sols showing well-defined structure-turbulence also show marked shear-elasticity. E. S. Hedges.

Jelly formation of ceric hydroxide hydrosol. W. Biltz (Z. anorg. Chem., 1927, 168, 96).—A claim for priority over Chakravarti, Ghosh, and Dhar (A., 1927, 934). H. F. Gillbe.

Relation between viscosity and electrolytic dissociation of colloidal solutions. I. Behaviour of gelatin hydrosols before and after treatment with proteolytic substances. S. Visco (Arch. sci. biol., 1926, 8, 471—479; Chem. Zentr., 1927, i, 2402).—From p_H 4·6, the viscosity of gelatin solutions increases with addition of hydrochloric acid to a maximum value at p_H 2·8 and thereafter diminishes. After treatment with trypsin, the gelatin solutions did not exhibit this maximum. The changes in viscosity are hence ascribed to changes, possibly the presence of sub-microscopic particles, in the protein solution, and not to ionisation variations.

A. A. Eldridge.

Viscosity factor in emulsification. R. C. Smith (Phil. Mag., 1927, [vii], 4, 820—826).—It is pointed out that it is not the viscosity of the dispersion medium but rather the viscosity of the interfacial film between the suspensoid and the dispersion fluid which is the limiting factor in emulsification. An examination of a large number of suspensions of solids in liquids has shown that solids which are readily emulsifiable exhibit as a rule high interfacial tensions with the dispersion medium.

A. E. Mitchell.

Solubility of cellulose esters. I. II. Solubility of cellulose acetate in acetone. I. Sakurada and T. Nakashima (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 153—164, 165—171).—I. Di- and tri-esters of cellulose with palmitic, stearic, and lauric acids, which are partly soluble in organic liquids, have been prepared by the action of the acid chloride on cotton cellulose in a mixture of pyridine and benzene. By heating the insoluble portions of the stearic esters in naphthalene at 200°, or with stearic acid or benzenesulphonic acid, they are rendered more or less completely soluble. Since this process is in no case accompanied by hydrolysis, and since the cellulose regenerated from the esters corresponds in properties with Hess' cellulose-*A*, it is concluded that the change in solubility is associated with physical changes, probably in molecular arrangement. Determinations of the mol. wt. in camphor by the cryoscopic method indicate that the soluble esters are associated.

II. By acetylation of secondary cellulose acetate which is soluble in acetone, it becomes partly insoluble. From a comparison between the solubilities of the cellulose acetates and the cellulose esters of the fatty acids, and the methods by which the solubility may be increased, it appears probable that in both sets of compounds the changes in solubility must be due to the same causes. By means of this hypothesis, some explanation of the "ripening" of primary cellulose acetate can be derived (cf. Ost, B., 1919, 355). R. Cuthill.

Application of the Aitken effect to the study of aerosols. H. L. Green (Phil. Mag., 1927, [vii], 4, 1046—1069).—A continuous-action Wilson cloud apparatus has been devised in which the counting of the particles is effected by a photographic method. The apparatus has been used for the study of ammonium chloride and cadmium oxide clouds. In the case of ammonium chloride the rate of coagulation of the cloud could be expressed by the equation $1/n=1/n_0+Kt$, where n is the number of particles per c.c. at time t, n_0 is the initial number of particles, and K the coagulation constant. K decreases as the initial concentration increases and it is suggested that the degree of dispersion of a cloud depends both on the degree of supersaturation of the vapour and the number and size of the nuclei present in the air. Similar results were obtained with cadmium oxide clouds. The results have been verified with a visual ultramicroscope. A. E. Mitchell.

Structural-chemical contributions to colloid-chemical problems. M. Bergmann (Gerber, 1926, 52, 195—196; Chem. Zentr., 1927, i, 2520).—Simple molecules can assume the properties of proteins. Alanylserine anhydride, by loss of a molecule of of water, yields three methylenedioxymethylpiperazines, having mol. wt. 140, of which two are very sparingly soluble in water. From the *iso*-form a substance is obtained with formaldehyde which yields colloidal solutions in water, gelatinises, and precipitates tannin. The postulate of very large "principal valency molecules" is unnecessary in protein chemistry. A. A. Eldridge.

Change in viscosity and electrical conductivity of sols on ageing, and formation of gels of inorganic substances. N. R. Dhar and D. N. Chakravarti (Z. anorg. Chem., 1927, 168, 209—217).—With increasing age, sols of thorium hydroxide (prepared either in the hot or in the cold), ceric hydroxide (prepared in the hot), ferric hydroxide (prepared in the cold), and benzopurpurin manifest increasing conductivity and decreasing viscosity, thus behaving like the other hydrophobic colloids previously examined (A., 1927, 629). Gelatin sols, however, first become more viscous, and do not change in conductivity. With silicic acid sols prepared either in the hot or in the cold, both viscosity and conductivity increase, this phenomenon being attributed to the aggregation of particles of molecular dispersity on the one hand, and to the release of adsorbed electrolytes on the other. A ceric hydroxide sol prepared in the cold, and kept until it has stiffened to a gel (*ibid.*, 934), ultimately becomes mobile again, the conductivity increasing at the same time; silicic acid sols behave similarly. If to a dilute solution of ferric or chromic chloride or aluminium nitrate are added sodium acetate, and then, after the mixture has been partly neutralised with ammonia, a little ammonium sulphate, a stiff gel of the corresponding hydroxide ultimately results. It is considered that the particles in gels such as these, which are formed by the slow coagulation of sols through the whole of their mass, are not arranged in a network. The arsenate gels, however, obtained by adding dipotassium hydrogen arsenate to manganous or zinc sulphate have probably a honeycomb structure, and are more stable. Von Weimarn's gels represent the third and least stable group. R. Cuthill.

Effect of the degradation products of gelatin on its separation by sulphosalicylic acid, and a technical method for testing gelatin. Wo. Ostwald and R. Köhler (Kolloid-Z., 1927, 43, 345—348).—The volume of liquid separating out from a gelatin sol on addition of sulphosalicylic acid is less after the gelatin sol has been heated. The volume of separated liquid falls linearly with the amount of degradation products contained in the gelatin. The effect can be used as a method of characterising different grades of gelatin. E. S. Hedges.

Separation of gelatin sols into two liquid layers by sulphosalicylic acid in relation to the phase rule. Wo. Ostwald and R. Köhler (Kolloid-Z., 1927, 43, 131—150).—For a given concentration of gelatin, separation occurs between two limiting concentrations of the sulphosalicylic acid, these limits becoming narrower for higher concentrations of gelatin. The effect is not observed in gelatin sols more concentrated than 14%. The two liquid layers do not have a constant composition, but the variation is least for a given concentration of gelatin when the concentration of sulphosalicylic acid is near one or other of the limiting values. Greater differences in composition of the layers are noticed at low concentrations of gelatin than in concentrated solutions. Rise of temperature diminishes the difference between the layers, ultimately leading to the formation of a single liquid phase. Although at first sight the behaviour of the system appears to be similar to that of a ternary molecularly dispersed system, comparison of the equilibrium diagram of the system gelatin–sulphosalicylic acid–water with that of the system potassium carbonate–alcohol–water reveals important differences. The two-phase system gelatin–sulphosalicylic acid–water has at least one degree of freedom more than is to be expected from the point of view of the phase rule. E. S. Hedges.

Effect of neutral salts on the formation of two liquid layers from the system gelatin–sulphosalicylic acid–water. Wo. Ostwald and R. Köhler (Kolloid-Z., 1927, 43, 151—155).—The separation of gelatin–sulphosalicylic acid mixtures into two liquid phases on the addition of potassium nitrate, chloride, bromide, and thiocyanate, and ammonium sulphate at a concentration of 4 g.-mol. per litre has been examined at 25°. Small quantities of the neutral salts are favourable to the separation, larger amounts exert a preventive influence, whilst still larger quantities again assist the separation. The relative effects of the different salts are in accordance with their position in the Hofmeister series. Gelatin solutions separate into two layers, not only on addition of sulphosalicylic acid, but also by addition of any acid the anion of which falls near the thiocyanate end of the Hofmeister series.

E. S. Hedges.

Gelation of silicic acid. Formation of gas bubbles and drops in silicic acid during gelation. H. A. Fells and J. B. Firth (Trans. Faraday Soc., 1927, 23, 623—630).—The form taken by bubbles, or by drops of liquid such as chloroform or mercury, passing through a silicic acid sol during the process of gelation has been studied, and the pressure required to blow the bubbles at various stages has been measured. The spherical shape assumed by the bubble or drop before gelation gradually flattens to a thin film in succeeding bubbles as gelation proceeds. Once a bubble or drop is formed in the gel the shape is permanent, and the air or liquid can be withdrawn or replaced at will. Any subsequent development of the bubble or drop appears as a growth on the original. After gelation, up to the condition for the formation of the extremely thin, film-like bubble which causes a permanent fracture in the gel, the only apparent change in the latter is that of continued increase of rigidity. After this stage there is external syneresis. The pressure required to blow a bubble increases as the gel ages, and once a bubble passes through the semi-rigid gel, subsequent bubbles follow the same path and pass with reduced resistance because the gel is fractured. Syneresis takes place along the path, due to the pressure caused by the first bubble. From the form of the bubbles or drops produced in different portions of the same sol, it is evident that gelation does not take place uniformly, but round a series of gelation centres. The water present in the gel is of two types, "fixed" and "free" (cf. A., 1927, 935). With the passage of time fixed water changes to free and is lost by evaporation, when the gel shrinks and ultimately forms anhydrous crystalline silica or quartz (Zsigmondy, A., 1911, ii, 880). Silicic acid gel has been found naturally, side by side with quartz, in the Simplon Tunnel (Z. Krist., 1901, 34, 289). M. S. Burr.

Influence of salts on the optical rotation of gelatin. I. D. C. Carpenter (J. Physical Chem., 1927, 31, 1873—1879).—The specific rotations of 0·7% solutions of potassium gelatinate (calfskin) containing potassium chloride, bromide, or iodide have been measured at p_H 6·0 and at 0·5° after 1, 2, and 7 days, and also at 40°. Each salt produces a characteristic lowering of the optical activity, the effect being in the descending order, iodide, bromide, and chloride. The change is attributed to the equilibrium between the gel and sol forms of gelatin, together with the changes in the equilibrium of water produced by the added halide.

L. S. Theobald.

Solvation of the disperse phase in jellies. H. Gaunt and F. L. Usher (Trans. Faraday Soc., 1928, 24, 32—36).—The degree of hydration of the disperse phase in silicic acid jellies has been derived from the changes in the concentration of indifferent solutes (sulphuric and nitric acids, chloride and oxalate ions) which occur on gelatinisation (cf. McBain and

Jenkins, J.C.S., 1922, **121**, 2336). The necessary data were obtained from a comparison of the original liquid and the intermicellary liquid which exudes from the jellies by syneresis. The degree of hydration of "precipitated" silicic acid, ferric hydroxide, and aluminium hydroxide was also determined, the broken materials being allowed to remain in contact with the reference liquids for several days. Attempts to prepare jellies of stannic, cupric, mercuric, and arsenic sulphides were unsuccessful.

L. F. Gilbert.

Method for determining the tensile strength of gelatin jellies. A. Rosinger and J. J. Vetter (J. Amer. Chem. Soc., 1927, 49, 2994—3003).—The tensile strength of gelatin jellies is determined by measuring the dimensions of the spherical segment which is produced when a circular membrane of the jelly, supported rigidly at its circumference, is subjected on one side to air pressure. A suitable apparatus is described, which can also be used to study the time of relaxation of stretched membranes.

S. K. Tweedy.

Influence of hydrolysed gelatin on the precipitation of silver chromate. T. R. Bolam and B. N. Desai (Trans. Faraday Soc., 1928, 24, 50—52; cf. A., 1926, 1005).—The influence of hydrolysed and unhydrolysed gelatin on the separation of silver chromate from aqueous solutions of silver nitrate and potassium chromate has been studied. The time for the appearance of a precipitate is decreased by hydrolysis. Evidence is adduced that this is not due to the slight change in acidity which occurs (cf. Ganguly, A., 1927, 19). With hydrolysed gelatin the precipitate appears uniformly at all parts, whereas with the unhydrolysed substance the precipitate is formed locally at certain points and settles comparatively rapidly. It is obvious that protection and inhibition are not closely associated.

L. F. Gilbert.

Influence of alkalis on the coagulation of silica and clay suspensions by alkali chlorides. H. B. Oakley (J.C.S., 1927, 3054—3065; cf. this vol., 16).—The addition of alkalis decreases the turbidity of a clay suspension as measured in a Klett nephelometer. The effect increases in the order: barium, calcium, ammonium, potassium, sodium, and lithium. The effect of mixtures of hydroxides with the corresponding chlorides on the coagulation of clay suspensions has been investigated. Below a certain alkalinity, increasing concentration of the mixtures results first in flocculation, then failure to flocculate, and finally flocculation again. The phenomenon is also shown by kaolin, and by silica coagulated by a small quantity of alumina, but not by pure silica, the flocculating powers of the chlorides considered increasing in the order: lithium, sodium, potassium, and calcium, calcium being about ten times as powerful as sodium. Between p_H 9 and 10 there is a pronounced maximum in the concentration of sodium chloride required to flocculate clay, kaolin, or aluminated silica. The behaviour observed is probably the outcome of two opposing factors in the stability of clay. The formation of a sodium compound tends to stabilise the suspension, the effect reaching a maximum at p_H 9—10 (*loc. cit.*). The presence of the electrolyte, on the other hand, tends to flocculate it. Calcium chloride behaves similarly to sodium chloride in the coagulation of clay, but the maximum is at p_H 7. Clay is more readily flocculated by calcium hydroxide than by calcium chloride at equivalent concentrations, provided these exceed 0·003*N*. At lower concentrations the opposite is the case. A suspension of silica is coagulated by calcium or sodium chloride in an alkaline medium only, and the minimum concentration required for flocculation rises rapidly as alkalinity diminishes. Silica is flocculated by 0·0001*M*-aluminium chloride. Greater concentrations give a stable electropositive suspension, whilst subsequent addition of increasing quantities of sodium hydroxide at first flocculates the suspension, and then gives a stable electronegative suspension. The flocculating powers of sodium hydroxide, carbonate, and hydrogen carbonate have been compared, and decrease in the order given.

M. S. Burr.

Kinetic investigation of the peptisation of aluminium hydroxide. Wo. Ostwald and H. Schmidt (Kolloid-Z., 1927, 43, 276—295).—The course of the peptisation of aluminium hydroxide gel prepared from ammonium alum was followed by gravimetric and potentiometric methods. The general character of the peptisation–time curves resembles that of a coagulation–time curve, being autocatalytic, or S-shaped. No relation could be found between peptisation and hydrogen-ion concentration, the effect depending rather on the anion of an acid. Buffer solutions of the same hydrogen-ion concentration but containing different amounts of neutral salt behave quite differently. Many strong acids, such as sulphuric acid and phosphoric acid, do not peptise aluminium hydroxide.

E. S. Hedges.

Thixotropy of concentrated ferric oxide sols. H. Freundlich and W. Rawitzer (Koll.-Chem. Beih., 1927, 53, 231—278).—A study has been made of the thixotropy of ferric oxide sols, especially with regard to the limiting concentrations of ferric oxide and sodium chloride. Below a certain concentration of sodium chloride no change in the viscosity of the system occurs, and above a critical ratio of sodium chloride to ferric oxide thixotropy is replaced by irreversible syneresis. The inhibitive action of amino-acids is not shared by other organic compounds. This effect is reversible and can be removed by dialysing away the amino-acid; it is due to an adsorption of the amino-acid. The inhibitive action of the amino-acid increases with the number of CH_2 groups contained therein. The amino-acids have no effect, however, on the velocity of cataphoresis. The curve connecting the velocity of gelation of ferric oxide sols with the concentration of sodium chloride reaches a maximum, which is independent of the concentration of the ferric oxide. A study was also made of some physical properties of ferric oxide sols. Using an apparatus similar to that of Couette, the tensile strength was found to increase during gelation to a constant end-point. The final value is different from that obtained when the transformation merely appears to have come to an end. The modulus of elasticity increases with the load but the extension is still quite reversible. During the measurement of viscosity in the Couette apparatus, the degree of liquidity of the sol depends on the shear gradient, and an end-point is reached by the stirring which is not the same as that produced by shaking the sol. E. S. HEDGES.

Influence of serum on the diffusion of acid dyes in gelatin gel. H. BENNHOLD (Kolloid-Z., 1927, 43, 328—335).—Serum has the power of radically changing the diffusion of acid dyes, in the sense that highly-dispersed substances diffuse slowly in its presence. Naphthol-yellow-*S* is almost completely dissociated in solution, whilst brilliant-Congo-*R* is at the other extreme, since it exists as a coarse dispersion. The two dyes exhibit widely different rates of diffusion in the presence of gelatin gel, but if serum is used in certain defined proportions the rates of diffusion become almost identical. Sera from different animals all possess this property, so that the phenomenon may possess biological significance.

R. A. MORTON.

Influence of acids on the water-binding capacity of serum. A. ADLER (Kolloid-A., 1927, 43, 313—328).—The integral water-binding capacity (sol-swelling+sol osmosis) of sheep-blood serum in the presence of 19 different acids has been investigated. When the acids are placed in the order of their optimal swelling effects on the serum, the series is approximately the same as for the swelling of gelatin. The dissociation constant or the hydrogen-ion concentration of an acid does not determine the water-binding power of the serum. Weak organic acids may show larger effects than strong mineral acids. The biologically important acids, phosphoric, lactic, β-hydroxybutyric, and glycollic acids, exhibit the phenomenon more strongly than the other acids investigated. R. A. MORTON.

Proteins and acids. F. MODERN (Anal. Asoc. Quím. Argentina, 1927, 15, 160—186).—Previous work on the effect of the addition of small amounts of acids to proteins stable in the isoelectric zone (cf. Modern and Pauli, A., 1925, ii, 518; Pauli, A., 1927, 19) has been supplemented by some observations of the displacement of the isoelectric point (determined by minimum viscosity) reached by addition of acids, towards a lower C_H with lower concentrations of proteins, and of the "fixation" of acid added to pure proteins.

These results are discussed in the light of Michaelis' theory and an adaptation of Bjerrum's theory (A., 1923, i, 444). The latter affords an explanation on the assumption that the protein solution contains $\overset{+}{N}H_3{\cdot}R{\cdot}CO_2H$ (A^+), $NH_3OH{\cdot}R{\cdot}CO\overset{-}{O}$ (A^-), $\overset{+}{N}H_3{\cdot}R{\cdot}CO\overset{-}{O}$ ($^+A^-$), and neutral molecules (A). The reaction $A^- + HCl \longrightarrow {}^+A^- + Cl^- + H_2O$ then accounts for the disappearance of the hydrogen ion of added acid and the necessity of adding 150 times the calculated quantity of acid to bring the solution to the isoelectric point, whilst the accompanying increase of conductivity is due to chlorine ions, and the migration of the protein to the cathode (Pauli and Samec, Biochem. Z., 1914, 62, 247) is due to residual A^+ ions. The formation of neutral particles as acid is added explains the displacement of the point of minimum viscosity.

When more acid is added to solutions of ovalbumin, the p_H of which is less than that of the isoelectric point, the "fixation" of hydrochloric acid by the protein increases with addition of acid up to $0{\cdot}025N$, and then remains constant. The activity of the chlorine ion of the protein salt also increases to a maximum at a concentration of $0{\cdot}01N$ of added acid and then falls slowly. R. K. CALLOW.

Viscosity and hydration. III. Kinetics of syneresis. S. LIEPATOV (Kolloid-Z., 1927, 43, 396—400).—The velocity of syneresis of geranin gel was followed by measuring the volume of liquid phase produced after various time intervals. The velocity increases with rise of temperature and with the concentration of the gel. With more concentrated gels, syneresis starts earlier and the total amount of liquid phase produced is less. Syneresis is not observed in gels more concentrated than 3%. Addition of alcohol accelerates the process of syneresis, the degree of acceleration increasing with the amount of alcohol. The results agree with the view that the particles are hydrated and tend to grow together. The degree of hydration calculated from the syneresis agrees with that calculated from the viscosity by means of Hatschek's equation. E. S. HEDGES.

Theory of electrolytic dissociation. W. NERNST (Z. Elektrochem., 1927, 33, 428—431).—Recent measurements (Nernst and Orthmann, A., 1926, 579; 1927, 733) of heats of dilution, *Q*, of dilute salt solutions show that the data for lithium chloride solutions can be represented approximately by the relation $Q=320\sqrt{c}$ for concentrations up to $c=0{\cdot}1N$, a relation of the form to be expected from Debye's theory of strong electrolytes. But with potassium nitrate solutions, *Q* is positive only in very dilute solutions and becomes increasingly negative with increasing concentration. This behaviour is ascribed to incomplete electrolytic dissociation and the relation $Q=320\sqrt{c}-Q_0(1-\alpha)$ may therefore be expected to hold, where α is the true degree of dissociation and Q_0 the heat of dissociation. From the temperature coefficient of the heat of dilution, Q_0 for potassium nitrate is estimated to be 4000 g.-cal. and $1-\alpha=0{\cdot}05$ when $c=0{\cdot}1$. Values of *Q* calculated from these figures agree approximately with the observed values. Values of $1-\alpha$ are also obtained for $0{\cdot}1N$-solutions of sodium nitrate, sodium chloride, and potassium chloride. The apparent degree of association $(1-\alpha')$ from f.-p. data being $0{\cdot}13$ for $0{\cdot}1N$-lithium chloride, the addition of $0{\cdot}13$ to the true degrees of association of other salts gives values which are compared with the corresponding data for $1-\alpha'$, and an approximate agreement is obtained. Hückel's development of the Debye theory is criticised. H. J. T. ELLINGHAM.

Theory of concentrated solutions. IV. Rosanov's method for the study of the composition of the vapour phase in equilibrium with a binary mixture of volatile liquids. E. PAHLAVOUNI (Bull. Soc. chim. Belg., 1927, 36, 533—547).—Rosanov's method has been modified to give accurate results when only about one quarter of the usual quantity of liquid is employed. The new method has been tested and results are given for mixtures of carbon disulphide and carbon tetrachloride, dichloro-ethane and benzene, *cyclo*hexane, and acetone, and butyl alcohol and benzene. H. F. GILLBE.

Change of the mass action law for strong electrolytes. P. GROSS (Oesterr. Chem. Ztg., 1927, 30, 207—210).—A survey of modern views on strong electrolytes. H. F. GILLBE.

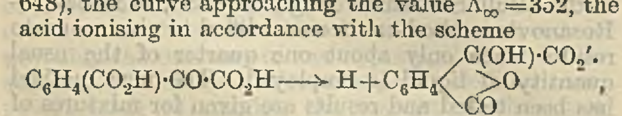
"Ebullioscopic paradox." A. MAZZUCCHELLI (Gazzetta, 1927, 57, 856—858).—The ebullioscopic paradox (cf. Berthoud, Briner, and Schidlof, A., 1927, 1029) is explained in the author's text-book ("Elementi di chimica fisica," Turin, 1923).

E. W. WIGNALL.

Dilution law for strong electrolytes. R. T. LATTEY (Phil. Mag., 1927, [vii], 4, 831—836).—The formula $\lambda_0-\lambda=A/(\beta+V^{\frac{1}{2}})$, where A and B are constants peculiar to the solution in question, has been shown to be applicable, over a wide range, to the conductivity of strong electrolytes. According to Debye and Hückel A should be expressible in the form $K_1+K_2\lambda_0(l_1/l_2+l_2/l_1)$, where K_1 and K_2 are factors depending only on the solvent and l_1 and l_2 are the mobilities of the ions of the salt. According to Onsager (A., 1927, 1031) the mobility term above should be replaceable by another term b independent of the salt. A should therefore be either a linear function of $\lambda_0 b$ or of λ_0. It is shown, however, that A is additive only and can be expressed as the sum of terms which are characteristic of the anion and cation, respectively. From the approximately linear relationship between λ_0 and A for potassium chloride, sodium chloride, and sodium fluoride a linear relationship between a and l for the ions K^+, Na^+, Cl^-, and F^- has been assumed and values of A have been calculated for all the salts examined and found to be in fair agreement with actual determinations. B can still be regarded only as a correction term.

A. E. MITCHELL.

[Electrolytic] dissociation of α-keto-acids. R. BARRÉ and A. CORNILLOT (Ann. Chim., 1927, [x], 8, 329—339).—The electrolytic conductivities of phenylglyoxylic and phthalonic acids and of their sodium salts in aqueous solutions have been measured at various dilutions. The conductivity–dilution curve from $v=40$—1000 for the former acid differs from those obtained by Bader (A., 1891, 257) and by Böeseken and Felix (A., 1921, i, 844) and approaches asymptotically the value $\Lambda_\infty=352$, which is in good agreement with the value (353) calculated from the curve for the sodium salt, which approaches the value $\Lambda_\infty=83$. Hence the anion has a mobility of only 41, the value obtained by the application of Ostwald's law being 64. With the above value of Λ_∞ for the acid, the dissociation constant has a value 10×10^{-2}, phenylglyoxylic acid being a strong acid, and in agreement with this a sharp neutralisation point is obtained by electrometric titration of the acid with sodium hydroxide solution. Similar results are obtained in the case of phthalonic acid ($v=12\cdot9$—648), the curve approaching the value $\Lambda_\infty=352$, the acid ionising in accordance with the scheme



$$C_6H_4(CO_2H)\cdot CO\cdot CO_2H \longrightarrow H+C_6H_4\left<\begin{matrix}C(OH)\cdot CO_2{}'.\\ >O\\ CO\end{matrix}\right.,$$

whence $k=3\cdot2\times10^{-2}$, and the mobility of the anion is 39, in disagreement with the value 64 calculated on the basis of Ostwald's law. For the neutral sodium salt the value $\Lambda_\infty=217$ is found experimentally, in moderate agreement with the value 242 calculated on the assumption that the bivalent ion has twice the mobility of the univalent ion. Electrometric titration shows a well-defined minimum corresponding with the monosodium salt, no subsequent minimum being obtained on further addition of sodium hydroxide. The supposed anomalies in the dissociation of α-ketonic acids are due to the erroneous values which have been assumed for the ionic mobilities and have no real existence. J. W. BAKER.

Dissociation constants of cystine, cysteine, thioglycollic acid, and α-thiolactic acid. R. K. CANNAN and B. C. J. G. KNIGHT (Biochem. J., 1927, 21, 1384—1390).—The apparent constants at 30° at different stages of dissociation have been determined for the above compounds, the methylene-blue–methylene-white electrode being used in the case of cystine and the hydrogen electrode for the other compounds. S. S. ZILVA.

Pseudo-electrolytes. Condition of ammonia in aqueous solution. E. BAARS (Samm. chem. u. Chem.-tech. Vorträge, 1927, 29, 53 pp.; Chem. Zentr., 1927, i, 2792—2793).—The equilibrium between ammonia and water in an indifferent medium (nitrobenzene) was investigated; the solubility of ammonia in dry and aqueous nitrobenzene and of water in benzene was determined. Values of $K=[NH_4OH]/[NH_3][H_2O]$ increase with the ammonia concentration. Values of K' for the reaction $2NH_3+H_2O=2NH_3,H_2O$ change to a similar extent, but in the opposite sense. Hence both hydrates are considered to be present. The partial pressures of water and ammonia over solutions of ammonia, and the contraction on admixture of ammonia and water vapour at the ordinary temperature were also investigated.

A. A. ELDRIDGE.

F. p. of concentrated solutions. II. Solutions of formic, acetic, propionic, and butyric acids. III. Solutions of phenol. E. R. JONES and C. R. BURY (Phil. Mag., 1927, [vii], 4, 841—848, 1125—1127; cf. A., 1927, 619).—The activities of formic, acetic, propionic, and butyric acids have been determined by the f.-p. method over a wide range of concentration. In general the results are in agreement with those of other observers. The rapid change of the activity of butyric acid with the concentration is attributed to the close proximity of the f.-p. curve to the critical solution point, which lies in the metastable region within a degree of and below the curve.

III. Previous work has been extended to the determination of the activity of phenol by the f.-p. method. From the results the free energy of formation of phenol hydrate, $2PhOH,H_2O$, from ice and solid phenol at about −1° is −306 g.-cal. per g.

A. E. MITCHELL.

Hydrolysis of solutions of sodium palmitate as measured by extraction with *p*-xylene. J. W. MCBAIN and R. BUCKINGHAM (J.C.S., 1927, 2679—2689).—The hydrolysis of soap solutions has been investigated by studying the distribution of palmitic acid between water and *p*-xylene. Two kinds of experiments are described, viz., those in which soap solutions are extracted with the non-aqueous solvent and therefore changed in composition, and those in which the right amount of fatty acid is previously added to the non-aqueous layer, so that the final equilibrium is determined without appreciable alteration of the aqueous solution. The results show that true equilibrium is attained, and that a soap solution, even when it is appreciably hydrolysed, contains only the merest trace of uncombined fatty acid, which is completely dissolved and not in the emulsified or free condition. Practically all the fatty acid corresponding with the hydrolysis alkalinity is in combination as insoluble acid soap. Soap solutions are excellent buffers, as their hydrolysis alkalinity is less dependent on extraneous additions than is usually the case with standard buffers. The effect of electrolytes is to diminish the extractability, and probably the hydrolysis, of dissolved soap. O. J. WALKER.

Superacid solutions. I. Use of chloranil electrode in glacial acetic acid and strength of certain weak bases. N. F. HALL and J. B. CONANT (J. Amer. Chem. Soc., 1927, **49**, 3047—3061).—Superacid solutions (*i.e.*, solutions of substances, like salts of amides, in which salt formation is exceptionally complete) are investigated with the aid of cells of the type Pt|tetrachlorobenzoquinone (satd.), tetrachloroquinol (satd.), HX (*c*) in acetic acid|LiCl in acetic acid|aqueous calomel electrode. Such cells have large *E.M.F.*, which are uniformly reduced on addition of basic substances, thus permitting the titration of the various acids with bases. Titration curves for sulphuric acid with many bases (pyridine, carbamide, acetanilide, etc.) are recorded; they resemble the curves obtained in water systems, and the bases studied are arranged in order of increasing strength and characterised by constants allied to the hydrolysis constants of their salts in water solution. The dissociation constants at 25° of *p*-toluidine and triethylamine are $1{\cdot}29\times10^{-9}$ and $5{\cdot}62\times10^{-4}$, respectively. The activity coefficients of molar solutions in acetic acid of trichloroacetic, sulphuric, and perchloric acids are 6·7, 700, and 25,000. The cause of superacidity in a solution is attributed to abnormally high hydrogen-ion activity. The *E.M.F.* of the above cells are depressed on addition of alcohol and especially of water to the acetic acid solution. S. K. TWEEDY.

Superacid solutions. II. Chemical investigation of the hydrogen-ion activity of acetic acid solutions. J. B. CONANT and N. F. HALL (J. Amer. Chem. Soc., 1927, **49**, 3062—3070).—Data are recorded for five arylcarbinols and five unsaturated ketones with the aid of acetic acid buffer solutions containing sulphuric acid and very weak bases. The results, which are consistent with those obtained by the methods of the preceding abstract, show that the substances used constitute a graded series of indicators suitable for use in superacid solutions. Addition of alcohol seems to produce an alcoholysis of the carbinol salt besides diminishing the acidity of the solution. The rate of sucrose inversion in 98% acetic acid solution is approximately proportional to the hydrogen-ion activity as measured either by the chloranil electrode or by means of indicators. The chemical behaviour of acids and bases in different solvents is discussed. S. K. TWEEDY.

Oxidation – reduction. XI. Potentiometric and spectrophotometric studies of Bindschedler's-green and toluylene-blue. M. PHILLIPS, W. M. CLARK, and B. COHEN (U.S. Public Health Service, Suppl. 61).—The equilibrium potentials of mixtures of Bindschedler's-green and its leuco-compound and of toluylene-blue and its leuco-compound in buffered solutions have been determined. Electrode equations have been derived relating the potentials to the hydrogen-ion concentration and the dissociation constants of the reactants. These constants have been evaluated from the electrode data and checked by hydrogen electrode titration curves of the leuco-compounds or by spectrophotometric observations. Bindschedler's-green is subject to spontaneous decomposition the rate of which is a function of the hydroxyl-ion concentration and leads to serious drifts of potential beyond about p_H 9·5. The behaviour of the indamines is compared with that of the thiazines. The basic indamines form useful alternative indicators to the acidic indophenols for the determination of oxidation–reduction intensity in biological systems. R. K. CANNAN.

Oxidation – reduction. XII. Schardinger reaction. W. M. CLARK, B. COHEN, and M. X. SULLIVAN (U.S. Public Health Rep., Suppl. 66, 1927). —The observations of Clark, Cohen, and Gibbs (A., 1925, ii, 1164) on the changes in electrode potential which occur on the addition of aldehyde to fresh milk have been confirmed. Various possible causes of failure in the experiments of Kodama (A., 1926, 1175) are discussed and illustrated experimentally. Kodama's observation that the addition of hypoxanthine to xanthine oxidase does not lead to the development of increased negative potentials is confirmed. R. K. CANNAN.

Dissociation of some organic and inorganic substances at high temperatures. G. M. WOOD and T. C. POULTER (Proc. Iowa Acad. Sci., 1926, **33**, 172—173).—Vapours were passed through a tube (at 500°) provided with wire electrodes to which a *P.D.* of 1—15 volts was applied, and the current was measured. The following showed a significant conductivity: glacial acetic acid, ethyl acetoacetate, hydrogen chloride, "AmOH," iodine, and nitrobenzene. Conductivity could be detected with 75% acetic acid, amylene, carbon tetrachloride, chlorobenzene, formic acid, bromine, bromobenzene, and methyl acetate. Conductivity was not observed with benzene, methyl alcohol, ammonia, toluene, chloroform, water, ethyl alcohol, benzaldehyde, or ethyl bromide. CHEMICAL ABSTRACTS.

Equilibrium diagram of the system thallium–phosphorus. Q. A. MANSURI (J.C.S., 1927, 2993—2995).—Molten thallium alloys with phosphorus, especially above 400°. When more than 2·5% of phosphorus is added, two layers are formed. The upper layer is a dark, brittle, homogeneous solid X, melting at 420° and dissolving excess of phosphorus to form solid solutions which freeze at temperatures above 420° and over a temperature range. The excess phosphorus may be present as the yellow variety, since the alloys inflame when rubbed on emery paper. The lower layer is a solution of a small quantity of X in thallium, but on cooling it gradually loses phosphorus and freezes at the m. p. of thallium. The substance X tends to dissociate into its constituents at all temperatures. A high pressure is, therefore, necessary for its formation.

M. S. Burr.

Vapour pressures of potassium amalgams. R. W. Millar (J. Amer. Chem. Soc., 1927, 49, 3003—3010).—The mercury vapour pressures of amalgams containing a mol. fraction N_2 of potassium are given by $\log p(\text{mm.})=a-b/T$. Corresponding values of N_2, a, and b are 0·0492, 7·799, 3125; 0·0552, 7·779, 3125; 0·0877, 7·717, 3125; 0·180, 7·569, 3212; 0·321, 7·968, 3950. The activities of the mercury, a_1, are calculated for each amalgam at 200°, 250°, 310°, and 390° and van Laar's relation between a_1/N_1 and N_1/N_2 is shown to hold at each temperature (cf. Hildebrand, "Solubility," p. 45). The deviations from Raoult's law are among the greatest yet observed and decrease with rising temperature. The heat of vaporisation of mercury from amalgams containing up to 8 mols. % of potassium is equal to that of pure mercury; possibly a mercuride is formed which behaves as a perfect solute with respect to pure mercury as solvent. At concentrations above 8 mols. % the partial molal heat content of the mercury is negative.

S. K. Tweedy.

Vapour pressure of sodium and cæsium amalgams. H. E. Bent and J. H. Hildebrand (J. Amer. Chem. Soc., 1927, 49, 3011—3027; cf. preceding abstract).—The vapour pressures were measured between 554° and 651° Abs., the mol fraction of mercury, N_1, varying between 1 and 0·5. The correction of experimental errors is discussed. If $\log a_1/N_1=0{\cdot}5\beta N_2^2$, then β (a function of T) expresses the deviation of both solvent and solute from Raoult's law (cf. Hildebrand, A., 1927, 936) and its values are compared for sodium, potassium, cæsium, and barium. From the connexion between β and T the relations $\log a_1/N_1=-(1965/T+3{\cdot}42)N_2^2$, $=-5815N_2^2/T$, $=-7810N_2^2/T$ are derived for the first three amalgams. The activities of the alkali metals are determined by integration of the Duhem equation and the *E.M.F.* of cells in which alkali metal is transferred to amalgam are calculated. On the assumption that each molecular species obeys Raoult's law and that dissociation occurs in accordance with the mass action law, the formation of the compounds $NaHg_2$, $NaHg_4$, and $NaHg_6$ will explain the vapour pressures of amalgams from $a_1=0{\cdot}1$ to 0·9, whilst in very dilute amalgams the compound $NaHg_{16}$ will account for both the vapour pressure and the *E.M.F.* data (cf. Poindexter, A., 1926, 897). The apparent molal volume of mercury in cæsium is negative when the mercury concentration is less than 30 mols.-%.

S. K. Tweedy.

Volatile hydrides. Formation of a compound HCl,HBr, and the binary system hydrogen chloride–nitrous oxide. A. Klemenc and O. Kohl (Z. anorg. Chem., 1927, 168, 163—176).—Pressure measurements have shown that at −85° to −75° hydrogen chloride and hydrogen bromide give a solid *compound*, HCl,HBr, which in the vapour state or in solution in either of its components is practically completely dissociated. Down to −120°, its vapour pressure, P, is connected with the temperature (Abs.), T, by the relation $\log P=-811/T+6{\cdot}818$. Attempts to detect the formation of a compound between hydrogen chloride and nitrous oxide in the liquid state in the same way have been unsuccessful.

R. Cuthill.

Equilibrium of the system potassium oxalate–water. N. K. Voskresenski (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 458; cf. A., 1926, 898).—The eutectic point of this solution, −6·3°, corresponds with a solution containing 25·19 g. of the salt per 100 g. of water. At ordinary atmospheric temperature the saturated salt solution boils at 107°.

T. H. Pope.

Equilibria in certain binary systems of 2 : 4 : 6-trinitromethylnitroaniline (tetryl). N. N. Efremov and A. M. Tichomirov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 269—301).—Binary systems of tetryl with the following compounds have been subjected to thermal analysis. (1) *o*-Nitrophenol (m. p. 44·9°); eutectic point, 40·2°, corresponds with 87·8 mols. % of nitrophenol; the mixtures are stable, and solid solutions, containing up to about 5·5% of tetryl, are formed. (2) *p*-Nitrophenol (m. p. 113·8°); mixtures are viscous and prone to supercooling; eutectic point, 80·6°, corresponds with 50·6 mols. % of nitrophenol; mixtures are not very stable, and solid solutions containing up to 8·5 mols. % of *p*-nitrophenol and up to 10·5 mols. % of tetryl are formed. (3) *p*-Nitrotoluene (m. p. 52·4°); mixtures are stable and colourless; eutectic point, 46·6°, corresponds with 84·7 mols. % of *p*-nitrotoluene (cf. Giua, A., 1915, i, 950); no solid solutions are formed. (4) *o*-Nitroaniline (m. p. 69·4°); mixtures are yellowish-red and, after crystallisation, violet; they show only slight stability; eutectic point, 49·7°, corresponds with 73·2 mols. % of *o*-nitroaniline. (5) *m*-Nitroaniline (m. p. 114·0°); mixtures are unstable and are yellow when fused and grey when crystallised; eutectic point, 78·3°, corresponds with 55·3 mols. % of *m*-nitroaniline; no solid solutions are formed. (6) *p*-Nitroaniline (m. p. 147·3°); mixtures, yellow when fused and brown when crystallised, are unstable, and the eutectic point, 87·2°, corresponds with 40·6 mols. % of *p*-nitroaniline. (7) *m*-Dinitrobenzene (m. p. 89·5°); mixtures are colourless and no solid solutions are formed; eutectic point, 65·5°, corresponds with 66·5 mols. % of *m*-dinitrobenzene. (8) 2 : 4-Dinitrotoluene (m. p. 68·0°); mixtures are stable and pale yellow, and no solid solutions are formed; eutectic point, 59·1°, corresponds with 79·5 mols. % of the dinitrotoluene. (9) 2 : 4-Dinitrophenol (m. p. 111·4°); solid solutions containing 0—16% of tetryl and 0—18·5% of dinitrophenol are formed; eutectic point, 83·1°, corresponds with 57·7 mols. % of dinitrophenol. (10) Picric acid; mixtures are stable, and the eutectic point, 75—77°, corresponds with about 43 mols. % of picric acid. (11) Styphnic acid (m. p. 175·5°); mixtures with 73—90% of the acid are unstable, and solid solutions are probably formed; eutectic point, about 83°, corresponds with about 25·5 mols. % of the acid. (12) 2 : 4 : 6-Trinitrotoluene; eutectic point, 58·8°, corresponds with 63·4 mols. % of trinitrotoluene, and there is no reason to assume the existence of a molecular compound of the two components; this result differs from that obtained by Giua (A., 1915, i, 950). (13) 2 : 4 : 6-Trinitrocresol (m. p. 101·2°); eutectic point is about 78° and corresponds with 63—64 mols. % of trinitrocresol. T. H. Pope.

Gas–solid equilibria. I. Pressure–temperature equilibria between benzene and (*a*) ferric oxide gel, (*b*) silica gel in sealed systems of known and unalterable total composition. B. Lambert and A. M. Clark (Proc. Roy. Soc., 1927, A, **117**, 183—201).—The equilibria between benzene and ferric oxide gel and silica gel, respectively, have been investigated by a method involving (1) the introduction into an all-glass apparatus, part of which consists of an evacuated mercury manometer, of an accurately known weight of the "activated" gel; (2) evacuation of the system, followed by the distillation into the apparatus of a known weight of benzene; (3) heating the sealed system in a vapour-bath to definite temperatures (30—130°), the equilibrium pressure for each temperature being read on the manometer. A series of such closed systems was investigated, containing gradually increasing weights of benzene per g. of gel used. Details are given for the weighing of portions of gel in a vacuum, the construction of evacuated mercury manometers, and the introduction of accurately known weights of benzene into the system. The pressure–concentration relationships derived from the pressure–temperature curves are described. L. L. Bircumshaw.

Thermal decomposition of ferrous sulphate. E. Greulich (Z. anorg. Chem., 1927, **168**, 197—202.)—The dissociation pressure of anhydrous ferrous sulphate between 235° and 698° has been determined, the pressure reaching 1 atm. at 680°. Using available data for the relation between the constant of the equilibrium $2SO_3 \rightleftharpoons 2SO_2+O_2$ and the temperature, T, to calculate the partial pressure, p, of sulphur trioxide in the gaseous phase resulting from the dissociation, the results agree with the equation $\log p = -2691{\cdot}8/T + 5{\cdot}1526$. From this equation, the heat of dissociation between 316° and 554° is calculated to be 12·3 kg.-cal., giving 189·5 kg.-cal. for the heat of formation of ferrous sulphate. R. Cuthill.

Reactions in the solid state at high temperatures. III. Heterogeneous equilibria in systems in which gas is evolved. W. Jander (Z. anorg. Chem., 1927, **168**, 113—124; cf. A., 1927, 1037).—The gas pressures corresponding with the equilibrium $BaCO_3+SiO_2 \rightleftharpoons BaSiO_3+CO_2$ have been determined at various temperatures, and found to obey the Nernst approximation formula satisfactorily if the heat of reaction from left to right is taken as −34 kg.-cal. at 0° Abs. R. Cuthill.

System lime–alumina–silica. E. Jänecke (Z. Elektrochem., 1927, **33**, 477; cf. Hansen, Dyckerhoff, Ashton, and Bogue, A., 1927, 519).—Evidence for the existence of the compound $8CaO,Al_2O_3,2SiO_2$ is discussed and the conclusions of Hansen and collaborators are disputed. H. J. T. Ellingham.

Crumbling of fused masses in the system calcium oxide–alumina–silica. T. Suzuki and K. Kasai (Sci. Papers. Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 173—188).—The crumbling after solidification of molten mixtures of calcium oxide, alumina, and silica has been examined, the extent to which the phenomenon occurs being measured by the relative amount of the mass which is converted into powder. By measurements of refractive indices, it is found that the powder resulting from masses containing little alumina consists mainly of Rankin and Wright's γ-$2CaO,SiO_2$ (A., 1915, ii, 50), whereas in mixtures rich in alumina the compound $3CaO,Al_2O_3,SiO_2$ preponderates. Of the mixtures examined, that containing 32 mols. % of silica and no alumina crumbled most readily. R. Cuthill.

Ternary systems copper acetate–acetic acid–water and lead acetate–acetic acid–water at 25°. K. Sandved (J.C.S., 1927, 2967—2974).—Investigation of the system copper acetate–acetic acid–water at 25° indicates that the following three compounds are capable of existence: (1) $Cu(OAc)_2,H_2O$; (2) $Cu(OAc)_2,AcOH,H_2O$; (3) $Cu(OAc)_2,AcOH$. The ternary invariant point between (1) and (2) lies at 0·79% of copper acetate and 74·06% of acetic acid, and that between (2) and (3) at 0·17% and 95·40%, respectively. The solubility of copper acetate in water at 25° is 6·79% and it is depressed by the addition of acetic acid. The system belongs to the same type as the alkali acetate–acetic acid–water systems examined by other investigators. When lead acetate is substituted for copper acetate, totally different behaviour is observed. The solubility of lead acetate trihydrate increases on addition of acid, the latter reaching a maximum at 28·99%, when the concentration of the anhydrous salt is 52·1%. At 67·90% of salt and 22·01% of acid there appears to be a ternary point between the trihydrate and the anhydrous salt. No acid salt has been identified. The results are discussed with reference to other data on the solubility of lead salts and also on the conductivity of electrolytes in acetic acid. The solutions of lead acetate in concentrated acetic acid probably contain very soluble complex salts of the type xAcOH,yPb(OAc)$_2$, dissociated to a small extent only into complex ions. M. S. Burr.

Systems uranyl nitrate, alkali nitrate, water, at 25°. A. Colani (Compt. rend., 1927, **185**, 1475—1476).—The double nitrates of uranyl and sodium or potassium do not crystallise from aqueous solutions in the cold. The ammonium double salt $UO_2(NH_4)_2(NO_3)_4,2H_2O$ separates, in slowly deliquescing crystals which are decomposed by water. The anhydrous double salt $UO_2NH_4(NO_3)_3$ probably results from the crystallisation of an equimolecular mixture of the above nitrates from cold nitric acid (d 1·33), but is readily decomposed by cold water.

J. Grant.

Empirical formula expressing mutual solubility of two salts with a common ion. T. S.

WHEELER (J.S.C.I., 1927, **46**, 420—423T).—The expression $s_0-s=kx^m$, where s_0 is the solubility of the saturating salt in a unit volume of its own aqueous solution at temperature t, s is the quantity of the saturating salt dissolved in a unit volume of solution at temperature t in presence of a quantity x of added salt (s_0, x, and s are in the same units), and m and k are empirical constants, expresses within the limits of experimental error the mutual solubility in water of salts with a common ion, provided that the salts separate from the aqueous solution in crystals containing no water of crystallisation, and that there is no formation of mixed crystals or double salts. The constant m depends only on the saturating salt.

Calcium cyanamide. II. Equilibrium of the reaction $CaC_2+N_2\rightleftharpoons CaCN_2+C$. H. FRANCK and H. HEIMANN (Z. Elektrochem., 1927, **33**, 469—475).—The system has been investigated by measurements of the pressure of nitrogen developed at 940—1300°, calcium cyanamide of 99·6% purity being obtained by the reaction between calcium oxide and hydrogen cyanide. The curves obtained by plotting the pressure of nitrogen against temperature show two branches, the lower, corresponding with a solid solution of cyanamide and carbide, being exponential, and the upper, corresponding with the molten system, being linear. The lowest value of the "break" occurs at 1146°, and is assumed to indicate the m. p. of the eutectic, cyanamide–carbide. The break also corresponds with an arrest in the cooling curve. The addition of calcium fluoride depresses this break and also the pressure of nitrogen. The value of the heat of the reaction obtained from the curves is 68,400 g-cal. between 1080° and 1130°, in good agreement with that obtained directly by Franck and Hockwald (B., 1926, 88). L. S. THEOBALD.

Liquid immiscibility in the system FeO–Fe_2O_3–Al_2O_3–SiO_2. J. W. GREIG (Amer. J. Sci., 1927, [v], **14**, 473—484).—The occurrence of two liquid phases in the system FeO–Fe_2O_3–SiO_2 has been studied; fusion of iron oxide with silica results in general in the formation of two liquid layers, of which the more siliceous layer is the less fluid. Over a small temperature interval in the neighbourhood of 1660° cristobalite is in equilibrium with the two liquids. Mixtures having a ferrous : ferric ratio of about 1 : 1 are the least miscible. The quantity of aluminium oxide necessary for the production of a homogeneous liquid varies with the ferrous : ferric ratio and with the silica content, a maximum of about 6·5% being required for a 1 : 1 ratio. It is shown that the hypothesis of siliceous magmas separating into two liquid layers is incorrect. The bearing of the results on the problems of furnace linings is discussed. Addition of iron oxide to a mixture of silica and alumina may in certain cases raise the fusion temperature of the whole. H. F. GILLBE.

Determination of the composition of the solid phase in equilibrated systems. V. P. SCHISCHOKIN (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 421–425).—The graphic method devised by Schreinemakers (A., 1893, ii, 260) for determining the composition of a solid phase in equilibrium with a liquid phase does not give exact results for small angles between the two straight lines, representing respectively the composition of the liquid phase and of the residual mixture of solid and liquid phases. This defect may be remedied by expressing the composition in terms of a fixed weight of the solvent. This modified procedure is applied to the systems guanidine nitrate–silver nitrate–water, and ammonium chloride–cupric chloride–water (cf. Rivett and Clendinnen, J.C.S., 1923, **123**, 1634). T. H. POPE.

Analytical and graphical methods of investigating complex equilibrium systems. V. P. SCHISCHOKIN (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 333—369).—Algebraic and geometric methods are considered. It is shown that various physical properties, and the relation between the concentrations of the components of systems which are formed by the mixing of m components may be expressed as linear non-homogeneous functions with m variables. On removal of n complexes from a system with m components, the relation between the concentrations of the components is, in the general case, determined by a linear non-homogeneous function with $(m+n)$ variables.

For determining the connexion between the concentrations of the components of complex systems, use may be made of the graphical methods of ordinary descriptive geometry and those of Fedorov's new graphical geometry (parallel vectors). In operations involving four or more variables Bieberbach's method is simpler than Federov's inclined vector method. The group to which a system belongs may be determined by D'Ocagne's and Masso's nomographic methods.

From the character of the relations between the concentrations of the components of a complex system, it is possible to judge, both qualitatively and quantitatively, of the physico-chemical processes which have taken place in the system prior to the establishment of the existing equilibrium.

These analytic and graphic methods are applied to the solution of several hydrological and chemico-mineralogical questions. Various mineral springs are shown to be formed by the mixing of two different waters, one more saline that the other and both resulting from metamorphosis of the water of the Black Sea. The formula attributed to tourmaline by Penfield and by Foote is readily verifiable by means of the characteristic equation for the mineral. T. H. POPE.

Concept of substance and the phase rule. R. WEGSCHEIDER (Z. anorg. Chem., 1927, **168**, 33—40).—A substance, in the sense of the phase rule, is defined as including all homogeneous bodies the properties of which, after subjection to variations, become the same when they are subjected to identical external conditions; the changes produced when the bodies are subjected to changes of external conditions, at least within certain limits, are not concerned with changes of composition. H. F. GILLBE.

Theory of static and dynamic displacement. II. D. REICHINSTEIN (Z. Elektrochem., 1927, **33**, 455—469; cf. A., 1926, 130).—Theoretical. The author's displacement theory is further extended and set out as a unified system. The theory not only applies to the statics and dynamics of adsorption processes, but also serves to characterise solutions and solid solutions. The philosophical significance of the theory is discussed and its applications to adsorption, solubility, passivation of metals, and decrease in velocity of oxidation with increasing concentration of oxidising agent are demonstrated.

H. J. T. Ellingham.

Equations of state of adsorbed phases. B. Tamamushi (Bull. Chem. Soc. Japan, 1927, 2, 299—303; cf. A., 1927, 199).—On the assumption that the equation of state for an adsorbed substance involves the potential energy due to intermolecular forces as well as the thermal energy of the adsorbed molecules, and applying the theory of dipoles, the term kE in Cofman's equation (A., 1926, 674) is converted into the form iRT. Applying Volmer's surface correction (A., 1925, ii, 539), the value of i for the adsorption of various organic substances at liquid–gas and liquid–liquid interfaces is found not to exceed 1, indicating that the adsorbed molecules attract each other. In the adsorption of acetic acid at a water–carbon interface, on the other hand, the acid molecules apparently repel each other, the value of i being greater than 1. R. Cuthill.

Reaction regions. XVII. Reaction regions in which a dichromate is the substance supplying oxygen. W. P. Jorissen and G. M. A. Kayser (Rec. trav. chim., 1927, 46, 885—890; cf. this vol., 21).—Reaction regions in the systems potassium dichromate–sulphur–iron and potassium dichromate–sulphur–aluminium have been investigated and are represented diagrammatically. In presence of silica, the narrow neck in the reaction region of the system ammonium dichromate–sulphur–iron becomes a gap and the reaction space becomes divided into two regions. J. S. Carter.

Free energy of transition in the system calcite–aragonite. J. L. Buchan (Trans. Faraday Soc., 1927, 23, 668—671).—The *E.M.F.* at 25° of a cell consisting of two hydrogen electrodes dipping into saturated solutions of calcite and aragonite, respectively, in *N*-potassium chloride solution containing 25% of alcohol, and connected by the same potassium chloride solution, is $0{\cdot}009 \pm 0{\cdot}0002$ volt, the electrode in the calcite solution being positive. The value of the free energy of transition of aragonite to calcite, calculated from this, is -414 cal./g.-mol., which is in approximate agreement with that determined from Kohlrausch's solubility data (A., 1903, ii, 528).

M. S. Burr.

Methods of determining the heat equivalent of calorimetric bombs. W. Swientoslawski (J. Russ. Phys. Chem. Soc., 1927, 59, 563—565).—The merits of a universal relative determination of heats of combustion using benzoic acid as a standard are discussed and compared with methods used for determining absolute values. A. Ratcliffe.

Methods of determining the heat equivalent of calorimetric bombs. A. Schukarev (J. Russ. Phys. Chem. Soc., 1927, 59, 567—572).—Disadvantages of relative determinations of heats of combustion are discussed (cf. preceding abstract).

A. Ratcliffe.

Calorimetric researches. XIV. Heats of combustion of successive members of homologous series: the normal primary aliphatic alcohols. P. E. Verkade and J. Coops, jun. (Rec. trav. chim., 1927, 46, 903—917; cf. A., 1926, 686, 1210).—In order to substantiate the suggestion that alternation is confined to the crystalline state, the heats of combustion of seven normal aliphatic alcohols have been determined. All the heats of combustion relate to isothermal reactions at 19·5°. The values thus obtained for the molecular heats of combustion (kg.-cal. 15°) at constant pressure, Qp, are: butyl, 639·5; amyl, 795·6; hexyl, 951·9; heptyl, 1108·4; octyl, 1265·0; nonyl, 1420·9; decyl, 1576·9. Combining these results with those of Richards and Davis (A., 1920, ii, 589) for the lower alcohols it is found that there is no indication of any alternation, the increment due to each increase of CH_2 being 156·3 kg.-cal. Contrary to previous experience, it is found that initial terms with abnormally high energy contents are missing.

In order to investigate the variation in molecular volume with mol. wt. the densities of nine normal alcohols were determined. The values of $d_4^{19\cdot6}$ thus obtained are: butyl, 0·7986; amyl, 0·8041; hexyl, 0·8082; heptyl, 0·8116; octyl, 0·8146; nonyl, 0·8174; decyl, 0·8198; undecyl, 0·8217; dodecyl, 0·8234. The derived molecular volumes show a constant increment of the order 16·59—16·80 c.c. Neither the b. p. nor the molecular refractivities (existing data) show any indication of alternation.

Approximate values for the degrees of association of the normal aliphatic alcohols have been calculated by standard methods. Whilst such values are admittedly approximate they nevertheless show that the degree of association decreases as the series is ascended. Possibilities whereby variation in degree of association may be reconciled with constant increment in physical constants are discussed. J. S. Carter.

Thermochemistry of organic compounds. E. Berner (Arch. Math. Naturvidenskab., 1926, 39, 6; reprint).—The heats of combustion of a series of stereoisomeric racemic and *meso*-compounds of the types represented by racemic acid and mesotartaric acid have been determined in a specially designed bomb calorimeter. Temperatures were measured by a platinum resistance thermometer and the substances were carefully purified by alternate crystallisation and distillation in a vacuum. In all cases, it was found that the *meso*-isomerides have the greater heats of combustion when corrections are applied for the difference in the lattice energy of the solids; these corrections were derived from measurements of the heats of dissolution of the isomerides. Calculations from existing data indicate that the energy of the atomic linkings in paraffins, at any rate in those containing less than ten carbon atoms in the molecule, is constant. The energy of the unsaturated linkings in unsaturated aliphatic compounds is nearly constant, and the energy in these linkings is in agreement with the ease with which they are attacked chemically. Alicyclic hydrocarbons containing five or more carbon atoms in the molecule have normal linking energies; the configuration of the rings is therefore multiplanar, and it is suggested that isomeric forms of these compounds may be detectable at low temperatures. G. A. Elliott.

Fictitious heat of dissolution of thallous sulphate. F. Ishikawa (Bull. Chem. Soc. Japan, 1927, 2, 294—299).—If the *E.M.F.* of the cell 50% thallium amalgam|saturated solution of thallous sulphate in equilibrium with the solid, mercurous sulphate|mercury and the similar cell with an unsaturated solution of thallous sulphate are E_A and E_B, respectively, application of the Gibbs–Helmholtz equation shows that the differential heat of dissolution, Q, of thallous sulphate is given by the expression $Q=nF[(E_B-E_A)-T\{(dE/dT)_B-(dE/dT)_A\}]$, where n, F, and T have their usual significance. By extrapolation to the saturation concentration of the values of Q obtained from *E.M.F.* measurements with the above cells, values of the fictitious heat of dissolution are obtained which approximate closely to those derived previously by another method (A., 1923, ii, 537). R. Cuthill.

Heats of dilution of strong electrolytes in the limiting region of the Debye–Hückel theory. W. Lange and G. Messner (Z. Elektrochem., 1927, 33, 431—440).—By means of an adiabatic differential calorimeter reading to about a millionth of a degree, measurements have been made at 25° of the heats of dilution, Q, of dilute solutions of the following salts: (1) potassium chloride, sodium chloride, lithium chloride, lithium bromide; (2) calcium nitrate, sodium sulphate; (3) magnesium sulphate, calcium sulphate; (4) potassium nitrate, cæsium chloride. Concentrations, c, as low as 0·001 g.-mol./litre were used in some cases. Salts of group (1) all gave practically identical values of Q at $c=0{\cdot}01$, but these values are definitely lower than the calculated value. Since the latter involves the temperature coefficient of the dielectric constant of water, however, it may be somewhat inaccurate. For salts of group (2), values of Q agree with each other, but are also less than the calculated value, whereas values obtained for group (3) are considerably higher than the theoretical and these salts are definitely anomalous. In all cases, Q is positive at sufficiently low concentrations as required by the theory, and for lithium bromide Q is practically proportional to $\sqrt{c}$ up to $c=0{\cdot}1$. With salts of group (4) the $Q-\sqrt{c}$ graphs are definitely curved and exhibit a maximum, Q eventually becoming negative with increasing concentration, for potassium nitrate at any rate. For potassium chloride and lithium bromide measurements of Q were also made at lower temperatures and for each salt the ratio of the values of Q at two different temperatures agreed closely with the theoretical value. From the data for lithium bromide it is shown that the partial molal heat capacity of water, c_{p_1}, in solutions of this salt is given by $c_{p_1}=17{\cdot}98-0{\cdot}098c^{1{\cdot}5}$, a relation of the same form as that obtained empirically by Randall and Ramage (A., 1927, 208), the value of the constant (0·098) being of the same order as that found by these authors for sodium chloride solutions. H. J. T. Ellingham.

Free energy and heat of dilution of concentrated solutions. R. Fricke and L. Havestadt (Z. Elektrochem., 1927, 33, 441—455).—Vapour pressures of aqueous solutions of various substances, including electrolytes and non-electrolytes, at various concentrations have been measured by a differential method at 0° and at either 10° or 15°. For each solute at each temperature values of vapour pressure, p, are plotted against the dilution, φ, of the solution (g.-mol. of water/g.-mol. of solute) or against the mol. fraction of the water. For solutions of carbamide and silver nitrate, values of p are higher in concentrated solutions than those corresponding with the mixture law, $p=p_0\varphi/(\varphi+1)$, where p_0 is the vapour pressure of water, but in more dilute solutions values for carbamide approach the theoretical values closely. For most of the other substances examined the vapour pressures were notably lower than the theoretical, especially in the more concentrated solutions of substances having a high positive heat of dilution. From the data obtained, the free energy of dilution, A, and the heat of dilution, U, were calculated for each solution, values of U being obtained by means of Kirchhoff's equation. For each solute values of A and U were plotted against φ. For silver nitrate and the salt $2KI,HgI_2$, U is negative and the A and U curves diverge with increasing concentration. Most of the other substances examined have a high positive value of U, and in these cases the A and U curves intersect, A being $>U$ in more dilute solutions but $<U$ in more concentrated solutions. In no case do the A and U curves run parallel over a considerable range of concentration so that the "theory of the ideal concentrated solution" (Nernst) cannot be applied without further considerations to concentrated solutions with a high positive heat of dilution. H. J. T. Ellingham.

Diffusion coefficients and ionic mobilities. E. N. Gapon (Z. anorg. Chem., 1927, 168, 125—128).—Examination of some of the existing data for the diffusion coefficients, D, of organic substances in water shows that if n is the number of atoms in the molecule the relation $D\sqrt{n}=$constant is approximately true, the value of the constant being rather greater for associated substances than for non-associated substances. A similar empirical formula, $u\sqrt{n}=$ constant, connects n with the ionic mobility, u, in the case of numerous electrolytes. This latter expression may be used to calculate ionic hydrations, the results being in general in agreement with those obtained by the usual methods. R. Cuthill.

Transport numbers of hydrochloric and picric acids. T. Erdey-Grúz (Z. physikal. Chem., 1927, 131, 81—89).—The transport numbers of picric and hydrochloric acids at 25° in water, ethyl alcohol, acetone, and glycerol, and in aqueous solutions of the last three as well as of mannitol, chloral hydrate, dextrose, and sucrose, have been determined by an electrometric method. The transport number of the hydrogen ion in alcohol and glycerol solutions at first increases with the concentration of the solutions, and then decreases. In the acetone solutions there is a continual decrease. Similar variations are observed in the other solutions. The results are explained on the assumption that the picrate ion is non-hydrated and non-solvated, and that, in the hydrochloric acid solutions, the hydration or solvation has relatively less influence on the chlorine ion than on the hydrogen ion. The changes must therefore be due principally to a diminution in hydration of the hydrogen ion with increasing concentration of the non-electrolyte, followed by increase in solvation. The large value of the transport number in pure water, compared with the low value in pure acetone, glycerol, or alcohol, is explained by supposing that transport in aqueous solution is mainly of the Grotthus type, whilst this plays only a small part, or none at all, in transport in other solvents. M. S. BURR.

Electrolytic transport of water in solutions of hydrochloric and hydrobromic acids. A. WAGNER (Chem. Listy, 1927, **21**, 543—548).—By means of transport experiments with Baborovsky's apparatus the following values have been obtained for the transport number of the cation, and the transport of water, respectively: *N*-hydrochloric acid, 0·874, 0·43; 0·1*N*-hydrochloric acid, 0·873, 0·64; *N*-hydrobromic acid, 0·878, 0·50. The transport numbers are probably somewhat too high, owing to electro-osmosis at the membranes. Assuming, however, that this effect is negligible in *N*-solutions, and that in such solutions the chloride ion fixes 4 molecules of water, the hydrogen ion is calculated to fix 1 molecule, and the bromide ion 3 molecules. R. CUTHILL.

Electrical conductivity of binary liquid systems. S. I. TSCHERBOV (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 459—460).—The electrical conductivities of the system aniline–acetic acid at 21° are in agreement with those given by Konovalov (A., 1893, 356). The curve expressing the conductivity of the system acetic anhydride–water at 17° consists of two branches intersecting at an obtuse but distinct angle at a point corresponding with 50 mols. % of water. The conductivity isotherm recalls the viscosity isotherm for this system (cf. Kurnakov, J. Russ. Phys. Chem. Soc., 1918, **50**, 157), except that the conductivity exhibits a pronounced maximum for 96 (not 75) mols. % of water.

T. H. POPE.

Electrochemistry of non-aqueous solutions. VIII. Conductivity of dilute organic solutions of silver nitrate, silver thiocyanate, and lithium bromide. R. MÜLLER, V. RASCHKA, and M. WITTMANN (Monatsh., 1927, **48**, 659—672).—The work of Müller, Griengl, and Mollang (A., 1926, 1212) is extended, and the results are again in agreement with the Debye–Hückel theory. The following figures give respectively the dielectric capacity of solvents, from recorded data, followed by (each at 25°) the solubility of silver nitrate in the solvent (in g. per litre), the range of *v* in conductivity measurements, the lowest value of *v* at which the square root law is valid, and the value of Λ_∞: *o*-toluidine, 6·3, 0·128, 1327—170,000, 15,000, 11; piperidine, 5·8, 40·07, 10—20,000, 320, 0·24; acetonitrile, 35·8, 875·7, 10—80,000, 78, 270; methyl ethyl ketone, 17·8, 1·72, 100—100,000, 12,000, 140; acetophenone, 18 or 15·6, 0·0755, 2250—144,000, 6,000, 36. Since phenylthiocarbimide is attacked explosively by silver nitrate, silver thiocyanate is used as solute; the respective figures are: 11, 0·926, 1·724—220,000, 13,000, 21·5; the results are uncertain, especially when *v* exceeds 100,000. For lithium bromide in benzaldehyde solution, the figures are: 18·0, 136·28, 0·637—1632, 10, 6·3. E. W. WIGNALL.

Specific adsorption volume and the electromotively effective space. D. REICHINSTEIN (Z. anorg. Chem., 1927, **168**, 189—196).—Theoretical. The conception of electromotively effective space previously developed in connexion with the determination of the rate of reactions occurring at electrodes during the passage of a current (A., 1923, ii, 468) has been applied to the elaboration of a theory of galvanic polarisation. It is found that it is really an adsorption problem which is involved, and the electromotively effective space is, in fact, equal to the adsorption space on the electrode. An equation for the polarisation *E.M.F.* is derived, which accounts for Le Blanc's point of inflexion on the voltage curve.

R. CUTHILL.

Decomposition potentials of the fused halides of the alkali and alkaline-earth metals. II. L. CAMBI and G. DEVOTO (Gazzetta, 1927, **57**, 836—855).—Further experiments have been made by the method described (cf. Giorn. Chim. Ind. Appl., 1926, **8**, 303). In addition to further observations on the chlorides, results are given for lithium, sodium, potassium, and barium bromides and iodides, calcium and strontium bromides, and magnesium iodide between 600° and 1000° with graphite anodes and nickel cathodes. Further measurements are also recorded for calcium, strontium, and barium chlorides with nickel and iron cathodes. The decomposition potentials at 800° are: (chlorides) potassium 3·37, lithium 3·30, sodium 3·20; (bromides) potassium 2·98, lithium 2·95, sodium 2·83; (iodides) potassium 2·53, lithium 2·48, sodium 2·30. The decomposition potentials of the fluorides of lithium, potassium, and calcium are much lower than those of the corresponding chlorides or bromides. The results indicate the occurrence of depolarisation phenomena. Neumann's method (cf. A., 1925, ii, 797), which gives markedly lower values of the decomposition potential, is criticised. Two thermodynamic methods of calculating the decomposition potential are given and the results, as exemplified in the case of sodium chloride, are in good agreement with the experimental figures. O. J. WALKER.

Current density–potential curves and time phenomena in the passivation of various metals. W. J. MÜLLER (Z. Elektrochem., 1927, **33**, 401—406).—The influence of the method of experiment on the form of current density–potential curves for anodes exhibiting active and passive states is discussed. The importance of the time factor is emphasised and a method of drawing the curves to show time effects is indicated. Curves for chromium are similar in form to those for iron and nickel, but at given current density passivity sets in after a very much shorter active period. True passivity, as shown by these metals, is regarded as due to a change in the atoms of the metal itself. The formation of a non-conducting film of salt, basic salt, or hydroxide causes high current densities at points which are not covered by the film, and passivity is brought about by the high current density. Metals which do not exhibit true passivity may show "mechanical passivity," but in such cases the high anode potential is due merely to the ohmic resistance of a film, the metal being really still active. H. J. T. Ellingham.

New method of measuring overvoltage. L. J. P. Byrne (Trans. Faraday Soc., 1927, 23, 661—667).—A new method for measuring overvoltage while the current is flowing is described. The *P.D. E* between the electrodes, the current *I* flowing through the cell, and the ohmic resistance *R* of the cell are all determined simultaneously. The overvoltage is $E-IR$. The method gives the true overvoltage existing during electrolysis without introducing extraneous factors, and is applicable over a wide range of current densities. Curves are given showing the relation between current density and overvoltage at copper electrodes in neutral and acid copper sulphate solutions of various concentrations, and at platinised platinum electrodes in sulphuric acid solution. A method is suggested by which oxygen and hydrogen might be obtained by using alternating current. M. S. Burr.

Electrolytic reduction potentials of organic compounds. I. Polarographic method. II. *iso*Valeraldehyde. III. Pyridine. IV. Nicotinic acid. M. Shikata (Mem. Coll. Agric. Kyoto, 1927, 4, 1—8, 9—18, 19—33, 35—48).—I. A description is given of the use of polarograms, produced by the automatic registration of current–voltage curves on a rotating drum, for the determination of the reduction potentials of organic compounds at the dropping mercury cathode.

II. [With I. Tachi.]—Polarographic measurement of the reduction potential π of *iso*valeraldehyde shows the equation $\pi=-(RT/2F)\log[k'/\{[H^{\cdot}]^2\times C_{R\cdot CHO}\}]$ to be valid; thus the reduction is reversible, in both acid and alkaline solution. For a 0·1868*M*-solution in 0·1*N*-hydrogen chloride, $\log k'=34{\cdot}672$. Corrected for adsorption the equation becomes $\pi=-(RT/2F)\log[k'/\{[H^{\cdot}]^2\times C_{R\cdot CHO}^{1/m}\}]$ in which for a strongly acid solution *m* is 1·380, for neutral solution 0·287, for alkaline solution 1·33, and for a solution in ammonium chloride 0·272. The results suggest negative adsorption of *iso*valeraldehyde at a mercury cathode in neutral solution. Schiff's reaction for the detection of aldehydes is only one twentieth as sensitive as the polarographic method. The influence of *iso*amyl alcohol on the reduction potential suggests that this substance is the product of the reaction.

III. [With I. Tachi.]—The two waves in the current–voltage curves obtained in the reduction of pyridine are due to reduction of the pyridine ion and molecule respectively. In acid solution moderate agreement exists between the theoretical and observed values of the reduction potential, although greater deviations occur than when the reduction is reversible. In neutral and alkaline solutions the agreement is less satisfactory. For moderate pyridine concentrations the adsorption coefficient *m* of the pyridine ion is 0·219 in acid solution and 0·089 in neutral solution. For the molecule in alkaline solution *m* is 0·223.

IV. [With I. Tachi.]—The reduction of nicotinic acid at the dropping mercury cathode takes place in two stages, of which the first is the reduction to aldehyde of the carboxyl group and the second the reduction of the pyridine ring. Reduction does not occur in presence of an excess of alkali, owing probably to desorption of the negatively-charged nicotinic acid ion at the cathode. A study of the reduction potential of benzoic acid indicates that the pyridine ring facilitates the reduction of the carboxyl group to a greater degree than does the benzene ring. H. F. Gillbe.

Applications of the polarographic method. I. Analysis of abnormal mineral constituents. II. Copper complex salts. III. Microanalysis of reducible substances in fermentation products. M. Shikata (Mem. Coll. Agric. Kyoto, 1927, 4, 49—57, 59—74, 75—90).—I. [With I. Tachi and N. Hozaki.] The polarographic method is applicable to the micro-detection of lead and copper.

II. The deposition potentials of copper complexes have been determined. On the assumption of the formation of lithium trichlorocuprate in solutions of cupric and lithium chlorides, the equilibrium constant $K=[Cu^{\cdot\cdot}][Cl']^3[CuCl_3']$ is $3{\cdot}98\times10^{-9}$ for lithium chloride concentrations from 0·05*N* to *N*. The equilibrium constants of sulphate complexes are in general greater than those of chloride complexes. The existence of current maxima and minima in the current–voltage curves is ascribed to varying adsorption of the copper complexes.

III. [With K. Shoji.]—Reducing substances such as cinnamaldehyde, furfuraldehyde, and acetaldehyde in various fermented liquids may be detected by the polarographic method. H. F. Gillbe.

Behaviour of nickel anodes. F. Foerster and F. Krüger (Z. Elektrochem., 1927, 33, 406—425).—Solutions of nickel sulphate containing varying amounts of nickel chloride and 2% of boric acid were electrolysed at 20° between nickel electrodes at fixed current densities, the electrolyte being well stirred. The bath voltage, anode potential, anodic and cathodic current efficiencies, and the p_H value of the electrolyte were measured during each electrolysis. When the current density is low or the chloride concentration high, the anode is continuously active and dissolves with high current efficiency at potentials (ε_h) between +0·40 and +0·58 volt, the p_H value of the electrolyte increasing gradually during the process. With high current density or low chloride concentration, the anode is in a permanently passive condition, for although it still dissolves with a current efficiency of 15—35%, its potential lies between +1·69 and +1·75 volt: the p_H value of the electrolyte falls rapidly at first but eventually approaches a constant low value. Under intermediate conditions, the p_H value decreases at first to a minimum and then rises again, whilst the anode exhibits temporary passivity. At first the anode potential varies periodically between a value which corresponds with activity and one somewhat less than that which is characteristic of permanent passivity, these higher values being more persistent; but as electrolysis proceeds the frequency of the pulsations decreases and the active phases become more persistent until permanent activity is eventually established. The maximum current density at which the anode remains continuously active increases rapidly with the chloride concentration, but decreases somewhat with increase in the sulphate concentration; it was also found to be higher with technical anodes than with specially prepared electrolytic anodes. High anode potentials are attributed to the partial covering of the anode surface by the observed peroxide film, but true passivity is regarded as due to a change in the electronic structure of the nickel atoms, a change which is produced by local high current densities, but which can persist in the presence of oxygen even if the current density falls owing to dissolution of part of the film. In "temporary passivity" the film forms but redissolves by interaction with chloride ions before true passivity is established. The current density–potential relations for a nickel anode in a nickel chloride solution and in a solution containing chloride and sulphate were also investigated.

As long as the p_H value of the electrolyte is below 5·5 good cathodic deposits of nickel are obtained. Flaking and cracking, which occur at high p_H values, are ascribed to strains due to inclusion of nickel hydroxide in the deposit. Presence of the hydroxide also enables hydrogen bubbles to adhere to the cathode and hence leads to pitting. The cathodic current efficiency runs parallel with the anodic efficiency, but is somewhat greater than the latter unless the anode is permanently active. The best conditions for electrodeposition of nickel in practice are discussed. The chloride concentration must be sufficient to avoid temporary passivity; the p_H value must be kept down, a condition favoured by low current concentration, and the iron content of the solution kept as low as possible, since iron in the deposit leads to flaking, and deposition of ferric hydroxide to pitting. H. J. T. ELLINGHAM.

Electroendosmosis of aqueous solutions through glass diaphragms. H. C. HEPBURN (J.C.S., 1927, 3163—3164).—The measurements by Fairbrother and Varley (A., 1927, 826) of the electro-endosmosis of dilute hydrochloric acid through a diaphragm of sintered Jena glass powder are criticised and their apparently inconsistent results corrected for the lowering of the electrokinetic potential produced by given concentrations of hydrochloric acid. Consecutive series of measurements then show good agreement, and, contrary to the view of Fairbrother and Varley, do not indicate any change in the effective size of the diaphragm pores corresponding with a progressive swelling process at the glass surface. Errors are introduced by failure to remove the last traces of adsorbed electrolyte remaining from the strong acid used in cleaning the diaphragm between the series of observations. The use of an entirely fresh diaphragm for each series of measurements is recommended. R. A. PRATT.

Flame and combustion. A. EGERTON (Nature, 1928, 121, 10).—A general view of gaseous combustion is presented. Reaction will commence when a sufficiently energetic molecule of fuel combines momentarily with an energetic oxygen molecule, forming a peroxide in a high energy state. Resulting breakdown may involve the formation of an aldehyde and water; these molecules would possess not only the initial energy of activation but also the reaction energy, and on their next encounter with other fuel (or oxygen) molecules would communicate sufficient energy to enable combination to occur, and so start a reaction chain. This view is discussed. A. A. ELDRIDGE.

Ionisation and chemical change during slow combustion. J. A. J. BENNETT and E. W. J. MARDLES (J.C.S., 1927, 3155—3161).—The temperatures of spontaneous ignition in a heated tube of vapour or spray of *m*-xylene, *n*-butyl alcohol, undecane, benzyl alcohol, amyl ether, and cymene are recorded, and it is concluded that a system containing liquid droplets is more ionised and more sensitive to ignition than the corresponding vapour mixture. Similarly, chemical changes occurring below the ignition temperature were usually more marked and occurred at lower temperatures with the liquid drops present than with the vapours alone. Slight ionisation was shown at higher temperatures with some gaseous mixtures. It is concluded that a thermionic emission occurs at the commencement of combustion, followed during combustion by the formation of centres of chemical change from ions as soon as they are liberated. The formation of peroxides from hydrocarbons is indicated. The action of iron carbonyl, lead tetraethyl, and other "anti-knocks" inhibits peroxide formation during the period of slow combustion. Experiments with hydrogen, and with hydrogen–air, hexane–air, coal gas–air, and acetylene–air mixtures, with and without puffs of "anti-knocks," were made at temperatures up to 600°, when no appreciable increase in ionisation was found. R. A. PRATT.

Decomposition of diacetone alcohol in alkali hydroxide solutions. G. ÅKERLÖF (J. Amer. Chem. Soc., 1927, 49, 2955—2981).—The velocity of the above decomposition was measured by a physical method which gave reasonably accurate results with reaction velocities having half-periods up to 35 sec. The velocity/alkali concentration ratio as a function of increasing concentration (0·1—2·2*N*) shows an almost continual decrease for lithium hydroxide, but for solutions of the other two hydroxides used it passes through a minimum between 0·6*N* and 1*N*, afterwards increasing, rapidly for potassium hydroxide but comparatively slowly for sodium hydroxide solutions. The corresponding activity coefficient–concentration curves for the pure hydroxides behave similarly, indicating that the above decomposition velocity is proportional to the hydroxide activity.

The experiments were repeated after addition of the corresponding chlorides, the total salt concentration being kept constant (up to 6*N*); log (velocity constant/alkali concentration) was a linear function of the hydroxide concentration, as in the case of the pure hydroxides, the lines being parallel for each alkali metal. Extrapolation of these lines to zero salt concentration gave values for the velocity of decomposition of diacetone alcohol in very concentrated alkali solution which agreed with those calculated from activity coefficients. An expression is deduced for the reaction velocity in solutions of high electrolyte concentration which agrees with Hückel's simplified general equation for the activity coefficient of a strong electrolyte (A., 1925, ii, 513) and holds also for the conversion of acetylchloroaminobenzene into *p*-chloroacetanilide in acid solution (Harned and Seltz, A., 1922, ii, 631). The decomposition velocity of diacetone alcohol seems to be a function of the activity of the electrolytes present at all concentrations. A review of relevant results is given. S. K. Tweedy.

Velocity measurements on the opening of the lactone ring in derivatives of phthalide. A. Tasman (Rec. trav. chim., 1927, 46, 922—924).—Errors in the calculation of the velocity coefficients previously published (A., 1927, 1186) are corrected. The conclusions remain valid and some of the " exceptions " now accord better with the general scheme.
J. S. Carter.

Inactivation of the surface of metals by diffusion. III. Diffusion of tungsten into iron and the resistance limits of iron–tungsten alloys. G. Grube and K. Schneider (Z. anorg. Chem., 1927, **168**, 17—30).—The extent of the diffusion of tungsten into iron when a bar of the latter is heated in contact with finely-divided tungsten for 15—72 hrs. at 1280°, 1330°, and 1400° has been determined by analysis of successive layers, each of thickness 0·05 mm., ground from the surface of the bar. The curves showing the relationship between the distance below the surface and the percentage of tungsten present exhibit a well-defined break at a point corresponding with a depth which increases with the time and temperature of heating. The mean diffusion coefficients for a short period of heating at the three temperatures given are 3·2, 21, and 26×10^{-5} cm.^{2}/day respectively, but the coefficient increases very greatly with increased time of heating, *i.e.*, with increase of the depth of penetration of the tungsten. It is suggested that the thin film of foreign matter deposited on the crystals of iron greatly influences the diffusion velocity.

Corrosion measurements have been made on iron–tungsten alloys containing 0—75% of tungsten, prepared by fusing a compressed mixture of the finely-divided metals, tempering the alloy at 1350° for 72 hrs., and cooling fairly slowly. Immersion of the alloys in *N*-hydrochloric acid for 24 hrs. and measurement of the weight of metal dissolved show that as the tungsten content increases up to 6% the amount of corrosion decreases to a value of about 0·33 of that of pure iron, and thereafter remains practically constant until 68·7% of tungsten, corresponding with Fe_3W_2, is approached, when the corrosion rises to a maximum and finally diminishes. Similar results are given by sulphuric acid. In 0·1*N*-nitric acid the amount of corrosion diminishes continuously as the tungsten content increases up to about 40%, and thereafter rises to a maximum.

Alloys containing up to 8% of tungsten consist of homogeneous mixed crystals; from 8% to 33% the structure exhibits large mixed crystals interspersed with small crystals of Fe_3W_2. The diminished susceptibility of the alloys to corrosion is ascribed to the formation of a protective film of tungstic oxide.
H. F. Gillbe.

Corrosive effect of nitric, hydrochloric, and sulphuric acids on pure lead and lead containing small amounts of copper and antimony. J. C. Olsen, M. H. Quell, and W. G. Holley (Trans. Amer. Inst. Chem. Eng., 1926, **18**, 19—36).—Corrosion in sulphuric acid increases with the temperature (20—100°) and concentration, and is minimal when the lead contains 0·1% of copper. With hydrochloric acid, corrosion is least with pure lead and greatest with lead containing antimony. Pure lead is least attacked by nitric acid, and least by concentrated acid.
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Paradox of corrosion and protective film [on iron] theory. T. Fujihara.—See B., 1927, 967.

Theory of intermediate reaction ions. I. H. von Euler and A. Ölander (Z. physikal. Chem., 1927, **131**, 107—126).—The reactivity of a substance is greatly increased by its ionisation. Hence the reaction is catalysed by a compound which, by salt-formation with the reacting substance, causes the increased formation of suitable ions of the latter. This does not exclude the possibility that the neutral substance may be reactive, or that it can form compounds with other substances, *e.g.*, neutral salts, which possess a higher specific reactivity than the free molecule. Substances catalysed by either acids or bases may function as amphoteric electrolytes and possess an isoelectric point. The acid amides are typical examples of this group. The basic dissociation constant of acetamide has been determined electrometrically. If no correction is made for the change in activity of the hydrogen ion in presence of the undissociated acetamide, the basic dissociation constant is $2·5\times10^{-15}$ at 20° and $2·0\times10^{-14}$ at 50°. If correction is made on the assumption that the acetamide has the same effect on the hydrogen-ion activity as an equal percentage of sucrose, the values are $3·8\times10^{-15}$ and $3·1\times10^{-14}$, respectively. The rate of hydrolysis of acetamide at 50° has been determined, under conditions of approximately constant p_H, in presence of different concentrations of hydrochloric acid between 0·1*N* and 3·12*N*. The ratio of the velocity coefficient to the amount of ionised acetamide, calculated from the corrected dissociation constant, is practically constant up to a concentration of acid of 2·0*N*, above which it falls rapidly. If calculated, however, from the uncorrected value, although approximately constant it shows a gradual small decrease with increase of hydrochloric acid. The ratio of the velocity coefficient to the hydrogen-ion concentration shows that the former increases more slowly than the latter. The mechanism of the reaction is discussed. It probably depends on the reaction with water of the intermediate ion $CH_3·CONH_3^+$, or an isomeride of this ion, the velocity of hydrolysis being proportional to the concentration of the acetamide ion, and not to that of the hydrogen ion. The system ethyl ether–hydrochloric acid–water has been studied electrometrically, and it is concluded that the basic dissociation constant of ethyl ether is less than 3×10^{-16}. This is much smaller than the value suggested by Skrabal (A., 1927, 943).
M. S. Burr.

Organic catalysts with hydrogen-ion optimum. G. Ljunggren (XII Int. Cong. Physiol., 1926, 97—98; Chem. Zentr., 1927, i, 2505).—Amino-compounds exert a catalytic effect on the decomposition of acetoacetic acid; the optimal p_{H}, which is near the neutral point, varies for different amines. The reaction is unimolecular. The effect is due chiefly to the primary amino-group; the total concentration of the solution is of importance. A. A. ELDRIDGE.

Catalytic action of aluminium chloride. H. J. PRINS (Chem. Weekblad, 1927, 24, 615—619).—A theoretical discussion of the causes of the activity of aluminium chloride as a catalyst. S. I. LEVY.

Nickel as catalyst in thermal decomposition of methane. B. YAMAGUTI (Bull. Chem. Soc. Japan, 1927, 2, 289—294).—Metallic nickel prepared by precipitating nickel sulphate solution with sodium carbonate and heating the precipitate in a current of hydrogen is most effective in catalysing the thermal decomposition of methane if the reduction temperature is about 600°, and if about 20% of oxide is left unreduced. The carbon produced by the decomposition of the methane does not appear to affect the activity of the catalyst. R. CUTHILL.

Auto-poisoning phenomenon shown by catalytically active copper at moderate temperatures. F. H. CONSTABLE (J.C.S., 1927, 2995—3000; cf. A., 1926, 250; 1927, 839).—When a copper catalyst is used to dehydrogenate alcoholic substances above 280° the activity decays with time. The dehydrogenation of ethyl alcohol was studied over ranges of temperature 270—350° and 375—400° and the corresponding decay curves were plotted, but no simple law of decay could be deduced. The initial rate of decay fell rapidly as poisoning of the catalyst proceeded. The results indicated the possibility of this being a particular case of the selective poisoning of a distribution of centres of activity. R. A. PRATT.

Catalysts and their effects on the oxidation of mineral oils. G. W. CUPIT.—See B., 1927, 960.

Hydrogen activated by the electrical discharge. A. DE HEMPTINNE (Ann. Soc. Sci. Bruxelles, 1927, 47, *B*, i, 143—149).—In a continuation of previous work on the reduction of metallic oxides by hydrogen in presence of an electrical discharge (A., 1923, ii, 121) it is shown that lead dioxide and mercuric oxide, but not copper oxide or lead monoxide, are reduced when not directly exposed to the electronic or ionic bombardment. The values of N/N' are, however, smaller. These observations are interpreted as indicative of the existence of non-ionised, active hydrogen, monatomic, triatomic, or excited, in the tube. Reduction at the cathode is effected by means of positive ions and at the anode by the intervention of negative ions or by non-ionised active hydrogen. Actual bombardment favours the reduction. J. S. CARTER.

Salt of bivalent silver. G. A. BARBIERI (Ber., 1927, 60, [*B*], 2424—2427).—Electrolysis in a divided cell in which the anolyte is an 8—10% solution of silver nitrate containing 40% of pyridine and the catholyte 10—15% sulphuric acid, the anode and cathode being respectively a platinum capsule and a thick platinum wire, gives small yields of the unstable, orange-red, crystalline *compound*, $Ag(NO_3)_2,4C_5H_5N$, which liberates iodine from potassium iodide and oxidises chromium and manganous salts to chromic and permanganic acids. H. WREN.

Comparison of certain methods for determining the ultra-violet intensity of a light source. A. E. GILLAM and R. A. MORTON (J.S.C.I., 1927, 46, 417—420T).—Various chemical methods for the determination of ultra-violet intensity have been described and the influence of screens of window-glass and vitaglass in retarding the reactions has been investigated. Webster, Hill, and Eidinow's acetone-methylene blue gauge is sensitive chiefly to rays between 200 and 280 μμ, as only some 12% of the chemical change can be ascribed to rays transmitted by vitaglass. The effective rays in the photolysis of potassium nitrate are also very largely absorbed by vitaglass.

The photolysis of oxalic acid sensitised by uranyl salts is much more sensitive to wave-lengths in the near and middle ultra-violet. Mackenzie and King have suggested that the photochemical decomposition of pure carbon tetrachloride can serve as a useful actinometric reaction, but it is found that rays of wave-length longer than 265 μμ do not bring about decomposition. With shorter radiations the method works well. The possibility of using the decomposition of hydrogen peroxide is discussed and certain difficulties are indicated. Experiments on the deterioration of mercury-vapour lamps show that the output of ultra-violet radiation may fall to 60% or even 40% after 150 hrs. (See this vol., 140.)

Self-integrating chemical actinometry for ultra-violet dosage or other specific purposes. M. J. DORCAS and G. S. FORBES (J. Amer. Chem. Soc., 1927, 49, 3081—3086).—Reddish-purple Corex glass, backed with a 1 cm. layer of $0{\cdot}00025M$-picric acid solution, transmits, at each frequency, a light-wattage proportional to the efficiency in producing erythema (sunburn) in human skin. A 50% solution of benzoquinone in alcohol was photolysed behind this filter, which was compensated, at each wave-length, for the photochemical efficiency of this photolysis. By this means changes in total intensity and in spectral energy distribution are integrated. If y is the iodine value of the benzoquinone photolysed per hr., and x is the reciprocal of the times in which the same sources, without filters, produce a standard erythema, then $y=ax$ approximately, or, for the more efficient light sources, $y=ax+b$, where a and b are constants, b being very small. Thus, the reciprocity law does not appear to hold exactly for the erythema reaction (cf. Hausser and Vahle, Strahlentherapie, 1923, 13).

S. K. TWEEDY.

Interaction of chlorine and sulphur monochloride. Preparation of sulphur dichloride. Use of antimony pentachloride as catalyst. R. P. BOTHAMLEY (Trans. Faraday Soc., 1928, 24, 47—50).—The period of induction during the reaction between sulphur monochloride and chlorine (cf. A., 1906, ii, 157) is reduced by substituting sunlight for diffused daylight, and the reaction proceeds more rapidly thereafter than under the latter conditions. The reaction is catalysed by antimony pentachloride (cf. A., 1905, ii, 22). In experiments carried out at the ordinary temperature, absorption of chlorine ceased when the liquid contained about 70% of chlorine (SCl_2=68·9% Cl). At 0°, however, absorption proceeded beyond this point. L. F. Gilbert.

Formation of nitrite from nitrate as a measure of ultra-violet intensity. A. E. Gillam and R. A. Morton (J.S.C.I., 1927, **46**, 415—417T).—The photolysis of potassium nitrate buffered at p_H 9·4 may be used as an actinometer for measuring the ultra-violet output of mercury-vapour lamps. The Griess–Ilosvay colorimetric method of determining nitrite concentration has been adapted for the purpose. The photolysis is primarily sensitive to wave-lengths in the far ultra-violet, so that it is suitable for detecting the first stages in the ageing of the lamps. It is also suitable for controlling the bactericidal action and other reactions occurring in the same spectral region. The use of a screen of vitaglass enables the test to be used as a theoretically sound method for controlling the output of a light source in respect of the stimulative rays. The reaction is, however, too slow for general use as an easy routine test for dosage in actinotherapy. (See this vol., 139.)

Photochemical studies. VI. Photochemical reaction between oxygen and mercury vapour at relatively low pressures. W. A. Noyes, jun. (J. Amer. Chem. Soc., 1927, **49**, 3100—3106).—The above reaction occurs largely between ozone and mercury vapour. The former, it is shown, cannot be produced by both sensitised and unsensitised reactions (cf. Dickinson and Sherrill, A., 1926, 485), and it is suggested that a relatively unstable complex of excited mercury and oxygen is formed which yields ozone through collision with activated or unactivated oxygen molecules or with ozone molecules. S. K. Tweedy.

Influence of radiation on thermal unimolecular reactions. J. E. Mayer (J. Amer. Chem. Soc., 1927, **49**, 3033—3046).—A detailed account of previously published results (Lewis and Mayer, A., 1927, 948). The absorption coefficients of nitrogen pentoxide at low pressures for black-body radiation (cf. Daniels, A., 1926, 108) are the same whether the black body is at 100° or 200° and are of the same order of magnitude as the coefficients for wave-lengths less than 7 μ. The velocity coefficient of thermal decomposition is calculated to be 1×10^{-10} sec.$^{-1}$, which is $2{\cdot}5\times10^{-6}$ times the experimental value (cf. Lewis and Smith, A., 1925, ii, 799). Pinene at low concentrations is not racemised at 830—1053° Abs. by a molecular stream of radiation. The concentration of the latter over the greater part of the frequency range exceeds that in a hohlraum at a temperature high enough to produce racemisation within the time of exposure used. Thus for both reactions the rate of activation by radiation alone is of insufficient rapidity to account for the observed decomposition rate, although a theory necessitating both radiation and collision is not incompatible with the experimental results. Recalculation of Kröger's results (A., 1926, 41) shows that the rate of dissociation of iodine by radiation is lower than the rate of reaction normally found in thermal reactions of the same activation energy. S. K. Tweedy.

Supposed photoactivity of irradiated substances. O. Beck (Monatsschr. Kinderheilk., 1926, **33**, 320—329; Chem. Zentr., 1927, i, 2396).—The observed darkening of the photographic plate is due to ultra-violet rays of relatively long wave-lengths. Irradiation of cod-liver oil and milk produces an extension of the absorption spectrum towards the ultra-violet, and that of paraffin oil a contraction. The iodine value of cod-liver oil, but not of paraffin, suffers a temporary reduction. A. A. Eldridge.

Light effect in the system caoutchouc–sulphur. H. Pohle (Naturwiss., 1927, **15**, 162—163; Chem. Zentr., 1927, i, 2396).—Exposure to light of caoutchouc–sulphur mixtures results in a separation of the sulphur; the effect, which is due to the violet and blue rays, can be followed ultramicroscopically, and the beginning of vulcanisation can be observed. Except in the presence of substances which absorb the blue and violet rays, the effect is observed so far below the surface as the light penetrates.

A. A. Eldridge.

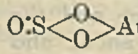
Activation of hydrogen by electric discharge. G. Glockler (Nature, 1927, **121**, 93).—Elliott's observations (A., 1927, 187) may be due to the hydrogen leaving the discharge tube carrying ions (H_2^+, H^+, or both) and electrons, the latter then combining with the sulphur atoms, and hydrogen sulphide being produced by simple ionic combination.

A. A. Eldridge.

Reduction of alkali carbonates by carbon, and action of alkali metals on carbon. G. Tammann and A. Sworykin (Z. anorg. Chem., 1927, **168**, 218—220).—Heating curves of mixtures of sugar charcoal or graphite with sodium carbonate or potassium carbonate have points of inflexion, indicating that the carbonate has commenced to "wet" the carbon, at 1040—1085°. Gas-carbon rods exposed to the vapour of sodium or potassium above about 500° begin to crumble, probably owing to the formation of solid solutions of the alkali metals in the carbon. Sodium vapour begins to act on porcelain at 570°, and at a particular temperature acts more rapidly than potassium, and less rapidly than lithium.

R. Cuthill.

Oxidation of sodium amalgam by means of oxygen. A. Feldmann.—See B., 1928, 12.

Formation and constitution [and anti-tubercular action] of sodium aurosulphite. B. Oddo and Q. Mingoia (Gazzetta, 1927, **57**, 820—826; cf. Rosenheim, Hertzmann, and Pritze, A., 1908, ii, 860).—*Sodium aurosulphite*, $Na_5Au(SO_3)_4(+5H_2O)$, is obtained by neutralising an aqueous auric chloride solution with sodium hydroxide and adding a solution of sodium sulphite; on adding alcohol to the filtered liquid, a yellow compound with a reddish-green fluorescence is obtained. Determinations of mol. wt. cryoscopically in water give a value $\frac{1}{8}$ to $\frac{1}{10}$ of the theoretical; μ_∞=720. It is therefore concluded that the substance dissociates thus: $3SO_3^{--}+AuSO_3^{+}+5Na^{+}$, the ion $AuSO_3^{+}$ having the structure  $O{:}S{<}\overset{O}{\underset{O}{}}{>}Au^{+}$ and the conductivity 88·5 (cf. Mollgaard, "Chemotherapy of Tuberculosis," Copenhagen, 1924).

The substance is completely absorbed from hypodermic or intramuscular injection; whilst there is a definite bactericidal action on Koch's bacillus, the anti-tubercular action is not great. In man the optimum tolerated dose is 0·1—0·2 g.

E. W. Wignall.

Magnesium peroxide. H. Křepelka and J. Červinka (Časopisu ceskosloven. lek., **6**, No. 11—12, 14 pp.; Chem. Zentr., 1927, i, 2404).—Treatment of ethereal (concentrated) hydrogen peroxide with magnesium hydroxide yields a hygroscopic substance of composition between MgO_2,H_2O and $MgO_2,2H_2O$, passing into the dihydrate and then into the compound MgO_2,MgO,H_2O, and in one case into $4(MgO_2,2H_2O),MgO$, but in absence of water into indefinite compounds with evolution of oxygen.

A. A. Eldridge.

Colour changes of double iodides when rubbed. G. Tammann and G. Veszi (Z. anorg. Chem., 1927, **168**, 46—48).—The transient red colour produced when an emulsion of silver mercuric iodide, $2AgI,HgI_2$, in gelatin, deposited on a glass plate, is rubbed is due to local rise of temperature to above 50°, the transition temperature of the double salt. The same is true of the change from red to violet of cuprous mercuric iodide, $2CuI,HgI_2$, which takes place at 65°.

H. F. Gillbe.

Chemical effects of high-frequency sound waves. I. Preliminary survey. W. T. Richards and A. L. Loomis (J. Amer. Chem. Soc., 1927, **49**, 3086—3100; cf. Phil. Mag., 1927, [vii], **4**, 417; A., 1927, 849, 1008).—The chemical effects of high-frequency (289,000 sec.$^{-1}$) compression waves are considered. Many sensitive metastable systems are discharged; *e.g.*, nitrogen trichloride is exploded and yellow mercuric iodide becomes red below 120°. Superheated liquids evaporate with explosive violence and substances at a liquid or gas interface are readily dispersed; *e.g.*, fairly stable emulsions of mercury in water may be prepared. Mercurial thermometers and thermocouples give readings elevated by several degrees, and air-free liquids boil below their normal b. p. Dissolved gases are expelled from solution to the pressure lowering in the tensional region of the waves. Some chemical reactions are accelerated, *e.g.*, the hydrolysis of methyl sulphate and the iodine "induction period" reaction. Tentative explanations of the above phenomena are offered.

S. K. Tweedy.

Action of sodium amalgam on carbon disulphide. B. Fetkenheuer [with H. Fetkenheuer and H. Leous] (Ber., 1927, **60**, [*B*], 2528—2537).—Carbon disulphide when shaken with 0·8% mercury amalgam forms a complex mixture of compounds which cannot readily be separated into its methylated derivatives after treatment of the product with methyl sulphate. The crude material is therefore treated with 90% alcohol, which leaves undissolved a product (not yet completely investigated) containing almost all the mercury. The solution is treated with methyl chloride, thus leading to the isolation of the following substances: methyl sulphide; *methyl tetrathio-oxalate*, $(CS\cdot SMe)_2$, m. p. 100·9°, b. p. 210°/0·1 mm. (decomp.), d_4^{20} 1·619, hydrolysed to oxalic acid [Sakurada's observation that ethyl tetrathio-oxalate is formed by the action of hydrogen chloride and cyanogen followed by hydrogen sulphide on an ethereal solution of ethyl mercaptan could not be confirmed (cf. A., 1926, 950)]; *methyl methylxanthate*, $C_3H_5OS_2$, b. p. 168°/765 mm., converted by alcoholic ammonia into ammonium thiocyanate; methyl trithiocarbonate, b. p. 224°/760 mm.; an isomeric *methyl tetrathio-oxalate*, m. p. 71·6°, d_4^{20} 1·658, apparently stereoisomeric with that described above; *tetramethylthiolethylene*, $(SMe)_2C\colon C(SMe)_2$, m. p. 61·5°, d_4^{18} 1·397 (corresponding *bromo*-derivative, $C_6H_{12}Br_4S_4$). The production of methyl methylxanthate is due to a subsidiary reaction, since the compound is not produced when the crude product of the reaction is treated directly with methyl sulphate. The production of sodium sulphide is not accompanied by the separation of carbon and the mechanism cannot at present be explained. Carbon disulphide appears able to add sodium, giving the compounds $\cdot CS\cdot SNa$ and $\colon C(SNa)_2$. Sodium in the absence of mercury does not react with carbon disulphide in a sealed tube at 150°, the slight brown layers formed being due to unavoidable production of layers of oxide or hydroxide on the surface of the metal. Sodium–potassium alloy forms yellowish-brown, exceedingly explosive crusts. When carbon disulphide is added to a solution of sodium in liquid ammonia, a vigorous action results in the production of a brown mass which, with methyl sulphate, affords the two forms of methyl tetrathio-oxalate, methyl trithiocarbonate, tetramethylthiolethylene, and methyl sulphide.

H. Wren.

Frosting of glass by mixtures containing hydrofluoric acid and alkali fluorides. C. D. Spencer and L. Ott.—See B., 1928, 52.

Behaviour of thorium oxide in tungsten filaments. W. Geiss and J. A. M. van Liempt (Z. anorg. Chem., 1927, **168**, 107—112).—Thorium oxide in tungsten filaments is reduced at temperatures above 2700° Abs. to metallic thorium, which does not form mixed crystals with tungsten. Diffusion of thorium oxide to the outer portions of the filament takes place through the interstices between the tungsten particles, and not through the crystal lattice.

H. F. Gillbe.

Preparation of $Th(OH)_4$ from the solution of a salt as function of the hydrogen-ion concentration. J. A. Atanasiu (Ber., 1927, **60**, [*B*], 2507—2509).—Thorium hydroxide is quantitatively formed when pyridine is added to the solution of a thorium salt at about its neutral point (p_H 7); the solution may be very feebly acid or alkaline. The quantity of pyridine has no marked effect on the precipitate. The metals of the cerium group and the ordinary heavy metals are not precipitated under these conditions.

H. Wren.

Appearance of visible impurities in chemical preparations with lapse of time. G. Kassner (Festschr. A. Tschirch, 1926, 80—84; Chem. Zentr., 1927, i, 2523).—The cause of a white preparation of bismuth nitrate becoming grey after 1 year proved to be the separation of tellurium effected by decomposition products of the cellulose of the filter paper employed.

A. A. Eldridge.

Reaction between potassium carbonate and sulphur in alcoholic solution. T. L. Davis and

J. W. Hill (J. Amer. Chem. Soc., 1927, **49**, 3114—3116).—The reaction is essentially the same as in aqueous solution; it is of much greater rapidity, however, since alcohol dissolves an appreciable amount of both substances, whereas water dissolves only a minute quantity of sulphur. 100 C.c. of ethyl alcohol solution contain, at 25°, 0·1114 g. of anhydrous potassium carbonate, 0·0088 g. of anhydrous sodium carbonate, and 0·03926 g. of sulphur.

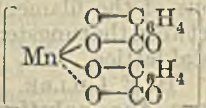
S. K. Tweedy.

Seleno-compounds of tungsten. V. Lenher and A. G. Fruehan (J. Amer. Chem. Soc., 1927, **49**, 3076—3080).—The saturation of cold, concentrated ammonium tungstate solution with hydrogen selenide yields green orthorhombic crystals of *ammonium selenotungstate*, $(NH_4)_2WSe_4$; incomplete saturation yields red, triclinic crystals of *ammonium diselenotungstate*, $(NH_4)_2WSe_2O_2$. Both salts are readily soluble in water (the solutions decomposing slowly in air), somewhat soluble in alcohol, and insoluble in ether, benzene, and carbon disulphide. Crystallographic properties are recorded. S. K. Tweedy.

Oxidation of iodic acid by compounds of bivalent silver. G. A. Barbieri (Ber., 1927, **60**, [*B*], 2427—2428).—Oxidation of a boiling solution of iodic acid by potassium persulphate in the presence of silver nitrate affords silver periodate. When a dilute solution of silver nitrate is treated with sodium carbonate and potassium persulphate at 70—80°, silver peroxide is precipitated; in the presence of an iodate, almost homogeneous silver periodate, Ag_3IO_5, is nearly quantitatively precipitated in place of the oxide. H. Wren.

New compounds of tervalent manganese. G. A. Barbieri (Ber., 1927, **60**, [*B*], 2421—2424).—When an ammoniacal solution of ammonium salicylate is treated successively with aqueous solutions of manganous sulphate and potassium persulphate the *compound* (I) is precipitated as a grey mass. It liberates iodine from potassium iodide; its brown solutions in dilute sulphuric acid are decolorised by hydrogen peroxide, sulphurous acid, hydrazine, and other reducing agents; it is converted by potassium cyanide into potassium manganicyanide. The presence of a relatively stable complex containing tervalent manganese is established by the formation of *precipitates* after addition of solutions of silver, thallium, and *luteo*-cobalt salts. Ammonium manganisalicylate is transformed by warm pyridine into the green *compound*, $Mn[CO_2H\cdot C_6H_4\cdot O]_2NH_4,3C_5H_5N,5H_2O$, which loses part of its pyridine when treated with chloroform and is converted by addition of glacial acetic acid to its saturated alcoholic solution into the *substance* $Mn[CO_2H\cdot C_6H_4\cdot O]_2H,2C_5H_5N,2H_2O$.

H. Wren.



$NH_4,4H_4O$

(I.)

Oxides of iron, especially ferrous oxide. H. Groebler and P. Oberhoffer.—See B., 1928, 12.

Reduction of metallic oxides by hydrogen. III. Nickel oxide. IV. Cobalt oxide. G. Gallo.—See B., 1928, 56.

Black nickel oxide. M. Le Blanc and H. Sachse (Z. anorg. Chem., 1927, **168**, 15—16; cf. Lunde, A., 1927, 815).—Polemical. H. F. Gillbe.

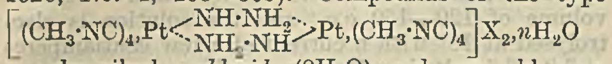
Bivalent ruthenium. H. Gall and G. Lehmann (Ber., 1927, **60**, [*B*], 2491—2497; cf. A., 1927, 123).—Repetition of the experiments of Remy (A., 1921, ii, 209) and Remy and Wagner (A., 1927, 328) on the reduction of ruthenium trichloride by sodium amalgam shows that the consumption of hydrogen never exceeds one equivalent proportion and that under these conditions only bivalent and metallic ruthenium are produced, whereas univalent ruthenium is incapable of existence. The green colour regarded by Remy as indicative of a definite valency stage is only a mixed colour produced whenever the blue solution of ruthenium dichloride is mixed with ruthenium trichloride. It invariably appears when reduction is effected slowly and its apparent dependence on the acidity of the solution is attributed to the variation caused thereby in the ratio of molecular to atomic hydrogen evolved by the amalgam. The behaviour of ruthenium dichloride when heated in a current of carbon dioxide at 200° excludes the possibility that it can have the composition $HRuCl_2$. Oxidation of the blue solutions of ruthenium dichloride by alkaline permanganate (cf. Ruff and Vidic, A., 1925, ii, 480) shows a consumption of four equivalents of oxygen indicating the transition from the bivalent to the sexavalent state, but the results are not very accurate, since the permanganate is partly transformed into manganate with liberation of gaseous oxygen. The use of manganate, however, yields exact and confirmatory results. H. Wren.

Platinum metals. VII. Reduction of ruthenium trichloride by sodium amalgam and by alcohol. H. Remy and T. Wagner (Z. anorg. Chem., 1927, **168**, 1—14).—Water-soluble ruthenium trichloride may be converted into potassium pentachlororuthenate without loss of chlorine by evaporation of a solution of the trichloride with the theoretical quantity of potassium chloride. Titrations of sodium amalgam with solutions of the ruthenate yield the same results as when ruthenium trichloride is employed, the successive changes of valency being clearly indicated. Assuming a valency of three for ruthenium in the trichloride and in the pentachlororuthenate, the first stage in the titration corresponds with a change to the bivalent, and the second stage to the univalent state. The deep blue solution formed when insoluble ruthenium trichloride is treated with aqueous alcohol contains ruthenium in the same valency state as the blue solution obtained by reduction with sodium amalgam; a complex acid H_2RuCl_3 is probably present. Pure anhydrous ruthenium trichloride may be prepared from the dark brown solution formed when ruthenium tetroxide is treated with hydrogen chloride by evaporation to constant weight at about 150—160° in a current of dry hydrogen chloride. The product, which contains free hydrogen chloride and water, is heated at 400° in a high vacuum in presence of soda-lime for 2—2·5 hrs.

H. F. Gillbe.

Platinum compounds of hydrazine and carbylamines. L. A. Tschugaev, M. S. Skanavi-

Grigoréva, and A. Posnjak (Ann. Inst. Platine, 1926, No. 4, 299—305).—Compounds of the type



$$\left[(CH_3\cdot NC)_4,Pt{<}\begin{matrix}NH\cdot NH_2\\ NH_2\cdot NH\end{matrix}{>}Pt,(CH_3\cdot NC)_4\right]X_2,nH_2O$$

are described: *chloride* ($8H_2O$), red, emerald-green when heated; *iodide* ($4H_2O$), emerald-green; *perchlorate* ($2H_2O$), strawberry-red; *azide*, dark blue. With ethylcarbylamine: *nitrate* ($2H_2O$), red; *perchlorate*, red; *iodide*, yellow; *chloroplatinate*, red; *chloride*, orange-yellow. Treatment of the chlorides with concentrated hydrochloric acid yields the *compounds* $4CH_3\cdot NC,Pt_2,2N_2H_3,2HCl,Cl_2$ and $4C_2H_5\cdot NC,Pt_2,2N_2H_3,Cl_2,2HCl$, respectively.

Chemical Abstracts.

New series of acido-amido-tetrammine derivatives of quadrivalent platinum. L. A. Tschugaev (Ann. Inst. Platine, 1926, No. 4, 37—43).—Chloropentammineplatinic chloride and alkali yield *chloroamidotetrammineplatinic chloride*, $[Pt,4NH_3,NH_2,Cl]Cl_2$; the corresponding (chloro-) *bromide* and *nitrate* and *bromoamidotetrammineplatinic bromide* were prepared. Chemical Abstracts.

Use of the quinhydrone electrode in electrometric acid titration. A. Klit (Z. physikal. Chem., 1927, **131**, 61—80).—The following acids have been titrated, using the quinhydrone electrode: hydrochloric, oxalic, acetic, malonic, and citraconic acids, and potassium dihydrogen phosphate. As comparison electrode a quinhydrone electrode in $0{\cdot}01N$-$HCl+0{\cdot}09N$-KCl was used (cf. Veibel, J.C.S., 1923, **123**, 2203). A weak acid, of initial concentration $0{\cdot}1N$, may be titrated by this method with $0{\cdot}1N$-base, provided its dissociation constant is not less than 10^{-7}. If the initial concentration is $0{\cdot}005N$ the dissociation constant must not be less than 10^{-6}. To avoid any error due to carbonic acid, a stream of nitrogen must be passed through the solution during titration. The dissociation constants (in the case of the polybasic acids the second dissociation constants) calculated on the basis of the p_H value when half-neutralised, and taking into account the ionic strengths concerned, are in good agreement with existing data.

M. S. Burr.

Apparatus for potentiometric titrations. J. F. Spencer (J.S.C.I., 1927, **46**, 423—424T).—An apparatus for carrying out titrations in highly coloured solutions, and suitable for use in general volumetric work, is described. A rheostat is used as a potentiometer, its ends being connected through a switch to an accumulator, and a sliding contact enables any fraction of the potential drop across the potentiometer to be opposed to the *E.M.F.* between the electrodes in the titration cell. When these are equal (no deflexion on the galvanometer) the *E.M.F.* is read on a voltmeter, and readings are made after each addition of standard solution until the end-point is passed, the end-point being found from the curve in which the *E.M.F.* is plotted against the volume of solution added. W. J. Powell.

Permanently saturated electrode for p_H determination. Swyngedauw (Compt. rend. Soc. Biol., 1927, **96**, 693—695; Chem. Zentr., 1927, i, 2756).—An arrangement is suggested whereby permanent hydrogen saturation is possible, and the p_H determination carried out in the original vessel.

A. A. Eldridge.

[**Platinum electrodes.**] S. Popoff and A. H. Kunz (Proc. Iowa Acad. Sci., 1926, **33**, 169).—The optimal conditions for plating platinum-black deposits are described. "Poisoned" hydrogen electrodes are restored by treatment with concentrated nitric acid.

Chemical Abstracts.

Electroanalysis. H. Paweck and R. Weiner (Z. anal. Chem., 1927, **72**, 225—248).—The novel feature of the method described is the use of electrodes of fusible alloy—Wood's or Lipowitz' metal. Electrolysis is carried out at a temperature at which the cathode is fluid, and when deposition is completed cold water is added to the electrolyte to cause the cathode to solidify. The deposited metal alloys with the fusible alloy and the button of solidified metal is washed quickly with water, alcohol, and ether in succession, dried at 50° in a vacuum desiccator, and weighed. The procedure recommended for the determination of copper, zinc, cadmium, mercury, bismuth, and lead is described in detail, and except for lead and cadmium does not vary appreciably from that previously described when using a mercury cathode (A., 1924, ii, 562). The deposition in most cases is effected more smoothly owing to the overvoltage of hydrogen on Wood's metal being higher than on mercury. Cadmium is deposited from a sulphate solution containing 10 g. of ammonium oxalate with a current of 2—3 amp. at 4·5—6 volts. For the deposition of lead the acetate solution is treated with 10—15 g. of ammonium oxalate, 10—15 c.c. of hydrochloric acid, and 0·5 g. of hydroxylamine hydrochloride and electrolysed for 2 hrs. with 3—4 amp. A. R. Powell.

Stirrer for rapid electro-analysis. H. Rom (Chem.-Ztg., 1927, **51**, 985).—The stirrer consists of a rod covered with vulcanite and provided with means for attaching any type of electrode at its lower end and with three driving pulleys of different diameters at its upper end, the whole being mounted on a suitable support. A number of stirrers connected together with a common driving belt may be operated by one motor. A. R. Powell.

"Greasy" burettes. W. Lowson (Nature, 1928, **121**, 14).—Inaccuracy due to "greasiness" is avoided by the addition of a trace of saponin to standard acid. A. A. Eldridge.

Mercury method of calibrating microburettes. E. Schilov (Z. anal. Chem., 1927, **72**, 261—263; cf. A., 1927, 221).—In the method previously described the limiting diameter of the burette is 3 mm.; this may be increased to 4·2 mm. by supporting the mercury on a column of air above the lower column of water. A. R. Powell.

Determination of p_H of fluids containing carbon dioxide at different partial pressures. A. Beck (Biochem. Z., 1927, **190**, 75—83).—A full description of the apparatus and method is given.

A. Wormall.

Use of sodium borate instead of sodium hydroxide in the titration of weak bases. H.

Baggesgaard-Rasmussen and C. E. Christensen (Festschr. A. Tschirch, 1926, 263—282; Chem. Zentr., 1927, i, 2756).—Sodium borate is substituted for sodium hydroxide in the titration of excess of acid in the determination of alkaloids or ammonia.

A. A. Eldridge.

Determination of hydrogen in fire-damp. Heyer.—See B., 1928, 42.

Reaction between iodic and hydriodic acids in very dilute solution and the titration of the liberated iodine with thiosulphate. P. Putzeys (Ann. Soc. Sci. Bruxelles, 1927, 47, *B*, i, 159—172; cf. Vosburgh, A., 1922, ii, 863; Rice, Kilpatrick, and Lemkin, A., 1923, ii, 574; Bray and Miller, A., 1924, ii, 870; Popoff and Whitman, A., 1925, ii, 1093).—An investigation of reactions involved in iodometry, primarily concerned with their application to micro-analysis. The reaction occurring in solutions about $0{\cdot}001N$ with respect to iodate and containing excess of iodide and acid has been investigated, special attention being devoted to the elimination of the oxygen error, and it is shown that the theoretical quantity of iodine is liberated and a satisfactory end-point obtained on subsequent titration only when the product of the concentrations of iodide and acid lies between certain limits. In the present instance these limits are 0·01 and 0·075 and apply to measurements made in artificial light. The limits are narrower for daylight. As the concentration of iodate is increased the quantity of iodine determined by titration becomes more independent of these factors. Reacting mixtures should be kept for 5 min. before titration. Although reaction between sodium thiosulphate and iodine is practically instantaneous, it is, nevertheless, advisable to add the thiosulphate rather slowly towards the end of the titration, especially when extremely dilute solutions are involved. Owing to the relative slowness of the reaction, titration with very dilute solutions of arsenite should be avoided. Alkaline absorption of iodine commences at p_H 6. Dilute solutions of thiosulphate should be prepared by dilution of $0{\cdot}1N$-solution with water approximating to conductivity water, and although when protected against acid vapours such solutions are not markedly unstable, they should be standardised immediately prior to use by means of a solution of potassium iodate of corresponding concentration, the quantities of potassium iodide and acid added to this latter being in accordance with the conditions stipulated above. $0{\cdot}1N$-Solutions of thiosulphate should be standardised by the dichromate–iodide method (Vosburgh; Bray and Miller, *loc. cit.*).

J. S. Carter.

Determination of the constituents of a gaseous mixture containing hydrogen sulphide, carbon dioxide, hydrogen arsenide and phosphide, and acetylene. M. Wilmet.—See B., 1928, 13.

Determination of selenium by rapid electro-analysis. A. Jilek and J. Lukas (Chem. Listy, 1927, 21, 576—583).—The nitric acid solution containing not more than 50 mg. of selenium as selenious acid is treated with a solution of copper or bismuth nitrate containing at least as much copper or three times as much bismuth as there is selenium present; 3 c.c. of nitric acid and 3·5—5·5 g. of tartaric acid, dissolved in water and neutralised with sodium hydroxide, are added, followed by water to give a volume of 120—150 c.c., and the solution is electrolysed at 18° with a current of a few centiamperes at 2·0—2·2 volts in a Classen crucible using a rotating platinum spiral as anode. The deposited copper or bismuth contains all the selenium and adheres well to the cathode; it is washed with a stream of cold water without breaking the current, then with alcohol, dried at 100°, and weighed. The weight of selenium is obtained by subtracting from this weight the weight of the copper or bismuth added.

A. R. Powell.

Qualitative precipitation of phosphoric acid with lead salts. G. G. Kandilarov (Z. anal. Chem., 1927, 72, 263—264).—After removal of the hydrogen sulphide from the solution obtained by digesting the ammonia and ammonium sulphide precipitate with dilute hydrochloric acid, the liquid is diluted to 150—200 c.c. and treated drop by drop with a dilute solution of lead acetate until no further precipitate forms. All the phosphoric acid is thus removed as lead phosphate. The filtrate is treated with ammonium sulphide and the precipitate digested with dilute sulphuric acid to remove the lead from the zinc, iron, and manganese. Chromium is mainly precipitated with the lead phosphate and should therefore be tested for in a separate portion of the original solution (cf. Balarev, A., 1922, ii, 525; 1924, ii, 700).

A. R. Powell.

Electrometric titrations: chloramine-*T* as a titrating agent. A. McMillan and W. Easton (J.S.C.I., 1927, 46, 472T).—"Chloramine-*T*" may be used for analytical work (Noll, A., 1925, ii, 66) in the oxidising operations involving the use of iodine to replace the latter if a few drops of potassium iodide containing a little starch are added to serve as indicator. The same substance may be used as titrating reagent in conjunction with the electrometric apparatus for the determination of arsenic, antimony, tin, and iron, no indicator being required in this case.

Volumetric determination of arsenic acid. K. Pedersen-Bjergaard (Dansk Tidsskr. Farm., 1928, 2, 1—7).—A discussion of the reaction $H_3AsO_4 + 3I' + 2H^{\cdot} \rightleftharpoons H_3AsO_3 + I_3' + H_2O$ involved in the volumetric determination of arsenic with respect to the mass-action equation $K = ([H_3AsO_4][H^{\cdot}][I'])/([H_3AsO_3][I_3'])$, the results of previous workers being briefly cited. In the direct determination of arsenic acid by reduction with hydriodic acid and subsequent titration of the liberated iodine, the reaction is affected adversely by dilution, which leads to low results. The solution should contain $4N$-hydrochloric acid and 1% of potassium iodide, and should be kept at the ordinary temperature for 15 min., when the liberated iodine is titrated with thiosulphate solution, using starch as indicator. If a mixture of arsenious and arsenic acids be present, the former is first determined in a portion of the solution by titration with iodine in presence of sodium hydrogen carbonate. Another portion is acidified strongly with hydrochloric acid, some ferrous sulphate and potassium bromide are added, and the whole of the arsenic is distilled off as chloride. The arsenious acid in the distillate is determined as above, and the arsenic acid found by difference. H. F. Harwood.

Determination of the purity of elementary boron. J. W. Andrews.—See B., 1928, 51.

Determination of carbon monoxide by means of mercuric oxide. P. N. Grigorjev (Z. anal. Chem., 1927, 72, 263—266).—The determination of carbon monoxide by oxidation with yellow mercuric oxide at 100° (cf. Moser and Schmid, A., 1914, ii. 384) yields high results if the gas mixture contains aldehydes or hydrocarbon vapours. These may be removed by passing the gas successively through concentrated sulphuric acid and liquid paraffin cooled below 0°. A. R. Powell.

Determination of carbon monoxide with iodine pentoxide. J. Tausz and K. Jungmann.—See B., 1928, 13.

Solubility of magnesium oxalate, and its importance for separation of calcium and magnesium. M. Bobtelsky and (Frau) Malkowa-Janowski (Z. angew. Chem., 1927, 40, 1434—1436).—The solubilities of magnesium oxalate in solutions of ammonium oxalate, oxalic acid, and ammonium chloride at 15° and 100° are recorded; from the data, a table of corrections for the determination of magnesium by precipitation as oxalate is given. Determination of the calcium becomes inaccurate if the amount present is too low, but may be carried out accurately if the proportion is increased by addition of a known quantity of a calcium chloride solution. S. I. Levy.

Precipitation of magnesium ions by tropæolin-*OO* and the use of this reaction for its colorimetric determination. J. Zahradníček (Biochem. Z., 1927, 191, 61—73).—Tropæolin-*OO* precipitates magnesium ions from solution, the maximum precipitation being obtained in 30 min. The best reaction is obtained with 2 c.c. of 0·1% tropæolin with 1 mg. of magnesium at a reaction p_H 6·8—7·0. In the absence of other electrolytes, 0·001 mg. of magnesium may be detected, but in their presence the reaction is interfered with, potassium sulphate inhibiting least and sodium phosphate most. Most other salts and salts of the alkaline earths react with the dye only in very concentrated solution and the precipitate dissolves on dilution. Organic solvents inhibit the reaction. The use of the dye is adapted to the determination of magnesium in small amounts of serum, plasma, blood, and tissues. P. W. Clutterbuck.

Potentiometric determination of silver, copper, and gold. E. Zintl, G. Reinäcker, and F. Schloffer (Z. anorg. Chem., 1927, 168, 97—106).—In absence of other metals, silver may be determined in a sulphate solution by potentiometric titration with chromous sulphate solution. Silver and copper, when both present, may be determined by the same method after addition of ammonium chloride, sodium acetate, and acetic acid; two breaks in the potential curve are obtained, corresponding with the successive reduction of the silver and copper salts. Mixtures of silver with lead, quadrivalent tin, or tervalent gold or arsenic may be determined in the same manner. The velocity of reduction of auric chloride being less than that of the catalytic decomposition of the chromous salt by the finely-divided metallic gold, accurate results cannot be obtained by direct titration. The presence of a cupric salt in the solution renders the titration quantitative; lead, cadmium, bismuth, mercury, and silver do not interfere. Gold and copper may be determined simultaneously in presence of lead, cadmium, or bismuth. Consecutive determination of gold, copper, and mercury in a solution containing 2—5% of hydrochloric acid may be effected by titration with chromous sulphate first of the gold, and then, after addition of bismuth and ammonium chlorides, of the copper and mercury. Copper and gold may be titrated directly in presence of silver and 2—5% of hydrochloric acid; the silver may then be determined by rendering the solution alkaline with ammonia, adding sodium acetate and ammonium chloride, and, after keeping the solution for several hours, continuing the titration with chromous chloride. H. F. Gillbe.

Detection and determination of metals by means of 8-hydroxyquinoline ("oxine"). I. M. Kolthoff (Chem. Weekblad, 1927, 24, 606—610).—The isoelectric point of the pure compound is at p_H 7·2, and the solubility at this point at 18° has the minimum value of about $3{\cdot}6\times10^{-3}$ g.-mol. per litre; solubilities have been determined for the p_H range 6·0—8·4. The sensitiveness of the reagent under various conditions towards metals is tabulated. In alkaline solution (with sodium potassium tartrate to hold the metal oxide in solution if necessary) copper, cadmium, zinc, and magnesium are completely precipitated, cobalt and nickel nearly so; zinc and magnesium may be completely separated by precipitating the former first in acetic acid solution, the latter afterwards in ammoniacal solution.

Various gravimetric determinations are described, in which the metal compound of 8-hydroxyquinoline is precipitated under suitable conditions, dried, and weighed as such; aluminium is readily determined in presence of calcium and magnesium. The volumetric method with bromine is best carried out by adding excess and titrating back; the determination of zinc, magnesium, calcium, and aluminium in this way is described. S. I. Levy.

Applications of the polarographic method. M. Shikata.—See this vol., 136.

Determination of rare metals and separation from other metals. X. Three new gravimetric determinations of beryllium, and separations depending thereon. L. Moser and J. Singer (Monatsh., 1927, 48, 673—687).—A method for preparing pure beryllium sulphate, depending on the use of tannic acid (cf. A., 1927, 846), is described.

Beryllium may be determined gravimetrically as oxide in three ways. The first, precipitation by ammonia (cf. Bleyer and Boshart, A., 1912, ii, 1211), gives low values, since the solubility of beryllium hydroxide is 2·0 mg. of oxide per litre, rising to 4·5 mg. in presence of 1% of ammonia, even when 1% of ammonium chloride is also present; it is unsatisfactory owing to the ease with which impurities are adsorbed on the hydroxide (which is furthermore very difficult to filter), and is abandoned. A second method is adapted from that used by Schirm (A., 1909, ii, 834) for the determination of aluminium, and consists in the precipitation of the hydroxide from neutral solution by an ammonium nitrite solution; when this is used for beryllium, the hydroxide forms a compact precipitate, easily filtered, but low values are obtained, owing to the formation of nitric acid by decomposition of the nitrous acid liberated. This is avoided by adding methyl alcohol, and thus eliminating nitrous acid in the form of its very volatile methyl ester. The beryllium hydroxide is washed with hot water, ignited to the oxide, and weighed; accurate results are obtained.

Thirdly, tannic acid may be used. Whereas aluminium is precipitated (and separated from beryllium; cf. A., 1927, 846) by tannic acid in weakly acid solutions, beryllim is purecipitated from a solution by adding ammonium nitrate and then tannic acid, followed by ammonia solution. The precipitate is washed and ignited; accurate values are obtained, provided that the solution contains no other metal (except the alkali metals) and no acetate. The method is applicable to the smallest quantities of beryllium.

A satisfactory method of determining beryllium as pyrophosphate is now described (cf. Travers and Perron, A., 1924, ii, 677). By analogy with magnesium, which forms a crystalline ammonium phosphate only in neutral or weakly acid solutions (Schmitz, A., 1925, ii, 67), beryllium ammonium phosphate can be prepared crystalline if an acetate is present. The beryllium solution is treated with a solution of diammonium hydrogen phosphate, ammonium nitrate, and ammonium acetate. After heating, enough nitric acid is added to dissolve the precipitate; dilute ammonia solution is then added very slowly while cloudiness develops, and then rapidly. The crystalline beryllium ammonium phosphate is washed with ammonium nitrate solution and is ignited. Precipitation can also be obtained in presence of sulphosalicylic acid, but not of tartaric acid.

Beryllium is separated from ferric iron and from chromium, thorium, and tungsten by precipitating these as tannic acid complexes in acid solution (cf. A., 1927, 846), and similarly from titanium and vanadium, which form tannic acid complexes insoluble in concentrated acetic acid, and from zirconium, which forms a complex insoluble in concentrated acetic acid or even dilute hydrochloric acid. Beryllium cannot be separated from molybdenum by the tannic acid method, and is accordingly precipitated by ammonium nitrite, a little ammonia solution being added to dissolve any adsorbed molybdenum compound.

E. W. Wignall.

Potentiometric determination of cerium. K. Someya (Z. anorg. Chem., 1927, 168, 56—60).—Cerous sulphate solution, containing free sulphuric acid, is boiled with sodium bismuthate, and the resulting solution, after cooling and diluting, is titrated with ferrous sulphate solution.

H. F. Gillbe.

Separation and determination of tin in the analysis of stannates by their decomposition in a current of hydrogen chloride. G. Jander and F. Busch (Ber., 1927, 60, [*B*], 2594—2597).—Determination of sodium and barium in their respective stannates is accurately effected by gently heating the salts in a current of hydrogen chloride and weighing the residual chloride. The volatilised tin tetrachloride is absorbed in two tubes containing water and dilute ammonia, respectively; the tin is determined as stannic oxide after precipitation with ammonia and ammonium nitrate. Attempts to determine tin volumetrically by a reductive process gave low results since volatile tin compounds were carried away by the gases evolved during the process.

H. Wren.

Germanium. XXV. Arc spectrographic detection and determination of germanium. Occurrence of germanium in certain tin minerals. Enargite as a possible source of germanium. J. Papish, F. M. Brewer, and D. A. Holt (J. Amer. Chem. Soc., 1927, 49, 3028—3033).—The arc spectrum lines of germanium are tabulated for germanium solutions of different concentrations. Except when the germanium is present in very low concentrations the presence of tin has no influence. Certain tin minerals are found to contain small quantities of germanium (0·005, 0·001%). Some specimens of enargite contain 0·1% of the metal, and a method of extraction from this mineral is described.

S. K. Tweedy.

Electrolytic separation of bismuth at low potential. J. Lukas and A. Jílek (Chem. Listy, 1927, 21, 541—543).—To 3 c.c. of concentrated nitric acid, containing not more than 0·3 g. of bismuth, is added a solution of 6 g. of tartaric acid neutralised with 20% sodium hydroxide, and the mixture is electrolysed at 70° in a Classen capsule with a rotating gauze anode with a current of 0·1 amp. and a *P.D.* of 2 volts. When the current has fallen to a few hundredths of an ampere, indicating the completion of the separation, the deposit is washed with water without stopping the current, then with alcohol, and dried at 100°.

R. Cuthill.

Red-sensitive photo-electric cells. C. C. Paterson (Nature, 1928, 121, 58).—Photo-electric cells of the Elster–Geitel type sensitive to the extreme red.

A. A. Eldridge.

Application of interference refractometer to the measurement of the concentration of dilute solutions. R. Macy (J. Amer. Chem. Soc., 1927, 49, 3070—3076).—The necessary precautions attending the use of the Zeiss interference refractometer for determining the concentrations of dilute solutions are described and discussed (cf. Barth, A., 1926, 779). The instrument is more sensitive to aromatic than to aliphatic compounds.

S. K. Tweedy.

Method for the determination of specific heats and heat tone from temperature-time curves. W. M. Cohn (Z. angew. Chem., 1927, 40, 1557—1559).—The substance under examination is placed in a small crucible containing also a thermo element within an electric furnace. The method is intended principally for silicates and ceramic masses for which variations in the thermal conductivity may be neglected. Then the rate of transmission of heat to the substance $dQ/dt=f(t,G)$, where t is the temperature of furnace and G the temperature difference between the furnace walls and the crucible. This function is a constant for a given furnace. A substance is chosen the specific heat of which has been ascertained. For the same substance the temperature–time curve is measured and thus dQ/dt is obtained. A series of curves is produced for varying values of G, and the temperature–time relations for various substances are transformed into temperature–heat quantity relations. Specific heats are determined by tangents and the thermal effect of any chemical reactions which occur can be measured. C. IRWIN.

Mercury oscillating pump. J. T. DONNELLY, C. H. FOOTT, H. NIELSEN, and J. REILLY (J.S.C.I., 1927, **46**, 437—438T).—A column of mercury in a U-tube is kept in oscillation by a water suction pump. The suction applied to one leg of the U-tube draws the mercury upwards. When the mercury reaches a certain height a float opens a valve to the atmosphere which breaks the partial vacuum. The mercury then drops to its original position, closes the valve, and restarts the cycle.

Micro-method for the determination of surface-tension and density. V. R. DAMERELL (J. Amer. Chem. Soc., 1927, **49**, 2988—2991).—The technique of the micro-determination of density and surface-tension with simple apparatus is described. About 0·1 c.c. of liquid is required; the accuracy is of the order of 1%. S. K. TWEEDY.

Distillation cooler. W. SCHULEMANN (Chem.-Ztg., 1927, **51**, 985).—The apparatus, which is for use in vacuum distillations, consists of a round-bottom flask the neck of which is narrowed and constricted at the upper end and turned downwards into a bulb-shaped tube; this is provided with outlets at its upper end for the insertion of a thermometer and for conducting the vapours to the condenser, and at its lower end to return condensed liquid and spray into the lower part of the round flask away from the stream of vapour which is admitted through a small tube on the opposite side of the neck of the flask. A. R. POWELL.

Apparatus. H. J. FUCHS (Biochem. Z., 1927, **190**, 241—246).—An apparatus for preparation of pure, sterile distilled water, an improved stalagmometer, and an apparatus for bubbling the same quantity of gas through several liquids in the same time, are described. P. W. CLUTTERBUCK.

Apparatus for removal of dissolved gases from water. J. R. LORAH, K. T. WILLIAMS, and T. G. THOMPSON (J. Amer. Chem. Soc., 1927, **49**, 2991—2994).—An apparatus is described in which the advantages of the Van Slyke apparatus (A., 1917, ii, 422) are combined with those of Treadwell's. S. K. TWEEDY.

Platinum electrode for laboratory and demonstration use. S. WIECHOWSKI (Chem.-Ztg., 1927, **51**, 984—985).—The electrode comprises a rectangular platinum sheet, 25×12 mm., to which is welded a piece of stout platinum wire 3·5 cm. long which is sealed into a small glass test-tube. The end of the wire in the tube is flattened and turned up to form a small hook into which a similar hook of brass or copper wire is fixed and the joint hammered flat. The brass wire is held in position by a plug of cement in the mouth of the tube and is provided with a brass contact and screw for making connexion with the source of current. A. R. POWELL.

Change of state on heating of silver mirrors deposited on glass. I. SAWAI and O. MORISAWA (Z. anorg. Chem., 1927, **168**, 49—55).—The distance between the particles forming a silver mirror on glass is on heating altered to an extent which varies with the temperature of heating, the thickness of the mirror, and the nature of the atmosphere in which the heating is conducted. H. F. GILLBE.

Cover-glass for conducting microchemical reactions in the Zeiss quartz cell. J. JOCHIMS (Z. wiss. Mikroskop., 1927, **44**, 214—216; Chem. Zentr., 1927, ii, 1285).

Illinium. W. A. NOYES (Z. anorg. Chem., 1927, **168**, 264).—Polemical against Rolla and Fernandes (A., 1927, 501). R. CUTHILL.

Geochemistry.

Theory of the upper atmosphere and meteors. (EARL OF) BERKELEY (Nature, 1927, **120**, 954).

Composition of the air in the streets of Paris. D. FLORENTIN (Compt. rend., 1927, **185**, 1538—1541).—The air of the streets in the centre of Paris contains about 0·5 litre/m.^{3} of carbon dioxide and small quantities of carbon monoxide. The actual amounts depend on the atmospheric conditions. Pollution of the air by these gases is considerably less on the upper floors of the buildings and in the suburbs. J. GRANT.

Temperature and salinity observations in the Gulf of Aden. D. J. MATTHEWS (Nature, 1927, **121**, 92).—A comparison of published observations. A. A. ELDRIDGE.

Variations in the salinity of estuaries measured *in situ* by electrical conductivity. A. CHAUCHARD and (MME.) CHAUCHARD (Compt. rend., 1927, **185**, 1503—1504).—A modified Kohlrausch conductivity method is described for the determination from a boat of the salinities of rivers and lakes in terms of the electrical conductivity of the water. A correction must be applied for temperature, but for depths of less than 10 m. the pressure has no appreciable effect. J. GRANT.

"Activity" of the best-known iron springs. A. SIMON and K. KÖTSCHAU [with G. BUSS] (Z. anorg. Chem., 1927, **168**, 129—144).—Examination of the waters of various German iron springs has shown that, as with the solutions of active iron employed in previous experiments (A., 1927, 843), the intensity of the benzidine and guaiacum resin reactions is a function of the concentration of ferrous ions. If air is excluded, and the escape of carbon dioxide prevented, the water apparently retains its activity indefinitely. R. Cuthill.

Acidity of the waters of some Puget Sound bogs. T. G. Thompson, J. R. Lorah, and G. B. Rigg (J. Amer. Chem. Soc., 1927, **49**, 2981—2988).—The carbon dioxide content of the above waters was measured (cf. Bot. Gaz., 1927, **84**, 264). The acidity is due to an acid (or acids) in addition to, and stronger than, carbonic acid, since the maximum acidity that carbonic acid could produce is less than that observed. Colorimetric and electrometric methods of measuring p_H gave different results. The p_H value is unaffected by boiling, showing that the acid substance is non-volatile, and is unaffected by temperature change; the substance either forms a true solution and is very soluble, or else it is a reversible colloid. The effect of dilution on acidity is similar to that occurring when an acid is buffered by a small quantity of one of its salts. The acidity increases with intensity of colour, *i.e.*, with the stage of plant succession. Water from "wet" bogs (*i.e.*, those surrounding a pond) contains dissolved methane and has a smaller acidity than that from "dry" bogs. The percentage of organic matter in the bogs is a logarithmic function of acidity, indicating that the amount of organic matter is the controlling factor of acidity. S. K. Tweedy.

Relation between the reducing power of sea water and the distribution of sea-shore organisms. E. Fischer (Compt. rend., 1927, **185**, 1525—1527).—Dissolved reducing substances in sea water favour the distribution of *Sabella pavonia*, Sav., and *Nassa reticulata*, L. H. Burton.

Determination of refractive indices of minerals by Becke's immersion method. V. Billiet (Natuurwetensch. Tijds., 1927, **9**, 97—103).—An account of the method and of the practical detail of manipulation, with a discussion of the theoretical basis. S. I. Levy.

Specific gravities of minerals: index of some recent determinations. L. J. Spencer (Min. Mag., 1927, **21**, 337—365).—The determination of density by floating in heavy liquids affords a useful "first-aid" in the identification of minerals. A number of crystals of known density act as indicators in a series of tubes containing methylene iodide diluted to different degrees with benzene. The same fragment of the mineral tested can then be used for confirmatory optical and micro-chemical tests. 2277 determined values of density collected from the literature since 1910 are listed numerically from 1·03 (retinite) to 19·0 (native platinum), with a reference to the original literature in each case. A second list gives the minimum and maximum recorded values for each mineral arranged alphabetically. A frequency-curve shows a very pronounced peak at 2·65 for 196 determinations, whilst the arithmetical mean of all the values is 3·62. L. J. Spencer.

Origin of Chile saltpetre. E. Wilke-Dörfurt (Z. anorg. Chem., 1927, **168**, 203—208).—Polemical against Stoklasa (Chem.-Ztg., 1924, **48**, 4, 949). The possible superiority of Chile saltpetre as compared with the synthetic nitrate as a fertiliser for sugar-beet is probably a consequence of the facts that beet, unlike similar cultivated plants, possesses certain inherited halophytic characteristics, and that small amounts of iodine are essential for the life of halophytes. It is considered that Stoklasa's volcanic theory of the origin of the saltpetre is untenable in view of the fact that the iodine content of the nitrate rock as well as the nature and proportions of the other salts present approximate much more closely to what would be expected in a deposit of marine origin than in one produced by volcanic activity. The nitrogen is therefore to be regarded as originating in marine organisms, and the occurrence of iodine, stored up by such organisms, in the nitrate deposits is then in line with its presence in coal, and in phosphate deposits of organic origin. R. Cuthill.

Composition of two Madagascar minerals: ampangabeite and columbite. G. Tschernick (Bull. Soc. Franç. Min., 1926, **49**, 127—135; Chem. Zentr., 1927, i, 2529).—Ampangabeite, *d* 4·45, almost black, contained Nb_2O_5 50·78, Ta_2O_5 1·80, TiO_2 5·22, SnO_2 0·27, ThO_2 1·65, UO_2 11·98, yttrium earths 4·71, cerium earths 0·67, Fe_2O_3 10·03, CaO 0·87, H_2O 11·04%; lighter-coloured specimens had *d* 4·39 and 3·36, respectively. Columbite contained Nb_2O_5 62·71, Ta_2O_5 12·42, SiO_2 0·65, TiO_2 1·30, SnO_2 0·41, U_3O_8 2·28, FeO 11·02, MnO 8·24, Al_2O_3 0·11, CaO trace, K_2O+Na_2O 0·09%. A. A. Eldridge.

Tourmaline and mica groups. W. Kunitz (Fortschr. Min. Kryst. Pet., 1927, **11**, 313—314; Chem. Zentr., 1927, i, 2640).—The compositions of the tourmalines, particularly the ratios $SiO_2 : B_2O_3 : Na_2O : H_2O$, are generally constant. In the magnesium iron tourmalines there is a regular increase in refractive power and decrease in the axial ratio $c : a$ with increase in the iron content. Partial substitution of the magnesium by lithium and aluminium gives a series analogous to the lithium micas. The member $H_5Na(LiAl)_2Al_8Si_8B_8O_{41}$ has ω 1·6401, ε 1·6202, $a : c=1 : 0{\cdot}4508$; $H_5NaFe_4Al_8Si_8B_8O_{41}$ has ω 1·698, ε 1·658, $a : c=1 : 0{\cdot}440$. A. A. Eldridge.

Rhyolites and hyperalkaline, quartziferous trachytes, with special reference to those of Korea. A. Lacroix (Compt. rend., 1927, **185**, 1410—1415).—The rhyolites, which are characterised by their richness in alkalis and by the presence of iron and sodium silicates, are divided into two groups, the comendites and the pantellerites. Analyses of samples from Korea show, however, that the members of the groups constitute a continuous series, although two mineralogical types are distinguished throughout the whole independently of the chemical composition. One is produced in a glass-like form by rapid cooling, and the other, which has a membrane structure, may be the result of a transformation of the first. Trachytes containing free silica (hakutoite) are associated with rhyolites and fall into the same mineralogical groups. As with all the hyperalkaline rocks, the types richest in coloured minerals are the richest in quartz. The term hakutoite is applied to all the siliceous α-hyperalkaline trachytes. J. Grant.

Chemical composition of the lavas of Ahaggar, Central Sahara. M. E. Denaeyer and J. Bourcart (Compt. rend., 1927, **185**, 1492—1494).—Analyses are given of a number of volcanic rocks, and the relationship between the origins of basalts from the valleys, plateaux, and other volcanic centres of the Sahara is indicated. J. Grant.

Natrojarosite from Kingman, Arizona. E. V. Shannon and F. A. Gonyer (J. Washington Acad. Sci., 1927, **17**, 536—537).—Jarosites are commonly found in the oxidised portions of ore deposits. The formula $(Na,K)_2O,3Fe_2O_3,4SO_3,6H_2O$ has been established by analysis for the earthy, yellowish-brown jarosite described. J. Grant.

Almandite–spessartite garnet from Gwynns Falls, Baltimore. E. V. Shannon and F. A. Gonyer (J. Washington Acad. Sci., 1927, **17**, 534—536).—Analysis has shown that, like most garnets from granitic pegmatites, the present example is a member of the almandite-spessartite series, but contains the ferrous iron molecule a little in excess of the manganese molecule. The almandite : spessartite ratio is 49·87 : 40·17, and andradite (4·58%), grossularite (2·26%), pyrope (1·62%), and free alumina (1·82%) are also present. The colorimetric determination of manganese is preferable to the basic acetate method in such cases. J. Grant.

Anthraxolite of Sudbury. A. P. Coleman (Amer. J. Sci., 1928, [v], **15**, 25—27).—A material resembling anthracite occurs in some abundance filling veins which cut across the stratification of the pre-Cambrian slates near Chelmsford, Sudbury region, Ontario. It breaks up into lustrous plates and cuboidal fragments, and is much intermixed with quartz and pyrite, showing up to 36·5% of ash. Analysis of selected fragments gave C 94·92, H 0·52, O 1·69, N 1·04, S 0·31, ash 1·52%. The material is referred to anthraxolite and is considered to represent an end-product of the metamorphism of petroleum, which was perhaps of organic origin in the pre-Cambrian seas (cf. A., 1926, 143). L. J. Spencer.

Vermiculite from the Bare Hills, near Baltimore, Maryland. E. V. Shannon (Amer. J. Sci., 1928, [v], **15**, 20—24).—A pale-green foliated mineral resembling talc in appearance has been found in the old chromite mines and quarries in serpentine. When heated, it exfoliates like the vermiculites. It encloses some shreds, apparently remnants, of fibrous serpentine or of actinolite. It is optically uniaxial and negative with perfect basal cleavage; ω=1·545, ε=1·525. Analysis gave SiO_2 36·12, TiO_2 0·24, Al_2O_3 13·90, Fe_2O_3 4·24, FeO 0·68, NiO 0·28, MnO trace, MgO 24·84, CaO 0·18, H_2O (>130°) 10·74, H_2O (<130°) 8·20, total 99·42, agreeing with the formula $4MgO,Al_2O_3,4SiO_2,6{\cdot}5H_2O$. The analyses and optical data of some other vermiculites are tabulated for comparison. L. J. Spencer.

Dehydration and optical studies of alunogen, nontronite, and griffithite. E. S. Larsen and G. Steiger (Amer. J. Sci., 1928, [v], **15**, 1—19).—The water content of these three minerals is variable, depending on the temperature and on the humidity of the atmosphere, and the optical data show a corresponding variation. Dehydration and rehydration curves are given for each, and optical determinations were made on the partly dehydrated material at different stages. Alunogen from New Mexico consisting of white flattened fibres with n_α 1·460, n_β 1·461, n_γ 1·470 gave on analysis of air-dried material SO_3 37·74, Al_2O_3 16·59, H_2O 44·64, insol. 0·94, total 99·91, agreeing with the formula $Al_2O_3,3SO_3,15{\cdot}5H_2O$. The dehydration curve shows a break at 90°, and the material is then optically isotropic with n 1·502. Nontronite from Woody, California, gave analysis I for dark olive-green material with n_α 1·56, n_β 1·585, n_γ 1·585, d 2·495; and II for citron-green material with n_α 1·57, n_β 1·59, n_γ 1·60.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O (+105°).	H_2O (−105°).	Total.
I.	47·51	0·37	35·17	nil	1·40	2·50	5·90	7·16	100·16*
II.	43·51	2·94	28·62	0·99	0·05	2·22	6·62	14·05	100·02†

* Including Na_2O 0·09, K_2O 0·06. † Including CuO 1·02.

Analysis I agrees with a formula $R^{II}O,3R_2^{III}O_3,10SiO_2,9H_2O$. The published analyses and optical data for nontronite, morencite, hœferite, and müllerite (=zamboninite) are tabulated and compared, and it is concluded that these are all identical, differing mainly in the variable amount of water present. The formula of nontronite may be given as $Fe_2O_3,3SiO_2,nH_2O$, and this shows a gradual passage to the isomorphous mineral beidellite, $Al_2O_3,3SiO_2,nH_2O$ (A., 1926, 143). Data are also given for griffithite (A., 1917, ii, 148). L. J. Spencer.

South African occurrences of willemite. Fluorescence of willemite and some other zinc minerals in ultra-violet rays. L. J. Spencer (Min. Mag., 1927, **21**, 388—396).—Willemite (Zn_2SiO_4) is described from Broken Hill and from two other localities in Northern Rhodesia, where it appears to be of abundant occurrence, at one place in association with native silver. Another occurrence is with copper ores at Guchab in South-West Africa. A complete list of localities known for willemite is compiled. The willemite from Franklin Furnace in New Jersey shows a brilliant green fluorescence in ultra-violet rays; that from other localities may show a dark green or a bright yellow, but in most cases no fluorescence at all. Similarly, with some other zinc minerals fluorescence is shown by some specimens and not by others. Of a set of 23 diamonds from British Guiana, a green crystal showed a bright green fluorescence, three colourless crystals a good blue, and the rest gave no effect. Fluorescence in ultra-violet rays is not a constant and essential character of a mineral species, and it evidently depends on the presence of some admixed impurity in the material. L. J. Spencer.

β-Quartz twins from some Cornish localities. J. Drugman (Min. Mag., 1927, **21**, 366—382).—β-Quartz or high-temperature quartz, stable above 575°, is represented by the porphyritic crystals in quartz-porphyry (the Cornish "elvans"). The twin-laws of this quartz are enumerated, and are distinct from those of α-quartz or low-temperature quartz. L. J. Spencer.

Occurrence of niccolite and ullmannite in Northumberland, and of serpierite in Killarney,

Ireland. Arthur Russell (Min. Mag., 1927, **21**, 383—387).—The Settlingstone mine in Northumberland is the largest producer of witherite ($BaCO_3$). Here, in a pipe of galena, the nickel minerals ullmannite (NiSbS) and niccolite (NiAs) have recently been found. Serpierite, as small greenish-blue radial aggregates of minute flattened crystals, has been detected in the waste heaps of the old copper mine on Ross Island in Lough Leane, Killarney. The formula of serpierite given in text-books is based on an error. The only analysis of this mineral (Frenzel, 1894) gives the ratios $(Cu,Zn,Ca)O : SO_3 : H_2O = 2{\cdot}21 : 1 : 3{\cdot}07$. L. J. Spencer.

Uranium minerals from Lotsmanskaja near Ekaterinoslav and from Khutor Golowin near Shitomit and their radioactivity. N. Leschenko (Nachr. Berginst. Ekaterin., 1926, **19**, 171—175).—The former (undefined) has radioactivity 50%, and the latter (wiikite) 60%, of that of pitchblende. Both originate from pegmatites. Chemical Abstracts.

Refractive index of becquerelite, curite, kasolite, fourmarierite, parsonite, dumontite, and janthinite. V. Billiet (Bull. Soc. Franç. Min., 1926, **49**, 136—140; Chem. Zentr., 1927, i, 2528).—Values of n_α, n_β, and n_γ, respectively, are: becquerelite, rhombic, 1·750, 1·88, 1·87; schœpite, $UO_3,3H_2O$, rhombic, 1·690, 1·735, 1·714; janthinite, $2UO_2,7H_2O$, rhombic, 1·674, 1·92, 1·90; fourmarierite, $PbO,4UO_3,5H_2O$, rhombic, —, 1·94, 1·92; curite, $2PbO,5UO_3,4H_2O$, rhombic, —, 2·12, 2·07; soddite, $12UO_2,5SiO_2,14H_2O$, rhombic, 1·645, —, 1·662; kasolite, $3PbO,3UO_3,3SiO_2,4H_2O$, monoclinic, 1·89, —, 1·90; sklodowskite, $MgO,2UO_3,2SiO_2,7H_2O$, rhombic, 1·613, 1·657, 1·635; parsonite, $2PbO,UO_3,P_2O_5,H_2O$, monoclinic, 1·85, 1·862, —; dumontite, $2PbO,3UO_3,P_2O_5,5H_2O$, rhombic, 1·88, —, 1·89; dewindite, $3PbO,5UO_3,2P_2O_5,12H_2O$, rhombic, 1·762, —, 1·763. A. A. Eldridge.

Villiaumite. T. Barth and G. Lunde (Zentr. Min. Geol. Paläont., 1927, A, 57—66; Chem. Zentr., 1927, i, 2529).—*X*-Ray analysis of carmine-red villiaumite shows its identity with pure sodium fluoride; the colour and double refraction are therefore ascribed to the effect of radioactivity. The properties of villiaumite are (incompletely) acquired by sodium fluoride on exposure to *X*-radiation.
A. A. Eldridge.

Pleochroic haloes and the age of the earth. F. Lotze (Nature, 1927, **121**, 90).—It is concluded that the coloration of the mineral is accompanied by an alteration in its cohesion properties, with a corresponding increase (revealed especially in the innermost uranium ring) in the range of the α-particles. Hence, it is supposed that with advancing development the outer periphery of the halo advances radially, whereby the part of the ring directed towards the centre is no longer darkened to the same extent as previously. Such a mechanism would explain the discrepancies observed by Joly. The absence of the anomaly in thorium haloes is attributed to the fact that the integral ionisation curve of thorium is less steep than that of uranium, and that no marked maximal absorption of the α-rays coincides with the innermost rings. This explanation invalidates Joly's calculation of geological age. A. A. Eldridge.

Organic Chemistry.

Hydrogen–ethylene reaction in presence of excited mercury atoms. A. R. Olson and C. H. Meyers (J. Amer. Chem. Soc., 1927, **49**, 3131—3134; cf. A., 1926, 364).—Methane, ethane, propane, and butane are produced when a mixture of hydrogen and ethylene is exposed to ultra-violet light in presence of mercury vapour. Ethane is unaffected under similar conditions. The results obtained appear to indicate the intermediate formation of atomic hydrogen, methylene by fission of the ethylene, and ethylene activated by loss of hydrogen. It is concluded that the energy required for rupture of the carbon–hydrogen linking in ethylene, and the ethylene linking itself, is less than 4·9 volts. F. G. Willson.

Hydrogenation of substances with conjugated double linkings. G. Vavon (Bull. Soc. chim., 1927, [iv], **41**, 1598—1600).—Gillet's interpretation of the hydrogenation of conjugated double linkings as due to addition of two sodium atoms in the αβ-positions, followed by isomeric change >CNa·CHNa·CH:C< $\longrightarrow$ >CNa·CNa:CH·CH< (A., 1927, 921) fails to account for hydrogenation of conjugated systems by agents other than sodium which afford nascent hydrogen, *e.g.*, aluminium amalgam and zinc and acetic acid. It is only catalytic methods of hydrogenation that have failed when applied to conjugated systems and any interpretation of the hydrogenation of such systems must account for this difference (cf. A., 1926, 934; 1927, 336). R. Brightman.

Ethylenic hydrocarbons obtained by semi-reduction of the corresponding acetylenes. M. Bourguel (Bull. Soc. chim., 1927, [iv], **41**, 1475—1479).—Δ^α-Olefines boil at lower temperatures than the Δ^β-isomerides, but the difference is less pronounced than with the corresponding acetylenes, being only about 2° with the higher members of the series. With hydrocarbons containing the same number of carbon atoms the Δ^β-acetylene, Δ^α-acetylene, paraffin, Δ^β-olefine, and Δ^α-olefine are in order of decreasing b. p. Similarly differences in density are less pronounced in the olefine series than in the acetylene series, the Δ^α-olefines being the lighter. The following data are recorded: Δ^α-pentene, b. p. 32·5°, d^{20} 0·644, n_D^{20} 1·371; Δ^β-pentene, b. p. 34·5°, d^{19} 0·647, n_D^{19} 1·375; Δ^α-hexene, b. p. 64·5—65°, d^{14} 0·684, n_D^{14} 1·393; Δ^α-heptene, b. p. 94—94·5°, d^{20} 0·705, n_D^{20} 1·404; Δ^α-octene, b. p. 122—122·1°, d^{19} 0·718, n_D^{19} 1·408; Δ^β-octene, b. p. 125—126°, d^{20} 0·725, n_D^{20} 1·415; Δ^α-nonene, b. p. 146°, d^{21} 0·721, n_D^{21} 1·414; Δ^β-nonene, b. p. 148·5°, d^{21} 0·738, n_D^{21} 1·420; cyclo*hexyl*-Δ^α-*propene*, b. p. 152°, d^{21} 0·808, n_D^{21} 1·449; cyclo*hexyl*-Δ^α-*butene*, b. p. 174°/760 mm., 62°/14 mm., d^{21} 0·810,

n_D^{21} 1·450; cyclo*hexyl*-Δ^{β}-*butene*, b. p. 177°/760 mm., 66°/14 mm., d^{21} 0·813, n_D^{20} 1·453; cyclo*hexyl*-Δ^{α}-*pentene*, b. p. 196°/760 mm., 83°/14 mm., d^{2} 0·816, n_D^{20} 1·454; cyclo*hexyl*-Δ^{β}-*pentene*, b. p. 198—199°/760 mm., 85°/16 mm., d^{20} 0·822, n_D^{20} 1·458; cyclo*hexyl*-Δ^{α}-*hexene*, b. p. 219°/760 mm., 99°/16 mm., d^{21} 0·820, n_D^{21} 1·457; cyclo*hexyl*-Δ^{β}-*hexene*, b. p. 221°/760 mm., 102°/17 mm., d^{21} 0·823, n_D^{21} 1·459; cyclo*hexylpropane*, b. p. 155°, d^{21} 0·791, n_D^{21} 1·437; cyclo*hexylbutane*, b. p. 177°/760 mm., 68°/16 mm., d^{20} 0·797, n_D^{20} 1·440; cyclo*hexylpentane*, b. p. 199°/760 mm., 84·85°/16 mm., d^{20} 0·802, n_D^{20} 1·444; cyclo*hexylhexane*, b. p. 221°/760 mm., 102°/16 mm., d^{20} 0·806, n_D^{20} 1·446. Δ^{α}-Butinene was prepared by catalytic dehydration of *n*-butyl alcohol with alumina, fixation of 2 atoms of bromine on the mixture of Δ^{α}- and Δ^{β}-butenes, treatment of the dibromobutane with alcoholic potassium hydroxide, and finally decomposition of the bromobutene, b. p. 88°, with sodamide in light petroleum at 150—160°. Δ^{β}-Pentinene, b. p. 57°, d^{19} 0·712, n_D^{19} 1·404, is obtained by treatment of Δ^{α}-butinene with sodamide and methyl sulphate.

R. BRIGHTMAN.

Properties of conjugated compounds. III. Bearing of hexatriene chemistry on the reactive form of conjugated hydrocarbons. E. H. FARMER, B. D. LAROIA, T. M. SWITZ, and J. F. THORPE (J.C.S., 1927, 2937—2958).—The addition of bromine to *cis*- and to *trans*-$\Delta^{\alpha\gamma\epsilon}$-hexatriene occurs primarily at the αβ-positions. Since bromine migrates easily in this series, terminal addition, the recorded evidence of which is reviewed, is considered to be probably fallacious and based on phenomena of only a secondary nature. The relation of *cis*-hexatriene to benzene is distant and the electronic formula, $\begin{matrix}\mathrm{CH{:}CH{:}CH_2}\\ \cdots\qquad\cdot\\ \mathrm{CH{:}CH{:}\dot{C}H_2}\end{matrix}$, does not represent any observed fact.

s-Divinylethylene glycol yields two stereoisomeric forms of s-*diethylethylene glycol*, b. p. 87—88°/15 mm., and m. p. 88°, each of which is oxidisable to propionic acid, together with some ethylpropylcarbinol. Bromination of *s*-divinylethylene glycol yields γδ-*dibromo*-$\Delta^{\alpha\epsilon}$-*hexadiene* (*A*), b. p. 94—96°/11 mm., αζ-*dibromo*-$\Delta^{\beta\delta}$-*hexadiene*, m. p. 85° (*B*), and a *tribromohexene*, b. p. 135—140°/11 mm. All attempts to determine the constitution of the first-named dibromide by oxidative methods or by attempts to prepare the corresponding glycol or diacetate, which afforded complex mixtures, failed. Alcoholic sodium hydroxide yielded $\Delta^{\alpha\epsilon}$-*hexadien-γ-in* (?), b. p. 80—95°, and γ-*bromohexatriene*, b. p. 52—55°/20 mm., both of which rapidly polymerise. Bromination in chloroform solution yields probably αβγδ-*tetrabromo*-Δ^{ϵ}-*hexene*, b. p. 155—158°/11 mm., whereas zinc dust and alcohol convert it into cis-*hexatriene*, b. p. 78·5°/760 mm., d_4^{20} 0·7175, n_D^{20} 1·4577, $[R_L]_D$ 30·41° (a lower value than that of the *trans*-), in 30% yield. αζ-Dibromo-$\Delta^{\beta\delta}$-hexadiene yields the two stereoisomeric forms of αβεζ-*tetrabromo*-Δ^{γ}-*hexene*, m. p. 111°, and m. p. 46° (the more soluble), which exhibit considerable stability towards ozone and potassium permanganate. On treatment with pyridine the dibromide yields the *dipyridinium* salt, m. p. 212°, and with glacial acetic acid and potassium acetate, αζ-*diacetoxy*-$\Delta^{\beta\delta}$-*hexadiene*, b. p. 155—160°/14 mm. αζ-*Diethoxy*-$\Delta^{\beta\delta}$-*hexadiene*, b. p. 116°/20 mm., prepared by the action of alcoholic sodium ethoxide on the dibromide, gives αζ-*diethoxyhexane*, b. p. 86°/14 mm., on reduction with hydrogen in the presence of colloidal palladium, and αζ-di-iodohexane by repeated treatment with hydrogen iodide at 100°. The last-named compound may be converted into suberic acid through the dinitrile by the usual methods. αδ-Diethoxy-$\Delta^{\beta\delta}$-hexadiene is oxidised by ozonised oxygen to an *ozonide* (syrup) which decomposes at 85° to give γ-*ethoxycrotonaldehyde*, b. p. 80°/21 mm., and its decomposition products, ethoxyacetic acid and ethoxyacetaldehyde.

Bromination of *cis*-hexatriene in chloroform solution at 0° affords cis-αβ-*dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene*, b. p. 90—96°/11 mm., which, unlike the other dibromides, is colourless. A small amount of αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene is formed at the same time. Tetrabromohexene, b. p. 155—158°/11 mm., together with a small amount of an *isomeride*, m. p. 91°, may be obtained by the same method using 4 atoms of bromine. By the gradual addition of an alcoholic solution of the dibromide *C* to alcoholic sodium ethoxide, cis-α(or β)-*bromohexatriene*, b. p. 46—65°/20 mm., is obtained.

trans-αβ-*Dibromo*-$\Delta^{\gamma\epsilon}$-*hexadiene* (an oil which distils at 1—2 mm.), obtained by the bromination of a glacial acetic acid solution of *trans*-hexatriene with quinoline dibromide at 0°, rapidly isomerises into the dibromide *B*. trans-α(or β)-*Bromohexatriene*, b. p. 53°/22 mm., obtained in the usual way, polymerises very rapidly. Reduction of cinnamaldehyde by Thiele's method (A., 1899, i, 616) yields *s*-distyrylethylene glycol together with an oily residue which on heating gives phenyl-α-naphthylethylene, m. p. 206° (unimolecular in benzene solution and unreduced by hydrogen in the presence of colloidal palladium). *Dibromo*-αζ-*diphenylhexadiene*, m. p. 124—125°, obtained by the action of phosphorus tribromide on the glycol, affords αζ-diphenylhexatriene, m. p. 196°, on treatment with zinc dust in chloroform or with diethylamine or pyridine, identical with that obtained by Smedley (J.C.S., 1908, 93, 376). Addition of bromine to a carbon disulphide solution of the hydrocarbon yields the original dibromide, the *tetrabromide*, m. p. 165°, and the *hexabromide*, m. p. 228—230°. Similarly bromination of *s*-dipropenylethylene glycol affords a mixture of the isomeric dibromides, b. p. 92—100°/14 mm., which in turn may be converted into αζ-*dimethylhexatriene*, b. p. 125—130°, d_4^{18} 0·8394, n_D^{18} 1·45193, and large amounts of polymerides, by treatment with zinc dust and alcohol. ση-*Dimethyl*-$\Delta^{\gamma\eta}$-*decadiene*-εζ-*diol*, b. p. 163—165°/23 mm., d_4^{19} 0·9400, obtained by the reduction of methylethylacraldehyde, affords εζ-*dibromo*-δη-*dimethyl*-$\Delta^{\gamma\eta}$-*decadiene*, m. p. 99—100°, by treatment with ethereal phosphorus tribromide. Repeated treatment of the latter dibromide affords impure βε-*dimethyl*-αζ-*diethylhexatriene*, b. p. 65—70°/26 mm., together with large amounts of waxy polymerides.

G. A. C. GOUGH.

Preparation of $\Delta^{\alpha\epsilon}$-heptadi-inene and $\Delta^{\beta\zeta}$-octadi-inene. URION (Compt. rend., 1927, **185**, 1286—1287).—Methyl sulphate reacts with the dimagnesium derivative of dipropargyl to form $\Delta^{\alpha\epsilon}$-*heptadi-inene*, b. p. 26—27°/30 mm., d^{21} 0·810, n_D^{21} 1·4521, and

$\Delta^{\beta\zeta}$-*octadi-inene*, m. p. 26·5—27°, b. p. 62°/19 mm., d^{30} 0·828, n_{D}^{30} 1·4658. Starting with a mixture of diallyl tetrabromides used in the above preparations, an attempt was made to reproduce the dibromodiallyl, b. p. 205—210°, and diallyl hexabromide, m. p. 76—77°, of Henry (cf. A., 1873, 1215). The action of sodium ethoxide on the diallyl tetrabromides yielded a mixture of isomeric dibromides, $C_6H_8Br_2$, giving two fractions, b. p. 85—89° and 89—94°, both of which, on bromination, yielded the same *diallyl hexabromide*, $C_6H_8Br_6$, m. p. 93·5—94°, differing from Henry's product. B. W. ANDERSON.

Preparation of *iso*propyl iodide. A. RÉCSEI (Biochem. Z., 1927, **190**, 57—58).—The method of Markownikoff (Annalen, 1866, **138**, 364) for preparing *iso*propyl iodide from glycerol, iodine, and white phosphorus has been modified by an alteration in the amounts of the reagents and the use of red phosphorus. The redistilled product has a brown colour, probably due to some compound containing iodine; this may be removed by sodium hydroxide but not by sodium thiosulphate solution. A. WORMALL.

Allyl transposition and the mechanism of esterification. C. PRÉVOST (Compt. rend., 1927, **185**, 1283—1285; cf. A., 1927, 851).—Of 13 known reactions in which the allyl ion, $(R'CH^{+}\cdot CH^{-}\cdot CH^{+}R'')$, may be involved, the only two which are quite normal are those in which this ion is not necessarily free during the reaction. Conversely, it may be assumed that when normal reactions occur the tripolar ion is not separated. The esterification of substituted allyl alcohols by acetic acid is quite normal, and thus the reaction must be written: $(MeCO)(OH)+(RO)(H) \rightleftharpoons (MeCO)(OR)+(H)(OH)$ (I); esterification by mineral acids, however, is of the type: $(MeCO_2)(H)+(R)(OH) \rightleftharpoons (MeCO_2)(R)+(H)(OH)$ (II), whilst esterification with trichloroacetic acid follows the equation (II), but the reverse process of hydrolysis is of the type (I). B. W. ANDERSON.

Ultra-violet absorption spectra of *cyclo*hexene, ethyl ether, methyl *n*-amyl ether, and ethylene chlorohydrin. A. W. SMITH, C. E. BOORD, C. S. ADAMS, and C. S. PEASE (J. Amer. Chem. Soc., 1927, **49**, 3137—3139; cf. A., 1927, 608, 918).—Re-examination of the materials used for the former experiments has confirmed the presence of benzene as an impurity, which appears to originate from alcohol denatured with benzene which is frequently used for the manufacture of ether, and the use of such ether in Grignard syntheses (*e.g.*, for methyl *n*-amyl ether) will contaminate the products with benzene. Examination of four brands of anæsthetic ether revealed a faint trace of benzene in only one case. The validity of de Laszlo's theoretical criticisms is challenged.
F. G. WILLSON.

Interpretation of the acetyl value and ester transformation of glycerides by acetic anhydride. II. D. HOLDE and W. BLEYBERG (Ber., 1927, **60**, [*B*], 2497—2507; cf. A., 1926, 1123).—The saponification values of the products obtained by the action of acetic anhydride on tristearin (Merck or Kahlbaum) are independent of the period of action and of the quantity of acetic anhydride used. Reaction is due to the presence of mono- or di-glycerides and not to ester transformation (cf. Willstätter and Madinaveitia, A., 1912, ii, 1104). Pure tristearin and tripalmitin, prepared by the method of Bellucci (A., 1911, i, 259, 515; 1912, i, 935) with subsequent repeated crystallisation of the products from acetone, after treatment with acetic anhydride are neutral when titrated with 0·1*N*-alcoholic potassium hydroxide in benzene solution and have a saponification value not greater than that of the original material. They therefore do not contain acid anhydride, combined acetic acid, or free fatty acid derived by hydrolysis of the acetylated product. Similar observations with regard to the first point are recorded for ethyl stearate. Tristearin and ethyl stearate when heated with glacial acetic acid under pressure at 200° during several hours suffer ester transformation to the extent of about 14% and 7%, respectively, whereas this change is not effected by acetic anhydride under similar conditions; acetic acid has a scarcely appreciable action on tristearin at atmospheric pressure. Ester transformation is observed to a limited extent when tristearin is boiled with acetic anhydride containing a trace of concentrated sulphuric acid. H. WREN.

Constitution of the glycerides in natural fats. T. P. HILDITCH and C. H. LEA (J.C.S., 1927, 3106—3117).—Oxidation of neutral fats with potassium permanganate in acetone has no action on the saturated glycerides, but converts the mono-, di-, and trioleins into the corresponding acid azelaic esters. Similarly oxidation with an acetic acid solution of hydrogen peroxide gives unaltered saturated glycerides and the dihydroxystearic esters corresponding with the three oleins (A., 1926, 938). Since both methods are almost quantitative and give products which are fairly easily isolated, they may be used to determine the constitution of fats. The vegetable fats contain only small amounts of fully saturated glycerides; the oleic acid is combined chiefly with two molecules of the saturated acid. Cacao butter contains palmitic, stearic, and oleic acids in approximately equal amounts and consists mainly of mono-oleic disaturated glycerides. In cotton-seed oil the palmitic acid is uniformly combined with the saturated fatty acids and the proportion of the saturated to the unsaturated acids is approximately 3 : 1. Mutton tallow contains 25—26% of fully saturated glycerides together with dioleic glycerides. No evidence is obtained for the existence of trioleins in cacao butter or in mutton tallow. G. A. C. GOUGH.

Separation of glycerides. I. Linseed oil. II. Soya-bean oil. B. SUZUKI and Y. YOKOYAMA (Proc. Imp. Acad. Tokyo, 1927, **3**, 526—528, 529—530).—I. Bromination of linseed oil in light petroleum, and subsequent separation of the bromides by dissolution in various solvents, results in the separation of *dilinoleo-linolenin bromide*, m. p. 78°, yielding, on hydrolysis with hydrochloric acid, tetrabromo-, m. p. 115°, and hexabromo-stearic acids, m. p. 179°, two *linoleo-dilinolenin bromides*, m. p. 117—118° and 158° (hydrolytic products, tetra- and hexa-bromostearic acids), and *dilinoleo-olein bromide* (hydrolytic products, di- and tetra-bromostearic acids).

II. From soya-bean oil, there were obtained, dilinoleo-linolenin bromide, m. p. 78°, linoleo-dilinolenin bromide, m. p. 118°, dilinoleo-olein bromide, and *trilinolenin bromide,* m. p. 166° (hydrolytic product, hexabromostearic acid). H. BURTON.

Separation of glycerides. III. Train oil. B. SUZUKI and Y. MASUDA (Proc. Imp. Acad. Tokyo, 1927, **3**, 531—532; cf. preceding abstract).—Bromination of train oil affords *arachidono-clupanodono-olein bromide*, m. p. 95° (hydrolytic products, octabromoarachidic acid, m. p. 220° (decomp.), decabromobehenic acid, m. p. 161—162°, and dibromostearic acid), *diclupanodono-olein bromide*, m. p. 132° (hydrolytic products, decabromobehenic and dibromostearic acids), two isomeric *diarachidono-olein bromides*, m. p. 200° (decomp.) and 216° (decomp.) (hydrolytic products, octabromoarachidic and dibromostearic acids), and *dizoomaro-olein bromide.* Treatment of this last bromide with zinc dust and acetic acid, with subsequent oxidation by potassium permanganate, yields dihydroxypalmitic acid, m. p. 115°, and dihydroxystearic acid, m. p. 132—133°.

H. BURTON.

Chlorination of ββ′-dichlorodiethyl sulphide. I and II. W. E. LAWSON and T. P. DAWSON (J. Amer. Chem. Soc., 1927, **49**, 3119—3125, 3125—3129).—I. Treatment of ββ′-dichlorodiethyl sulphide with chlorine in carbon tetrachloride at −5° to 0° affords *ββ′-dichlorodiethylsulphonium chloride* as a white precipitate, which decomposes at the ordinary temperature with evolution of hydrogen chloride and formation of αββ′-trichlorodiethyl sulphide, this decomposition being apparently autocatalytic. In presence of water it yields ββ′-dichlorodiethyl sulphoxide. *αββ′-Trichlorodiethyl sulphide* has d_4^{20} 1·4038, $n_D^{22\cdot5}$ 1·5309, and decomposes on distillation, at ordinary or reduced pressure, with formation of β-*chloroethyl* β-*chlorovinyl sulphide* (I), b. p. 73·5—74·5°/4 mm., d_4^{20} 1·3280, $n_D^{22\cdot5}$ 1·5483, and β-*chloroethyl* α-*chlorovinyl sulphide* (II), b. p. 69·5—70·5°/4 mm., d_4^{20} 1·3193, $n_D^{22\cdot5}$ 1·550, the former predominating. *ββ′-Dichlorodiethylsulphonium bromide* decomposes when kept in air with formation of *ββ′-dichloro-α-bromodiethyl sulphide*, a yellow liquid, unstable at the ordinary temperature, which yields (I) when distilled. When treated with alcoholic sodium naphthionate, (I) and (II) yield, respectively, β-*naphthoxyethyl* β-*naphthoxyvinyl sulphide*, m. p. 129·5°, and α-*chlorovinyl* β-*naphthoxyethyl sulphide*, m. p. 56—57°. Of the above, only (I) and (II) are irritating and slightly vesicant.

II. Treatment of the crude mixture of (I) and (II) in carbon tetrachloride with 1 mol. of chlorine affords *αβββ′-tetrachlorodiethyl sulphide* (III), b. p. 118·5—119°/3 mm., and β-*chloroethyl* αβ-*dichlorovinyl sulphide*, (IV), b. p. 79·7—80·5°/4 mm., b. p. 108·5—109°/15 mm. The latter is also formed by treatment of ββ′-dichlorodiethyl sulphide with 2 mols. of chlorine in carbon tetrachloride, and is apparently identical with Mann and Pope's supposed αββ′-trichlorodiethyl sulphide (J.C.S., 1922, **121**, 594). When oxidised with dilute nitric acid, it yields β-chloroethylsulphonic acid. When heated under reflux at 150—160° for 14 hrs. (III) yields β-*chloroethyl* ββ-*dichlorovinyl sulphide*, b. p. 90—91°/3·5 mm. Treatment of (IV) with 1 mol. of chlorine in carbon tetrachloride yields *ααβββ′-pentachlorodiethyl sulphide*, liquid, which decomposes on distillation into hydrogen chloride and β-*chloroethyl* αββ-*trichlorovinyl sulphide*, b. p. 97—98°/4 mm., b. p. 123·5—124·5°/15 mm., apparently identical with Mann and Pope's supposed αβββ′-tetrachlorodiethyl sulphide (*loc. cit.*). Treatment of ββ′-dichlorodiethyl sulphide with excess of chlorine at the ordinary temperature affords hexachlorodiethyl sulphide, together with chlorinated hydrocarbons and the above β-chloroethyl αββ-trichlorovinyl sulphide. ααββ′-Tetrachlorodiethyl sulphide decomposes when distilled, with formation of β-chloroethyl αβ-dichlorovinyl sulphide. None of the above compounds is vesicant. F. G. WILLSON.

Oxidation of certain fatty acids. J. B. RHINE (Plant Physiol., 1926, **1**, 349—361).—When the mixed fatty acids from linseed oil are submitted to enzymic hydrolysis at 60—95° in an abundant supply of oxygen, there are formed unidentified volatile and non-volatile aldehydes and short-chain volatile acids fermentable by yeast. CHEMICAL ABSTRACTS.

Simple compounds containing asymmetric carbon. H. J. BACKER (Chem. Weekblad, 1924, **24**, 630—633).—A *résumé* of work carried out at Groningen during the past two years. Following the resolution of chlorosulphoacetic acid by crystallisation of alkaloidal salts in the cold, the same method has been applied to the chlorine and bromine substitution products of sulphopropionic acid, and higher sulphocarboxylic acids. The effect of salt formation on the rotation in this series has been systematically studied, as well as the effect of hydrogen-ion concentration on racemisation in this series and with the three sulphopyrotartaric acids. Resolution of sulphonyldipropionic acid and of arsenylpropionic and arsenylbutyric acids, $AsO_3H_2\cdot CHMe\cdot CO_2H$ and $AsO_3H_2\cdot CHEt\cdot CO_2H$, has also been effected by cold crystallisation. Chlorobromoacetic acid has been resolved in the same way, using the quinine and brucine salts, as well as bromoiodomethanesulphonic acid; a small rotation (1·5°), has also been obtained in aqueous solution with chlorobromomethanesulphonic acid, which had up to now defeated all efforts at resolution. S. I. LEVY.

Interaction of bromine with acetic anhydride. III. Arrest of the reaction. Comparison with bromination of acetone. H. B. WATSON (J.C.S., 1927, 3065—3068).—The inhibitory influence of quinoline on this reaction (A., 1927, 1168) is shown to be removed if 1·6 equivalents of sulphuric acid are concurrently added. The relatively feeble influence of aliphatic primary and secondary amines is ascribed to their inactivation on conversion into the acetyl derivatives and the powerful influence of acetyl nitrate to the oxidation of the hydrogen bromide necessary for the sequence of reactions. Quinoline similarly inhibits the bromination of acetone in carbon tetrachloride until neutralised by the hydrogen bromide liberated by direct substitution of the acetone. After this stage the reaction proceeds rapidly owing to the enolisation of the acetone under the influence of the hydrogen bromide.

G. A. C. GOUGH.

Steric series. VIII. Configuration of α-bromopropionic acid. K. FREUDENBERG and L. MARKERT

(Ber., 1927, 60, [*B*], 2447—2458; cf. A., 1926, 53).—On the assumption that analogous compounds of similar configuration undergo corresponding displacement of rotation when subjected to the same changes, an attempt has been made to elucidate the configuration of α-bromopropionic acid by comparison of the optical behaviour of its esters, chloride, and substituted amides with the similar compounds of *d*-methoxy-, acetoxy-, benzoyloxy-, and *p*-toluenesulphonyloxy-propionic acid. With all four derivatives of *d*-lactic acid a strong displacement in the dextro-direction accompanies the change from dimethylamide to ester. (The esters exhibit irregularities among themselves and the ethyl member is chosen on account of its mean position.) From dimethylamide to chloride dextro-displacement is observed in three instances, whereas the remaining case is doubtful. From chloride to ester dextro-displacement occurs in three instances, lævo-displacement in one. Only the dextrorotatory bromopropionic acid fits into this picture, showing dextro-displacement from dimethylamide to chloride and ester and from chloride to ester. Of the fifteen possible comparisons, thirteen are confirmatory, one is contradictory, and one doubtful. According to these and previous observations inversion occurs during the action of ammonia on bromopropionic acid and its esters, of phosphorus pentabromide on lactic acid and its esters, of potassium hydroxide on bromopropionic acid, and of nitrosyl bromide on alanine esters. Inversion is not observed during the action of nitrous acid on alanine, silver oxide on bromopropionic acid, and nitrosyl bromide on alanine. The following physical data, among others, are recorded: (−)-α-bromopropionic acid, b. p. 80—81°/2 mm., d^{20} 1·706, $[\alpha]_{578}^{20}$ −30·4°; (−)-α-bromopropionyl chloride, b. p. 47—49°/35—37 mm., d^{0} 1·756, $[\alpha]_{578}^{0}$ −28·7°; *methyl* (−)-*α-bromopropionate*, b. p. 61—63°/32 mm., d^{5} 1·522, $[\alpha]_{578}^{5}$ −59·3°; *ethyl* (−)-*α-bromopropionate*, b. p. 75—77°/38 mm., d^{24} 1·370, $[\alpha]_{578}^{24}$ −40·5°; *propyl* (−)-*α-bromopropionate*, b. p. 92—93°/38 mm., d^{0} 1·321, $[\alpha]_{578}^{5}$ −32·1°; (−)-*α-bromopropionamide*, m. p. 125—126°, $[\alpha]_{578}^{20}$ −24·2° in alcohol (c=10); (−)-*α-bromopropiondimethylamide*, b. p. 44—45°/2 mm., d^{0} 1·336, $[\alpha]_{578}^{0}$ +15·6°; (−)-*α-bromopropiondiethylamide*, b. p. 86—88°/2 mm., d^{20} 1·298, $[\alpha]_{578}^{20}$ +5·6°; *d*(+)-*methoxypropionic acid*, b. p. 113—115°/30—32 mm., d^{20} 1·095, $[\alpha]_{578}^{20}$ +74·2° (this and the succeeding values for the optical rotation are probably 4% low); *d*(+)-*α-methoxypropionyl chloride*, b. p. 38—39°/41 mm., d^{20} 1·118, $[\alpha]_{578}^{20}$ +91·8°; methyl *d*(+)-methoxypropionate, b. p. 36—40°/23 mm., d^{0} 1·030, $[\alpha]_{578}^{0}$ +96·5°; ethyl *d*(+)-methoxypropionate, b. p. 57—59°/28—30 mm.; *propyl* d(+)-*methoxypropionate*, b. p. 70—71°/25 mm., d^{0} 0·964, $[\alpha]_{578}^{0}$ +87·1°; d(+)-*methoxypropionamide*, m. p. 81°, d^{90} 1·027, $[\alpha]_{578}^{90}$ +38·2°; d(+)-*methoxypropiondimethylamide*, b. p. 90—91°/18—19 mm., d^{0} 1·015, $[\alpha]_{578}^{0}$ +67·9°; d(+)-*acetoxypropionyl chloride*, b. p. 51—53°/11 mm., d^{20} 1·177, $[\alpha]_{578}^{20}$ +51·6° (the optical values of this and the succeeding compounds are probably 10% low); methyl *d*(+)-acetoxypropionate, b. p. 63—65°/10 mm., d^{0} 1·112, $[\alpha]_{578}^{0}$ +50·5°; ethyl *d*(+)-acetoxypropionate, b. p. 73—74°/11—12 mm., d^{2} 1·076, $[\alpha]_{578}^{2}$ +46·7°; *propyl* d(+)-*acetoxypropionate*, b. p. 85—86°/13 mm., d^{0} 1·044, $[\alpha]_{578}^{0}$ +50·9°; d(+)-*acetoxypropionamide*, m. p. 67°, d^{17} 1·117, $[\alpha]_{578}^{17}$ +15·2°; r-*acetoxypropionamide*, m. p. 57°, b. p. 104—105°/2 mm.; r-*acetoxypropiondimethylamide*, m. p. 48°, b. p. 105°/3 mm.; d(+)-*acetoxypropiondimethylamide*, m. p. 57—58°, b. p. 76—78°/0·5 mm., d^{16} 1·083, $[\alpha]_{578}^{16}$ +17·7°; d(−)-*benzoyloxypropionyl chloride*, m. p. 24°, b. p. 135—137°/12 mm., d^{20} 1·213, $[\alpha]_{578}^{20}$ −62·7°; *methyl* d(−)-*benzoyloxypropionate*, d^{20} 1·143, $[\alpha]_{578}^{20}$ −17·0°; *propyl* d(−)-*benzoyloxypropionate*, b. p. 157—159°/11—12 mm.; d(−)-*benzoyloxypropiondimethylamide*, m. p. 128°, d^{135} 1·078, $[\alpha]_{578}^{135}$ −37·3°; r-*benzoyloxypropiondimethylamide*, m. p. 106°; d(−)-*benzoyloxypropiondiethylamide*, b. p. 157—160°/2 mm., d^{20} 1·087, $[\alpha]_{578}^{20}$ −37·6°; r-*benzoyloxypropiondiethylamide*, b. p. 157—160°/2 mm.; d(+)-*toluenesulphonyloxypropionyl chloride*, m. p. 42—43°, d^{35} 1·298, $[\alpha]_{578}^{35}$ +55·2° (this and the succeeding optical data are probably about 5% low); r-*toluenesulphonyloxypropionyl chloride*, m. p. 59°; d(+)-*toluenesulphonyloxypropionamide*, d^{118} 1·201, $[\alpha]_{578}^{118}$ +33·4°; d(+)-*toluenesulphonyloxypropiondimethylamide*, m. p. 80°, d^{30} 1·222, $[\alpha]_{578}^{30}$ +18·9°; r-*toluenesulphonyloxypropiondimethylamide*, m. p. 80°; d(+)-*toluenesulphonyloxypropiondiethylamide*, m. p. 62—63°, d^{40} 1·148, $[\alpha]_{578}^{40}$ +5·1°, and the corresponding r-*compound*, m. p. 62—63°. H. WREN.

Esters of α-linoleic acid tetrabromide from lumbang oil. (MISS) I. SANTOS and A. P. WEST (Philippine J. Sci., 1927, 34, 199—203).—The following esters of tetrabromo-α-linoleic acid have been prepared by the general method of interaction of the acid chloride with appropriate alcohols: *methyl*, m. p. 56—60°, *ethyl*, m. p. 58—60°, *propyl*, m. p. 45—50°, iso*propyl*, m. p. 50—52°, and *allyl*, m. p. 72—80°. Qualitative solubilities in the usual organic solvents are given. E. HOLMES.

Constitution of zoomaric acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1927, 30, 603—607).—Zoomaric acid, a hexadecenoic acid found in cod-liver oil, has also been isolated from humpback whale oil, sei-whale oil, California grey whale oil, and others (cf. B., 1926, 286). On oxidising methyl zoomarate with potassium permanganate in acetone solution, heptoic and azelaic acids were obtained. The ozonide peroxide of zoomaric acid yielded, on boiling with water, heptoic acid, heptaldehyde, and azelaic acid. Therefore the structure of zoomaric acid is $\mathrm{Me\cdot[CH_2]_5\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H}$, which is the same as that of palmitoleic acid isolated from a specimen of South Georgia whale oil by Armstrong and Hilditch (J.S.C.I., 1925, 44, 180T). K. KASHIMA.

Constitution of cetoleic acid. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1927, 30, 597—602).—Cetoleic acid, $C_{22}H_{42}O_2$ (isomeric with erucic acid), was first discovered by the author in humpback oil and also in sei-whale oil, cod-liver oil, herring oil, and others (cf. B., 1926, 286), and hence is of common occurrence in marine-animal oils. Although the occurrence of erucic acid in certain marine-animal oils has been frequently recorded, no erucic acid could be found in the above-mentioned marine-animal oils. The author suggests that the acid which occurs in marine-animal oils and has been considered as

erucic acid by the earlier authors is in reality cetoleic acid. On oxidising methyl cetoleate isolated from sei-whale oil with potassium permanganate in acetone solution, *n*-undecoic acid and nonane-αι-dicarboxylic acid were obtained. The ozonide peroxide of cetoleic acid yielded, on boiling with water, *n*-undecoic acid, *n*-undecaldehyde, nonane-αι-dicarboxylic acid, and possibly also the semi-aldehyde of nonane-αι-dicarboxylic acid. Therefore cetoleic acid has the constitution $Me\cdot[CH_2]_9\cdot CH\colon CH\cdot[CH_2]_9\cdot CO_2H$.
K. Kashima.

Rotatory dispersion of certain derivatives of hydroxy-acids. C. E. Wood (J.S.C.I., 1927, **46**, 424—427T).—The optical properties of several series of compounds are described with the object of emphasising the differing effects of the alkyl, *cyclo*hexyl, and phenyl groupings when directly attached to the asymmetric centre, the prevailing type of dispersion observed being complex in character. The dispersion curves of typical members of each of these series show how the positive rotations of the lactates change progressively through the *cyclo*hexahydromandelates to the strongly negative rotation of the mandates. The movement in rotation due to the increasing alkyl chain is in the same direction in the *l*-hexahydromandelates as in the *l*-lactates, which is indicative of the configuration relationship of the two acids; two of the higher esters of the former acid exhibit visual anomaly in the positive region. Certain simple cases of compounds containing two centres of optical asymmetry are quoted, and it is concluded that one of the factors in the condition for visual anomaly is that the partial rotations of the two asymmetric centres are of comparable magnitude.

Formation of the hydrazones of ethyl γ-chloroacetoacetate. G. Favrel (Bull. Soc. chim., 1927, [iv], **41**, 1601—1603).—Ethyl chloroacetate does not behave like monochloroacetone (this vol., 166) with diazonium hydroxides, benzenediazonium chloride in presence of sodium acetate affording about 15% of the phenylhydrazone of ethyl γ-chloroacetoacetate, m. p. 91—92°, and not the expected phenylhydrazone of ethyl chloro-oxalate (cf. Wislicenus, A., 1911, i, 107). It is suggested that the ethyl chloroacetate first condenses with itself to form ethyl γ-chloroacetoacetate.
R. Brightman.

Derivatives of ethyl acetoneoxalate. G. Favrel and J. Chrz (Bull. Soc. chim., 1927, [iv], **41**, 1603—1607).—Alkyl derivatives of ethyl acetylpyruvate cannot be obtained by the action of alkyl iodides or sulphates on ethyl sodioacetylpyruvate (cf. Kötz and Lemien, A., 1915, i, 247). Acyl derivatives are readily obtained by the action of acyl chlorides on ethyl sodio-acetylpyruvate in ether. Thus acetyl chloride affords the hydrated form of *ethyl diacetylpyruvate*, $CHAc_2\cdot C(OH)_2\cdot CO_2Et$, also obtained by the action of ethyl chloro-oxalate on sodioacetylacetone. Benzenediazonium hydroxide in aqueous acetic acid at 0° converts it into the phenylhydrazone of ethyl acetylpyruvate, m. p. 112—114° (A., 1926, 48). Ethyl acetylpyruvate and 1 mol. of sulphuryl chloride in benzene yield *ethyl β-chloroacetylpyruvate*, b. p. 115—118°/25 mm. (*cupric* derivative), which with benzenediazonium hydroxide in acetic acid at 0° affords the phenylhydrazone of pyruvyl chloride, m. p. 135—136°. With 2 mols. of sulphuryl chloride the reaction affords *ethyl βδ-dichloroacetylpyruvate*, b. p. 128—129°/25 mm. (*copper* derivative). These reactions distinguish ethyl acetylpyruvate from the β-diketones generally.
R. Brightman.

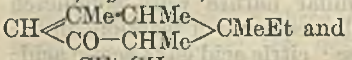
Mechanism of the formation of citric and oxalic acids from sugars by *Aspergillus niger*. II. T. K. Walker, V. Subramaniam, and F. Challenger (J.C.S., 1927, 3044—3054; cf. A., 1927, 228).—Fermentation of dextrose by *A. niger* in the presence of ammonium nitrate and potassium dihydrogen phosphate yielded saccharic acid and traces of citric acid, which may also be formed from the fermentation of calcium gluconate. Dipotassium saccharate yields similarly citric acid. The following fermentations of a similar nature were conducted in order to determine the sequence of reactions in the fermentation of dextrose: citric acid gave acetic acid; ammonium acetonedicarboxylate gave oxalic acid; malonic acid gave glyoxylic acid (isolated as the dixanthylhydrazone) and oxalic acid; calcium glycollate (or the ammonium salt) gave glyoxylic acid and oxalic acid.
G. A. C. Gough.

Optical resolution of *dl*-α-*iso*propylglutaric acid. J. Read and W. G. Reid (J.S.C.I., 1928, **47**, 11T).—*dl*-α-*iso*Propylglutaric acid, prepared by the oxidation of benzylidene-*dl*-piperitone (Earl and Read, A., 1926, 1040), has been resolved into optically active components by fractionally crystallising the acid brucine salt from absolute alcohol. The less soluble salt, *lBdA*, yielded the free *d*-acid with m. p. 88—89° and $[\alpha]^{15}_{D}$ +9·35° in absolute alcohol; the corresponding anhydride has m. p. 55—56° and $[\alpha]^{15}_{D}$ −10·0°, whilst the anilic acid has m. p. 155—156° and $[\alpha]^{15}_{D}$ +11·5°.

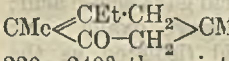
Synthesis of formaldehyde and acetone from oxides of carbon and hydrogen or water by contact substances. T. Sabalitschka and C. Harnisch (Biochem. Z., 1927, **190**, 265—277).—The production of formaldehyde and acetone by passing various gas mixtures (carbon dioxide and hydrogen; carbon dioxide, hydrogen, and water; carbon dioxide and water; carbon monoxide and hydrogen) through a tube at about 300° containing a large number of contact substances is investigated and the results are tabulated.
P. W. Clutterbuck.

Reactions of α-bromoaldehydes. A. Kirrmann (Compt. rend., 1927, **185**, 1482—1483; cf. A., 1927, 751).—Oxidation of α-bromoheptaldehyde with sulphuric acid and dichromate affords α-bromoheptoic acid, b. p. 147°/12 mm., d^{18} 1·319, n^{18} 1·471, *R* 44·28 (barium salt). α-Bromoheptaldehyde condenses normally with urethane to form a *compound*, m. p. 112°; it furnishes heptoic acid when boiled with an aqueous suspension of silver oxide and reacts with zinc methyl iodide to give methyl hexyl ketone, b. p. 73°/12 mm., m. p. −20°, d^{20} 0·818. *Heptoyl bromide* has b. p. 80°/12 mm., d^{19} 1·210, n^{19} 1·460. The unsubstituted fatty acid and the ketone are formed, probably through an intermediate keten (cf. Kötz and Rathert, A., 1922, i, 236).
H. Burton.

Catalytic condensation of methyl ethyl ketone. A. Petrov (Ber., 1927, 60, [*B*], 2548—2551; cf. A., 1926, 1130; 1927, 449).—At the ordinary temperature under the influence of condensing agents such as hydrogen chloride, sulphuric acid, and sodium ethoxide, methyl ethyl ketone yields products analogous to those derived from acetone, but the yield of triethylbenzene is remarkably small. At 380—400° in the presence of aluminium oxide and under a pressure of 80—100 atm., the total yield of hydrocarbons from methyl ethyl ketone is lower than from acetone and attains scarcely 8%; triethylbenzene is produced in very small quantity. Homomesitylene oxide and homo*iso*phorone are obtained. The action of sodamide on methyl ethyl ketone at 0° affords a mixture of the four possible homo*iso*phorones, $C_{12}H_{20}O$, b. p. 129—133°/15 mm., d_{25}^{25} 0·9315, n_D^{18} 1·4855, in which the isomerides



$CH<\begin{matrix}CMe\cdot CHMe\\CO-CHMe\end{matrix}>CMeEt$ and



$CMe<\begin{matrix}CEt\cdot CH_2\\CO-CH_2\end{matrix}>CMeEt$ appear to predominate. At 220—240° the mixture is hydrogenated under pressure in the presence of nickel oxide to the saturated ketone, $C_{12}H_{22}O$, b. p. 226—236°, d_{25}^{25} 0·9200, n_D^{18} 1·4790, whereas at 260—280° in the presence of the oxides of nickel and aluminium it gives a cyclic hydrocarbon, $C_{12}H_{24}$, b. p. 188—198°, d_{25}^{25} 0·8217, n_D^{18} 1·4558. H. Wren.

Relationship of the reduction of cupric oxide by dextrose to the concentration of copper sulphate used. Cupric oxide as a by-product in this reduction. S. Adler (Biochem. Z., 1927, 190, 433—443).—The amount and composition of the reduction product obtained in Bertrand's determination of sugar with varying concentrations of sugar and copper sulphate and times of heating are studied. When the time of heating and the concentration of sugar are constant, the amount of reduction product increases with increasing amount of copper sulphate to a maximum and then decreases. The smaller the excess of copper, the less is the result affected by lengthening the time of heating. If a large excess of copper sulphate is used or if the time of heating is increased, there is formed, besides cuprous oxide, the same hydrated brown cupric oxide as can be obtained by heating together copper sulphate, sodium potassium tartrate, and sodium hydroxide or copper sulphate and sodium hydroxide. Whereas the reduction product when heated for 3 min. is almost entirely cuprous oxide, after 50 min. it consists of about equal amounts of the two oxides. With a small excess of cupric sulphate, cuprous oxide is almost exclusively formed and with increasing concentration of copper sulphate the amount of cuprous oxide decreases and of cupric oxide increases.

P. W. Clutterbuck.

Oxide-ring structure of normal and γ-derivatives of mannose. Preparation and oxidation of γ- and δ-mannonolactones, with an addendum on the formulation of normal and γ-sugars as derivatives of pyran and furan and the suggestion of a new nomenclature. E. H. Goodyear and W. N. Haworth (J.C.S., 1927, 3136—3146).—Methylation of γ-mannonolactone with methyl iodide in the presence of methyl alcohol and silver oxide yields *tetramethyl γ-mannonolactone*, m. p. 108°, $[\alpha]_D^{15}$ +65·2° to 61·2° in water (period 9 days; *phenylhydrazide*, m. p. 167°). Treatment of γ-mannonolactone with acetone containing 0·1% of hydrogen chloride yields *γ-mannonolactone* iso*propylidene ether*, m. p. 133°, $[\alpha]_D^{20}$ +55·4 in water (*dimethyl* derivative, m. p. 110°), and *γ-mannonolactone di*iso*propylidene ether*, m. p. 126°, $[\alpha]_D^{20}$ +50·6 in chloroform, +73·65—45·9° in alcohol (50%; period 20 days). Hydrolysis of the dimethyl compound yields *dimethyl γ-mannonolactone*, m. p. 109—110° $[\alpha]_D^{20}$ +61·1° to 60·5° in water (period 19 days). *Tetra-acetyl-γ-mannonolactone*, m. p. 120°, prepared by treatment of the lactone with acetic anhydride and pyridine, has $[\alpha]_D$ +44·9° in chloroform. Oxidation of tetramethyl-γ-mannonolactone with nitric acid (*d* 1·42), followed by esterification of the product, yields methyl *i*-dimethoxysuccinate (identified by the methylamide). Tetramethyl-δ-mannonolactone yields similarly methyl *i*-dimethoxysuccinate and *d*-arabotrimethoxyglutarate. These results confirm the assignation of the butylene-oxide structure to γ-mannose and the amylene-oxide structure to normal mannose. The similar structural relations of other sugars already established allows the formulation of normal sugars and γ-sugars as pyran and furan derivatives respectively and it is suggested that a new method of naming the sugars, based on this, should be adopted. According to this method the normal sugars would be named pyranoses, *e.g.*, arabinose would become arabopyranose, and the labile sugars furanoses, *e.g.*, γ-fructose would become fructofuranose.

G. A. C. Gough.

Coefficients of diastatic inversion. E. Saillard (Compt. rend., 1927, 185, 1302—1303).—Coefficients of diastatic inversion for solutions of sucrose are given, as calculated from the formula $K=[100(A+B)+0{\cdot}5St]/S$ (cf. A., 1924, ii, 632). The coefficients are lower than those for inversion with hydrochloric acid and show a progressive diminution as the sugar content is lowered. In applying the method to the determination of sugars in beetroot or molasses, a quantity of potassium or sodium chloride equivalent to that in the sample must first be added to the pure sugar solutions. B. W. Anderson.

Constitution of the disaccharides. XVII. Maltose and melibiose. W. N. Haworth, J. V. Loach, and C. W. Long (J.C.S., 1927, 3146—3155).—Melibionic acid, prepared by the oxidation of melibiose with aqueous bromine, is converted by methylation with methyl sulphate into methyl octamethylmelibionate, b. p. 173—175°/0·06 mm., $[\alpha]_D^{13}$ +106·4°, n_D^{14} 1·4640. Hydrolysis of this ester with hydrochloric acid yields only two products: βγδζ-tetramethylgalactose, m. p. 71—72°, $[\alpha]_D^{21}$ +117·8° (equilibrium value), and tetramethylgluconic acid, distilling at 0·05 mm. (bath temperature 164°). The latter acid, on oxidation with nitric acid followed by esterification of the product, affords methyl tetramethylsaccharate, m. p. 77—78°, which may be converted into the diamide, m. p. 237—239°. Repetition of Karrer and Peyer's preparation (A., 1922, i, 809) gave a product, m. p. 76—77°, identical with the latter ester. These results (see also Charlton, Haworth, and Hickinbottom, A., 1927, 859) confirm the formulation of melibiose as a glucose-α-galactoside. The relation of this formula with the constitutions of the six commonly occurring disaccharides is discussed.

G. A. C. Gough.

Optical rotation and atomic dimension. VII. Halogeno-hepta-acetyl derivatives of gentiobiose. D. H. Brauns (J. Amer. Chem. Soc., 1927, 49, 3170—3177; cf. A., 1927, 93).—α-Fluorogentiobiose hepta-acetate has m. p. 168—169°, $[\alpha]_D^{20}$ +43·85° (cf. Brauns, A., 1923, i, 441; Helferich, Bäuerlein, and Wiegand, A., 1926, 386). *α-Chlorogentiobiose hepta-acetate*, m. p. 148°, $[\alpha]_D^{20}$ +80·52°, *α-bromogentiobiose hepta-acetate*, m. p. 144°, $[\alpha]_D^{20}$ +101·08°, and *α-iodogentiobiose hepta-acetate*, m. p. 134°, $[\alpha]_D^{20}$ +126·10°, are described, the preparations being given in detail. The specific rotations of the above derivatives show agreement with the regular relationship observed amongst the corresponding derivatives of the monose sugars only if, as in the previous case (*loc. cit.*), the value for the fluoro-derivative is excluded. By modified procedures, β-*chloro-* and β-*iodo-gentiobiose hepta-acetates* were obtained from β-gentiobiose octa-acetate, contaminated with the corresponding α-derivatives, from which it is concluded that the formation of these α-halogeno-derivatives from β-gentiobiose octa-acetate proceeds in at least two stages, the β-halogeno-derivatives being formed intermediately.

F. G. Willson.

Acetolysis of mannocellulose. Formation of the new sugars tetramannoholoside and pentamannoholoside. G. Bertrand and J. Labarre (Compt. rend., 1927, **185**, 1419—1422).—Mannocellulose from *Phytelephas macrocarpa* is acetylated by acetic anhydride and sulphuric acid, then hydrolysed by cold alcoholic potassium hydroxide, and the resulting potassium derivatives are treated with perchloric acid. Fractionation of the syrupy mixture of sugars from various strengths of alcohol yields *tetramannoholoside*, $C_{24}H_{42}O_{21}$, m. p. 278—280°, $[\alpha]_D$ −25° 20′ to +20°, without mutarotation, in 5% aqueous solution (p-*bromophenylosazone*), and *pentamannoholoside*, $C_{30}H_{52}O_{26}$, m. p. 298—300°, $[\alpha]_D$ −31° 40′ to +20°, without mutarotation, in 5% aqueous solution (p-*bromophenylosazone*). The reducing power of these sugars is about one fifth that of mannose. They are hydrolysed by 1% hydrochloric acid at 100°.

H. Burton.

Oxycelluloses. IV. A. M. Nastukoff [with O. P. Goloff and A. J. Collie] (Ber., 1927, **60**, [*B*], 2591—2594).—Oxycellulose, prepared from filter paper by means of bleaching powder, is converted by phenylhydrazine in 10—12% alcoholic solution into the phenylhydrazone; the latter is oxidised, and the product again treated with phenylhydrazine, and the process is repeated until the nitrogen content of the phenylhydrazone is constant at 2·88%. *Oxycellulose*, regenerated from the phenylhydrazone by hydrochloric acid, has the composition $C_6H_{10}O_5,2C_6H_{10}O_6$ or $2C_6H_{10}O_5,4C_6H_{10}O_6$ if the proportion of nitrogen in the phenylhydrazone is taken into account. When freshly prepared it is completely soluble in water, aqueous ammonia, and dilute alkali hydroxides, but the solubility gradually diminishes. It reduces Fehling's solution.

H. Wren.

Complex salts of nickel with aliphatic diamines. F. G. Mann (J.C.S., 1927, 2904—2918).—β-Aminotriethylamine (*A*), prepared by the interaction of phthal-β-bromoethylimide and diethylamine in xylene at 100° followed by hydrolysis with hydrochloric acid, is converted by treatment with nickel succinimide followed by potassium thiocyanate into *bis*-β-*aminotriethylaminenickelous thiocyanate*, m. p. 213—214° (decomp.) [*chloroplatinate* darkens at 165—168° and shrinks at 179—181°]. Attempts to obtain the *d*-camphor-β-sulphonate resulted in the formation of non-ionic *bis*-d-*camphorsulphonatebisaminotriethylaminenickel*, m. p. 175—176°; the corresponding d-α-*bromo*-π-*camphorsulphonate*, m. p. 165—168°, is formed similarly together with some β-*aminotriethylammonium hydroxide* d-α-*bromocamphorsulphonate*, m. p. 80—82°. *Bis*-d-*camphornitronateaminotriethylaminenickel* has m. p. 258—260° (decomp.), $[\alpha]_{5461}$ +275° in chloroform. β-Bromo-αγ-diaminopropane, prepared by hydrolysis of αγ-*diphthalimido*-iso*propyl bromide*, m. p. 196—198°, in turn prepared by heating diphthalimido*iso*propyl alcohol with acetic acid and hydrogen bromide at 100°, gives *bis*-β-*bromo*-αγ-*diaminopropanenickelous thiocyanate*, m. p. 247—248°. αγ-Diamino*iso*propyl alcohol (*B*) gives with roseocobaltic chloride *dihydroxybis*-αγ-*diamino*-β-*hydroxydihydrochloride propane cobaltic monochloride* (corresponding *monothiocyanate*, dark red, decomp. 240—250° after shrinking at about 230°; corresponding *monoiodide*), and with hydrated nickel chloride *bis*-αγ-*diamino*-β-*hydroxypropanenickelous thiocyanate*, m. p. 161—163° [corresponding *di-iodide*, m. p. 239—242° (decomp.); d-*camphor*-β-*sulphonate*, $[\alpha]_{4062}$ +51·5° in water, unresolved by crystallisation]. The latter thiocyanate yields *bis*-d-*camphornitronate*-αγ-*diamino*-β-*hydroxypropanenickel*, blackening at 210°, $[\alpha]_{6161}$ +266° in chloroform. β-*Methyltrimethylenediamine dihydrochloride* (*C*), m. p. 195—197° [*dihydrobromide*, m. p. 227—229° (decomp.); *dibenzoyl* derivative, m. p. 92—93° (decomp.; solidifying and remelting at 136—138°)], is prepared by hydrolysis of αγ-*diphthalimido*-β-*methylpropane*, m. p. 169—171°, which in turn is prepared from potassium phthalimide and αγ-dibromo-β-methylpropane. This amine yields *bis*-β-*methyltrimethylenediaminenickelous thiocyanate*, m. p. 226—228° (decomp.), converted by silver *d*-camphorsulphonate into *bis*-β-*methyltrimethylenediaminenickelous* d-*camphor*-β-*sulphonate*, $[\alpha]_{4062}$ +48·0°, or its *monohydrate*, $[\alpha]_{1062}$ +51·2°, which yields an optically inactive thiocyanate. The *d*-camphorsulphonate combines with ammonium nitrocamphor to afford *bis*-d-*camphornitronate*-β-*methyltrimethylenediaminenickel*, m. p. 293—295° (decomp.), $[\alpha]_{5161}$ +322° in chloroform (constant). β-Methyltrimethylenediamine also yields *dichloro*-β-*methyltrimethylenediamineplatinum*, m. p. 273—276° (decomp.), and *bis*-β-*methyltrimethylenediamineplatinous chloride*, m. p. 266—267° after darkening at 240°, which gives no indication of existing in *cis*- and *trans*-forms. The above co-ordination compounds have been examined in order to determine whether they exhibit *cis–trans* or optical isomerism. No indication of *cis–trans* isomeric forms could be detected and, owing to experimental difficulties, attempts to resolve the compounds with amines *A*, *B*, and *C* failed. *Cis–trans* isomerism should exist if the four co-ordination valencies of nickel are directed to the corners of a square, whilst if they are directed towards the apices of a tetrahedron optical isomerism should exist. G. A. C. GOUGH.

Reversibility of the oxidative decomposition of amino-acids and its physiological significance. F. KNOOP (XII Int. Cong. Physiol., 1926, 90; Chem. Zentr., 1927, i, 2444).—α-Ketonic acids and ammonia, in presence of molecular hydrogen and palladium, yield 70% of the theoretical quantity of amino-acids. Ferrous salts and cysteine effect the reduction in the absence of free hydrogen and catalysts. A. A. ELDRIDGE.

Chemical constitution and rotatory power. II. Acyl derivatives of *l*-asparagine. S. BERLINGOZZI (Gazzetta, 1927, **57**, 814—819).—Some acyl derivatives of *l*-asparagine have been prepared by the Schotten–Baumann reaction and the rotatory powers of aqueous solutions of their potassium salts have been determined. The m. p. of the acyl-*l*-asparagine, $[\alpha]_D^{20}$ and $[M]_D^{20}$ for the potassium salts are respectively: *anisoyl-*, 190—191°, +15·11°, +40·2°; *benzoyl-*, 189°, +15·35°, +36·2°; m-*nitrobenzoyl-*, 176°, +12·55°, +35·3°; p-*nitrobenzoyl-*, 178°, +10·96°, +30·8°; p-*toluenesulphonyl-*, 175°, +6·83°, +19·5°; chloroacetyl-, 148—149°, +4·71°, +9·8°. The decreasing molecular rotatory power corresponds, except in the case of the chloroacetyl derivative, with increasing dissociation constant of the acid derived from the substituent group (cf. Betti and Bonino, Atti II Congr. Naz. Chim., Palermo, 1926). E. W. WIGNALL.

Condensation of ethyl acetoacetate with sodiomalononitrile. Explanation of similar reactions. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, **2**, 305—307).—The fact that ethyl sodiocyanoacetate will not condense with ethyl cyanoacetoacetate, as it condenses with ethyl acetoacetate (J.C.S., 1905, **87**, 1685; 1922, **121**, 2216), is explained by the greater affinity of the latter for sodium, which causes an interchange of the metal from one ester to the other. In extension of previous work (this vol., 49), it is found that sodiomalononitrile reacts with ethyl acetoacetate in alcoholic solution to yield a crystalline *sodio*-derivative which, when treated with acids, in turn affords ethyl γγ-dicyano-β-methyl-Δ^{β}-butenoate (an oil), which shows no tendency to combine with water to form the diamide.

G. A. C. GOUGH.

Properties of simple amides. A. PARTS (Ber., 1927, **60**, [*B*], 2520—2522).—Contrary to the observations of Rakshit (J.C.S., 1913, **103**, 1557), the main products of the action of sodium on propionamide and butyramide dissolved in benzene are the sodium amides $\mathrm{R{\cdot}CO{\cdot}NHNa}$. The amount of ammonia evolved increases in the sequence butyramide, propionamide, acetamide, but the production of sodium diacetamide is by no means quantitative. Hence there is no sharp distinction between the actions of sodium and potassium. Further evidence in favour of the view that sodium and propionamide yield sodium propionamide is found in the formation of dipropionamide from the latter and propionyl chloride. The formation of triacylamides from acyl chlorides and homogeneous sodium diacylamides is established by the smooth production of tribenzamide from benzoyl chloride and sodium dibenzamide. H. WREN.

Acyl*iso*carbamides. S. BASTERFIELD and M. S. WHELEN (J. Amer. Chem. Soc., 1927, **49**, 3177—3180).—The following acyl *iso*carbamides, $\mathrm{NHR{\cdot}C(OR'){:}NH}$, were obtained by treating the appropriate alkyl*iso*carbamide hydrochlorides in ethereal suspension with acyl halides: *phenylacetyl-*, m. p. 207° (decomp.); *chloroacetyl-*, m. p. 183°; *carbo*-n-*propoxy-*, m. p. 36—37°; *carbo*-n-*butoxy-*, m. p. 32°, and *carbo*iso*amyloxy-methyl*iso*carbamide*, m. p. 93°; *phenylacetyl-*, b. p. 160°/20 mm.; p-*nitrobenzoyl-*, m. p. 125°; *bromopropionyl-*, liquid (*polymeride*, m. p. 141°); *chloroacetyl-*, liquid (*hydrochloride*, m. p. 140°); *carbo*-n-*propoxy-*, liquid; *carbo*iso*amyloxy-*, m. p. −10°, and *benzenesulphonylethyl*iso*carbamide*, m. p. 86° when freshly prepared, changing to 101° on keeping. n-*Propyl*iso*carbamide*, liquid (*hydrochloride* of *benzoyl* derivative, m. p. 97°), was obtained through the *hydrochloride* by treatment of cyanamide in *n*-propyl alcohol with hydrogen chloride. n-*Butyl*iso*carbamide hydrochloride* was obtained similarly in an impure condition, and converted into the p-*nitrobenzoyl* derivative, m. p. 118°.

F. G. WILLSON.

Transformation of phenylated azodicarboxylamides into benzotriazines. F. ARNDT and B. EISTERT (Ber., 1927, **60**, [*B*], 2598—2602).—The constitutions $\mathrm{NHPh{\cdot}CS{\cdot}N(NH_2){\cdot}CO{\cdot}NH_2}$ and $\mathrm{NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2}$ have been assigned to the product obtained from phenylthiocarbimide and semicarbazide by Rosenthaler (A., 1927, 451) and Arndt (A., 1922, i, 375), respectively. In favour of the latter formulation it is pointed out that the compound is stable to short treatment with alkali hydroxide and is converted by methyl sulphate in such solution into the non-crystalline *S*-methyl ether, which is oxidised by excess of potassium ferricyanide to the red *azo* compound, $\mathrm{NPh{:}C(SMe){\cdot}N{:}N{\cdot}CO{\cdot}NH_2}$, decomp. 112—113°. The latter substance in boiling ethyl acetate is isomerised to the colourless 3-*methylthiol*-1 : 2-*dihydro*-1 : 2 : 4-*benzotriazine*-1-*carboxylamide*, m. p. 208—210° after softening and darkening, the constitution of which follows from its oxidation to 3-methylthiol-1 : 2 : 4-benzotriazine (cf. Arndt and Rosenau, A., 1918, i, 40). The azo-compound decomposes at 110—115° into phenylthiourazole methyl ether, m. p. 207—208°. The azo-compound $\mathrm{NPh{:}C(NH_2){\cdot}N{:}N{\cdot}C({:}NH){\cdot}SMe}$, decomp. 110° (cf. Arndt and Tschenscher, A., 1923, i, 1139), in boiling solvents, however, passes only into the hydrazo-compound and 4-phenylguanazole derived therefrom when heated in suitable solvents; when heated by itself it affords 3-amino-1 : 2 : 4-benzotriazine. H. WREN.

Ureides of bromovaleric acids. Influence of the migration of the halogen on their physicochemical and pharmacodynamic properties. E. FOURNEAU and G. FLORENCE (Bull. Soc. chim., 1927, [iv], **41**, 1518—1535).—In continuation of earlier work on the ureide of α-bromo*iso*valeric acid (bromural) and the ureide of α-bromo-α-ethylbutyric acid (adaline) the effect of displacement of the bromine atom in the chain and of accumulation of bromine atoms has been examined in relation to the physicochemical and narcotic properties. The results confirm the relation already observed by Overton between the partition coefficient in oil and water and the hypnotic properties. Tiffeneau's assertion that the parallel holds only within the same series is also supported by the present work. Bromural, containing varying proportions of the ureides of *iso*valeric and α-methylbutyric acids, is a stronger hypnotic than the pure ureide of α-bromo*iso*valeric acid prepared from synthetic *iso*valeric acid. Migration of bromine from the α- to the β-position decreases the hypnotic effect almost to zero, the solubility in water and the partition coefficient decreasing simultaneously. Accumulation of bromine atoms in the molecule exerts a similar influence. The hypnotic effect is thus attributed to the acid chain and not to the bromine atom, the latter decreasing the effect by decreasing the solubility of the ureide. The following data are recorded for the ureides, the percentage figures indicating the solubility in water, plain figures the partition coefficients for olive oil and water: bromural: m. p. 152°, 3·209%, 1·29; ureide of synthetic α-bromo*iso*valeric acid, m. p. 160°, 1·94%, 0·96; β-*bromo*isovaleric *ureide*, m. p. 195°, 1·86%, 0·19; αβ-*dibromo*isovaleric *ureide*, m. p. 172·5° (decomp.), 2·30%, 0·22. *iso*Valeric acid, b. p. 175°, was synthesised from magnesium *iso*butyl chloride in 82% yield. β-Bromo*iso*valeric acid and αβ-dibromo*iso*valeric acid were prepared from dimethylacrylic acid obtained by oxidation of mesityl oxide (Barbier and Léser, A., 1905, i, 628).

R. BRIGHTMAN.

Action of copper nitrite on thiocarbamide. A. CONTARDI and A. DANSI (Gazzetta, 1927, **57**, 802—813).—When copper nitrite is treated with thiocarbamide in aqueous solution, a green, gelatinous *product*, $CH_4O_4N_4SCu$, is obtained, which evolves nitric oxide to give a yellowish-white *substance* (I) regarded as $[Cu(CH_4N_2S)(NO_2)_2][Cu(CH_4N_2S)H_2O]$. In presence of carbon dioxide, the action of hydrochloric acid converts this into the additive product of thiocarbamide and cuprous chloride (cf. Rathke, A., 1884, 1017), whilst that of boiling water gives copper sulphide, nitric oxide, and cyanamide. If the initial reaction product is allowed to remain in the mother-liquor it is converted into copper thiocyanate and basic copper nitrate. The compound (I) is also obtained by treating the compound $[Cu(CH_4N_2S)_3]Cl$ with sodium nitrite solution, or the compound $[Cu(CH_4N_2S)Cl_2][Cu(CH_4N_2S)H_2O]$ with thiocarbamide followed by sodium nitrite. Excess of thiocarbamide in the latter reaction, or in reaction with (I), yields the *compound* $[Cu(CH_4N_2S)_2H_2O]NO_2$, converted by washing with water into (I) and the soluble $[Cu(CH_4N_2S)_3]NO_2$.

Aniline and copper nitrite in aqueous solution yield a *compound*, $C_{12}H_{10}O_2N_4Cu$. E. W. WIGNALL.

Carbolthionic acids and esters. IV. Thioamides and thiohydrazides. Y. SAKURADA (Bull. Chem. Soc. Japan, 1927, **2**, 307—310; cf. A., 1926, 950).—The following thioamides are prepared by treatment of the requisite thionester (the eliminated alcohol radical of which is given in parentheses) with ethereal solutions of amines: *thioacetoethylamide*, $CH_3{\cdot}CS{\cdot}NHEt$ (oily; propyl), *thiopropioethylamide* (oily; propyl), *thiobenzethylamide* (oily; butyl), *thiophenylacetoethylamide* (oily; *iso*amyl), *thio*-p-*toluethylamide* (oily; propyl), *thioaceto*iso*butylamide* (oily; *iso*amyl), *thiopropio*iso*butylamide* (oily; butyl), *thiobenz*iso*butylamide* (crystalline; methyl), *thiophenylaceto*iso*butylamide* (oily; *iso*butyl), *thio*-p-*tolu*iso*butylamide* (oily; butyl), *thioaceto*iso*amylamide* (oily; *iso*butyl), *thiopropio*iso*amylamide* (oily, *iso*amyl), *thiobenz*iso*amylamide* (crystalline; *iso*amyl), *thiophenylaceto*iso*amylamide* (oily; ethyl), *thio*-p-*tolu*iso*amylamide* (crystalline; methyl). Similarly phenylhydrazine affords the following crystalline *s*-thiophenylhydrazides: *thioacetophenylhydrazide*, *thiopropiophenylhydrazide*, *thiobenzphenylhydrazide*, *thiophenylacetophenylhydrazide*, *thio*-p-*toluphenylhydrazide*.

G. A. C. GOUGH.

Complex cyanides. G. A. BARBIERI and E. PARISI (Ber., 1927, **60**, [*B*], 2418—2421).—Solutions of potassium silver cyanide which, according to electromotive measurements of Bodländer and Eberlein (A., 1904, ii, 401), contain the compound $K_2Ag(CN)_3$, do not give additive compounds with hexamethylenetetramine; if, however, potassium is replaced by sodium, calcium, or magnesium, the *compounds* $Na_2Ag(CN)_3,C_6H_{12}N_4,2H_2O$, $MgAg(CN)_3,2C_6H_{12}N_4,9H_2O$, and $CaAg(CN)_3,C_6H_{12}N_4,3H_2O$ are readily isolated. From suitable solutions of copper cyanide the analogous *compounds* $Na_2Cu(CN)_3,C_6H_{12}N_4,2H_2O$ and $MgCu(CN)_3,2C_6H_{12}N_4,9H_2O$ are similarly derived. If a large excess of hexamethylenetetramine is added to a concentrated solution of vanadyl sulphate and sodium cyanide, the *substance* $Na_3VO(CN)_5,2C_6H_{12}N_4,5H_2O$ crystallises in blue octahedra. H. WREN.

Complex cyanides of molybdenum. W. R. BUCKNALL and W. WARDLAW (J.C.S., 1927, 2981—2992).—Improved methods for the preparation of tetrapotassium, tetrasilver, tetrathallous, and dicupric molybdenum octacyanide (cf. Rosenheim, A., 1907, i, 688; 1910, i, 101) are given. Treatment of the last-named salt with ammonia (*d* 0·88) yields *hexamminodicupric molybdenum octacyanide*, $Cu[(NH_3)_3]_2Mo(CN)_8$ (dark green), which is converted into the original compound on treatment with acids. By the use of ethylenediamine hydrate *tetramethylenediaminocupric molybdenum octacyanide*, $[Cu\,(en)_2]_2Mo(CN)_8$ (deep blue), is prepared. Conductivity measurements indicate that it exists as 3 ions (maximum) in very dilute solutions, whilst in more concentrated solutions the values are even less than those required for a binary electrolyte. *Trisilver molybdenum octacyanide* (cf. Olsson, A., 1914, i, i, 504), prepared by the addition of silver nitrate to a dilute solution of the tetrapotassium salt which had been oxidised with potassium permanganate until a faint pink colour persisted, yields *tripotassium molybdenum octacyanide*, $K_3Mo(CN)_8$, when triturated with potassium chloride in the dark, or *trihydrogen molybdenum octacyanide* ($+3H_2O$) when triturated with hydrochloric acid. The constitution of the new acid, which is very deliquescent, is demonstrated by conversion into the silver salt which may be quantitatively decomposed by hydrochloric acid. The "anomalous" oxidation of molybdenum (Ephraim, "Inorganic Chemistry," English transl., 1926, 280) from the quadri- to the quinque-valent state is explained by the tendency to revert to a compound in which molybdenum exerts its maximum effective atomic number 54.

Electrolysis of a 10% solution of molybdenum trioxide in 3*N*-hydrochloric acid in a diaphragm cell followed by concentration and addition of potassium iodide yields a red *cyanide*, $K_4[Mo(OH)_4(CN)_4],H_2O$, the dilute aqueous solutions of which are alkaline and contain more than 5 ions even at 1° [apparent mol. wt. in water (cryoscopic, $c=1{\cdot}517$) 97·9]. A co-ordination number of 8 is indicated since 2 mols. of the associated water are retained at 100° or in a vacuum in the presence of sulphuric acid. Repeated treatment of an aqueous solution of this substance with alcohol yields a blue *cyanide*, $K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O$, which again gives alkaline reaction to phenolphthalein in dilute solutions and is shown by conductivity and mol.-wt. determinations to contain more than 4 ions. By treatment of tetrapotassium molybdenum octacyanide with nitric acid varying amounts of molybdic acid are obtained together with a brick-red, insoluble *molybdenum cyanide*, $H[MoO_2(CN)_2,2H_2O]$, which is shown to contain quinquevalent molybdenum by quantitative oxidation. It is readily soluble in ammonia or alkalis. G. A. C. Gough.

Colour reactions of nitroprusside. N. Tarugi (Annali Chim. Appl., 1927, 17, 519—524).—Cambi's criticisms (A., 1927, 346) of the author's work (A., 1927, 46) are answered. T. H. Pope.

Reaction of molybdic acid with ferrocyanides. G. A. Barbieri (Ber., 1927, 60, [*B*], 2415—2418).—If an excess of ammonium or potassium ferrocyanide followed by a large excess of an ammonium salt is added to the solution of a molybdate acidified with acetic acid, a lemon-yellow *precipitate*, $(NH_4)_4Fe(CN)_6.2MoO_3.3H_2O$, is obtained which is so sparingly soluble in concentrated solutions of ammonium salts that the separation of molybdic acid is almost quantitative. The compound is also obtained by dissolving phosphomolybdic acid or its salts in ammonia, addition of potassium ferrocyanide and much ammonium acetate, and acidification with acetic acid. In neutral or alkaline solution the precipitation from polymolybdates is incomplete, but can be made quantitative by addition of a slight excess of an acid. Treatment of the yellow compound with weak acids or with water causes it to become red, whereas strong acids transform it into tile-red powder probably owing to hydrolysis, $(NH_4)_4Fe(CN)_6,2MoO_3+4HX \rightleftharpoons 4NH_4X+(MoO_2)_2Fe(CN)_6+2H_2O$. The reddish-brown, gelatinous precipitates obtained by the interaction of molybdates and potassium ferrocyanide in the presence of hydrochloric or sulphuric acid are converted by concentrated ammonium acetate into a crystalline *powder* (?), $(NH_4)_4Fe(CN)_6,2MoO_3,2H_2O$, thus indicating that they are probably formed exclusively from molybdenyl ferrocyanide, $(MoO)_2Fe(CN)_6$. Attempts to obtain similar compounds of potassium, sodium, rubidium, or cæsium were unsuccessful. H. Wren.

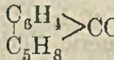
Catalysts and activated magnesium in the preparation of Grignard reagents. H. Gilman and J. M. Peterson (Proc. Iowa Acad. Sci., 1926, 33, 173—174).—When a magnesium–copper (12·75%) alloy is heated for 1 hr. in an evacuated tube at 200° with about half its weight of iodine, the activated alloy is superior to that of Baeyer.
Chemical Abstracts.

Qualitative colorimetric reaction for the Grignard reagent. H. Gilman and F. Schulze (Bull. Soc. chim., 1927, [iv], 41, 1479—1481).—Magnesium *tert.*-butyl chloride, bromide, and iodide, magnesium *tert.*-amyl chloride, and magnesium *tert.*-hexyl chloride give positive results in the colorimetric test for Grignard reagents previously described (A., 1925, ii, 1011), provided 5 min. are allowed for the reaction between the Grignard reagent and Michler's ketone. If the hydrolysis is effected immediately, on account of the lower reactivity of Grignard reagents containing butyl or higher alkyl groups, the coloration may be only faint or negligible, especially if the solutions are not concentrated. R. Brightman.

Apparatus for determining the quantity of gas evolved and the amount of reagent consumed in reactions with magnesium methyl iodide. E. P. Kohler, J. F. Stone, and R. C. Fuson (J. Amer. Chem. Soc., 1927, 49, 3181—3188).—The apparatus consists essentially of a reservoir for standard Grignard solution, connected through a graduated measuring vessel to a reaction flask of 40 c.c. capacity, the latter being connected in turn through a phosphorus pentoxide tube with a jacketed gas burette. Arrangements are provided for displacing the air in the entire apparatus with nitrogen, for filling the reservoir with filtered Grignard solution without access of air, and for the addition of measured quantities of water to the reaction flask. The Grignard reagent is prepared by adding methyl iodide (40 g.) to a stirred suspension of magnesium (8 g.) in *iso*amyl ether (100 g.) at 0—20°, diluting the resulting solution with *iso*amyl ether (175 g.), and heating the whole at 100° for 1½ hrs., all in an atmosphere of nitrogen. The solution is then filtered into the reservoir, and standarised by measuring the gas evolved when a measured volume of the solution is treated with water in the reaction flask. A sample (about 0·2 g.) of the substance to be studied is then placed in the reaction flask, the apparatus swept out with nitrogen, and a measured volume of the Grignard solution, considerably in excess of that required, added from the reservoir. The mixture is then heated until reaction ceases, and the volume of gas evolved is measured. The amount of Grignard reagent remaining unattacked is then determined by adding water to the reaction flask and measuring the volume of gas generated. Results are accurate to within about 3%, and examples of measurements with 14 substances are listed, including cases where ketonic and enolic modifications compete for the Grignard reagent (cf. Grignard and Savard, A., 1927, 567). If necessary, the substance under examination may be dissolved in xylene before the Grignard solution is added. F. G. Willson.

Cadet's oil. II. Oxidation of cacodyl oxide. A. Valeur and P. Gailliot (Bull. Soc. chim., 1927, [iv], **41**, 1481—1491).—Cacodyl oxide, b. p. 149—151°, d^{15} 1·486, when obtained by the action of sodium carbonate on cacodyl chloride, does not fume in air, and can be distilled without decomposition. When oxidised under water at 15—25° in a current of oxygen, 44·7% of the oxide is converted into cacodylic acid, the remainder being converted by intramolecular change mainly into trimethylarsine, monomethylarsine oxide, and arsenious acid, with a little trimethylarsine oxide and methylarsinic acid. These transformations are regarded as catalytic reactions consecutive on the oxidation, the catalyst being probably a peroxide. R. Brightman.

Friedel–Crafts' reaction with non-aromatically combined hydrogen. J. von Braun and M. Kühn (Ber., 1927, **60**, [*B*], 2557—2566).—Phenyl*cyclo*pentene is only partly and with difficulty reduced by hydrogen in the presence of palladium. It is slowly converted by hydrogen bromide in glacial acetic acid at 100° into 2-*bromophenyl*cyclo*pentane*, b. p. 138—140°/13 mm. The latter substance reacts vigorously with magnesium and the product after treatment with carbon dioxide affords phenyl*cyclo*pentane (see later), *di(phenyl*cyclo*pentyl)*, and 2-*phenyl*cyclo*pentanecarboxylic acid*, b. p. 190—192°/13 mm. The homogeneity of the acid and consequently of the parent bromide is established by its smooth conversion through 2-*phenyl*cyclo*pentanecarboxyl chloride*, b. p. 150—153°/12 mm., into 2-*phenyl*cyclo*pentanecarboxyanilide*, m. p. 93—95°. The chloride is converted by aluminium chloride in carbon disulphide into the *ketone*, $\begin{matrix}C_6H_4\\ |\\ C_5H_8\end{matrix}\!\!>CO$, b. p. 135—140°/14 mm. (*semicarbazone*, m. p. 170°). Phenyl*cyclo*pentane, as prepared above, is homogeneous, but the yields are poor and the compound is more readily prepared by reduction of 2-bromophenyl*cyclo*pentane by zinc dust and boiling glacial acetic acid. It has b. p. 215°, d_4^{23} 0·9553, n_D^{23} 1·5330, thus agreeing with the data of Borsche and Menz (A., 1908, i, 147); phenyl*cyclo*propane derived from ε-phenyl-*n*-amyl chloride and aluminium chloride has d_4^{20} 0·9385, n_D^{20} 1·5157, in agreement with previous data (von Braun and Deutsch, A., 1912, i, 433). The latter product appears to consist essentially of phenyl*cyclo*pentane, which itself is appreciably modified by aluminium chloride. The *ketones*, b. p. 190—200°/1 mm. and 200—210°/1 mm., obtained from phenyl*cyclo*pentane and benzoyl or anisoyl chloride are ill adapted for its identification; p(?)-cyclo*pentylacetophenone* readily yields a *semicarbazone*, m. p. 212—215° (obtained also from the product from ε-phenyl-*n*-amyl chloride). ε-Phenyl-Δ^{α}-amylene, d_4^{19} 0·8796, n_D^{19} 1·5040, is largely polymerised by aluminium chloride in light petroleum and does not afford phenyl*cyclo*pentane; the Friedel–Crafts reaction cannot therefore be due to loss of hydrogen chloride in the side-chain from ε-phenyl-*n*-amyl chloride followed by isomerisation of the hydrocarbon thus produced.



ε-Phenyl-β-methylamyl alcohol is converted with difficulty by the successive action of fuming hydrochloric acid at 125° and phosphorus pentachloride into ε-*phenyl*-β-*methylamyl chloride*, b. p. 128—130°/12 mm., which is transformed by aluminium chloride in the presence of light petroleum into 3-*phenyl*-1-*methyl*cyclo*pentane*, b. p. 93—94°/12 mm., d_4^{17} 0·9173, n_D^{17} 1·5136, oxidised by permanganate to benzoic acid. *N*-ε-Chloroamylbenzamide, toluene, and aluminium chloride afford ε-p-*tolylamylbenzamide*, b. p. 265—270°/10 mm., hydrolysed to benzoic acid and ε-p-*tolylamylamine*, b. p. 143°/11 mm. The benzoyl compound is converted by phosphorus pentachloride into the corresponding imidochloride, which decomposes when slowly distilled into benzonitrile and ε-p-*tolyl*-n-*amyl chloride*, b. p. 136—138°/11 mm., from which ε-p-*tolyl*-n-*amyl acetate*, b. p. 154—156°/11 mm., and ε-p-*tolyl*-n-*amyl alcohol*, b. p. 158—159°/11 mm., are successively obtained. With aluminium chloride ε-*p*-tolyl-*n*-amyl chloride yields a mixture of *p*-tolyl*cyclo*pentane and (predominatingly) methylbenzosuberane, oxidised by permanganate to a mixture of terephthalic and trimellitic acids. ε-p-*Xylyl*-n-*amylbenzamide*, b. p. 235—238°/1 mm., is hydrolysed to ε-p-*xylyl*-n-*amylamine*, b. p. 146—148°/12 mm. (*picrate*, m. p. 155°; non-crystalline *hydrochloride* and quaternary *methiodide*). ε-p-*Xylyl*-n-*amyl chloride*, b. p. 143—145°/12 mm., from which ε-p-*xylyl*-n-*amyl acetate*, b. p. 162—164°/12 mm., and ε-p-*xylyl*-n-*amyl alcohol*, b. p. 153—155°/14 mm., are successively obtained, is converted by aluminium chloride into 1 : 4-*dimethylsuberane*, b. p. 121—125°/13 mm., d_4^{21} 0·9373, n_D^{21} 1·5330, oxidised to benzene-1 : 2 : 3 : 4-tetracarboxylic acid. Magnesium *p*-xylyl bromide and *cyclo*pentenyl chloride afford a mixture of *p*-xylene, di*cyclo*pentadiene, di-*p*-xylyl, and p-*xylyl*cyclo*pentene*, b. p. 125—127°/14 mm., d_4^{23} 0·9613, n_D^{23} 1·5380. The last-named compound adds hydrogen bromide in glacial acetic acid, giving the *bromo*-derivative, $C_{13}H_{17}Br$, b. p. 163—165°/13 mm., reduced by zinc dust and acetic acid to p-*xylyl*cyclo*pentane*, b. p. 122°/13 mm., $d_4^{20.5}$ 0·9621, $n_D^{20.5}$ 1·5344. The course of the Friedel–Crafts reaction with substituted amyl chlorides is not readily explicable in the light of the work of Wieland and Bettag (A., 1922, i, 1033). H. Wren.

Alkylation of benzene, toluene, and naphthalene. T. M. Berry and E. E. Reid (J. Amer. Chem. Soc., 1927, **49**, 3142—3149; cf. A., 1922, i, 330).—Ethylene is absorbed by benzene in presence of aluminium chloride much more rapidly than is ethyl chloride. Benzene dried with sodium gives better results than when dried with calcium chloride. There is little variation in rate of reaction between 60° and 90°. Absorption is preceded by an induction period which may be shortened by prior refluxing or addition of 10% of ethylated benzenes, and the rate of reaction increases as the products accumulate, until a maximum is reached when about 4 mols. of ethylene have been absorbed. Whilst the reaction cannot be controlled to give a single product, there is preferential formation of triethylbenzene, which has been obtained in

80% yield, and 90% of hexaethylbenzene can be eventually obtained. The optimum molecular ratio of aluminium chloride to benzene appears to be 1 : 13. The reaction product comprises two phases, one of which contains practically all the aluminium chloride associated with an approximately equal weight of hydrocarbons, these latter being always the more highly alkylated, with an especial preference for the pentaethylbenzene. The highest rate of absorption of ethylene observed was 402 c.c. per min. per mol. of benzene. Toluene absorbs ethylene under the same conditions as benzene. The absorption of 0·9 mol. of ethylene by 3·04 mols. of toluene gave a mixture containing toluene, ethylbenzene and xylenes, ethyltoluenes, and higher substitution products of b. p. up to above 207°, the fraction of b. p. 198—203° being highly fluorescent. Bromobenzene affords similarly benzene, ethylbenzenes, brominated ethylbenzenes, and tar. Benzene reacts with propylene under similar conditions, with formation of *iso*propylbenzenes, but the reaction is only about 4% as rapid as that with ethylene, and a higher degree of alkylation than tetra*iso*propylbenzenes could not be obtained on account of tars. Of the di*iso*propylbenzenes formed, the *m*-derivative forms 65%, and the tri*iso*propylbenzenes contain 75% of the 1 : 3 : 5-derivative. 1 : 2 : 4-*Tri*iso*propylbenzene*, b. p. 237—237·5°/752 mm., b. p. 97—97·5°/4 mm., d_{25}^{25} 0·8593, n_D^{25} 1·4855, was identified by oxidation to the corresponding benzenetricarboxylic acid, and 1 : 2 : 4 : 5-*tetra*iso*propylbenzene*, m. p. 117°, b. p. 260°/775 mm., was isolated. Propylation of toluene takes place more rapidly than that of benzene, the products being benzene, toluene, xylenes, triethylbenzene, and cymenes (*p*-cymene preponderating) and products of higher b. p. Di*iso*propylbenzene, naphthalene, and aluminium chloride yield, when stirred together at 90° for 4½ hrs., a product, b. p. 264—266°, probably iso*propylnaphthalene*, together with unchanged naphthalene and other unidentified products. *cyclo*Hexene reacts vigorously with benzene in presence of aluminium chloride, and the mixture boils when rapidly stirred for 30 sec. The product contained a small proportion of *cyclo*hexylbenzene.

F. G. WILLSON.

Derivatives of ethylbenzene. E. L. CLINE and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 3150—3156)—Benzene can be completely converted into ethylbenzene by treatment with ethylene in presence of aluminium chloride with rapid stirring (11,000 r.p.m.; cf. A., 1922, i, 330) if the more highly ethylated benzenes are added to the succeeding batch. Treatment of ethylbenzene (700 g.), stirred at 3000 r.p.m., with a mixture of nitric acid (510 g., *d* 1·42) and concentrated sulphuric acid (675 g.) below 40°, the reaction mixture being subsequently maintained at the ordinary temperature for 3 hrs., then heated to 100° during 4 hrs. and kept at 100° for 2 hrs., affords *o*-nitroethylbenzene, b. p. 135°/37 mm., and *p*-nitroethylbenzene, b. p. 154°/37 mm. (cf. Schultz and Flachsländer, A., 1902, i, 751), in the proportion 1·2 : 1 (cf. Béhal and Choay, A., 1894, i, 280), together with some 2 : 4-dinitroethylbenzene (cf. Weisweiller, A., 1900, i, 291). Both mononitro-derivatives can be reduced to the corresponding amines by means of tin and hydrochloric acid, but the *o*-nitro-derivative is only slowly reduced by iron and hydrochloric acid or ammonium sulphide. Reduction of the 2 : 4-dinitro-derivative with ammonium sulphide affords mainly the 2-nitro-4-amino-derivative, m. p. 45° (*acetyl* derivative, m. p. 110°), but some 4-nitro-2-aminoethylbenzene is also formed. The o-*aminoethylbenzene* salt, m. p. 237—239°, and p-*aminoethylbenzene* salt, m. p. 247—249°, of anthraquinone-1-butylthiol-5-sulphonic acid were prepared. Sulphonation of *p*-aminoethylbenzene affords 4-*aminoethylbenzene-2-sulphonic acid* (*amide*, m. p. 86°), from which 4-*dimethylamino-4'-ethylazobenzene-3-sulphonic acid*, closely resembling helianthine, was obtained in the usual manner. Treatment of *p*-aminoethylbenzene hydrochloride in aqueous solution with bromine yields 3 : 5-*dibromo-4-aminoethylbenzene*, m. p. 85°. 4-*Ethyldiazoaminobenzene*, yellow, m. p. 75°, is obtained either from diazotised aniline and *p*-aminoethylbenzene or from diazotised *p*-aminoethylbenzene and aniline. o-*Ethylphenylhydrazine*, m. p. 49—50°, b. p. 156°/28 mm. (*hydrochloride*), and p-*tolualdehyde*-o-*ethylphenylhydrazone*, m. p. 102·5—103°, are described. *o*-Ethylphenylhydroxylamine could not be obtained. 4 : 4'-*Diethylazoxybenzene* is obtained by reduction of *p*-nitroethylbenzene with zinc dust and calcium chloride in aqueous alcohol, and yields 4 : 4'-diethylazobenzene, m. p. 63°, when distilled with iron filings. Only a trace of *p*-ethylbenzaldehyde was obtained from ethylbenzene by the Gattermann–Koch reaction. Dyes obtained by coupling diazotised *o*- and *p*-aminoethylbenzenes with 1-naphthol-4 : 8-disulphonic and 1-naphthol-4-sulphonic acid are slightly deeper in colour than the corresponding dyes from *o*- and *p*-toluidines.

F. G. WILLSON.

***m*-Diethylbenzene and some of its derivatives.** J. E. COPENHAVER and E. E. REID (J. Amer. Chem. Soc., 1927, 49, 3157—3164).—*m*-Diethylbenzene, b. p. 180·55°, d_{25}^{25} 0·8597, n_D^{25} 1·4926, can be separated from the mixture of isomeric diethylbenzenes, b. p. 180—185°, obtained by condensation of ethylene and benzene in presence of aluminium chloride, by sulphonation of the mixture with 12·5 mols. of sulphuric acid at 15—20°, fractional crystallisation of the barium salts, of which the *m*-isomeride is the least soluble (cf. Voswinkle, A., 1889, 1193), and then hydrolysing the barium *m*-diethylbenzenesulphonate with sulphuric acid (cf. Armstrong and Miller, J.C.S., 1884, 45, 148). Treatment of *m*-diethylbenzene (100 g.) with a mixture of 70% (60 g.) and 90% (40 g.) nitric acids at below 30° affords mainly 4-nitro-*m*-diethylbenzene, b. p. 133°/4 mm., d_{25}^{25} 1·0644, n_D^{25} 1·5300. Reduction of the latter with iron filings and acetic acid yields 4-*amino*-m-*diethylbenzene*, b. p. 116·5°/12 mm., b. p. 141°/30 mm., d_{25}^{25} 0·9545, n_D^{25} 1·5395 (*hydrochloride*; *acetyl* derivative, m. p. 112—113·5°; *benzoyl* derivative, m. p. 176·5°), from which the following are obtained by the usual methods: 4-*hydroxy*-, b. p. 124·5—125·5°, d_{25}^{25} 0·9794, n_D^{25} 1·5218; 4-*chloro*-, b. p. 94·5°/12 mm., d_{25}^{25} 1·0119, n_D^{25} 1·5149; 4-*bromo*-, b. p. 106·5°/12 mm., d_{25}^{25} 1·2462, n_D^{25} 1·5359; 4-*iodo*-, b. p. 131·5°/12 mm., d_{25}^{25} 1·4740, n_D^{25} 1·5729 (*iodoso-chloride*, unstable, m. p. 51—53° decomp.); 4-*cyano*-1 : 3-*diethylbenzene*, b. p. 134°/12 mm., d_{25}^{25}

0·9507, n_D^{25} 1·5195, and 2 : 4 : 2′ : 4′-*tetraethylthiocarbanilide*, m. p. 144·5°. Dyes made from this amine by coupling with a series of sulphonic acids have similar but more intense colours than those prepared analogously from aniline and the corresponding xylidine. F. G. Willson.

Hydrogenation of tetraphenylmethane and of *p*-hydroxytetraphenylmethane under pressure. V. N. Ipatiev and B. N. Dolgov (Bull. Soc. chim., 1927, [iv], **41**, 1621—1625).—Hydrogenation of tetraphenylmethane at 80—100 atm. and 275—285° in presence of nickel for 5—6 days affords only di*cyclo*hexylmethane, b. p. 251—253°, d_0^{20} 0·8743, n_D^{21} 1·4755, together with tri*cyclo*hexylmethane, m. p. 48°, d_0^{50} 0·9274, n_D^{50} 1·4967, and probably a little phenyl*cyclo*hexylmethane. Similarly *p*-hydroxytetraphenylmethane affords *cyclo*hexanol, di*cyclo*hexylmethane, and tri*cyclo*hexylmethane. Tetra*cyclo*hexylmethane was not obtained, probably on account of the greater affinity of the central carbon atom for hydrogen than for a fourth *cyclo*hexyl group. (Cf. this vol., 169.) R. Brightman.

Reactivity of halogens in various types of naphthalene derivatives. J. B. Shoesmith and H. Rubli (J.C.S., 1927, 3098—3106; cf. A., 1926, 389, 1247; 1927, 962).—The halogen in halogenonaphthalene derivatives is found to be more labile than that of the corresponding benzene derivatives. Thus 1-bromo-β-naphthol is more easily reduced by an acetic acid solution of hydrogen iodide than 4-bromo-α-naphthol and, probably owing to quinonoid tautomerisation, either is more easily reduced than the corresponding bromophenol, where the order of reducibility is the reverse. The order of the ease of hydrolysis of the substituted naphthylmethyl bromides is in exact parallel to the corresponding benzene series, although the influence of the second benzene nucleus approximately doubles the rate. Evidence of the transmission of influence from the 1- to the 5-position is obtained by the ease of hydrolysis of the following α-naphthylmethyl bromides which are in the order 5-methoxy->unsubstituted>5-bromo-. 4-*Methoxy-α-naphthylmethyl bromide*, m. p. 119—120° (decomp.), is prepared by the action of a benzene solution of hydrogen bromide on the corresponding carbinol. 3-*Methoxy-α-naphthoyl chloride*, m. p. 79°, obtained by the action of thionyl chloride on the acid, yields 3-*methoxy-α-naphthaldehyde*, m. p. 60° (*oxime*, m. p. 102°; p-*nitrophenylhydrazone*, m. p. 197°; *semicarbazone*, m. p. 200°), which may be converted into 3-*methoxynaphthylcarbinol*, m. p. 88°. 4-*Bromo-α-naphthyl methyl ether*, b. p. 181°/18 mm., is described. 4-*Methyl-α-naphthylcarbinol*, m. p. 75°, prepared by the interaction of the magnesium compound of 4-bromo-1-methylnaphthalene and paraformaldehyde, yields 4-*methyl-α-naphthylmethyl bromide*, m. p. 77°. *Aceto-4-bromo-2-methyl-α-naphthalide*, m. p. 223°, obtained by the bromination of the corresponding acetomethylnaphthalide (Lesser, A., 1914, i, 33), yields 4-*bromo-2-methyl-α-naphthylamine*, m. p. 82°, on hydrolysis. 5-Bromo-α-naphthaldehyde (p-*nitrophenylhydrazone*, m. p. 263°) yields similarly 5-*bromo-α-naphthylcarbinol*, m. p. 124°, and 5-*bromo-α-naphthylmethyl bromide*, m. p. 101°. 5-*Methoxy-α-naphthylcarbinol*, m. p. 98°, and 5-*methoxy-α-naphthylmethyl bromide*, m. p. 65°, are also described. G. A. C. Gough.

Derivatives of fluorene: 2-chloro-fluorene and -fluorenone. P. Chanussot (Anal. Asoc. Quím. Argentina, 1927, **15**, 216—220, and Bull. Soc. chim., 1927, [iv], **41**, 1626—1627; cf. A., 1927, 962).—2-Chlorofluorene, m. p. 96—97°, was prepared from 2-diazofluorene by Sandmeyer's reaction and yielded 2-*chlorofluorenone*, m. p. 125—126°, on oxidation. Direct chlorination of fluorene also yields 2-chlorofluorene (cf. Courtot and Vignati, A., 1927, 348, 654). R. K. Callow.

2-Iodofluorene. P. Chanussot (Bull. Soc. chim., 1927, [iv], **41**, 1625—1626; cf. preceding abstract).—2-Iodofluorene was obtained by the author prior to Korczyński, Karlowska, and Kierzek (A., 1927, 347) in 25—30% yield by the action of potassium iodide on fluorene-2-diazonium chloride (Actas Trab. II. Congr. Quim., 1924, **3**, 77). 2-Chloro- and 2-bromofluorene were similarly prepared. R. Brightman.

Unsaturated residues in chemical and pharmacological relationship. VI. J. von Braun and M. Kühn (Ber., 1927, **60**, [*B*], 2551—2557; cf. A., 1926, 850, and previous abstracts).—The outstanding influence of a double linking in the βγ-position is exhibited by the *cyclo*pentenyl group, since *cyclo*pentenyl and allyl derivatives show close analogy in their stabilities and pharmacological action. cyclo*Pentenyldiethylamine*, $NEt_2{\cdot}CH{<}\begin{matrix}CH{=}CH\\ CH_2{\cdot}CH_2\end{matrix}$, b. p. 164—165° (*hydrochloride*, m. p. 127°; *picrate*, m. p. 124°), is prepared in 70% yield by the action of *cyclo*pentenyl chloride on diethylamine in benzene at 0°; it is converted by cyanogen bromide in ethereal solution exclusively into diethylcyanamide, b. p. 70°/11 mm. *cyclo*Pentenyl chloride and methylamine afford a mixture of cyclo*pentenylmethylamine*, $C_5H_9{\cdot}NHMe$, b. p. 123° (*hydrochloride*, m. p. 124°; *picrate*, m. p. 136°), and *dicyclopentenylmethylamine*, b. p. 100°/15 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 129°). The tertiary base yields cyclo*pentenylmethylamine*, b. p. about 110°/12 mm., when treated with cyanogen bromide. cyclo*Pentenylmethylbenzylamine*, b. p. 130°/12 mm. (*picrate*, m. p. 115°), and cyanogen bromide yield the hydrobromide of the original base, a quaternary bromide which could not be obtained pure, and a mixture of methylbenzyl- and *cyclo*pentenylmethyl-cyanamides. The *cyclo*pentenyl group is therefore loosely attached to nitrogen, although more firmly than the allyl radical. *cyclo*Pentenyl chloride is converted by ammonium thiocyanate suspended in benzene or toluene into cyclo*pentenylthiocarbimide*, b. p. 80°/14 mm. (cyclo*pentenylphenylthiocarbamide*, non-crystalline; cyclo*pentenyl*-p-*tolylthiocarbamide*, m. p. 186°; cyclo*pentenyl*-β-*naphthylthiocarbamide*, amorphous). Magnesium phenyl bromide and *cyclo*pentenyl chloride afford cyclo*pentenylbenzene*, b. p. 92—93°/13 mm., d_4^{19} 0·9668, n_D^{19} 1·5396 (*dibromide*, b. p. 130—135°/1 mm.), isomeric or possibly identical with the compound obtained by Borsche and Menz (A., 1908, i, 147). *cyclo*Pentenyl chloride and sodium or potassium phenoxide suspended in toluene give *cyclo*pentadiene, phenol (derived from primarily formed *cyclo*pentenyl phenyl ether), and *o*-cyclo*pentenylphenol*, b. p. 133—135°/12 mm. (non-crystalline *acetyl* and *benzoyl* derivatives; *methyl ether*, b. p. 125°/15 mm.); the portion insoluble in alkali hydroxide gives analyses indicating a compound of 1 mol. of phenol with 2 mols. of *cyclo*pentadiene or 1 mol. of *cyclo*pentenylphenol with 1 mol. of *cyclo*pentadiene. *cyclo*Pentadiene reacts vigorously with phenols but not with phenolic ethers in presence of a trace of hydrogen chloride. N-cyclo*Pentenylnorcodeine*, m. p. 113° (*hydrochloride*, m. p. 188° after softening at about 180°), prepared from norcodeine and *cyclo*pentenyl chloride in toluene, closely resembles allylnorcodeine in pharmacological behaviour, whilst 5-cyclo*pentenyl*-5-iso*propylbarbituric acid*, m. p. 171—172°, from *cyclo*pentenyl chloride and the sodium derivative of 5-*iso*propylbarbituric acid in toluene, is almost as powerful a soporific as "noctal."

H. Wren.

Alternating effect in carbon chains. XXII. Attempt further to define the probable mechanism of orientation in aromatic substitution. C. K. Ingold and F. R. Shaw (J.C.S., 1927, 2918—2926).—Experiments on the relative speeds of nitration of aromatic compounds of certain classes are used in an attempt to ascertain the comparative degrees of activation induced by substituents at the *o*-, *m*-, and *p*-positions of the benzene nucleus. The classes of compound investigated are chosen to include cases of simple inductive effect (toluene and benzyltrimethylammonium salts) and of combined inductive and tautomeric effect (halogenobenzenes) (cf. Ann. Reports, 1926, 140). Inductive effects of either sign are shown to operate primarily on the *o*- and *p*-positions, whilst an appreciable second-order effect, always of the same sign as the primary effect, is relayed on to the *m*-position. Tautomeric effects operate powerfully on the *o*- and *p*-positions but no similarly appreciable second-order effect reaches the *m*-position. It is concluded tentatively that, whilst inductive effects give rise to an essentially permanent (not necessarily constant) molecular condition, the tautomeric effect (apart, possibly, from a small permanent residuum) is essentially a temporary phenomenon, of main significance at the moment of attack by a reagent. The mechanism of transmission through the nucleus of the inductive and tautomeric effects is discussed. M. Clark.

Sulphonation in basic or neutral media. Arylsulphonanilidosulphonic acids ($Ar{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$). M. Battegay and A. Schneider (Bull. Soc. chim., 1927, [iv], **41**, 1491—1494).—Sulphonation of *p*-toluenesulphonanilide with pyridinium anhydrosulphate at 180—190° yields a *sulphonic acid* affording the *calcium* salts $(C_7H_7{\cdot}SO_2{\cdot}N{\cdot}C_6H_4{\cdot}SO_3)Ca,\frac{1}{2}H_2O$ and $(C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3)_2Ca$, the sulphonic group entering the *para*-position. The corresponding derivatives of the three *p*-toluenesulphotoluidides are similarly obtained. In the sulphonation of naphthalene by this method at 140° and 170°, rise of temperature favours the formation of the α-sulphonic acid, which with this method is always formed in greater amount than the β-isomeride. R. Brightman.

Synthesis of substituted carbamides and thiocarbamides. R. M. Roy and J. N. Rây (J. Indian Chem. Soc., 1927, **4**, 339—342).—Carbamide when treated with aniline, *o*-, *m*-, and *p*-toluidines, and *p*-phenetidine in presence of phosphorus pentoxide at 110—125° gives the corresponding monophenylcarbamides. Small quantities of the *s*-diphenylcarbamides are produced also. Thiocarbamide with aniline and *o*- and *p*-toluidines yields the monophenylthiocarbamides. Urethane and thiourethane react with aniline to give *s*-diphenylcarbamide and *s*-diphenylthiocarbamide. H. Burton.

Derivatives of *n*-hexylamine with chlorodinitro- and chlorotrinitro-naphthalenes. A. P. J. Hoogeveen (Rec. trav. chim., 1927, **46**, 918—924).—*n*-Hexylamine, n_D^{17} 1·4255, is prepared by Frentzel's method (A., 1883, 1075), improved details being given. When heated with the appropriate chloronitronaphthalene in alcohol solution at 100° for 5 hrs. it yields, respectively, 2 : 4-*dinitro*-1-n-*hexylamino*-, m. p. 64°; 2 : 4 : 5-*trinitro*-1-n-*hexylamino*-, m. p. 97°, and 1 : 6 : 8-*trinitro*-2-n-*hexylamino*-, m. p. 164°, -*naphthalenes*. These m. p. are in close agreement with those predicted by Talen (Diss., Leiden, 1927) and by van der Kam (A., 1926, 1240).

J. W. Baker.

Higher alkyl derivatives of toluene-*p*-sulphonyl-β-naphthylamine. 2-*n*-Butyl-2-toluene-*p*-sulphonyl-1 : 2-naphthylenediamine. J. Reilly, F. J. Drumm, and (Miss) K. O'Sullivan (J.S.C.I., 1927, **46**, 436—437T; cf. Morgan and Micklethwait, J.C.S., 1912, **101**, 143).—On heating β-naphthylamine with *n*-butyl iodide in *n*-butyl alcohol, β-*naphthyl*-n-*butylamine*, b. p. 348—350°, $d_4^{16·5}$ 1·02, is obtained; it is a colourless oil with a faint violet fluorescence; *hydrochloride*, m. p. 176—178°; p-*bromobenzoyl* derivative, m. p. 125°. When heated with toluene-*p*-sulphonyl chloride in pyridine solution, β-naphthyl-*n*-butylamine yields *toluene*-p-*sulphonyl*-n-*butyl*-β-*naphthylamine*, m. p. 55—56°, which may also be prepared in better yield by butylation of toluene-*p*-sulphonyl-β-naphthylamine. Nitration of this product in glacial acetic acid solution at 40—50° yields 1-*nitro*-2-*toluene*-p-*sulphonyl*-n-*butylnaphthylamine*, m. p. 129—130°, which is reduced by ammonium chloride and zinc dust to 2-*toluene*-p-*sulphonyl*-n-*butyl*-1 : 2-*naphthylenediamine*, m. p. 119° (*benzoyl* derivative, m. p. 150°). The diazonium salt of this base is comparatively stable in glacial acetic acid solution at the ordinary temperature; it yields with β-naphthol a scarlet *dye*, which with sulphuric acid gives a pure blue solution not changing on dilution, with chromotropic acid a purple and with γ-acid a chocolate-brown *dye*. The diamine couples with diazosulphanilic acid to give a violet *dye*, the sodium salt of which is a scarlet powder giving a purple coloration with sulphuric acid.

W. J. Powell.

Trypanocidal action and chemical constitution. VII. *s*-Carbamides and arylamides of naphthylamine-di- and -tri-sulphonic acids, with observations on the mesomorphic state. I. E. Balaban and H. King (J.C.S., 1927, 3068—3097).—The corresponding *m*-nitrobenzoyl derivatives have been prepared by the action of *m*-nitrobenzoyl chloride on the sodium salts of 1-naphthylamine-3 : 6-disulphonic acid (I), 2-naphthylamine-6 : 8-disulphonic acid (II), 2-naphthylamine-4 : 8-disulphonic acid (III), 2-naphthylamine-5 : 7-disulphonic acid (IV), 8-hydroxy-1-naphthylamine-3 : 6-disulphonic acid (V), 8-hydroxy-2-naphthylamine-3 : 6-disulphonic acid (VI), and 1-naphthylamine-4 : 6 : 8-trisulphonic acid (VII). The nitro-group has, in each case, been reduced by ferrous hydroxide and the amino-compounds so formed have been converted (*a*) into the *s*-carbamides by the action of carbonyl chloride and (*b*) into the *m*-nitrobenzoyl derivatives. These new nitro-compounds (*b*) have been reduced to the *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives, which have again been phosgenated to give a further series of *s*-carbamides, having the general structure: $CO(NH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}NHR)_2$. *s*-Carbamides have also been prepared from the original amino-acids with the exception of (V), which yields, with carbonyl chloride, 1 : 8-ON-*carbonylaminonaphthol*-3 : 6-*disulphonic acid* (*disodium* salt $+4H_2O$; *barium* salt). The toxic and trypanocidal action of these substances has been tested on mice and on mice infected with *Trypanosoma equiperdum.* Trypanocidal action appears only at the *s*-carbamide stages of the aminobenzoyl and aminobenzoylaminobenzoyl derivatives and no activity is exhibited by derivatives of (I) and (VI). The substantive dyeing action on cotton was determined for derivatives of (V) and (VI) by measuring the colour intensities developed on immersion in diazotised *p*-nitroaniline of a cotton skein, which had been previously heated at 100° with an aqueous solution of the derivative and sodium chloride. The most pronounced substantive effect appeared at the *s*-carbamide stage in each case and this was confirmed for Bayer 205 (*s*-carbamide of *m'*-aminobenzoyl-*m*-aminotoluoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid), which, at a dilution of 1 in 50,000, gives a precipitate with clupeine sulphate in presence of 20% sodium chloride solution. It is considered that substantivity to cotton is roughly paralleled by the substantivity either to the tissues of the mammalian host or to the trypanosomes or to both. Many of the derivatives of the disulphonic acids exhibit to a pronounced degree the phenomenon of anisotropy in aqueous solution. The following are described: Derivatives of (I): s-*carbamide* ($+14H_2O$); *sodium* m-*nitrobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+5\frac{1}{2}H_2O$); *sodium* m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+5H_2O$) [*sodium hydrogen* salt ($+4\frac{1}{2}H_2O$); *calcium, barium*, and *silver* salts; corresponding *diazo*- and *azoxy*- ($+12H_2O$) compounds; s-*carbamide* ($+14\frac{1}{2}H_2O$)]; *sodium*, m'-*nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+4H_2O$); *sodium hydrogen* m'-*aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonate* ($+10H_2O$) [*diazo*-compound; s-*carbamide* ($+14H_2O$) derived from disodium salt (*barium* salt)]. Derivatives of (II): s-*carbamide* ($+10H_2O$) (*barium* salt); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+7H_2O$); *sodium hydrogen* m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+5\frac{1}{2}H_2O$) [*diazo*-compound; s-*carbamide* ($+13H_2O$) from disodium salt]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* ($+6H_2O$); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonate* [*sodium hydrogen* ($+5\frac{1}{2}H_2O$), *magnesium, calcium*, and *barium* salts; *diazosulphonate*; s-*carbamide* ($+16\frac{1}{2}H_2O$) (*magnesium, calcium*, and *barium* salts)]. Derivatives of (III): s-*carbamide* ($+5H_2O$); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+5H_2O$); *sodium* m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+7\frac{1}{2}H_2O$) [*sodium hydrogen* salt ($+5\frac{1}{2}H_2O$); *diazosulphonate*; s-*carbamide* ($+12H_2O$) (*calcium* and *barium* salts)]; m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* [*disodium* salt ($+5H_2O$); *barium, calcium*, and *magnesium* salts]; *sodium hydrogen* m'-*aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonate* ($+6\frac{1}{2}H_2O$) [s-*carbamide* ($+14\frac{1}{2}H_2O$) (*magnesium, barium*, and *calcium* salts)]. Derivatives of (IV): s-*carbamide* ($+7H_2O$); *sodium* m-*nitrobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* ($+5\frac{1}{2}H_2O$); *sodium* m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* [*sodium hydrogen* salt ($+4H_2O$); *diazo*-compound; s-*carbamide* ($+15H_2O$) (*barium* salt)]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* ($+9H_2O$); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonate* [*sodium hydrogen* salt ($+5\frac{1}{2}H_2O$); s-*carbamide* ($+8H_2O$) (calcium and barium salts)]. Derivatives of (V): *sodium* 1-m-*nitrobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7H_2O$) (*barium* salt); *sodium* 1-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* [*sodium hydrogen* salt ($+5H_2O$); *calcium, magnesium*, and barium salts; s-*carbamide* ($+13\frac{1}{2}H_2O$)]; *sodium* 1-m'-*nitrobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7\frac{1}{2}H_2O$); *sodium hydrogen* 1-m'-*aminobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+6\frac{1}{2}H_2O$) [s-*carbamide* ($+17\frac{1}{2}H_2O$) from disodium salt]. Derivatives of (VI): s-*carbamide* ($+10H_2O$) (*barium* salt); *sodium* 2-m-*nitrobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+4\frac{1}{2}H_2O$) (*barium* salt); *sodium hydrogen* 2-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+4H_2O$) [*barium* salt; *diazosulphonate*; s-*carbamide* ($+8\frac{1}{2}H_2O$) (*calcium* and *barium* salts) from disodium salt]; *sodium* 2-m'-*nitrobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+7H_2O$) (*calcium* and *barium* salts); *sodium hydrogen* 2-m'-*aminobenzoyl*-m-*aminobenzamido*-8-*naphthol*-3 : 6-*disulphonate* ($+8\frac{1}{2}H_2O$) [s-*carbamide* ($+9H_2O$) (*magnesium, calcium*, and *barium* salts) from disodium salt]. Derivatives of (VII): s-*carbamide*; *sodium* m-*nitrobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+4\frac{1}{2}H_2O$) (*calcium* and *barium* salts); *sodium* m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* [s-*carbamide* ($+4H_2O$)]; *sodium* m'-*nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+8H_2O$) (*calcium* and *barium* salts); *sodium* m'-*aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonate* ($+3\frac{1}{2}H_2O$) [*disodium* salt; s-*carbamide* ($+8H_2O$); *barium* salt]. M. CLARK.

Substitution products of 3-nitro- and 3-aminodiphenyl. W. BLAKEY and H. A. SCARBOROUGH (J.C.S., 1927, 3000—3009; cf. A., 1927, 656).—*4'-Chloro-3-nitrodiphenyl* (I), m. p. 89°, 2' : 4'-*dichloro-3-nitrodiphenyl* (II), m. p. 115°, (2' : 4' : 5 ?)-*trichloro-3-nitrodiphenyl*, m. p. 211°, and (2' : 4' : 5 : 6' ?)-

tetrachloro-3-nitrodiphenyl, m. p. 175°, are obtained by direct chlorination of 3-nitrodiphenyl in presence of ferric chloride under varying conditions of temperature and duration of heating. Reduction of compounds (I) and (II) with alcoholic stannous chloride in presence of concentrated hydrochloric acid, followed by acetylation, gives 4′-*chloro*-3-*acetamidodiphenyl*, m. p. 184°, and 2′ : 4 : 4′-*trichloro*-3-*acetamidodiphenyl*, m. p. 170°, respectively, converted by hydrolysis into 4′-*chloro*-3-*aminodiphenyl*, m. p. 82°, and 2′ : 4 : 4′-*trichloro*-3-*aminodiphenyl*, m. p. 105°. Bromination of 3-nitrodiphenyl yields 4′-*bromo*-3-*nitrodiphenyl*, m. p. 95°, and further bromination does not occur. 4′-*Bromo*-3-*acetamidodiphenyl* has m. p. 193° and 4′-*bromo*-3-*aminodiphenyl*, m. p. 105°. Further bromination of the last-named compound gives 2 : 4 : 4′ : 6-*tetrabromo*-3-*aminodiphenyl*, m. p. 104°. Nitration of 3-nitrodiphenyl in fuming nitric acid solution gives a mixture of 3 : 4′-*dinitrodiphenyl*, m. p. 189°, and 2′ : 3-dinitrodiphenyl. Further nitration of either compound in sulphuric acid solution yields 2′ : 3 : 4 : 4′-*tetranitrodiphenyl*, m. p. 173°, which gives, on treatment with piperidine, 2′ : 3 : 4′-trinitro-4-piperidinodiphenyl. Treatment of 3-acetamidodiphenyl with sodium hypochlorite yields N-*chloro*-3-*acetamidodiphenyl*, m. p. 87°, converted by alcohol and acetic acid into 4-*chloro*-3-*acetamidodiphenyl* (III), m. p. 148°, alternatively obtained by direct chlorination of 3-acetamidodiphenyl in glacial acetic acid solution. 4-*Chloro*-3-*aminodiphenyl hydrochloride* has m. p. 247° (decomp.). Treatment of (III) with sodium hypochlorite gives an unstable *N*-chloroamine. Bromination of 3-aminodiphenyl in carbon tetrachloride solution gives 4-*bromo*-3-*aminodiphenyl hydrobromide*, m. p. 255° (decomp.), and, after prolonged treatment, 2 : 4 : 6-*tribromo*-3-*aminodiphenyl*, m. p. 141°, which is quantitatively obtained by bromination in acetic acid solution. Deamination gives 2 : 4 : 6-*tribromodiphenyl*, m. p. 64°. Direct bromination of 3-acetamidodiphenyl in glacial acetic acid at the ordinary temperature gives 4-*bromo*-3-*acetamidodiphenyl*, m. p. 163°, whilst, in the presence of excess of bromine and at 100—120°, 4 : 6-*dibromo*-3-*acetamidodiphenyl*, m. p. 149°, is obtained. These compounds were converted respectively into 3 : 4-*dibromodiphenyl*, b. p. 215°/15 mm., and 2 : 4-*dibromodiphenyl*, b. p. 235°/15 mm. Nitration of 3-acetamidodiphenyl in a mixture of glacial acetic acid and acetic anhydride at 70° gives 4-*nitro*-3-*acetamidodiphenyl*, m. p. 115°. 4-*Nitro*-3-*aminodiphenyl* has m. p. 116°. Nitration of 3-acetamidodiphenyl and of 4-bromo-3-acetamidodiphenyl in fuming nitric acid solution gives 4′-*nitro*-3-*acetamidodiphenyl*, m. p. 192°, and 4-*bromo*-4′-*nitro*-3-*acetamidodiphenyl*, m. p. 158°, respectively. 4′-*Nitro*-3-*aminodiphenyl* has m. p. 137° and 4-*bromo*-4′-*nitro*-3-*aminodiphenyl* has m. p. 145°.

M. CLARK.

Action of chloroacetone on diazonium hydroxides. G. FAVREL (Bull. Soc. chim., 1927, [iv], 41, 1494—1497).—The presence of the electronegative chlorine and carbonyl group confers on chloroacetone properties analogous to those of αγ-diketones. Thus an aqueous solution of benzenediazonium chloride at 0° in presence of sodium acetate gives with chloroacetone a reddish-yellow precipitate, probably the azo-derivative, COMe·CHCl·N:NPh, which is rapidly transformed into the phenylhydrazone of pyruvyl chloride, COMe·CCl:N·NHPh, m. p. 136—137° (yield 30%). The o- and p-*tolylhydrazones* of pyruvyl chloride, m. p. 109—110° and 145—146° respectively, are obtained analogously in yields of 25% and 15%.

R. BRIGHTMAN.

Side-chain derivatives of alkyl*cyclo*pentanes. Tertiary alcohols, unsaturated and saturated hydrocarbons. G. CHAVANNE and P. BECKER (Bull. Soc. chim. Belg., 1927, 36, 591—604).—Magnesium alkyl bromides react with *cyclo*pentanone to form 1-alkyl*cyclo*pentan-1-ols, which are sometimes accompanied by *cyclo*pentanol, thus demonstrating the reducing action of the Grignard reagent. The following data are recorded: ethyl*cyclo*pentanol, b. p. 154·5—155·2°/760 mm., d_4^{15} 0·9225 (*allophanate*, m. p. 169°); *n*-propyl*cyclo*pentanol, b. p. 175·2—175·7°/760 mm., d_4^{15} 0·9083, d_4^{20} 0·9044±0·0005 (*allophanate*, m. p. 178°); n-*butyl*cyclo*pentanol*, b. p. 195·4—195·9°/760 mm., $d_4^{14\cdot95}$ 0·9022, $d_4^{19\cdot6}$ 0·8989 (*allophanate*, m. p. 181°). Dehydration of these tertiary alcohols by passing over alumina at 300°, heating with dry aluminium sulphate at 120—130°, or application of Wuyts' method using *p*-toluenesulphonic acid as catalyst furnishes ethyl*cyclo*pentene, b. p. 106·5—107°/760 mm., m. p. −123·3°, d_4^{15} 0·8041, d_4^{20} 0·8000 (cf. Wallach and von Martius, A., 1909, i, 383), which is oxidised by chromic–acetic acids to propiobutyric acid; n-propyl*cyclo*pentene, b. p. 131·5—132·5°/760 mm., m. p. −100·3°, d_4^{15} 0·8056, d_4^{20} 0·8015 (cf. Eisenlohr, A., 1926, 718), which is oxidised by potassium permanganate, forming mainly butyrobutyric acid and small amounts of glutaric, succinic, propionic, and butyric acids; n-*butyl*cyclo-*pentene*, b. p. 157·5—158°/760 mm., m. p. −95·75°, $d_4^{17\cdot8}$ 0·8101. Reduction of these unsaturated hydrocarbons with hydrogen in presence of acetic acid and platinum-black affords ethyl*cyclo*pentane, b. p. 103—103·2°/760 mm., m. p. −137·9°, $d_4^{14\cdot9}$ 0·7711, $d_4^{19\cdot}$ 0·7669; *n*-propyl*cyclo*pentane, b. p. 131·3—131·5°/760 mm., m. p. −120·3°, $d_4^{14\cdot9}$ 0·7814, $d_4^{20\cdot}$ 0·7772; n-*butyl*cyclo*pentane*, b. p. 156·8°±0·1/760 mm., m. p. −108·2°, $d_4^{14\cdot95}$ 0·7887, $d_4^{20\cdot}$ 0·7848. Critical solution temperatures of these last hydrocarbons in aniline are given, together with numerous values of the refractive indices of all the compounds examined.

H. BURTON.

***cis–trans* Isomerism and steric hindrance. VI. 2-Propyl*cyclo*hexanols.** G. VAVON and P. ANZIANI (Bull. Soc. chim., 1927, [iv], 41, 1638—1649).—*o*-Propylphenol, b. p. 100—101°/10 mm., 214—216° 760 mm., obtained by hydrogenation of *o*-allylphenol in acetic acid in presence of platinum, on further hydrogenation affords a mixture of 2-propyl*cyclo*hexanols, b. p. 199—201°, rich in the *cis*-isomeride, and about 25—30% of propyl*cyclo*hexane, b. p. 154°, 2-propyl*cyclo*hexanone forming an intermediate stage. cis-2-*Propyl*cyclo*hexanol* has b. p. 84°/10 mm., d_4^{11} 0·9247, n_D^{11} 1·4688 (*phenylurethane*, m. p. 97—97·5°; *hydrogen phthalate*, m. p. 107—108°; *hydrogen succinate*, m. p. 31—32°; *benzoate*, b. p. 177—178°/14 mm.,

d_4^{16} 1·0262, n_D^{15} 1·5150; iso*valerate*, b. p. 138—139°/18 mm., d_4^{11} 0·914, n_D^{11} 1·450). trans-2-*Propyl*cyclo*hexanol*, b. p. 90°/14 mm., d_4^{11} 0·9160, n_D^{11} 1·4668 (*hydrogen phthalate*, m. p. 120—121°; *phenylurethane*, m. p. 69—70°; *hydrogen succinate*, m. p. 48—49°; *benzoate*, b. p. 179—180°/15 mm., d_4^{16} 1·0154, n_D^{16} 1·513; iso*valerate*, b. p. 129—130°/13 mm., d_4^{11} 0·9131, n_D^{11} 1·4490), is obtained by heating the sodium derivative of the *cis*-isomeride at 200°, or in 85% yield by hydrogenation of *propyl*cyclo*hexanone*, b. p. 83—84°/13 mm., 198—199°/760 mm., d_4^{13} 0·9145, n_D^{13} 1·4558. The latter is obtained by oxidising the crude mixture of 2-propyl*cyclo*hexanols, b. p. 199—201°. Its *oxime*, m. p. 67—68°, with hydrogen in aqueous hydrochloric acid in presence of platinum-black gives 2-*propyl*cyclo*hexyl*-β-*hydroxylamine*, m. p. 64—65°. The *semicarbazone*, m. p. 133·5—134°, similarly affords 2-*propyl*cyclo*hexylsemicarbazide*, m. p. 103—104° (*hydrochloride*, m. p. 146—148°).

cis-2-Propyl*cyclo*hexanol is esterified only a little more slowly than the *trans*-isomeride, the difference being rather more marked in presence of a catalyst. Similarly, the *trans*-hydrogen phthalate is hydrolysed more rapidly than the *cis*-isomeride, the ratio of the velocity coefficients in water being 3·6 at 39° and 2·9 at 69°; in 75% alcohol the corresponding ratios are 2·3 and 2·2. The steric effect of the propyl group is thus much less marked than that of the *iso*propyl group in the corresponding 2-*iso*propyl*cyclo*hexanol derivatives (cf. Vavon and Callier, A., 1927, 455), as the theory of steric hindrance requires. For the hydrogen succinates the ratio of the velocity coefficients for hydrolysis of the *trans*- and *cis*-forms in water at 17° is 4·0; for the benzoates in 75% alcohol at 17°, the ratio is 3·9; and for the *iso*valerates in 75% alcohol at 30°, 2·5. R. Brightman.

Dihydroxydiphenylsulphones (hydroxysulphobenzides). J. Zehenter and E. Fauser (J. pr. Chem., 1927, [ii], **117**, 233—244).—Treatment of phenol with fuming sulphuric acid (15—20% SO_3) at 180—190° (cf. Annaheim, A., 1874, 795) yields mainly 4 : 4′-dihydroxydiphenylsulphone, together with a small amount of an isomeric *compound*, m. p. 173—174° (*diacetate*, m. p. 121°; *dibenzoate*, m. p. 205°; *sodium* salt), which is converted by dilute nitric acid into a *dinitrodihydroxydiphenylsulphone*, m. p. 229—230°. Treatment of the sulphone with concentrated sulphuric acid at the ordinary temperature for 24 hrs. gives a water-soluble product, whilst similar treatment of 4 : 4′-dihydroxydiphenylsulphone affords a *disulphonic acid*, $[C_6H_3(OH)(SO_3H)]_2SO_2$, m. p. (anhydrous) 212—214°, m. p. ($+8H_2O$), 66—68° after previous softening [*potassium*, *barium* ($+4H_2O$), and *lead* ($+2H_2O$) salts]. Sulphuric acid at 90—100° converts the sulphone into a *phenoldisulphonic acid* [*barium* salt ($+5H_2O$), loses $3H_2O$ at 170°, and decomposes at higher temperatures], and at 180—190° to a *phenoltrisulphonic acid* [*potassium* salt ($+4H_2O$), loses $2H_2O$ at 150°]. H. Burton.

Alcohol additive products of the bromo-derivative of mixed ethers and bromo-derivative of ββ-diphenoxypropane. D. M. Birosel (Philippine J. Sci., 1927, **34**, 153—160).—A review of the literature leads to the conclusion that the action of alcohols on bromine derivatives of propenyl compounds, in which the side-chain is directly attached to the benzene ring, is a general reaction for the bromine derivatives of *n*-alkyl compounds. It is now shown to be applicable to compounds in which the side-chain is connected through oxygen to the aromatic nucleus. Direct bromination of *p*-bromophenyl *iso*propyl ether in chloroform solution gives 2 : 4 : 6-*tribromophenyl* β-*bromo*iso*propyl ether*, m. p. 93°, which when boiled with methyl alcohol in the presence of silver nitrate gives 2 : 4 : 6-*tribromophenyl* β-*methoxy*iso*propyl ether*, m. p. 118—120°, and with ethyl alcohol the corresponding *ethoxy*-compound, m. p. 130—132°. Interaction of the foregoing brominated mixed ether and phenol gives a *compound*, m. p. 125—130°, not further characterised, which on bromination gives ββ-*di*-2 : 4 : 6-*tribromophenoxypropane*, m. p. 86·5°. A comprehensive bibliography is included. E. Holmes.

Replacement of sulphonic groups by nitro-groups in aromatic amino-compounds. R. L. Datta and P. S. Varma (J. Indian Chem. Soc., 1927, 4, 321—324).—Nitrous fumes convert sulphanilic acid or anilinedisulphonic acid in aqueous suspension into 2 : 4 : 6-trinitrophenol. Aniline-*m*-sulphonic acid yields 2 : 5-dinitrophenol. Similarly, from *p*-nitroanilinesulphonic acid, dimethylanilinesulphonic acid, *o*-toluidine-5-sulphonic acid, *o*-toluidine-3 : 5-disulphonic acid, *m*-toluidinesulphonic acid, *p*-toluidine-3-sulphonic acid, *p*-toluidine-3 : 5-disulphonic acid, and *m*-xylidinesulphonic acid there were obtained 2 : 4-dinitrophenol, 2 : 3 : 4-trinitrodimethylaniline, 3 : 5-dinitro-*o*-cresol, 3 : 5-dinitro-*o*-cresol, 2 : 4 : 6-trinitro-*m*-cresol, 3 : 5-dinitro-*p*-cresol, oxalic acid, and 5-nitro-1 : 3 : 4-xylenol, respectively. H. Burton.

Replaceability of the halogen atom in 1-chloro-2 : 4-dinitro-5-ethoxy(methoxy)-benzene by alkoxy groups. H. F. J. Lorang (Rec. trav. chim., 1927, **46**, 891—902).—The velocity of replacement of the chlorine atom in 1-chloro-2 : 4-dinitro- or 1-chloro-2 : 4-dinitro-5-methoxy(and ethoxy)-benzene by a methoxy- or an ethoxy-group by the action of the sodium alkoxide has been measured at various temperatures. The values of the bimolecular reaction coefficients at 0°, 10°, 15°, 20°, and 25° for sodium ethoxide are: with 1-chloro-2 : 4-dinitrobenzene, 0·36, 1·05, 1·80, 2·91, and 4·90 (cf. Luloffs, A., 1902, i, 87, whose values require to be halved); with 1-chloro-2 : 4-dinitro-5-ethoxybenzene, 0·11, 0·22, 0·46, 0·61, and 1·11, respectively. With sodium methoxide and 1-chloro-2 : 4-dinitrobenzene, the values are 0·11, —, 0·59, —, and 1·49, and with 1-chloro-2 : 4-dinitro-5-methoxybenzene, 0·037, 0·091, 0·20, 0·30, and 0·47, respectively. The ratio of the velocities of replacement of the halogen atom in the unsubstituted and in the 5-alkoxy-chlorodinitrobenzenes are therefore 3·4 : 1 and 3 : 1, respectively, in the two series. J. W. Baker.

Action of light on colouring matters containing the nitro-group. A. Seyewetz and D. Mounier (Compt. rend., 1927, **185**, 1279—1281).—Textiles of animal or vegetable fibres impregnated with nitrophenols, nitroamines, or even colourless nitro-compounds turn brown when exposed to daylight or ultra-violet rays. Reduction apparently takes place, as reducing agents hasten, and oxidising agents retard, the effect. The brown *substance* thus formed from picric acid on calico was isolated, by extraction with alkali and precipitation with acid, and found to contain nitro- or nitroso-groups, but no amino-group. This substance may be an azo-compound derived from an azoxy-reduction product of picric acid. B. W. Anderson.

Acyl derivatives of *o*-aminophenol. R. E. Nelson, N. W. Shock, and W. H. Sowers (J. Amer. Chem. Soc., 1927, **49**, 3129—3131; cf. A., 1926, 833).—Treatment of *iso*amyl *o*-hydroxycarbanilate with *n*-butyl chloroformate affords the corresponding *carbo*-n-*butoxy*-derivative, m. p. 77°, the reverse reaction taking place on hydrolysis. Acylation of *n*-butyl *o*-hydroxycarbanilate with *iso*amyl chloroformate affords the same diacyl derivative, indicating the migration of the carbo-*n*-butoxy-group from the nitrogen to the oxygen atom. Treatment of *iso*amyl *o*-hydroxycarbanilate with *iso*butyl chloroformate affords the corresponding *carboisobutoxy*-derivative, m. p. 61·5°, which yields the original *iso*amyl *o*-hydroxycarbanilate on hydrolysis. The same diacyl derivative is obtained from *iso*butyl *o*-hydroxycarbanilate and *iso*amyl chloroformate, indicating the migration of the carbo*iso*butoxy-group. o-*Benzamidophenyl* n-*propyl carbonate*, m. p. 52°, is obtained normally from *o*-benzamidophenol and *n*-propyl chloroformate, and, by rearrangement, from *n*-propyl *o*-hydroxycarbanilate and benzoyl chloride, the carbo-*n*-propoxy-group migrating from nitrogen to oxygen. Acylation of *iso*propyl *o*-hydroxycarbanilate with benzoyl chloride proceeds normally, with formation of the corresponding *benzoate*, m. p. 82°. The latter is also obtained by treatment of *o*-benzamidophenol with *iso*propyl chloroformate, indicating migration of the benzoyl group from nitrogen to oxygen. F. G. Willson.

Use of hydrogen peroxide for iodine and other substitutions in aromatic compounds. J. E. Marsh (J.C.S., 1927, 3164).—Examples are given of the use of hydrogen peroxide (30%) in effecting iodination of phenol and β-naphthol; phenol can also be brominated or chlorinated using a bromide or chloride with hydrogen peroxide in acetic acid. The method has also been extended to the introduction of the thiocarbimido-group. The reaction between dimethylaniline and potassium thiocyanate in glacial acetic acid solution followed by the gradual addition of hydrogen peroxide produces a compound, probably a dimethylaminobenzthiazole. R. A. Pratt.

***m*-4-Xylenol and some derivatives.** L. Palfray and T. Duboc (Compt. rend., 1927, **185**, 1479—1481).—*m*-4-Xylenol, b. p. 97—98°/14 mm., d_4^{14} 1·0276, n_D^{14} 1·5420, R_D 37·41 (acetate, b. p. 107·5—108·5°/13 mm., $d_4^{15·5}$ 1·0298, $n_D^{15·5}$ 1·4990, R_D 46·79; *propionate*, b. p. 121·4—121·6°/(corr.)15 mm., d_4^{17} 1·0104, n_D^{17} 1·4944, R_D 51·28; *benzoate*, b. p. 110·5—111°/15 mm., m. p. 37—38°), reacts with ethyl chloroacetate to form *ethyl* m-4-*xylyloxyacetate*, b. p. 150—150·2°/14 mm., d_5^{25} 1·0563, n_D^{25} 1·4942, R_D 57·89 (free *acid*, m. p. 140·5°). Bromination of the xylenol in acetic acid yields the 5-bromo-derivative, b. p. 105·5—106·5°/14 mm., m. p. 8·5—9°, $d_4^{16·5}$ 1·4392, $n_D^{16·5}$ 1·5642, R_D 45·44 (cf. Orton and Coates, J.C.S., 1907, **91**, 53) (*acetate*, b. p. 137·6—137·9°/14 mm., d_4^{25} 1·3684, n_D^{25} 1·53115, R_D 54·97; *propionate*, b. p. 154—154·5°(corr.)/14 mm., d_4^{25} 1·3275, n_D^{25} 1·5246, R_D 59·31; *benzoate*, b. p. 216°(corr.)/15 mm., m. p. 54°). H. Burton.

Course of oxidation in arylthioarylides [derivatives of Ph·S·NHPh]. E. Gebauer-Fülnegg and E. Riesz [with A. Lorenz and R. Pollak] (Monatsh., 1927, **48**, 645—658).—The oxidation of the compounds formed by the reaction of 4-chloro-2-nitro-1-chlorothiolbenzene with aromatic amines is studied. 4-*Chloro*-2-*nitro*-1-*anilinothiolbenzene*, m. p. 100°, is oxidised by peracetic acid to a brownish-violet *nitro*-compound, $C_{24}H_{16\,(or\,14)}O_4N_4Cl_2S_2$, decomp. 135—137°, reduced by zinc and acetic acid to the corresponding *amine*, decomp. 115—116°, and unaffected by the Claasz reaction (A., 1912, i, 851). Reduction of the original anilide causes decomposition with formation of acetanilide. The action of chlorine yields 4-chloro-2-nitrobenzenesulphonyl chloride and ammonium chloride, and the same compounds are obtained from the oxidised product.

4-*Chloro*-2-*nitro*-1-*diphenylaminothiolbenzene*, m. p. 127°, is oxidised slowly by peracetic or chromic acid to unidentified products. Nitric acid in acetic acid nitrates the two phenyl groups, yielding thus a *trinitro*-compound, decomp. 140—176°.

Hydrazobenzene with the chlorothiolbenzene gives equal amounts of benzidine and azobenzene, with a large amount of 4 : 4′-dichloro-2 : 2′-dinitrodiphenyldisulphide. Benzidine yields *bis*-(4-*chloro*-2-*nitrophenylthiol*)-pp′-*diaminodiphenyl*, m. p. 235°; oxidation products could not be isolated. Dihydrophenazine yields the hydrophenazine hydrochloride double salt (Hinsberg and Garfunkel, A., 1897, i, 123), phenazine, and 4 : 4′-dichloro-2 : 2′-dinitrodiphenyldisulphide. *o*-Chloroaniline yields 4-*chloro*-2-*nitro*-1-o-*chloroanilinothiolbenzene*, m. p. 112°, which is oxidised by peracetic acid to a *substance*, $C_{24}H_{14}O_4N_4S_2Cl_4$, decomp. 170°. E. W. Wignall.

Direct methylthiolation. Application in the preparation of substituted thioanisoles. H. H. Hodgson and F. W. Handley (J.S.C.I., 1927, **46**, 435—436T).—The process, which is of general application for chloronitrobenzenes with labile chloro- or nitro-groups, consists in passing the gases evolved from a warm mixture of methyl sulphate and a 10% aqueous solution of sodium hydrosulphide into an alcoholic solution or suspension of the chloronitrobenzene in the presence of sodium hydroxide, or, in certain cases, of potassium carbonate. By this means 3-chloro-6-nitrothioanisole was obtained in excellent yield from 1-chloro-3 : 4-dinitrobenzene, as also were 2-nitro-, 4-chloro-2-nitro-, 2-nitro- and 4-nitro-5-methoxy-, and 2 : 4-dinitro-thioanisoles from 2-chloro- and 2 : 5-dichloro-nitrobenzenes, 3-chloro-4- and -6-nitro-anisoles, and 1-chloro-2 : 4-dinitrobenzene, respectively. An exception occurred with 4-chloronitrobenzene, which was mainly converted into 4 : 4′-dichloroazoxybenzene.

Action of aminosulphonic acid on diphenols. A. Quilico (Gazzetta, 1927, **57**, 793—802).—When aminosulphonic acid is heated with pyrocatechol, *ammonium pyrocatechol-4-sulphonate*, m. p. 260° (decomp.), is obtained, and with excess of aminosulphonic acid, the same product. Resorcinol yields similarly *ammonium resorcinol-4-sulphonate*, m. p. 190° (decomp.), identified by conversion by ammonia and ammonium chloride in a sealed tube into *ammonium* m-*phenylenediamine-4-sulphonate*, from which m-*dichlorobenzene-4-sulphonyl chloride*, m. p. 35°, is obtained, and finally, by the action of thionyl chloride, 1 : 3 : 4-trichlorobenzene. With excess of aminosulphonic acid, *ammonium resorcinol-4 : 6-disulphonate* (carbonises at 305°) is obtained; the *potassium* salt is converted into resorcinol-4 : 6-disulphonyl chloride (*-disulphonamide*, m. p. 263°, decomp.), and thence into *s*-tetrachlorobenzene. Quinol yields similarly *ammonium quinol-2-sulphonate*, m. p. 200—205°, and *-2 : 5-disulphonate* (carbonises at about 300°), converted into the *disulphonyl chloride*, m. p. 100°, and by thionyl chloride into *s*-tetrachlorobenzene.

E. W. Wignall.

Synthesis of some aralkylamines containing phenolic hydroxyl groups in the benzene nucleus. S. Kobayashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 149—165).—Vanillin and benzyl chloride react in presence of alcohol and anhydrous potassium carbonate to form 4-benzyloxy-3-methoxybenzaldehyde, b. p. 213—214°/5 mm., m. p. 63—64°, which condenses with nitromethane in presence of methylamine to give ω-*nitro-4-benzyloxy-3-methoxystyrene*, m. p. 122—123°. Reduction of this compound with zinc dust and alcoholic acetic acid at 5—10° affords *4-benzyloxy-3-methoxyphenylacetaldoxime*, m. p. 118—119°, which on further reduction with sodium amalgam and alcoholic acetic acid yields β-*4-benzyloxy-3-methoxyphenylethylamine*, b. p. 201—202°/4 mm., m. p. 67—69° [*hydrochloride*, m. p. 173—175°; *picrate*, m. p. 171—172°; *chloroplatinate*, m. p. 211° (decomp.); *chloroaurate*, m. p. 220—221° (decomp.)]. This amine hydrochloride is hydrolysed by concentrated hydrochloric acid, forming β-*4-hydroxy-3-methoxyphenylethylamine*, m. p. 156—157° [*hydrochloride*, m. p. 210—211°; *picrate*, m. p. 194—196; *chloroplatinate*, m. p. 211° (decomp.)]. ω-*Nitro-4-acetoxy-3-methoxystyrene* and ω-*nitro-3-methoxy-4-methoxymethoxystyrene* have m. p. 161—162° and 102—103°, respectively. Condensation of 4-benzyloxy-3-methoxybenzaldehyde with ethyl cyanoacetate gives *ethyl* α-*cyano-4-benzyloxy-3-methoxycinnamate*, m. p. 127—129°, hydrolysed by alcoholic potassium hydroxide to the corresponding *cyano-acid*, m. p. 202—203° (*potassium* and *silver* salts). Reduction of this acid with sodium amalgam and water gives α-*cyano*-β-*4-benzyloxy-3-methoxyphenylpropionic acid*, m. p. 125—126·5°, which when heated with pyridine at 130—140° furnishes β-*4-benzyloxy-3-methoxyphenylpropionitrile*, m. p. 78—79°. Reduction of this compound with sodium and alcohol affords γ-*4-hydroxy-3-methoxyphenylpropylamine*, m. p. 105—107° [*hydrochloride*, m. p. 154·5—155·5°; *picrate*, m. p. 165—166°; *chloroplatinate*, m. p. 198—199° (decomp.)], together with a small amount of β-*4-benzyloxy-3-methoxyphenylpropionic acid*, m. p. 98·5—99·5° (*amide*, m. p. 119—120°), also obtained by reducing *4-benzyloxy-3-methoxycinnamic acid*, m. p. 188—190°. An improved method of isolating vanillylamine [*hydrochloride*, m. p. 212—214°; *picrate*, m. p. 198—200° (decomp.)] is given (cf. Nelson, A., 1919, i, 543). *Di-(4-hydroxy-3-methoxybenzyl)amine*, m. p. 134° [*hydrochloride*, m. p. 235—236°; *picrate*, m. p. 205° (decomp.)], is obtained by the reduction of vanillinoxime with zinc dust and approx. 80% acetic acid. *4-Benzyloxy-3-methoxybenzaldoxime*, m. p. 113—115°, on reduction yields *4-benzyloxy-3-methoxybenzylamine* [*hydrochloride*, m. p. 207—208°; *picrate*, m. p. 173—175°; *chloroplatinate*, m. p. 211—212° (decomp.); *chloroaurate*, m. p. 143—144°].

3 : 4-Methylenedioxybenzyl chloride reacts with potassium and mercuric cyanides in presence of water to form 3 : 4-methylenedioxyphenylacetonitrile, m. p. 43—44° (cf. A., 1906, i, 421); in aqueous alcohol the nitrile and 3 : *4-methylenedioxybenzyl ethyl ether*, b. p. 118—120°/8 mm., were produced. Reduction of the nitrile with sodium and boiling alcohol gives β-3 : 4-methylenedioxyphenylethylamine (*hydrochloride*, m. p. 208—209°) together with 3 : 4-methylenedioxytoluene, b. p. 193—195°, 83/14 mm. (cf. Schepss, A., 1913, i, 1154).

H. Burton.

[Nuclear condensation of phenols with nitriles.] K. Hoesch (Ber., 1927, 60, [*B*], 2537; cf. A., 1927, 353).—A reply to Houben (A., 1927, 870).

H. Wren.

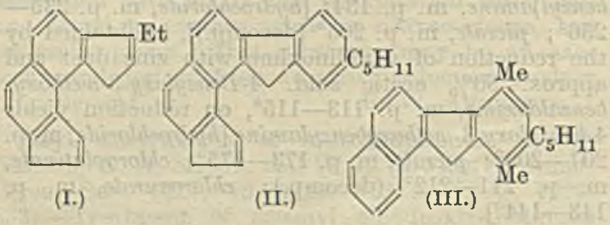
Catalytic hydrogenation under pressure of *p*-hydroxytriphenylcarbinol and *p*-hydroxydiphenylmethane. V. Ipatiev and B. Dolgov (Compt. rend., 1927, 185, 1484—1486).—Hydrogenation of *p*-hydroxytriphenylcarbinol in *cyclo*hexanol, in presence of nickel oxide, at 220° and an initial pressure of 80—100 atm., affords phenol, diphenylmethane, and p-*hydroxytriphenylmethane*, b. p. 250—253°/25 mm., m. p. 107—108°. Hydrogenation of this last substance at 270—275° gives *tri*cyclo*hexylmethane*, m. p. 48°, d_0^{30} 0·9265, n_D^{50} 1·4976. Hydrogenation of the carbinol at 280° yields mainly *di*cyclo*hexylmethane*, d_{20}^{16} 0·8776, n_D^{22} 1·4752, whilst at 320° a small amount of tri*cyclo*hexylmethane, some methane, and mainly di*cyclo*hexylmethane are produced.

Hydrogenation of *p*-hydroxydiphenylmethane, at 250—260° and 100 atm., gives di*cyclo*hexylmethane, dehydrogenated by sulphur at 280° to diphenylmethane.

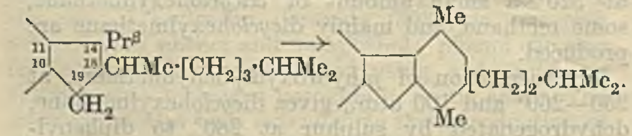
H. Burton.

Dehydrogenation of cholesterol. III. O. Diels, W. Gädke, and P. Körding (Annalen, 1927, 459, 1—26).—Dehydrogenation of cholesterol and some of its derivatives is smoothly effected at a lower temperature by the use of selenium instead of sulphur or palladised charcoal and the danger of alteration in the cholesterol skeleton is thus minimised. Dehydrogenation of the hydrocarbon $C_{19}H_{28}$ obtained by the thermal decomposition of cholesteryl chloride (Mauthner and Suida, A., 1896, i, 425) with palladised charcoal yields chrysene together with methane, ethane, propane, and octane. Similar dehydrogenation of cholesterol itself (Diels and Gädke, A., 1927, 241) yields hexane and *iso*octane in addition. Dehydrogenation of cholesteryl chloride with selenium at 240—310° yields an aromatic *hydrocarbon*, $C_{18}H_{16}$,

m. p. 123—124° (*picrate*, m. p. 117—118°), and a *hydrocarbon*, $C_{25}H_{24}$, m. p. 219—220° (*dinitro*-derivative, m. p. 261—262°), to which the structures (I) and (II) are respectively assigned. When the hydrocarbon (I) is treated with nitrous gases in ether and the product is heated with pyridine, formic or acetic acids, a *compound*, $C_{18}H_{13}O_2N$, m. p. 231—232° (decomp.) on slow heating, 238—240° on rapid heating, is obtained. The hydrocarbon (II) when oxidised with sodium dichromate and glacial acetic acid yields a *ketone*, m. p. 191—192°, which by reduction with magnesium and acetic acid yields an *alcohol*, m. p. 250—252°. When the acid $C_{26}H_{44}O_3$ obtained by the oxidation of cholesterone (Windaus, A., 1906, i, 579) is reduced by Clemmensen's method it yields a monobasic *acid*, $C_{26}H_{46}O_2$, m. p. 138°, which is dehydrogenated by selenium at 330° for 25 hrs. to yield a hydrocarbon, $C_{24}H_{26}$ (III), m. p. 171° (*dinitro*-derivative, m. p. 210), very similar to the hydrocarbon $C_{25}H_{24}$ (above), but readily oxidised by sodium dichromate and acetic acid directly to a *ketone*, $C_{24}H_{24}O$, m. p. 131°. Cholesterol itself by dehydrogenation with selenium for 30 hrs. yields the two hydrocarbons (I) and (II). On the basis of these results the authors consider that the existence of two five-membered rings in the cholesterol molecule is confirmed, in agreement with the conclusions of Wieland, Schlichting, and Jacobi (A., 1927, 247), the *iso*propyl and *iso*octyl groups being attached to the five-membered ring in positions 14 and 18, respectively. Six-membered ring formation during hydrogenation thus involves the interaction of the side-chains in accordance with the scheme



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



The formation of chrysene at the higher temperature results from the fission of the five-membered ring systems and subsequent ring closure to yield the six-rings present in this hydrocarbon. J. W. Baker.

Walden inversion. XI. Oxidation of secondary mercaptans to sulphonic acids; Walden inversion in series of secondary carbinols. P. A. Levene and L. A. Mikeska (J. Biol. Chem., 1927, 75, 587—605).—α-Naphthylethyl alcohol and *cyclo*hexylphenylcarbinol form exceptions to the compounds previously investigated (A., 1927, 53) in that the sign of rotation of their thio-derivatives is unaltered on oxidation to the sulphonic acids. However, in the former case a great increase in lævo-rotation is observed on passing from *l*-thiol to *l*-sulphonic acid, so that it is concluded that the *l*-carbinol and *l*-halide are configuratively related, whilst in the latter case the change of rotation from thiol to sulphonic acid is opposite in direction from that between carbinol and halide when the latter conversion is brought about by phosphorus pentachloride, so that in this case the carbinols are regarded as configuratively related to the halides of the opposite rotation. With this assumption it is possible to conclude in general that simple aliphatic carbinols and phenylbenzylcarbinol are converted into the halogen derivatives without Walden inversion, regardless of the halogenating reagent; with α-phenylethyl alcohol and α-phenyl-*n*-propyl alcohol and with *cyclo*hexylphenylcarbinol inversion takes place only when thionyl chloride is used; with α-phenyl-*n*-butyl, α-phenyl-β-methylpropyl, α-phenyl-*n*-amyl, and α-naphthylethyl alcohols inversion always occurs.

d-α-*Methyl*-n-*butyl alcohol* has $[\alpha]_D^{20}$ +18·5° in ether; l-α-*methyl*-n-*butyl alcohol*, $[\alpha]_D^{20}$ −9·06°, gave, with hydrobromic acid, *d*-β-bromo-*n*-pentane, b. p. 115—118°, $[\alpha]_D^{20}$ +9·14° in ether; with thionyl chloride it gave *di-α-methyl*-n-*butyl sulphite*, b. p. 113—119°, $[\alpha]_D^{20}$ +5·58°; *d*-β-*bromo*-n-*pentane*, $[\alpha]_D^{20}$ +6·8° in ether, gave l-β-*thiol*-n-*pentane*, b. p. 112°, $[\alpha]_D^{20}$ −4·66° in ether; d-β-*thiol*-n-*pentane*, $[\alpha]_D^{20}$ +7·92° in ether, yielded l-n-*pentane*-β-*sulphonic acid*, $[\alpha]_D^{20}$ −3·25° (*barium* salt, $[\alpha]_D^{20}$ −2·51°). d-cyclo*Hexylphenylcarbinol* has $[\alpha]_D^{20}$ +37·6° in ether; l-cyclo*hexylphenylcarbinol*, $[\alpha]_D^{20}$ −21·4° in ether, gave, with thionyl chloride, *chloro*-l-cyclo*hexylphenylmethane*, b. p. 105—107°/0·7 mm., $[\alpha]_D^{20}$ −29·4° in ether, and, with phosphorus pentachloride, the same compound, b. p. 112—113°/1·3 mm., $[\alpha]_D^{20}$ −3·43° in ether; d-cyclo*hexylphenylmethyl mercaptan*, $[\alpha]_D^{20}$ +27·7° in ether, yields d-cyclo*hexylphenylmethylsulphonic acid*, $[\alpha]_D^{20}$ +4·79° (*potassium* salt, $[\alpha]_D^{20}$ +4·10°). d-α-*Naphthylethyl alcohol*, $[\alpha]_D^{20}$ +11·06° in ether, gave, with thionyl chloride, l-α-*naphthylethyl chloride*, $[\alpha]_D^{20}$ −36·4° in ether, whilst l-α-*naphthylethyl alcohol*, $[\alpha]_D^{20}$ −35·2° in alcohol, gave, with phosphorus pentachloride, d-α-*naphthylethyl chloride*, $[\alpha]_D^{20}$ +5·42° in ether; the *l*-chloride, $[\alpha]_D^{20}$ −12·1°, gave d-α-*naphthylethyl mercaptan*, $[\alpha]_D^{20}$ +9·2°; the l-*mercaptan*, $[\alpha]_D^{20}$ −24·8° in ether, gave l-α-*naphthylethylsulphonic acid*, $[\alpha]_D^{20}$ −66·9°. d-α-cyclo*Hexylethyl alcohol*, $[\alpha]_D^{20}$ +7·40° in ether, gave, with phosphorus pentachloride, l-α-cyclo*hexylethyl chloride*, b. p. 70—72°/16 mm., $[\alpha]_D^{20}$ −5·02° in ether; the d-*chloride*, $[\alpha]_D^{20}$ +3·83°, gave *l*-α-cyclo*hexylethyl mercaptan*, $[\alpha]_D^{20}$ −3·60° in ether, which yielded d-α-cyclo*hexylethylsulphonic acid*, $[\alpha]_D^{20}$ +9·1° (*potassium* salt, $[\alpha]_D^{20}$ +7·4°). d-α-cyclo*Hexyl*-n-*propyl alcohol*, $[\alpha]_D^{20}$ +8·95° in ether, gave, with phosphorus pentachloride, l-α-cyclo*hexyl*-n-*propyl chloride*, b. p. 88—93°/16 mm., $[\alpha]_D^{20}$ −1·20° in ether, and, with thionyl chloride, the same compound, $[\alpha]_D^{20}$ −2·97°; this gave d-α-cyclo*hexyl*-n-*propyl mercaptan*, b. p. 95—100°/16 mm., $[\alpha]_D^{20}$ +0·64°, which yielded d-α-cyclo*hexyl*-n-*propylsulphonic acid*, $[\alpha]_D^{20}$ +2·97° (*barium* salt, $[\alpha]_D^{20}$ +1·79°). C. R. Harington.

Molecular migrations. [Mme.] P. Ramart and [Mlle.] P. Amagat (Ann. chim., 1927, [x], 8, 263—328; cf. A., 1926, 710; 1927, 241).—A large number of primary alcohols of the types CHArR·CH$_2$·OH (I), CHAr$_2$·CH$_2$·OH (II), and CAr$_2$R·CH$_2$·OH (III) have been prepared and the action of dehydrating agents on them has been investigated. In case (I) the corresponding amides were first prepared by hydrolysis of the alkylated benzyl cyanide with either 85% sulphuric acid or concentrated alcoholic potassium hydroxide and thus are obtained *α-phenyl-γ-methyl*-n-*valeramide*, b. p. 195—196°/15 mm., m. p. 80—82° (*acid*, m. p. 75°, b. p. 178—180°/30 mm.); *α-phenyl-Δ^{γ}-pentenamide*, m. p. 60°. In cases II and III the benzyl esters of the corresponding acids (obtained by alkylation of the diarylacetic esters) were first prepared by the silver salt method and thus are obtained *benzyl α-phenyl-α-tolylacetate*, b. p. 252°/12 mm.; *benzyl α-phenyl*-α-p-*anisylacetate*, m. p. 68—69°, b. p. 275—280°/20 mm.; *α-phenyl-α-tolylpropionic acid*, m. p. 128—129° (*amide*, m. p. 85—86°; *benzyl* ester, b. p. 252°/12 mm.); *benzyl α-phenyl-α-tolyl-Δ^{γ}-pentenoate*, b. p. 252°/10 mm. (*acid*, m. p. 91°); *benzyl αβ-diphenyl*-α-p-*tolylpropionate*, m. p. 83—84°, b. p. 255°/5 mm. (*acid*, m. p. 145—146°). When reduced with sodium and boiling alcohol with the addition of toluene these amides or esters yield the corresponding primary alcohols, the reaction being accompanied by a secondary reaction which results in the formation of the amine or the saturated hydrocarbon, and thus are obtained α-phenylethyl alcohol (*benzoate*, b. p. 198—200°/20 mm.) together with α-phenylpropylamine; β-phenyl-*n*-butyl alcohol (*benzoate*, b. p. 202—203°/18 mm.; *phenylurethane*, m. p. 58—59°), together with β-phenyl-*n*-butylamine (chloroplatinate); β-phenyl-γ-methylbutyl alcohol (*benzoate*, b. p. 212°/22 mm.; *phenylurethane*, m. p. 70°), together with β-*phenyl-γ-methylbutylamine*, b. p. 155—156°/24 mm. (*chloroplatinate*); β-*phenyl*-δ-*methyl*-n-*amyl alcohol*, b. p. 138—139°/14 mm. (*phenylurethane*, m. p. 78°); β-*phenyl-Δ^{δ}-penten-α-ol*, b. p. 130—135°/15 mm. (*phenylurethane*, m. p. 78°); βγ-diphenylpropyl alcohol (*phenylurethane*, m. p. 92—93°); ββ-*diphenylethyl alcohol*, m. p. 62°, b. p. 190—195°/20 mm. (*phenylurethane*, m. p. 138—139°; *benzoate*, m. p. 90—91°); β-*phenyl*-β-p-*tolylethyl alcohol*, m. p. 45—46°, b. p. 192—193°/12 mm. (*phenylurethane*, m. p. 79—80°); ββ-diphenylpropyl alcohol (*phenylurethane*, m. p. 148—149°; *benzoate*, m. p. 94—95°). β-Phenyl-β-tolylpropyl alcohol and βγ-diphenyl-β-tolylpropyl alcohol could only be obtained contaminated with the saturated hydrocarbon, from which they cannot be separated by distillation. Dehydration of the carbinols of type I was effected by passing the vapour of the alcohol over infusorial earth as a catalyst at 300—400°, the mixture of ethylenic hydrocarbons obtained being identified by conversion into their crystalline dibromides and by oxidation with chromic oxide in acetic acid, the various isomerides being synthesised for purposes of comparison. In this class of carbinols dehydration occurs mainly in accordance with the scheme $CHArR{\cdot}CH_2{\cdot}OH \longrightarrow CHAr{:}CHR$ (A) and only slightly in the direction $CHArR{\cdot}CH_2{\cdot}OH \longrightarrow CArR{:}CH_2$ (B), the amount of the hydrocarbon B produced decreasing as the mol. wt. of the alkyl radical increases, so that in the case of βγ-diphenylpropyl alcohol the product consists almost entirely of αγ-diphenyl-Δ^{α}-propene (*dibromide*, m. p. 112°). Dehydration of the diaryl alcohols (II) was effected by heating with phosphoric oxide in benzene. Migration of an aryl radical occurs in each case, ββ-diphenylethyl alcohol yielding stilbene and β-phenyl-β-tolylethyl alcohol yielding *ω-tolylstyrene*, m. p. 119—120°, b. p. 175—180°, as the sole products. In the dehydration of the diarylalkyl alcohols (III) by phosphoric oxide migration of the phenyl group always occurs. J. W. BAKER.

Amino-substituted tetraphenylethylenes, benzpinacols, and benzpinacolins. W. MADELUNG and M. OBERWEGNER (Ber., 1927, 60, [*B*], 2469—2491; cf. A., 1925, i, 1459).—Criticism is directed against the proposals of Wizinger and Fontaine (A., 1927, 764). It appears inadvisable simply to re-name Witt's chromophors and to contrast them as negative auxochromes or antiauxochromes with the positive auxochromes previously termed simply auxochromes. Further, the co-ordinatively unsaturated, electrically charged central atom of a coloured ion cannot be regarded as a chromophor, since there is no evidence that the electronic vibrations which may be regarded as responsible for selective absorption are exclusively or predominatingly proper to the central atom. Selective absorption is observed whenever a sufficient number of carbon atoms of co-ordination 3 or nitrogen atoms of co-ordination 2 form a continuous open chain or ring; a single atom cannot therefore be regarded as a chromophor, but rather a sequence of such atoms. In the triphenylmethane series, the whole triphenylmethyl residue and not the central carbon atom is to be regarded as chromophor.

Benzpinacol dissolved in benzene or carbon tetrachloride is converted by hydrogen chloride into *s*-tetraphenylethylene chloride; under similar conditions hydrogen bromide affords tetraphenylethylene and bromine.

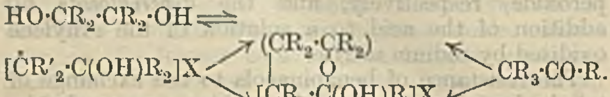
Octamethyltetra-aminotetraphenylethylene, m. p. 318° after softening at 312°, is converted by saturation of its solution in benzene with hydrogen chloride into the colourless *tetrahydrochloride*, $C_{34}H_{40}N_4,4HCl$, immediately hydrolysed by water to the ethylene; the corresponding *tetraperchlorate*, *tetramethiodide*, and tetramethoperchlorate are described. The base adds acid chlorides in benzene solutions, giving the *compounds* $C_{34}H_{40}N_4,4AcCl$ and $C_{34}H_{40}N_4,2COCl_2$. Symmetrical coloured salts are produced by the action of oxidising agents on the ethylene under conditions such that an anion of the salt is produced from the oxidising agent; they are quantitatively reconverted into the ethylene by alkalis, ammonia, alkali cyanide, sulphite, or sulphide, or by reducing agents. Thus chlorine gives the dichloride (cf. Wizinger, *loc. cit.*), whereas ferric chloride in glacial acetic acid affords the double *salt*, $C_{34}H_{40}N_4Cl_2,2FeCl_2$. The *dibromide* and *di-iodide* are described; with excess of halogen the perbromide or periodide is produced. Nitrogen peroxide gives the *dinitrite*, whilst potassium ferricyanide in acetic acid solution affords the *ferrocyanide*; the *disulphate* and *dibenzoate* are obtained by means of potassium persulphate and benzoyl peroxide, respectively, and the *diperchlorate* by addition of the acid to a solution of the ethylene oxidised by sodium nitrite.

The resistance of benzpinacols to the exchange of two hydroxyl groups for ionic residues is remarkable. Octamethyltetra-aminobenzpinacol in acetic acid and in mineral acid if not used in excess readily yields coloured monoacidic salts, whereas tetramethyldiaminobenzpinacol is stable in acetic acid and the solutions contain normal di- or tetra-acid salts such as *tetramethyldiaminobenzpinacol dihydrochloride.* With octamethyltetra-aminobenzpinacol, hydrogen chloride and carbonyl chloride afford the additive *compounds*, $C_{34}H_{42}O_2N_4,4HCl$ and $C_{34}H_{42}O_2N_4,2COCl_2$. With phosphorus chlorides or highly concentrated acids dye salts are produced which readily lose their colour owing to formation of pinacolins; nuclear substitution is not thereby observed.

Reconversion of the symmetrical coloured salts into ethylenes can frequently be effected simply by heating; thus octamethyltetra-aminotetraphenylethylene dichloride is converted into the base at 120°, nuclear substitution not being observed. Similarly, in hot concentrated hydrochloric acid the salt is gradually decomposed into the ethylene hydrochloride, whereas the corresponding tetramethyldiamino-derivative affords mainly the pinacolin which in both cases is produced exclusively in concentrated sulphuric acid. Although it appears impossible to oxidise the aminated tetraphenylethylenes to benzpinacols through their coloured salts, this can be effected readily by treatment with permanganate in acetone solution.

Unsymmetrically constituted coloured salts can be obtained from octamethyltetra-aminotetraphenylethylene by the use of less than 4 mols. of mineral acid, but their isolation as individuals has not been accomplished. The *compound* $[(NMe_2{\cdot}C_6H_4)_2\dot{C}{\cdot}C(OH)(C_6H_4{\cdot}NMe_2)_2]ClO_4$, obtained by the regulated addition of ammonia to an alcoholic solution of the colourless tetraperchlorate, behaves as a coloured salt of the di- or tri-phenylmethane series and has high electrical conductivity. Alkalis convert it into the pinacol, whilst with potassium cyanide it affords the *cyanohydrin*, $C_{35}H_{41}ON_5$, m. p. 229°, and with ammonia the *amino-alcohol*, $C_{34}H_{43}ON_5$. If, however, the temperature is somewhat raised during these reactions, octamethyltetra-aminobenzpinacolin is produced. The formation of pinacolin is also observed when the pinacol is boiled with absolute alcohol in the absence of acids, a coloured base appearing to be produced. Similarly, production of pinacolin occurs when the coloured salt is treated with boiling aqueous alcohol (but not with absolute alcohol) in the absence of alkali; the reaction is greatly facilitated by sodium acetate. The observations are considered to give experimental support to Meerwein's theory of the pinacolin transformation.

Octamethyltetra-aminobenzpinacolin is converted by treatment with boiling glacial acetic acid or with alcohol containing not more than 1 mol. of mineral acid into the monoacid coloured salt of the pinacol, thus realising a "direct" retro-pinacolin transformation probably in accordance with the scheme:



$$HO{\cdot}CR_2{\cdot}CR_2{\cdot}OH \rightleftharpoons [\dot{C}R'_2{\cdot}C(OH)R_2]X \rightarrow (CR_2{\cdot}CR_2{\cdot}O) \leftarrow CR_3{\cdot}CO{\cdot}R.$$
$$[\dot{C}R'_2{\cdot}C(OH)R_2]X \rightarrow [CR_3{\cdot}\dot{C}(OH)R]X \leftarrow CR_3{\cdot}CO{\cdot}R.$$

The initially colourless solution of octamethyltetra-aminobenzpinacolin in glacial acetic acid gradually becomes violet when preserved, a similar change being observed when the absolute-alcoholic solution of the blue pinacol monoperchlorate is boiled during several hours; the solution then contains the perchlorate of crystal-violet and dimethylaminobenzaldehyde in addition to unchanged pinacol salt. Tetramethyldiaminobenzpinacol appears to undergo similar fission with production of malachite-green in boiling glacial acetic acid or alcohol containing a little perchloric acid.

Tetramethyldiaminobenzpinacol is converted by very protracted treatment with boiling alcohol into *tetrabenzoylmethyldiaminotriphenylmethane*, m. p. 221° (*hydrochloride*), the constitution of which is established by its fission by alcoholic potassium hydroxide into benzoic acid and leuco-malachite-green. If, however, the solution of the pinacol in concentrated sulphuric acid is preserved or, preferably, heated at 100° the isomeric *p*-dimethylaminobenzoyldimethylaminotriphenylmethane, m. p. 255—256°, is produced; it converted by alkali into *p*-dimethylaminobenzoic acid and *p*-dimethylaminotriphenylmethane. H. Wren.

Photochemical reaction between bromine and cinnamic acid or stilbene. II. R. Purkayastha and J. C. Ghosh (J. Indian Chem. Soc., 1927, 4, 409—422; cf. A., 1926, 366).—The photobromination of cinnamic acid and stilbene has been studied in carbon tetrachloride and carbon disulphide solutions in blue and green light, and it is found that the value of the unimolecular velocity coefficient diminishes regularly with increase of time. The velocity coefficient varies as the square root of the intensity of incident radiation for blue light, but the increase is greater for green light. The rate of reaction depends on the concentration of the cinnamic acid and stilbene. The temperature coefficient of the reaction between cinnamic acid and bromine increases with the wave-length of the light. The number of mols. of cinnamic acid transformed per quantum of light absorbed varies from 22 (533 μμ) to 43 (488 μμ) in carbon tetrachloride solution and from 101 to 156 in carbon disulphide. For stilbene, the values are 16 to 34 in carbon tetrachloride and 52 to 99 in carbon disulphide. The molecular extinction coefficient of bromine in carbon disulphide solution for different wave-lengths is 1·5—2 times as great as in carbon tetrachloride. H. Burton.

Catalytic hydrogenations with platinum oxide. II. Mechanism of the process. F. Diaz Aguirreche (Anal. Fís. Quím., 1927, 25, 411—420; cf. A., 1927, 1188).—Examination of the course of hydrogenation of salicylic acid and phthalic anhydride in presence of platinum oxide shows that after an induction period the velocity rises to a maximum as the platinum oxide is reduced, and then falls slowly as the reaction proceeds. The platinum is actually found in colloidal form at the end of the reaction in decahydronaphthalene.

The great activity of colloidal noble metals is illustrated by measurements of the decomposition of hydrogen peroxide in the presence of colloidal gold, and compared with the smaller activity in the presence of a protective colloid.

In acetic acid the reduction of the platinum oxide is rapid, but the catalyst is soon fatigued. In decahydronaphthalene the reduction is slower and the activity lasts longer. In alcohol the behaviour is intermediate. This is consistent with an influence by the solvent, among other factors, on the formation of finely-divided platinum, followed by coagulation. The results are closely analogous to those obtained in catalysis with colloidal solutions (Madinaveitia and Aguirreche, A., 1921, ii, 390), when a maximum activity precedes coagulation, and are related to observations of the change of physical state of catalysts, demonstrating the close connexion between the change of state and catalytic activity.

The reactivation of platinum catalysts by oxygen is discussed and the literature reviewed. Reactivation is regarded as a superficial oxidation, followed by reduction, producing change in the surface or state of subdivision of the catalyst. R. K. Callow.

Isomeric derivatives of α- and β-naphthoic acids obtained by catalytic hydrogenation. J. Ranedo and A. León (Anal. Fís. Quím., 1927, 25, 421—433).—Hydrogenation was carried out in presence of platinum oxide. α-Naphthoic acid gave Δ^1-dihydro-α-naphthoic acid (*chloride*, b. p. 206°/64 mm.; *amide*, m. p. 186°), and Δ^3-*dihydro-α-naphthoic acid*, m. p. 138° (*chloride*, b. p. 205—206°/64 mm.; *amide*, m. p. 200°). Further hydrogenation gave *ar*-tetrahydro-α-naphthoic acid, m. p. 134—135° (*amide*, m. p. 176—177°), and (?)-*tetrahydro-α-naphthoic acid*, m. p. 146° (*chloride*, b. p. 190°/55 mm.; *amide*, m. p. 181—182°). Complete hydrogenation of α-naphthoic acid or of *ac*-tetrahydro-α-naphthoic acid (*chloride*, b. p. 182—183°/50 mm.; *amide*, m. p. 165°) gave *decahydro-α-naphthoic acid*, m. p. 127° (*chloride*, b. p. 200°/120 mm.; *amide*, m. p. 198—199°). β-Naphthoic acid gave decahydro-β-naphthoic acid, m. p. 76—79° (*chloride*, b. p. 210°/180 mm.; *amide*, m. p. 145°). The calcium, strontium, and barium salts are soluble, with the exception of the *calcium* salt of *decahydro-α-naphthoic acid*. The dihydro- and tetrahydro-acids, but not the decahydro-acids, give an intense red coloration in sulphuric acid on the addition of a drop of nitric acid. R. K. Callow.

Intermediate products for dyes [derivatives of β-naphthylthioglycollyl chloride]. Soc. Chem. Ind. in Basle.—See B., 1928, 8.

Derivatives of methyl 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylate. C. S. Gibson, K. V. Hariharan, and J. L. Simonsen (J.C.S., 1927, 3009—3015).—An improved method for the preparation of 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylic acid (J.C.S., 1904, **85**, 138) is described. The *methyl* ester, b. p. 158°/100 mm., yields, on bromination in acetic acid solution, a dibromo-ester regarded as *methyl* 4 : 4-*dibromo*-2 : 2-*dimethyl*cyclo*pentan*-3-*one*-1-*carboxylate*, m. p. 76—77°. This ester, on treatment with barium hydroxide, yields 4-*hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid* (I), m. p. 150—152° (slight decomp.) (*acetyl* derivative), oxidised by dilute nitric acid to dimethylmalonic and oxalic acids, and 4-*hydroxy*-2 : 2-*dimethyl*-Δ^4-cyclo*penten*-3-*one*-1-*carboxylic acid* (II), an oil, oxidised by nitric acid to *as*-dimethylsuccinic acid. On treatment with semicarbazide acetate or with *o*-phenylenediamine, the hydroxy-acid (I) reacts as the tautomeric diketo-acid, yielding respectively the *disemicarbazone* of 2 : 2-*dimethyl*cyclo*pentane*-3 : 4-*dione*-1-*carboxylic acid*, decomp. 200—201°, and a *quinoxaline* derivative, m. p. 175—177°, alternatively obtained from the acid (II). When the compound (I) is distilled under reduced pressure, a small quantity of an oil, probably 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione*, b. p. 80—100°/4 mm., is obtained together with unchanged starting material. The following are described: *ethyl* βγ-*dicyano*-β-*methylpentane*-γε-*dicarboxylate*, b. p. 184°/5 mm.; *ethyl* 3 : 3-*dimethyl*cyclo*pentan*-2-*one*-1 : 4-*dicarboxylate*, b. p. 145°/4 mm. M. Clark.

Preparation of phenyl salicylate. F. Chemnitius (Pharm. Zentr., 1927, 68, 795—797).—The details of a laboratory preparation from phenol and salicylic acid, in presence of phosphoryl chloride, are given. S. I. Levy.

Action of iodine in alkaline media on phenyl*iso*crotonic acid: some new mixed anhydride derivatives of benzoylacrylic acid. E. Cattelain (Bull. Soc. chim., 1927, [iv] **41**, 1500—1507; cf. A., 1927, 458).—For the preparation of mixed anhydride derivatives of benzoylacrylic acid by Bougault's method (A., 1908, i, 791, 983) the organic acid must be sparingly soluble in water. Thus, *o*-aminobenzoic acid gives no mixed anhydride, and β-phenylpropionic acid (solubility, 1 part in 168 parts) gives poor yields. Acids of high mol. wt., such as *o*-benzoylbenzoic acid or *o*-benzoyl-*p*-toluic acid, give no mixed anhydride or only indifferent yields. The purity of the acid is important; traces of salicylic acid in *o*-methoxybenzoic acid prevent the formation of the mixed anhydride; the presence of *m*-hydroxybenzoic acid in *m*-methoxybenzoic acid, or of cinnamic acid in hydrocinnamic acid, acts similarly. The iodine is added gradually to avoid the formation of the iodolactone of phenyl*iso*crotonic acid. The following *mixed anhydrides* of benzoylacrylic acid are new: o-*methoxybenzoic*, m. p. 91—92°; m-*methoxybenzoic*, m. p. 104°; o-*chlorobenzoic*, m. p. 106°; m-*chlorobenzoic*, m. p. 112°; o-*bromobenzoic*, m. p. 110°; p-*bromobenzoic*, m. p. 138°; o-*iodobenzoic*, m. p. 103°, m-*iodobenzoic*, m. p. 126°, and p-*iodobenzoic*, m. p. 163°; β-*phenylpropionic*. R. Brightman.

Preparation of *m*-iodobenzoic acid. Purification of *o*-iodobenzoic acid. E. Cattelain (Bull. Soc. chim., 1927, [iv], **41**, 1546—1548).—*m*-Iodobenzoic acid is obtained pure, m. p. 186·5°, by decomposing diazotised *m*-aminobenzoic acid with potassium iodide in 20% sulphuric acid; *o*-iodobenzoic acid obtained by the same method requires purification by crystallisation from 50% alcohol; the cumbersome purification method of Cohen and Raper is unnecessary. R. Brightman.

Action of carbon tetrachloride on certain mercaptans. S. Krishna and S. Singh (J. Indian Chem. Soc., 1927, **4**, 291—296).—Thiophenol when heated with carbon tetrachloride in presence of potassium hydroxide solution at 100—110° for 24 hrs., yields *o*-thiolbenzoic acid (12%), m. p. 177° (lit. 165°). *p*-Chlorothiophenol, under similar conditions, yields 4 : 4′-*dichloro*-6′(?)-*carboxydiphenyl disulphide*, m. p. 210—212°, which when reduced with zinc and hydrochloric acid gives *p*-chlorothiophenol and 5-*chloro*-o(?)-*thiolbenzoic acid*, m. p. 110°. 2 : 2′ : 5 : 5′-*Tetrachloro*-6′(?)-*carboxydiphenyl disulphide*, m. p. 176°, is obtained from 2 : 5-dichlorothiophenol, and on careful reduction with zinc dust and acetic acid yields 3 : 6-*dichloro*-o(?)-*thiolbenzoic acid*, m. p. 122°. *p*-Tolylmercaptan, *p*-nitrothiophenol, and *p*-bromothiophenol yield 4 : 4′-*dimethyl*-3′(?)-*carboxydiphenyl disulphide*, m. p. 156°, 4 : 4′-*diamino*-3′(?)-*carboxydiphenyl disulphide dihydrochloride*, chars at 280°, and 4 : 4′-*dibromo*-6′(?)-*carboxydiphenyl disulphide*, m. p. 241—242°, which on reduction furnish 6-*methyl*-m(?)-*thiolbenzoic acid*, m. p. 82°, 6-*amino*-m(?)-*thiolbenzoic acid hydrochloride*, and 6-*bromo*-m(?)-*thiolbenzoic acid* [5-*bromo*-o(?)-*thiolbenzoic acid* (?)], m. p. 210°, respectively.

H. BURTON.

Relative ease of formation of rings. I. J. VON BRAUN, O. BAYER, and L. CASSEL (Ber., 1927, 60, [*B*], 2602—2609).—The comparison is based on the exclusive or predominating formation of one ring from a compound from which two similar ring closures are theoretically possible. It is essential that the active groups should be identical.

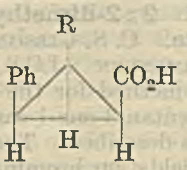
p-Benzylphenol is very readily reduced by hydrogen at somewhat above 200° under pressure in the presence of nickel to 4-*benzyl*cyclo*hexanol* (mixture of two stereoisomerides), b. p. 171°/14 mm. (*phenylurethane*, m. p. 154—157°), oxidised by chromic acid in glacial acetic acid to 4-*benzyl*cyclo*hexanone*, b. p. 165—166°/14 mm., m. p. 46—47° (*semicarbazone*, m. p. 145—147°). 4-*Hexahydrobenzyl*cyclo*hexanol*, b. p. 158°/14 mm. (*phenylurethane*, m. p. 153—155°), similarly prepared from 4-benzyl-phenol or -*cyclo*hexanol, is oxidised to 4-*hexahydrobenzyl*cyclo*hexanone*, b. p. 155°/14 mm. Oxidation of 4-benzyl*cyclo*hexanol by very dilute, alkaline permanganate at 0° gives β-*benzyladipic acid*, m. p. 110—111° (*anhydride*, b. p. 245—250°/16 mm., m. p. about 90°; *ethyl* ester, b. p. 220°/14 mm.); at higher temperatures, β-benzylglutaric acid is mainly produced. β-Benzyladipic acid is converted by successive treatment with phosphorus pentachloride in nitrobenzene and aluminium chloride into β-1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-3-*propionic acid*, m. p. 136—137°, in 55% yield; the corresponding *semicarbazone*, m. p. 260°, *oxime*, m. p. 148°, and *phenylhydrazone*, m. p. 152°, are described. Reduction by Clemmensen's method converts the ketonic acid into β-1 : 2 : 3 : 4-*tetrahydronaphthyl*-2-*propionic acid*, b. p. 73° (*ethyl* ester, b. p. 188—190°/14 mm., d_4^{22} 1·040, n_D^{22} 1·5153; *amide*, m. p. 130°). Naphthalene is formed when the ethyl ester is passed over heated lead oxide–pumice in an atmosphere of carbon dioxide. The four-membered carbon chain is therefore more readily attached to the benzene nucleus as a ring than the five-membered.

βγ-Diphenylpropylamine, b. p. 182°/18 mm., is obtained in poor yield by the reduction of α-phenylcinnamonitrile with sodium and alcohol, in 60% yield (accompanied by small amounts of the corresponding secondary *amine*, b. p. about 282°/18 mm.) by treatment with hydrogen in the presence of nickel at about 210°, preferably in the absence of solvent; its *benzoyl* derivative, b. p. about 280°/11 mm., is converted by phosphorus pentachloride into benzonitrile and βγ-*diphenylpropyl chloride*, b. p. 150°/11 mm. The base is converted by treatment with ethyl bromoacetate and hydrolysis of the ester thus produced followed by the action of *p*-toluenesulphonyl chloride on the portion soluble in alkali hydroxide into N-p-*toluenesulphonyl*-βγ-*diphenylpropylaminoacetic acid*, m. p. 135° (the corresponding *benzenesulphonyl* derivative is non-crystalline). Ring closure is effected by treating the glycine derivative with phosphoric oxide in boiling xylene, whereby carbon monoxide and 2-p-*toluenesulphonyl*-4-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, m. p. 158—160°, are produced in almost 100% yield. The sulphonyl compound is hydrolysed by hydrochloric acid at 160° to 4-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, b. p. 204—205°/15 mm., m. p. 49—50° (*hydrochloride*, m. p. 155°; *picrate*, m. p. 150°; non-crystalline *acetyl* derivative; *nitroso*-compound, m. p. 100°; *phenylthiocarbamide*, m. p. 166°; quaternary *methiodide*, m. p. 186°). Dehydrogenation to 4-benzyl*iso*quinoline, m. p. 119°, is effected by reduced nickel. The tendency towards the formation of the tetrahydro*iso*quinoline ring is therefore greater than that towards the homotetrahydro*iso*quinoline complex.

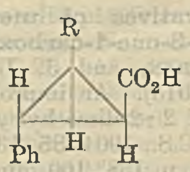
H. WREN.

Degradation of truxillic and truxinic acids. XIII. R. STOERMER and F. SCHENCK [in part, with E. PANSEGRAU] (Ber., 1927, 60, [*B*], 2566—2591).—Revision of the attempted decarboxylation of a truxillic acid to a diphenyl*cyclo*butanemonocarboxylic acid (Stoermer and Schmidt, A., 1926, 290) has been rendered necessary by the observation that four different anhydrides of *cis*-hydroxy-acids can be derived from a single truxillic acid, whereas only three such compounds are theoretically derivable from hydroxydiphenyl*cyclo*butanemonocarboxylic acids. An explanation is found in the contraction of the ring during the replacement of the amino- by the hydroxyl group in the aminodiphenyl*cyclo*butanemonocarboxylic acids so that these acids are phenyl-α-hydroxybenzyl*cyclo*propanecarboxylic acids. Since they contain four dissimilar asymmetric carbon atoms they exist theoretically in four pairs of racemic forms :

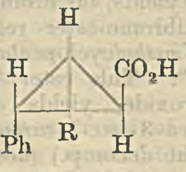
(I *a*, *b*.)



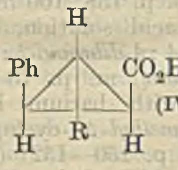
(II *a*, *b*.)



(III *a*, *b*.)



(IV *a*, *b*.)



(R=Ph·CH·OH), the isomerism within each pair being due to the spatial arrangement around the carbinol carbon atom. If the isomerism in this position is destroyed, four keto-acids (R=PhCO·) are produced. The constitution of the ketonic acids is established by the identity of two of them with the acids obtained in a completely different manner by Kohler (A., 1917, i, 566, 568; 1919, i, 530) and by the isolation from them of compounds in which the phenyl groups are separated from one another by a chain of four carbon atoms and not by two or three as in the *cyclo*butane formulation of the truxinic and truxillic acids. The configuration of the hydroxy-acids is tentatively based on that of the corresponding truxillic and truxinic acids on the supposition that if the phenyl and carboxyl groups maintain their relative positions after the action of nitrous acid it is possible that they also do so, at any rate as far as the main products of the change are concerned, when the ring contracts.

Degradation of γ-truxillic acid. γ-Truxillamic acid is converted by sodium hypochlorite at 35—37° into 3^c-*amino*-2^c : 4^t-*diphenyl*cyclo*butane*-1^c-*carboxylic acid*, decomp. 195—196° (*trihydrate*; *methyl* ester, m. p. 83·5—84°; *monoacetyl* derivative, m. p. 236—237°). The action of nitrosyl bromide on the amino-acid yields small amounts of diphenylbutadiene tetrabromide and a mixture of lactones (see later), mainly 2^c-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylactone* (cf. I*a*), m. p. 133·5—134°, obtained also by Barbels (Diss., Rostock, 1924) from α-truxillamic acid. When distilled in a vacuum the lactone yields *trans*-*trans*-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene. With piperidine at 160—170° it affords the *piperidide* of the corresponding hydroxy-acid, m. p. 162·5—163°, whilst it is transformed by boiling alcoholic potassium hydroxide into 2^c-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylic acid* (I*a*), m. p. 145—146° (decomp.) when rapidly heated (*methyl* ester, m. p. 124—125°, prepared by means of diazomethane). The latter ester is oxidised by an excess of chromium trioxide in glacial acetic acid to *methyl* 3^c-*benzoyl*-2^c-*phenyl*cyclo*propane*-1^c-*carboxylate* (cf. I), m. p. 115—116°, which is stable towards Fehling's solution and ammoniacal silver solution, moderately stable to alkaline permanganate and bromine in chloroform; the corresponding *oxime*, m. p. 201—202°, and *semicarbazone*, m. p. 253—255°, are described. Hydrolysis of the ester by acids affords 3^c-*benzoyl*-2^c-*phenyl*cyclo*propane*-1^c-*carboxylic acid*, m. p. 157—157·5°, isomerised by alcoholic potassium hydroxide to 3^t-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylic acid (see later), and reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid. The isomeric 2^c-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylactone* (cf. I*b*), m. p. about 167°, is obtained in very small amount from the mixture of lactones described above; the corresponding hydroxy-acid (I*b*) could not be investigated completely but its oxidation to the ketonic acid I is established.

2^t-*Phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylactone*, m. p. 120—121° (cf. II*a*), is most readily separated from lactone I*a* by isomerisation of the latter to the hydroxy-acid II*a* by alkali and preservation of the acidified mixture in which the lactone II*a* is slowly regenerated. Unlike lactone I*a* it can be distilled unchanged in a vacuum. It is hydrolysed to 2^t-*phenyl*-3^c-*hydroxylbenzyl*cyclo*propane*-1^c-*carboxylic acid* (II*a*), m. p. 122° (decomp.) (*methyl* ester, m. p. 73—74°; *piperidide*, m. p. 132—133°). The methyl ester is oxidised to *methyl* 3^c-*benzoyl*-2^t-*phenyl*cyclo*propane*-1 -*carboxylate*, m. p. 93°, hydrolysed by acids to 3^c-benzoyl-2^t-phenyl*cyclo*propane-1^c-carboxylic acid, m. p. 174—175° (ethyl ester, m. p. 103°), identical with the product described by Kohler and Steele (*loc. cit.*). The isomeric 2^t-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylic acid* (II*b*), m. p. 170° (decomp.) when rapidly heated (*methyl* ester, m. p. 86—87°), is identical with the compound obtained by Stoermer and Schmidt (*loc. cit.*) from ε-truxillamic acid and regarded as hydroxydiphenyl*cyclo*butanecarboxylic acid; the corresponding *lactone*, m. p. 112°, is obtained by the action of acetic anhydride on the acid and also from β-truxinic acid (see later). 2^t-*Phenyl*-3^t-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylic acid* (III*a*), decomp. 185—186°, is obtained by isomerisation of lactone I*a* by very concentrated alcoholic potassium hydroxide or from α-truxillamic acid through the corresponding amino-acid; the *methyl* ester, m. p. 75—76°, and the *potassium* salt are described. It is oxidised to 3^t-benzoyl-2^t-phenyl*cyclo*propane-1^c-carboxylic acid, m. p. 153—154° (*methyl* ester, m. p. 66—67°; ethyl ester, m. p. 93—94°), identified with the compound described by Kohler (*loc. cit.*); the keto-acid is reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid, whereas the ethyl ester is converted by zinc dust and boiling acetic acid into a mixture of α-phenacyl-β-phenylpropionic and γ-benzoyl-β-phenyl-*n*-butyric acids.

Methyl 3^c-benzoyl-2^c-phenyl*cyclo*propane-1^c-carboxylate is converted by boiling alcoholic potassium hydroxide into 3^t-*benzoyl*-2^c-*phenyl*cyclo*propane*-1^c-*carboxylic acid* (cf. IV), m. p. 136—137° (*methyl* ester, m. p. 66—67·5°; *oxime*, m. p. 166—167°), reduced by hydrogen in the presence of palladised barium sulphate to α-phenacyl-β-phenylpropionic acid. *trans*-*trans*-αδ-Diphenyl-$\Delta^{\alpha\gamma}$-butadiene, m. p. 152—153°, is obtained by the distillation of lactones I*a* and II*b*, by heating the methyl ester of hydroxy-acid I*a*, when the hydroxy-acid III*a* is melted, and during the preparation of its bromo-ester. The non-crystallisable residues obtained during the preparation of lactone I*a* are converted by distillation into *trans*-*trans*-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene and γ-phenyl-α-benzylidene-*iso*crotonolactone, m. p. 152°. Treatment of methyl 2^c-phenyl-3^c-hydroxybenzyl*cyclo*propane-1^c-carboxylate with phosphorus pentabromide in the presence of ether affords the *compound* $C_{18}H_{17}O_2Br$, m. p. 131—132° [? $CHPh{:}CH{\cdot}CH(CO_2H){\cdot}CHPhBr$], hydrolysed by alcoholic potassium hydroxide to α-benzylidene-γ-phenyl*iso*crotonic acid, m. p. 169—170°, and converted by successive reduction by aluminium amalgam and hydrolysis into γ-phenyl-α-benzyl*iso*crotonic acid, m. p. 125—126°. Treatment of the bromo-ester with hydrogen in the presence of palladised barium sulphate affords αδ-diphenylbutane-β-carboxylic acid, m. p. 55—57°.

Degradation of β-truxinic acid. β-Truxinamic acid is converted by sodium hypochlorite solution at 38—40° into 4^c-*amino*-2^t : 3^t-*diphenyl*cyclo*butane*-1^c-

carboxylic acid, m. p. 161° (decomp.) [*hydrochloride*; *hydrobromide*; *sulphate*; *monoacetyl* derivative, m. p. 194°, and its *methyl* ester, m. p. 127—128°; *methyl* ester, m. p. 64°; *compound*, $C_{34}H_{29}O_3N$, m. p. 161°, possibly a mixed anhydride of the amino- and corresponding hydroxy-acid). The amino-acid is transformed by nitrosyl bromide into 2^t-phenyl-3^c-hydroxylbenzy*cyclo*propane-1^c-carboxylactone (cf. II*b*), the corresponding hydroxy-acid (II*b*), and 2-*phenyl*-3-α-*bromobenzyl*cyclo*propanecarboxylic acid*, m. p. 167° (*methyl* ester, m. p. 112°, obtained also from phosphorus pentabromide and the methyl ester of the hydroxy-acid). Reduction of the bromo-acid by zinc dust and acetic acid, hydriodic acid, aluminium, or sodium amalgam or catalytic hydrogenation in the presence of palladised barium sulphate yields the unsaturated *acid*, $C_{17}H_{14}O_2$, m. p. 125—126°. *Methyl* 2^t-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylate*, m. p. 86—87°, and 2^t-*phenyl*-3^c-*hydroxybenzyl*cyclo*propane*-1^c-*carboxylamide*, m. p. 142°, are described.

β-Truxinic anhydride is converted by an excess of hydrazine hydrate at 0° into the *hydrazine* salt of β-truxinhydrazidic acid, hydrolysed by much boiling water to β-*truxinhydrazidic acid*, $C_{18}H_{18}O_2N_3$, m. p. 182° (*sodium* salt; *benzylidene* derivative, $C_{25}H_{22}O_3N_2$, m. p. 214°, and its *methyl* ester, $C_{26}H_{24}O_2N_3$, m. p. 142°). The acid is converted by hot 5% hydrochloric acid into the unimolecular *hydrazide*, $C_{18}H_{16}O_2N_2$, m. p. 106—107° (from which it is regenerated by boiling alkali hydroxide), and (?) a bimolecular, secondary hydrazide, m. p. 250—260°. Attempts to convert the hydrazidic acid into the azidic acid were unsuccessful, resulting apparently in the production of a carbamide *derivative*, $CO(NH{\cdot}C_{16}H_{14}{\cdot}CO_2H)_2$, m. p. 224°. H. WREN.

Photobromination of ethyl *m*-nitrobenzylidenemalonate. I. J. C. GHOSH and K. BASU (J. Indian Chem. Soc., 1927, 4, 375—386).—The photobromination of ethyl *m*-nitrobenzylidenemalonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light, and the ratio of the equilibrium constants measured equals the square root of the ratio of intensities of incident light. The equilibrium constant is slightly affected by temperature, rise of temperature causing an increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentration of ester, bromine, or dibromide. The temperature coefficient of *k* for 10° is 2·4. Application of Einstein's law of photochemical equivalence shows that more than one quantum of energy is necessary for the production of 1 mol. of the dibromide. H. BURTON.

Relation between chemical constitution and pungency in acid amides. S. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 166—184; cf. Jones and Pyman, A., 1926, 60).—The following acid amides have been prepared and their pungencies compared with that of undecenovanillylmethylamide (=1000), m. p. 60—61° (Nelson, A., 1920, i, 154, gives m. p. 53—55°; cf. Ott and Zimmermann, A., 1922, i, 137); undecovanillylmethylamide, m. p. 73—74° (Nelson, *loc. cit.*, gives m. p. 54—56°) (pungency 1000); *undeceno*-β-*vanillylethylamide*, m. p. 80—81° (O-*benzyl* derivative, m. p. 102—103°), *undeceno*-γ-*vanillylpropylamide*, m. p. 59—60°, *undecenopiperonylmethylamide*, m. p. 87—88°, and *undeceno*-β-*piperonylethylamide*, m. p. 81—82°, are all non-pungent. The pungencies of δ-*piperonylvinylacrylovanillylmethylamide*, m. p. 165—167°, and δ-*piperonyl*-n-*valerovanillylmethylamide*, m. p. 90—91°, are both 100, whilst the *piperonylmethylamide*, m. p. 187—189°, and β-*piperonylethylamide*, m. p. 198—200°, of δ-piperonylvinylacrylic acid are non-pungent, thus demonstrating the necessity of a hydroxyl group in the amine residue. Cinnamovanillylmethylamide, m. p. 146—147° (Ott and Zimmermann, *loc. cit.*, give m. p. 138°), β-*phenylpropiovanillylmethylamide*, m. p. 91—92°, and β-*piperonylacrylovanillylmethylamide*, m. p. 189—190°, have pungencies of 50; n-*valerovanillylmethylamide* has a value of 20, and β-*veratrylacrylovanillylmethylamide*, m. p. 145·5—147°, a value of 1. β-*Vanillylacrylobenzylamide*, m. p. 128·5—130° (O-*acetyl* derivative, m. p. 132—134°), β-*vanillylacrylopiperonylmethylamide*, m. p. 161—163° (O-*acetyl* derivative, m. p. 154·5—155·5°), and the *vanillylmethylamides* of β-vanillylacrylic, m. p. 179—181°, 4-hydroxycinnamic, m. p. 192—193°, and β-vanillylpropionic acids, m. p. 128—130°, are all non-pungent. The *carbethoxy*-derivative (*chloride*) of β-4-hydroxy-3-methoxyphenylpropionic acid has m. p. 88—90°.

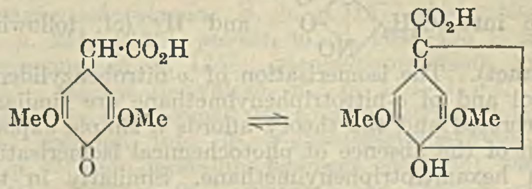
4-Benzyloxy-3-methoxybenzaldehyde condenses with acetaldehyde to form 4-*benzyloxy*-3-*methoxycinnamaldehyde*, m. p. 89—90° (*phenylhydrazone*, m. p. 144—146°). An improved method of preparing 3-methoxy-4-methoxymethoxycinnamaldehyde, m. p. 78—79° (cf. Pauly and Wäscher, A., 1923, i, 342), is given. Application of the Perkin reaction to this substance yields 3-*methoxy*-4-*methoxymethoxyphenylvinylacrylic acid*, m. p. 145·5—146·5°, which is hydrolysed by dilute hydrochloric acid to the corresponding 4-*hydroxy-acid*, m. p. 193—194° (decomp.) (*carbethoxy*-derivative, m. p. 143—145°). 3 : 4-Methylenedioxybenzylamine (hydrochloride, m. p. 238—239°; cf. A., 1912, i, 217) has b. p. 135—137°/12 mm., and *di*-(3 : 4-*methylenedioxybenzyl*)*amine hydrochloride* has m. p. 257—258° (decomp.). H. BURTON.

Double compounds of α-unsaturated acid amides with acid and ammonia. S. KOBAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 185—195).—Treatment of a solution of β-*O*-acetylvanillylacrylobenzylamide in acetic acid with concentrated sulphuric acid gives a *compound*, m. p. 147—150°, consisting of 1 mol. of β-vanillylacrylobenzylamide and 1 mol. of sulphuric acid, which on exposure to air loses 0·5 mol. of sulphuric acid forming a *compound*, m. p. 170—173°. β-Vanillylacrylobenzylamide and hydrochloric acid or ammonia yield the additive *compounds*, $C_{17}H_{17}O_3N,HCl$, m. p. 106° (decomp.), and $C_{17}H_{17}O_3N,NH_3$, m. p. 126° (decomp.). The hydrochloric acid *compound* of the *O*-acetyl derivative has m. p. 163° (decomp.). The following additive compounds have been isolated and, except where stated, contain 1 mol. of the amide and

1 mol. of the reagent: β-vanillylacrylopiperonylmethylamide [*sulphuric acid*, $+0\cdot5H_2SO_4$, m. p. 201° (decomp.); *hydrochloric acid*, m. p. 134° (decomp.); *ammonia*, m. p. 161—163°; O-*acetyl hydrochloric acid*, m. p. 118—142°]; β-vanillylacrylovanillylmethylamide [*sulphuric acid*, m. p. 161—162° (decomp.); *hydrochloric acid*, m. p. 132° (decomp.)]; β-O-*acetylvanillylacryloanilide*, m. p. 146—147° [*sulphuric acid*, m. p. 138° (decomp.); *hydrochloric acid*, m. p. 107° (decomp.)]; β-*vanillylacryloanilide*, m. p. 141—143° [*sulphuric acid* $+0\cdot5H_2SO_4$, m. p. 185° (decomp.); *hydrochloric acid*, m. p. 121° (decomp.); *ammonia*, m. p. 141°]; β-*vanillylacryloamide*, m. p. 150—151° [*ammonia*, m. p. 156°; *sulphuric acid*, m. p. 184° (decomp.); *hydrochloric acid*, m. p. 172° (decomp.)]; δ-piperonylvinylacrylo-β-piperonylethylamide (*sulphuric acid*, m. p. 140—141°, $+0\cdot5H_2SO_4$, m. p. 169—170°; *hydrochloric acid*, m. p. 198—200°); δ-piperonylvinylacrylopiperonylmethylamide [*sulphuric acid*, m. p. 142—145° (decomp.); *hydrochloric acid*, m. p. 187—189°]; δ-piperonylvinylacrylovanillylmethylamide [*hydrochloric acid*, m. p. 180° (decomp.)]; *p*-hydroxycinnamamide [*hydrochloric acid*, m. p. 202° (decomp.); *ammonia*, m. p. 188°]; 3 : 4-methylenedioxycinnamamide and cinnamamide yield hydrochloric acid *compounds* having m. p. 178° (decomp.) and 147° (decomp.), respectively. Most of these additive compounds are coloured, and the ammonia additive products generally lose ammonia when heated. H. BURTON.

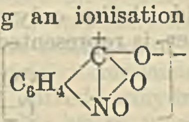
Perylene and its derivatives. XV. A. PONGRATZ (Monatsh., 1927, 48, 639—643).—The yield of perylene-3 : 9-dicarboxylic acid is increased to 90% by modifying the conditions of hydrolysis of the dinitrile (cf. A., 1927, 1190). If hydrolysis by heating with concentrated sulphuric acid is attempted, the solution deposits orange-red crystals of 9-*carboxyperylene*-4-*sulphon*-3-*carboxylimide*. Similarly, the action of concentrated sulphuric acid on perylene-3 : 9-dicarboxylic acid yields orange-red 9-*carboxyperylene*-4-*sulpho*-3-*carboxylic anhydride*. The action of concentrated sulphuric acid followed by manganese dioxide on 3 : 9-dibenzoylperylene yields a vat dye, *hydroxyisoviolanthrone* (cf. Zinke, A., 1925, i, 819; F.P. 612338; B., 1927, 698). E. W. WIGNALL.

Bios. III. B. SUZUKI and Y. HAMAMURA (Proc. Imp. Acad. Tokyo, 1927, 3, 521—525).—Treatment of crude bios with boiling 30% sodium hydroxide solution and an excess of alcohol yields resinous products, together with "*γ-acid*," $C_{10}H_{10}O_5$, m. p. 187—189° (decomp.) (*benzoyl* derivative, m. p. 216°; *ethyl* ester, m. p. 86°), which is methylated by methyl sulphate to a *methyl-γ-acid*, m. p. 130°, and its *methyl* ester, m. p. 100°. Oxidation of the methylated acid with potassium permanganate furnishes 3 : 4 : 5-*trimethoxybenzoic acid*, m. p. 169°. Ethylation of the acid yields *ethyl-γ-acid*, oxidised by potassium permanganate to 3 : 5-*dimethoxy*-4-*ethoxybenzoic acid*, m. p. 123°, also obtained by ethylation of syringic acid. Reduction of γ-acid by Willstätter's method affords *dihydro-γ-acid*, m. p. 102°, which yields a *methyl* derivative, m. p. 105° (*dibromo*-derivative, m. p. 122°). The original acid furnishes an *oxime*, decomp. 199—201°, in acid solution only. The acid, which is a colouring matter, is represented as

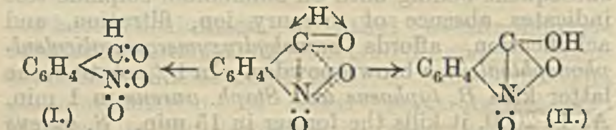


H. BURTON.

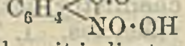
Salicylsulphonephthalein and its tetrabromo- and monomercury derivatives. W. C. HARDEN (J. Amer. Chem. Soc., 1927, 49, 3139—3142).—*Salicylsulphonephthalein*, red, amorphous, is obtained by heating together salicylic acid (50 g.), *o*-sulphobenzoic anhydride (24 g.), sulphuric acid (2 c.c.), and stannic chloride (10 c.c.) at 120—130° for 4 hrs., then at 160—180° for several hrs., and pouring the mass into 4 litres of hot water, purification being effected by repeated dissolution in, and reprecipitation with hydrochloric acid from, aqueous sodium carbonate. It forms an excellent indicator, being yellow at p_H below 6·6, brown at p_H 7·0—7·2, and bluish-red at p_H 8·2. Bromination in hot glacial acetic acid affords a *tetrabromo*-derivative, yellow, amorphous, which is yellow at p_H below 3·2, changing through a brownish-purple to clear purple at p_H 4·6. Colour standards prepared with these indicators showed no appreciable fading after several months' exposure to daylight; the names "salicyl-red" and "salicyl-purple" are suggested. Treatment of the disodium salt of salicylsulphonephthalein in aqueous solution with mercuric acetate and acetic acid, with subsequent boiling until an ammonium sulphide test indicates absence of mercury ion, filtration, and acidification, affords *monohydroxymercurisalicylsulphonephthalein*, a brown powder. In 1% solution, the latter kills *B. typhosus* and *Staph. aureus* in 1 min. At 1 : 2000, it kills the former in 15 min. *S. aureus* is killed at 1 : 500 in 5 min., but not in 15 min. at 1 : 1000. F. G. WILLSON.

Explanation of the mechanism of isomerisations and spontaneous reactions in organic chemistry with the aid of the theory of polar valencies. I. TANASESCU (Bull. Soc. chim., 1927, [iv], 41, 1468—1475).—It is suggested that organic molecules which do not form ions in the usual sense can be regarded as virtually divided into atomic groups, consisting either of atoms or radicals which carry equal and opposite electric charges. These electronegative and electropositive radicals represent the first phase in the division of the molecule. They are not necessarily ionised, but can become true ions in certain cases. Groupings in which the polar valencies are not perfectly neutralised are unstable and may undergo transformation into arrangements possessing a more pronounced positive or negative character, and representing the most stable configuration under given conditions. This theory is used to interpret a number of isomerisations effected by light. Thus the isomerisation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid is interpreted by assuming an ionisation of the *o*-nitrobenzaldehyde into  and H⁺ (cf. following abstract). The isomerisation of *o*-nitrobenzylideneglycol and of *o*-nitrotriphenylmethane are similarly interpreted and the theory affords a simple explanation of the absence of photochemical isomerisation with hexanitrotriphenylmethane. Similarly in the isomerisation of *o*-nitro-*p'p''*-diaminotriphenylmethane into *o*-nitroso-*p'p''*-diaminotriphenylcarbinol it is suggested that the unstable ions $[{}^{-}C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NO_2]^+$ and H^- are first formed which are rapidly transformed into $[{}^{-}C(C_6H_4{\cdot}NH_2)_2{\cdot}C_6H_4{\cdot}NO]^+$ and OH^-, an interpretation which accords with increase of basic properties in the carbonium bases with the accumulation of electropositive groups in the molecule observed by Bayer. Similarly, the stability of the "ions" $[{}^{-}\overset{(1)}{C}(C_6H_4{\cdot}\overset{(4)}{O}H)_3]^-$ and H^+ accounts for the nonexistence of the corresponding carbinol. *cis*- and *trans*-Isomerisations and the behaviour of *αγ*-diketones are similarly interpreted. R. BRIGHTMAN.

Tautomerism of *o*-nitrobenzaldehyde. I. TANASESCU (Bull. Soc. chim., 1927, [iv], 41, 1497—1499).—To account for the existence of a mobile hydrogen atom in *o*-nitrobenzaldehyde, the weak but appreciable acidity, and the readiness with which this substance isomerises in light, it is now suggested (cf. A., 1926, 1247) that the molecule of *o*-nitrobenzaldehyde represents an equilibrium between (I) and (II), determined by oscillation of a hydrogen atom between the carbon and oxygen atom. The formula



(I.) (II.)

(II) allows of a ready interpretation of the formation of arylanthranils by the action of aromatic hydrocarbons in presence of sulphuric acid, and of the appearance of the direct carbon–nitrogen linking in similar reactions. The structure  $C_6H_4{<}\begin{smallmatrix}C{:}O\\NO{\cdot}OH\end{smallmatrix}$ previously advanced is now abandoned, as it indicates much more pronounced acidic properties than *o*-nitrobenzaldehyde possesses. R. BRIGHTMAN.

Isomerism of the oximes. XXXII. Sulphates. O. L. BRADY and A. D. WHITEHEAD (J.C.S., 1927, 2933—2937).—Treatment of certain α-aldoximes (A) with concentrated sulphuric acid provides a convenient method of conversion into the β-aldoxime (cf. Luxmoore, J.C.S., 1896, 69, 180) if only small quantities are used. The sulphates of a number of oximes have been prepared and, in general, the α-form of these compounds is more stable than the corresponding hydrochloride. Sulphuric acid did not bring about isomeric change in those oximes (B) the α-hydrochlorides of which fail to change or change with difficulty to the β-form, nor was it possible to convert those α-oximes (C) which did not form hydrochlorides although the sulphates were isolated. Prolonged heating of aldoximes at 100° with concentrated sulphuric acid resulted in the formation of the corresponding amides. The following are described: (A) α-m-*nitrobenzaldoxime sulphate*, m. p. 71—76°, p-*nitrobenzaldoxime sulphate*, deliquescent, and α-p-*methoxybenzaldoxime sulphate*, m. p. 79—80°; (B) α-o-*methoxybenzaldoxime sulphate*, m. p. 143°, and α-o-*chlorobenzaldoxime sulphate*; (C) α-6-*bromo*-3 : 4-*dimethoxybenzaldoxime sulphate*, m. p. 105°, and α-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime sulphate*, m. p. 110—135°; and α-3 : 4-*methylenedioxybenzaldoxime sulphate*, unstable. M. CLARK.

Reimer–Tiemann reaction with *m*-bromo- and *m*-iodo-phenol. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1927, 3041—3044).—A mixture of 4-bromo-2-hydroxybenzaldehyde (I) [*sodium*, *potassium*, and *copper* salts; oxime, m. p. 168° (lit. 151°); p-*nitrophenylhydrazone*, m. p. 258° (decomp.); *semicarbazone*, m. p. 212°; *benzoate*, m. p. 115°] and 2-bromo-4-hydroxybenzaldehyde [p-*nitrophenylhydrazone*, m. p. 274° (decomp.); *semicarbazone*, m. p. 212°; oxime, m. p. 184° (lit. 128·5°)] in almost equal proportions is obtained from *m*-bromophenol by the Reimer–Tiemann reaction. *m*-Iodophenol yields in like manner approximately equal quantities of 4-*iodo*-2-*hydroxybenzaldehyde*, m. p. 87° [*alkali-metal*, *ammonium*, *silver*, and *copper* salts; *oxime*, m. p. 171°; p-*nitrophenylhydrazone*, m. p. 242° (decomp.); *semicarbazone*, m. p. 252°; *benzoate*, m. p. 62°], and 2-*iodo*-4-*hydroxybenzaldehyde*, m. p. 163° [*alkali-metal* and *copper* salts; p-*nitrophenylhydrazone*, m. p. 265° (decomp.); *semicarbazone*, m. p. 232° (decomp.); *oxime*, m. p. 155°; *benzoate*, m. p. 112°]. The constitutions of the aldehydes are determined by the method already described for the corresponding chlorohydroxybenzaldehydes (A., 1927, 877). The following are also described: 4-*bromo*-2-*methoxybenzaldehyde*, m. p. 71° (*oxime*, m. p. 132°; p-*nitrophenylhydrazone*, m. p. 215°; *semicarbazone*, m. p. 224°); 4-*bromo*-2-*methoxybenzoic acid*, m. p. 155°; 4-*bromo*-2-*hydroxybenzoic acid*, m. p. 214°; 2-*bromo*-4-*methoxybenzaldehyde*, m. p. 77° [*oxime*, m. p. 93°; p-*nitrophenylhydrazone*, m. p. 250° (decomp.); *semicarbazone*, m. p. 232°]; 2-*bromo*-4-*methoxybenzoic acid*, m. p. 199°; 2-*bromo*-4-*hydroxybenzoic acid*, m. p. 151°; 4-*iodo*-2-*methoxybenzaldehyde*, m. p. 85° [*oxime*, m. p. 138°; p-*nitrophenylhydrazone*, m. p. 238° (decomp.); *semicarbazone*, m. p. 228°]; 4-*iodo*-2-*methoxybenzoic acid*, m. p. 150°; 4-*iodo*-2-*hydroxybenzoic acid*, m. p. 230° (decomp.); 2-*iodo*-4-*methoxybenzaldehyde*, m. p. 115° [p-*nitrophenylhydrazone*, m. p. 247° (decomp.); *semicarbazone*, m. p. 211°; *oxime*, m. p. 101°]; 2-*iodo*-4-*methoxybenzoic acid*, m. p. 184°; 2-*iodo*-4-*hydroxybenzoic acid*, m. p. 179° (decomp.). M. CLARK.

Vanillin derivatives. G. C. HILMAN and O. H. ALDERKS (Proc. Iowa Acad. Sci., 1926, 33, 175).—A dibromovanillin (under investigation) gives an oxime which exists in but one form, and the nitrile derived from it is very resistant to hydrolysis. CHEMICAL ABSTRACTS.

Mechanism of the catalytic hydrogenation of phenols. V. GRIGNARD and G. MINGASSON (Compt. rend., 1927, 185, 1552—1556).—Catalytic reduction of phenol in *cyclo*hexanol solution (the critical temperatures above which dehydrogenation of the latter to *cyclo*hexanone occurs being 155°/18—22 mm., 157°/30 mm., 160°/50 mm., 170°/100 mm., 175°/200 mm., and 180°/760 mm.) at 150°/18—22 mm. with a nickel catalyst yields only the *enol* form, b. p. 55°/12 mm., of *cyclo*hexanone (12—15% yield), since the active hydrogen in the product, determined by the method of Job and Reich (A., 1924, i, 24), is 100%. Fractional distillation of the product obtained by treating the reduction mixture with acetic anhydride and fused sodium acetate yields *cyclo*hexyl acetate, phenyl acetate, and the *acetate*, b. p. 75—77°/17 mm., d_{15}^{4} 1·0237, n_{D}^{25} 1·4732, of the enol, which is stable to boiling water but is hydrolysed to the free enol by boiling with a 10% solution of oxalic acid for 5 hrs. By similar reductions of the appropriate phenols are obtained the *enols* of *p*-methyl*cyclo*hexanone, n_{D}^{13} 1·45507 for a mixture containing 80% of enol (*acetate*, b. p. 92—93°/12 mm., 191—192°/760 mm., d_{24}^{4} 0·9813; n_{D}^{14} 1·46086), and carvomenthone, b. p. 104—106°/11 mm., n_{D}^{20} 1·4624 (75% enol) (*acetate*, b. p. 103—105°/11 mm., d_{13}^{4} 0·947, n_{D}^{13} 1·46196). Reduction of phenols therefore occurs by direct addition of hydrogen to the two double linkings in the Kekulé formula not contiguous to the hydroxyl group, the resulting enol of the cyclic ketone then either ketonising or being further reduced to the secondary alcohol. J. W. BAKER.

Odour and molecular asymmetry. IV. The three 3 : 5-dimethyl*cyclo*hexanones and the four 3 : 5-dimethyl*cyclo*hexanols. J. VON BRAUN and E. ANTON (Ber., 1927, 60, [*B*], 2438—2446; cf. A., 1926, 1142).—*s*-*m*-Xylenol is hydrogenated to a mixture of 3 : 5-dimethyl*cyclo*hexanols, which is oxidised to a mixture of 3 : 5-dimethyl*cyclo*hexanones. Oximation of the latter gives a crystalline and a liquid oxime. Reduction of the liquid compound affords *r*-3 : 5-dimethyl*cyclo*hexylamine, which cannot be satisfactorily resolved by camphorsulphonic, bromocamphorsulphonic, or mandelic acids, but from which by means of *d*-tartaric acid in aqueous solution l-3 : 5-*dimethyl*cyclo*hexylamine* is obtained. Lack of material prevented the preparation of the homogeneous *d*-base by means of *l*-tartaric acid. The bases are converted by sodium nitrite in cold, dilute acetic acid solution into l-3 : 5-*dimethyl*cyclo*hexanol*, b. p. 89—90°/17 mm., d_{4}^{20} 0·9166, $[\alpha]_{D}^{17}$ −7·74°, and non-homogeneous d-3 : 5-*dimethyl*cyclo*hexanol*, b. p. 89—90°/17 mm., d_{4}^{20} 0·9146, $[\alpha]_{D}^{20}$ +4·55°, which are oxidised by potassium dichromate and sulphuric acid to l-3 : 5-*dimethyl*cyclo*hexanone*, b. p. 67—68°/16 mm., d_{4}^{20} 0·9074, $[\alpha]_{D}^{20}$ −7·91° (*semicarbazone*, m. p. 189°), and d-3 : 5-*dimethyl*cyclo*hexanone*, b. p. 67—68°/16 mm., d_{4}^{20} 0·9083, $[\alpha]_{D}^{20}$ +4·65° (*semicarbazone*, m. p. 187—189°).

The two inactive 3^{c} : 5^{c}-dimethyl*cyclo*hexylamines obtained by reduction of the crystalline oxime, m. p. 73° (see above), are separated from one another by crystallisation of their benzoyl derivatives from 96% alcohol. Hydrolysis of the homogeneous derivatives with concentrated hydrochloric acid affords 3^{c} : 5^{c}-*dimethyl*cyclo*hexylamine* A, b. p. 167° (*hydrochloride*, m. p. 235—237°; *picrate*, m. p. 205°; *acetyl* compound, m. p. 137°; *phenylthiocarbamate*, m. p. 181°; *benzoyl* derivative, m. p. 162—163°), and 3^{c} : 5^{c}-*dimethyl*cyclo*hexylamine* B, b. p. 167° (*hydrochloride*, m. p. 211—213°; *picrate*, m. p. 194—195°; *acetyl* compound, m. p. 125°; *phenylthiocarbamate*, m. p. 165°; *benzoyl* derivative, m. p. 116—117°). The base *A* is transformed by sodium nitrite in acetic acid solution into 3^{c} : 5^{c}-*dimethyl*cyclo*hexanol* A, m. p. 41° (non-crystalline *hydrogen phthalate*; *phenylurethane*, m. p. 96°), whereas the base *B* yields 3^{c} : 5^{c}-*dimethyl*cyclo*hexanol* B, m. p. 16—17° (*hydrogen phthalate*, m. p. 105—106°). The alcohol *A* appears to undergo partial isomerisation to alcohol *B* when distilled. The crystals which separate from the mixture of dimethyl*cyclo*hexanols derived from xylenol consist of a mixture of alcohols *A* and *B*, which can be separated into its components by conversion by the successive action of sodium in ether and phthalic anhydride into the corresponding hydrogen phthalates and crystallisation of the latter from dilute alcohol; treatment with phthalic anhydride at 140° results in the production of much dimethyl*cyclo*hexene. Oxidation of either alcohol affords 3^{c} : 5^{c}-dimethyl*cyclo*hexanone (oxime, m. p. 73°). The alcohol of m. p. 17° has a pronounced odour of mint, whereas that of m. p. 41° more closely resembles stored acetone. The optically active alcohols have sweeter odours analogous to those of certain amyl esters; the odour of the *d*-form is fresher and more powerful than the milder and heavier odour of the *l*-variety. Similar differences in odour are observed among the ketones.

The mixture of the two optically inactive dimethyl*cyclo*hexanols is converted by phosphorus tribromide at 0° into a mixture of the corresponding *bromides*, b. p. 81—82°/14 mm., which with magnesium and carbon dioxide affords a readily separable mixture of the 3^{c} : 5^{c}-*dimethyl*cyclo*hexylcarboxylic acids*, m. p. 68° (corresponding *amide*, m. p. 160°), and non-crystalline, d_{4}^{20} 0·9776 (corresponding *amide*, m. p. 148—149°). Probably other compounds of the 3 : 5-dimethyl*cyclo*hexane series containing a pseudo-asymmetric carbon atom in position 1 may be separated with comparative ease. H. WREN.

Pyrogenic decomposition of cyclic ketones. V. IPATIEV and A. PETROV (Ber., 1927, 60, [*B*], 2545—2548; cf. A., 1927, 1076).—Homo*iso*phorone, in the form of a mixture of four possible isomerides obtained by condensation of methyl ethyl ketone under the influence of sodamide, is decomposed when heated under high pressure at 470—480° in the presence of ferric oxide into gases, carbon, phenols approximating to xylenol in composition, and comparatively small amounts of hydrocarbons, b. p. 60—240°. 2-Methyl*cyclo*hexanone decomposes at 470—490°, giving a mixture of hydrocarbons closely analogous to that obtained from *cyclo*hexanone; toluene is present in traces, whereas phenols are completely absent. Condensation products of high b. p. are formed in small amount. At 380—400° pulegone affords phenols, cyclic and unsaturated hydrocarbons, and cymene. The absence of thymol is due to its conversion under these conditions into a complex mixture of phenols. H. WREN.

Azomethine derivatives of fluorene. A. Novelli (Anal. Asoc. Quím. Argentina, 1927, **15**, 187—209).—The formation of azomethines by the reaction of fluorene derivatives with nitroso-compounds is discussed in relation to the activation of methylene groups and the relation between colour and constitution. Although dibenzo*cyclo*pentadiene-imine is colourless, the substituted phenylimines (azomethines) are deep red. Condensation of 2 : 7-dibromofluorene with *p*-nitrosoalkylanilines takes place in boiling alcoholic solution, readily on the addition of alcoholic sodium ethoxide, less readily with potassium cyanide. The following 2 : 7-*dibromodibenzo*cyclo*pentadiene-imines* were prepared: p-*dimethylaminophenyl-*, m. p. 205—206°; p-*diethylaminophenyl-*, m. p. 176° (*hydrochloride*, m. p. 185—186°); p-*methylaminophenyl-*, m. p. 201—202°; p-*ethylaminophenyl-*, m. p. 171°, and p-*methylethylaminophenyl-*, m. p. 168°. These compounds are rapidly hydrolysed by dilute mineral acids to 2 : 7-dibromofluorenone and the corresponding amine.

R. K. Callow.

Isomeric relationships in the chalkone series. V. Dibenzoylmethane, *p*-bromodibenzoylmethane, and *p*-methylchalkone [phenyl *p*-methylstyryl ketone]. C. Weygand [with H. Hennig] (Ber., 1927, **60**, [*B*], 2428—2432; cf. A., 1926, 1248).—Hydrolysis of the α-form of phenyl β-ethoxystyryl ketone with alcoholic hydrogen chloride affords the phenyl β-hydroxystyryl ketone, m. p. 80—81°, of von Baeyer and Perkin. The known isomeric forms of phenyl β-ethoxystyryl ketone have m. p. 63°, 73—74°, 77—78°, and 80—81°, respectively. The varieties of phenyl β-methoxystyryl ketone have m. p. 65°, 77—78°, and 80—81°, and those of phenyl β-hydroxystyryl ketone have m. p. 72—73°, 77—78°, and 80—81°, respectively. In all cases the varieties of highest m. p. are unstable (cf. Dufraisse and Gillet, A., 1927, 58). The enolic form of *p*-bromodibenzoylmethane exists in two *varieties*, m. p. 94° and 86·5°, the latter being obtained by solidification of the undercooled melt of the former under certain conditions. Phenyl *p*-methylstyryl ketone exists in an unstable α-*variety*, m. p. 99°, a stable β-form, m. p. 96·5°, and a metastable γ-variety, m. p. 90°. The α- is obtained from the β-variety by cautious crystallisation from hot methyl alcohol. Contrary to Dufraisse and Gillet (*loc. cit.*), the authors propose to designate the form of highest m. p. as the α-variety until a reasonable explanation of the isomerism is forthcoming. Since the isomerides are not distinguished from one another by visible difference in colour, it is considered improbable that the isomerism is of the *cis–trans* type and all the isomerides are regarded as *cis*-forms in analogy with *cis*-dibenzoylethylene and *cis*-cinnamic acid. H. Wren.

Tautomerism of α-diketones. C. Dufraisse and H. Moureu (Bull. Soc. chim., 1927, [iv], **41**, 1607—1621).—The dimorphism of phenylbenzylglyoxal (cf. Widman, A., 1916, i, 406; Jörlander, A., 1907, i, 343) is attributed to the two stereoisomerides of the enolic form, COPh·C(OH):CHPh, the α-form, m. p. 67°, being the unstable form. The β-form has m. p. 90°. The appearance of either form in the preparation of phenylbenzylglyoxal is not to be attributed to differences in the technique of preparation (cf. Jörlander, *loc. cit.*). In support of the enolic structure is advanced the existence of the following coloured salts: *potassium*, *copper*, ferric, *uranium*, *zinc*, *lead*, *antimony*. The antimony salt, $COPh\cdot C(OSbCl_2):CHPh$, m. p. 179—180°, is obtained in 75% yield by the action of antimony trichloride on either the α- or β-form. On exposure to the atmosphere for a year phenylbenzylglyoxal yields benzoic acid, a substance, m. p. 235—236°, insoluble in ether and in alkali, and a substance, m. p. 193—194°, soluble in ether and alkali. With crystalline phenylbenzylglyoxal in the cold, magnesium methyl iodide affords 93% of the theoretical amount of methane. Hydroxylamine in aqueous alcohol yields mainly an *oxime*, $C_{15}H_{13}O_2N$, m. p. 114—115°, together with some oximinobenzylacetophenone, and, probably, a little dioxime, m. p. 220°. Attempts to obtain this oxime from α-piperidinobenzylideneacetophenone failed, the latter giving piperidine and oximinobenzylacetophenone when treated with hydroxylamine. When distilled at 192—193°/15 mm. crystalline phenylmethylglyoxal is converted (yield 90%) into a liquid *isomeride*, b. p. 137—138°/0·3 mm., n_D^{21} 1·5881, $d_4^{18\cdot5}$ 1·1333, which affords the same monoxime, m. p. 114—115°, and metallic derivatives, the latter on decomposition with acids yielding the crystalline form. Magnesium methyl iodide yields only about 50% of the theoretical amount of methane, a result indicating that whilst the crystalline form consists almost entirely of the enolic form, a large amount of the liquid isomeride is ketonic. Some of the enol present in the latter case may be due to enolisation by the Grignard reagent. Conversion of the liquid into the crystalline form is best effected through the antimony salt, the latter being decomposed with hydrogen sulphide or 40% tartaric acid. The liquid form on keeping (10 months) in a sealed tube changes to the β-form, m. p. 89°. Hydrolysis of oximinobenzylacetophenone with 25% sulphuric acid gives a little crystalline phenylbenzylglyoxal.

Similarly, phenylanisylglyoxal, m. p. 70°, gives coloured sodium, potassium, and ferric salts; the orange-yellow *antimony* salt has m. p. 199—200°. When distilled at 211—213°/8 mm. the crystalline form is converted into a liquid *isomeride*, n_D^{22} 1·5932, d_4^{22} 1·1656, giving the same metallic derivatives from which the crystalline form is regenerated. The crystalline form of benzylmethylglyoxal, m. p. 69—70°, is obtained by the action of piperidine on dibromobenzylideneacetophenone and cold hydrolysis of the piperidino-compound. The yellow *antimony* salt has m. p. 184—185°. When heated the crystalline form is converted into the liquid isomeride, b. p. 107°/17 mm. The crystalline form is regenerated by decomposition of the sodium salt.

R. Brightman.

Heteropolar carbon compounds. V. Influence of phenoxy- and substituted phenoxy-groups on the halochromy of chromogens. W. Dilthey, E. Bach, H. Grütering, and E. Hausdörfer (J. pr. Chem., 1927, [ii], **117**, 337—368).—p-*Phenoxyphenyl* β-*phenylvinyl ketone*, m. p. 85—86° (with previous sintering; *dibromo*-additive compound,

m. p. 137°), and p-*phenoxyphenyl* β-p-*methoxyphenylvinyl ketone*, m. p. 97°, are prepared by condensation of *p*-phenoxyacetophenone with the appropriate aldehyde. 4 : 4′-*Diacetyldiphenyl ether*, m. p. 100—101° (*dioxime*, m. p. 182—183°), prepared either by the interaction of diphenyl ether and acetyl chloride in carbon disulphide solution in the presence of aluminium chloride or from the potassium salt of *p*-hydroxyacetophenone and *p*-bromoacetophenone by Ullmann's method, yields pp′-*dicinnamoyldiphenyl ether*, m. p. 170° [*tetrabromo*-additive compound, m. p. 224° (decomp.)], and pp′-*di*-β-*anisylacrylyldiphenyl ether*, m. p. 207—208° [*tetrabromo*-additive compound, m. p. 198° (decomp.)]. pp′-*Dibenzoyldiphenyl ether*, m. p. 163—164° [*dioxime*, m. p. 215—216° (decomp.)], prepared by both the above methods from the suitable components, reacts with magnesium phenyl bromide to give finally pp′-*dichlorodiphenylmethyldiphenyl ether*, decomp. at 120° (melting and frothing at 165°), or pp′-*dibromodiphenylmethyldiphenyl ether*, m. p. 193° (decomp.). pp′-*Di*(*hydroxydiphenylmethyl*)*diphenyl ether*, m. p. 90—95° (frothing; *dimethoxy*-derivative, m. p. 138—139°), gives on reduction with acetic acid and zinc dust pp′-*di*(*diphenylmethyl*)*diphenyl ether*, m. p. 167—168° (darkening; when crystallising with $2C_6H_6$, m. p. 85—90°). p-*Phenoxytriphenylmethane*, m. p. 138—140°, is prepared by the interaction of *p*-phenoxybenzophenone and magnesium phenyl bromide. 4-p-*Tolyloxybenzophenone*, m. p. 68°, 4-p-*tolyloxyacetophenone*, m. p. 53—54° (*oxime*, m. p. 138°), 4-p-*nitrophenoxybenzophenone*, m. p. 126° (*oxime*, m. p. 162°; *phenylhydrazone*, m. p. 167°), and 4-p-*nitrophenoxyacetophenone*, m. p. 82—83°, are prepared from the ethers by the Friedel–Crafts method. p-*Tolyl* p-*cinnamoylphenyl ether*, m. p. 84°, p-*tolyl* β-p-*anisylacrylylphenyl ether*, m. p. 109—110°, p-*nitrophenyl* p-*cinnamoylphenyl ether*, m. p. 165—166°, p-*nitrophenyl* 4-β-p-*anisylacrylylphenyl ether*, m. p. 135°, and p-*nitrophenyl* p-*cinnamylideneacetylphenyl ether*, m. p. 138° [*chlorostannate* of corresponding amine, m. p. 263° (decomp.)], are prepared by condensation of the aldehydes with the acetophenone derivatives. 4-p-*Aminophenoxybenzophenone*, m. p. 85° (*acetyl* derivative, m. p. 156°; *benzoyl* derivative, m. p. 172°), and 4-p-*aminophenoxyacetophenone*, m. p. 123° (*compound* with benzaldehyde, m. p. 144—145°), are obtained by reduction of the corresponding nitro-compounds with stannous chloride in saturated hydrogen chloride solution. p-*Aminophenyl* 4-β-p-*anisylacrylylphenyl ether*, m. p. 148° [*chlorostannate*, m. p. 246° (decomp.); *hydrochloride*, m. p. 198—200° (decomp.); *picrate*, m. p. 207° (yellow); *monoperchlorate*, m. p. 218—220°; *diperchlorate*, m. p. indef.], and p-*aminophenyl* p-*cinnamoylphenyl ether*, m. p. 104° (*chlorostannate*, m. p. 239—240°; *acetyl* derivative, m. p. 171°; *monoperchlorate*, m. p. 223°; *diperchlorate*, m. p. indef.), are obtained similarly. The colours given when these compounds are treated with sulphuric acid or with sulphuric acid and glacial acetic acid are recorded and are found to confirm the theory previously published (A., 1926, 727).

G. A. C. Gough.

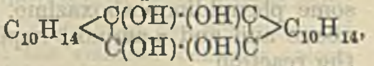
Action of primary amines on nitroso-β-naphthol. R. Lantz and A. Wahl (Compt. rend., 1927, **185**, 1489—1491).—2-Hydroxy-α-naphthaquinone-1-imine-4-anil (A., 1926, 617) is obtained by heating a mixture of nitroso-β-naphthol, aniline, and benzene for 12—15 min. The reaction is catalysed by copper, and when copper is used there is formed some phenyldinaphthoxazime, presumably from the above anil and α-amino-β-naphthol produced during the reaction. H. Burton.

Preparation of anthraquinone. P. S. Varma and J. L. D. Gupta (J. Indian Chem. Soc., 1927, **4**, 297—298).—Eleven methods of preparing anthraquinone are compared. The use of nitrous oxides in water or alcohol as oxidising agent is described. The highest yield, 4·3 g. from 5·0 g. of anthracene, is obtained using chromium trioxide and glacial acetic acid (Fischer's method). H. Burton.

Catalytic action of mercury in the sulphonation of anthraquinone. A. Meyer (Bull. Soc. chim., 1927, [iv], **41**, 1627—1638).—A more detailed account of work already published (A., 1927, 463). The transformation of anthraquinone-α-sulphonic acid into the β-sulphonic acid observed by Martinet and Roux (A., 1921, i, 257) is attributed to the presence of traces of mercury as impurity (cf. also Coppens, A., 1925, i, 1432; Clough, A., 1923, i, 46; Fierz-David, A., 1927, 463; Wibaut, A., 1927, 566). If the mercuric sulphate or oxide used is not ground up with the anthraquinone before charging into the sulphuric acid, erratic results may be obtained. Sulphonation of anthraquinone at 160° with 50% oleum in presence of 1% of mercuric sulphate affords 56·8% of anthraquinone-α-sulphonate, 20% of the 1 : 5- and 1 : 8-disulphonic acids, and 3·5% of trisulphonic acid, 19·6% of the anthraquinone being unattacked. R. Brightman.

Aromatic thionyl and chlorothionyl derivatives. III. Reactions of thionylalizarin. A. Green (J.C.S., 1927, 2930—2932).—Thionylalizarin reacts with the corresponding free weak organic acids to give the following 2-monoacyl derivatives of alizarin: 2-*monobenzoyl*-, m. p. 208—210° (lit. 214—216°); 2-*phenylacetyl*-, m. p. 165°; 2-*phenoxyacetyl*-, m. p. 179°; 2-*cinnamoyl*-, m. p. 209°; 2-o-*toluoyl*-, m. p. 192°; 2-m-*bromobenzoyl*-, m. p. 214°, and 2-p-*bromobenzoyl-alizarin*, m. p. 195°. With dichloro-, trichloro-, and dibromo-acetic acids, thionylalizarin yields alizarin only, whilst with chloroacetic acid it yields a mixture of alizarin and a substance assumed to be the chloroacetyl derivative. Benzoic anhydride condenses with thionylalizarin giving dibenzoylalizarin, isolated in a new labile *modification*, m. p. 160°, as well as in the ordinary modification, m. p. 187°. Only the latter is obtained when benzoyl chloride is used. When thionylalizarin is heated under pressure with acetyl chloride, diacetylalizarin is obtained. With succinic or phthalic anhydrides, and with alkyl halides or sulphates, no reaction occurs. With boiling absolute alcohol or hot phenol, sulphur dioxide is evolved with formation of alizarin. With hot primary aromatic amines the alizarin first formed undergoes further slow reaction with formation of secondary amines. M. Clark.

Nuclear hydrogenation of quinones in non-acidic media. A. Skita [with F. Keil and H.

WITTE] (Ber., 1927, 60, [*B*], 2522—2527).—Acenaphthenequinone, suspended in aqueous sodium hydroxide or ammonia, is converted by hydrogen in the presence of colloidal platinum into the tetrahydric *alcohol*,  $C_{10}H_{14}<\begin{matrix}C(OH)\cdot(OH)C\\ C(OH)\cdot(OH)C\end{matrix}>C_{10}H_{14}$, m. p. 207—208° (*tetra-acetate*, m. p. 138°), which is not identical with the tetrahydroxy-alcohol, m. p. 206° (now formulated $C_{24}H_{26}O_4$; *tetra-acetate*, m. p. 102—103°), obtained by hydrogenation of acenaphthenequinone in acid solution (cf. A., 1926, 173). Anthraquinone dissolved in decahydronaphthalene in the presence of a nickel catalyst is converted by hydrogen at 75° and 50 atm. almost exclusively into tetrahydroanthraquinol, which readily passes by atmospheric oxidation into tetrahydroanthraquinone, m. p. 158°. At 90° and 50 atm., hexahydroanthraquinol (*diacetate*, m. p. 215—216°), readily oxidised to hexahydroanthraquinone, m. p. 175°, is produced. At 150° and 50 atm., anthraquinone affords octahydroanthraquinone, m. p. 184°, mixed with about 30% of octahydroanthranol. If the temperature is reduced to 130°, the production of octahydroanthranol falls to 15% without any appreciable change in the rate of the reaction. At 130° and 25 atm., anthranol formation occurs only to the extent of 10%, whereas the yield of octahydroanthraquinone is proportionately increased. H. WREN.

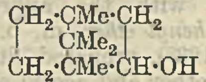
Dyes and intermediates [dibenzanthronyls]. R. F. THOMSON, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1928, 9.

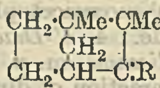
1-Diazoanthraquinone-2-carboxylic acids. I. G. FARBENIND. A.-G.—See B., 1928, 45.

Determination of santonin in *Flores cinæ*. H. BECKURTS (Festschr. A. Tschirch, 1926, 6—12; Chem. Zentr., 1927, i, 2586).—Loss of santonin on purification takes place as follows: with potassium permanganate solution, 6—10%; through the lead compound, 7·2—8·3%; by coagulation of the impurities with potassium alum (2·1—2·3%) or ferric chloride (1·3—1·5%); by using Pukall filters, 1·9—2·4%. Pure santonin may be obtained, although not quantitatively, by ultra-filtration.

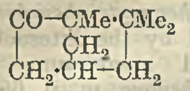
A. A. ELDRIDGE.

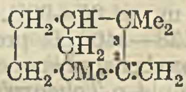
Structure of methyl*iso*borneol from α-methylcamphene, of β-methylcamphenilone, and of their derivatives. S. NAMETKIN and L. BRÜSSOV (Annalen, 1927, 459, 144—171).—The compound previously regarded as 6(β)-methyl*iso*borneol (cf. A., 1926, 619; Bredt, A., 1919, i, 125) has now been shown to be the 4-methyl derivative (I) as follows: (*a*) The hydrazone of the corresponding methylcamphor is converted by sodium ethoxide at 200° into 4-*methylcamphane*, m. p. 138—139°, b. p. 170—170·5°/752 mm. This yields as main product of nitration by Konovalov's method a *sec.*-*nitro*-derivative, m. p. 144—146°, which is oxidised by permanganate to the original methylcamphor. (*b*) Attempts to brominate the corresponding methylcamphoric acid using bromine and red phosphorus result only in anhydride formation. These reactions indicate the absence of hydrogen from the 4-position. By applying the usual pinacolin-type transformation to 4-methyl*iso*borneol, formulæ (II) [R=(*a*) :CH₂, (*b*) :O,

(I.) 

 (II.)

(*c*) :H₂] are obtained for (*a*) β-methylcamphene, (*b*) β-methylcamphenilone, and (*c*) β-methylcamphenilan. These are confirmed in the following ways: (1) When β-methylcamphenilan is nitrated by Konovalov's method it gives 4-*methylapofenchocamphoric acid* (3 : 3 : 4-*trimethyl*cyclo*pentane*-1 : 4-*dicarboxylic acid*), m. p. 187—188°, and a *sec.*-*nitro*-derivative, m. p. 110—114°, the constitution of which follows from its oxidation by permanganate to 4-*methyl*iso*camphenilone* (III), m. p. 146—147° (*semicarbazone*, m. p. 202—204°). The accepted formula required the formation of a *tert.*-nitro-derivative and of an acid, $C_7H_{12}(CO_2H)_2$. (2) When β-methylcamphenilonehydrazone is oxidised by freshly-precipitated mercuric oxide, *iso*cyclene, m. p. 119° (cf. Bredt, A., 1917, i, 655), not fenchocyclene, is obtained. (3) Free β-*methylcamphenylic* (camphenilolic) *acid* (1 : 1-*methyl*iso*propyl*cyclo*pentane* 3-*carboxylic acid*), b. p. 143—143·5°/10 mm., d_4^{20} 0·9853, n_{20} 1·4641, prepared from the amide (A., 1923, i, 690), has been treated with red phosphorus and bromine and the product hydrolysed by calcium carbonate to *calcium* 3-*hydroxy*-1 : 1-*methyl*iso*propyl*cyclo*pentane*-3-*carboxylate* (+18H₂O). The free acid is oxidised by lead dioxide and sulphuric acid to a new *ketone* [(?) 1 : 1-*methyl*iso*propyl*cyclo*pentan*-3-*one*], b. p. 195—196°/756 mm. (*semicarbazone*, m. p. 198—199°), which is not identical with 1-methyl-3-*iso*propyl*cyclo*pentan-5-one (Wallach, A., 1918, i, 442). Thus, the hydration of α-methylcamphene (IV) to 4-methyl*iso*borneol (I) must involve, first, hydration and simultaneous migration of a methyl group from the 3- to the 2-position, followed by ring-isomerisation, whilst the formation of the same compound from β-methylcamphene (II) is not accompanied by methyl-wandering. This apparently dissimilar behaviour of two closely-related substances is explained by the tendency of the hydroxyl group to enter such a position in the molecule (adjacent to a :CH group) that by ring-isomerisation a secondary alcohol is formed. The reverse change, dehydration of methyl*iso*borneol, appears to proceed in both directions and both schemes are applicable to the formation of *iso*borneol from camphene. H. E. F. NOTTON.

(III.) 

 (IV.)

Derivatives of camphorquinone. J. PALMÉN (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 9).—Magnesium phenyl bromide converts camphorquinone into hydroxyphenylcamphor, m. p. 78—80°; magnesium benzyl chloride gives hydroxybenzylcamphor (not isolated in a state of purity); magnesium ethyl bromide gives a product which may contain some dihydroxydiethylcamphane.

G. A. C. GOUGH.

Decomposition of the ozonides of semicyclic unsaturated systems. Ozonisation of sabinol. T. HASSELSTRÖM (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 5).—A glacial acetic acid solution of sabinol ozonide, prepared by the action of ozone on a solution of sabinol in that solvent, decomposes when heated for 3 hrs. at 100° to give formaldehyde, α-tanacetogendicarboxylic acid, α-tanacetogen acid aldehyde, and α-oxysabina ketone. G. A. C. Gough.

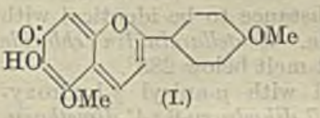
Furfuryl and furfurylidene compounds of menthone. E. Boedtker, B. Wiger, and T. Aagaard (J. Pharm. Chim., 1927, [viii], 5, 193—204).—Menthone condenses with furfuraldehyde in presence of sodium ethoxide to give *furfurylidenementhone*, yellow, b. p. 181°/12 mm., $[\alpha]_D^{15}$ −190° 51′, n_D^{15} 1·5649, which, by the action of magnesium alkyl halides is converted into the following alkyl (R) substituted furfurylmenthones, $C_{10}H_{17}O·CHR·C_4H_3O$; *methyl-*, b. p. 149—150°/9 mm., $[\alpha]_D^{15}$ −19° 7′, n_D^{15} 1·4986; *ethyl-*, b. p. 165°/12 mm., $[\alpha]_D$ nil, n_D^{15} 1·4941; n-*propyl-*, b. p. 164°/9 mm., $[\alpha]_D$ nil, n_D^{15} 1·4929; iso*propyl-*, b. p. 162°/9 mm., $[\alpha]_D^{15}$ +49° 58′, n_D^{15} 1·4938; n-*butyl-*, b. p. 174°/10 mm., $[\alpha]_D^{15}$ +13° 22′, n_D^{15} 1·4905; iso*butyl-*, b. p. 169—170°/10 mm., $[\alpha]_D^{15}$ +19° 33′, n_D^{15} 1·4911; iso*amyl-*, b. p. 181°/10 mm., $[\alpha]_D^{15}$ +21° 46′, n_D^{15} 1·4915; *phenyl-*, m. p. 93·5—94°, $[\alpha]_D^{18·5}$ +22° 45′, n_D^{19} 1·5415. Furfurylidenementhone reacts with hydroxylamine, giving a *compound*, $C_{11}H_{20}O_2N$, m. p. 139—140°. 2 : 6-Difurfurylidene-*cyclo*hexanone, m. p. 145°, has been prepared by a slight modification of the method of Wolff (A., 1922, i, 668). It gives a violet colour with concentrated sulphuric acid. E. H. Sharples.

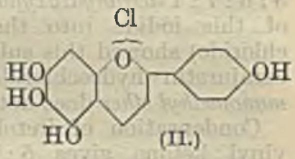
Reduction of furan derivatives. N. Williams (Ber., 1927, 60, [*B*], 2509—2514).—*Tetrahydrofurfuraldoxime*, b. p. 110°/8 mm., d^{18} 1·1314, n_D^{18} 1·4845, is prepared from the aldehyde or from its diacetate after treatment with sulphuric acid. It is reduced by sodium and alcohol to a mixture of *tetrahydro-2-furylmethylamine*, b. p. 54—56°/30 mm., 154°/750 mm., d^{17} 0·9792, n_D^{17} 1·4580 (*hydrochloride*; *chloroplatinate*; *chloroaurate*), and ε-hydroxy-*n*-amylamine, b. p. 110—112°/10 mm., n_D^{17} 1·4619 (chloroplatinate). *Tetrahydrofuran-2-carboxylonitrile*, b. p. 80—82°/23 mm., d^{25} 1·0295, n_D^{25} 1·4351, prepared by the action of acetic anhydride and sodium acetate on the corresponding oxime, gives only very small amounts of tetrahydro-2-furylmethylamine when treated with sodium and alcohol. Di-2-furylmethylamine (*hydrochloride*, $C_{10}H_{11}O_2N,HCl$, m. p. 170—172°) is obtained by the catalytic reduction of furfuraldoxime in the presence of palladised charcoal. 2-Furylmethylamine is not reduced by hydrogen in ethereal solution, but in glacial acetic acid in the presence of palladised charcoal affords tetrahydro-2-furylmethylamine.

H. Wren.

Derivatives of furfuraldehyde. V. Action of organo-magnesium compounds on furyl ketones; constitution of furylidenemethyl ethyl ketone. I. Kasiwagi (Bull. Chem. Soc. Japan, 1927, 2, 310—319).—The condensation product of furfuraldehyde with methyl ethyl ketone, previously described as α-furyl-Δ^{α}-penten-γ-one (A., 1926, 842), is shown to be actually α-furyl-β-methyl-Δ^{α}-buten-γ-one. α-Furyl-β-methylbutan-γ-one (previously described as α-furyl-γ-pentanone), prepared by the hydrogenation of the last-named, reacts with magnesium methyl iodide to give *α-furyl-βγ-dimethylbutan-γ-ol*, b. p. 82·5°/3·5 mm., d_4^{25} 0·9923, n_D^{25} 1·4779, and with magnesium ethyl iodide to give α-furyl-βγ-dimethylpentan-γ-ol, b. p. 90—91°/3 mm., d_4^{25} 0·9892, n_D^{25} 1·4800. Both these tertiary alcohols are dehydrated by phenylcarbimide and the alternative synthesis of the second from magnesium methyl iodide and α-furyl-β-methylpentan-γ-one indicates the actual structure of the furylidenemethyl ethyl ketone. Additional evidence is obtained by the oxidation of this ketone with sodium hypochlorite to β-*furyl-α-methylacrylic acid*, m. p. 110·5—111°, which may also be obtained (with m. p. 116°) by hydrolysis of the *ethyl* ester, b. p. 103—104°/4·5 mm., d_4^{25} 1·0800, n_D^{25} 1·5418, obtained by condensation of furfuraldehyde with ethyl acetate by Claisen's method. The following compounds are incidentally described: *α-furyl-γ-methylbutan-γ-ol*, b. p. 93·5—94°/8 mm., d_4^{25} 0·9972, n_D^{25} 1·4745 (*phenylcarbamate*, m. p. 126·5—127°; *acetate*, b. p. 83—85°/3 mm., d_4^{25} 1·0188, n_D^{25} 1·4583); *α-furyl-γ-methylpentan-γ-ol*, b. p. 83·5—84·5°/2 mm., d_4^{25} 0·9926, n_D^{25} 1·4780 (*phenylcarbamate*, m. p. 84·5—85°); β-*furylacrylic acid*, m. p. 139·5—140°; αε-*di-furyl*-β-*methylpentan*-γ-*one*, m. p. 61°.

G. A. C. Gough.


(I.)


(II.)

Colouring matters of carajura. E. Chapman, A. G. Perkin, and R. Robinson (J.C.S., 1927, 3015—3041; cf. Perkin, Proc. C.S., 1914, 30, 212).—Extraction of carajura with benzene and other suitable reagents affords the red substances *carajurin* (I), m. p. 205—207° (*hydrogen sulphate*; *hydrochloride*, blackens at 196° with partial fusion), and *carajurone*, m. p. 183—186° (decomp.). Bromination of (I) in acetic acid yields a *tetrabromide*, $C_{17}H_{14}O_5Br_4$, darkens at 195° and becomes black at 300°, which is converted by hot acetone into a *dibromocarajurin*, $C_{17}H_{12}O_5Br_2$, decomp. 300°. Fission of (I) with alcoholic potassium hydroxide affords *p*-acetylanisole, whilst acetylation with acetic anhydride in pyridine yields colourless O-*triacetyldihydrocarajurinol*, $C_{23}H_{22}O_9$, m. p. 142°. Reduction of (I) with hydriodic acid gives *carajuretin*, blackens at 330° (*hydriodide*; *hydrogen sulphate*; *hydrogen perchlorate*), which is acetylated in pyridine, forming O-*penta-acetyldihydrocarajuretinol*, $C_{25}H_{22}O_{11}$, m. p. 156—157°. *Carajuretin hydrochloride* (II), is obtained by decomposition of the hydriodide with silver chloride. Methylation of 2 : 6-dimethoxyquinol yields 1 : 2 : 3 : 5-tetramethoxybenzene and antiarol (3 : 4 : 5-trimethoxyphenol) (*sodium* salt; *acetyl* derivative, m. p. 74°). 3 : 6-*Dihydroxy-2 : 4-dimethoxybenzaldehyde*, m. p. 135—136°, and *antiarolaldehyde* (2-*hydroxy*-4 : 5 : 6-*trimethoxybenzaldehyde*), m. p. 65° [*semicarbazone*, m. p. 245° (decomp.)], are obtained by the Gattermann method from the corresponding phenols. 4 : 5-*Dimethoxyresorcinol*, m. p. 115—116°, is prepared by prolonged boiling of an aqueous solution of 3 : 5-diaminoveratrole hydrochloride containing a little stannous chloride. Antiarol reacts with acetyl chloride in presence of aluminium chloride and nitrobenzene to form 4 : 5-*dimethoxy*-2 : 6-*diacetylresorcinol*, m. p. 92—93°, a small amount of 4 : 5-*dimethoxy*-2-*acetylresorcinol*(?), m. p. 160—161°, and a trace of a *substance*, m. p. 78—84°. 4 : 5-Dimethoxyresorcinol reacts with methoxyacetonitrile in ethereal hydrogen chloride to yield ω : 5 : 6-*trimethoxyresacetophenone*, m. p. 129—130°.

Condensation of anisoylacetone, m. p. 57° (previously recorded m. p. 54·5°), best obtained by condensing *p*-acetylanisole and ethyl acetate in presence of sodamide, with 2 : 6-dimethoxyquinol in formic acid in presence of hydrogen chloride affords 6-*hydroxy*-5 : 7 : 4′-*trimethoxy*-4-*methylflavylium chloride*, $+1·5H_2O$, (III), m. p. 139—145° (decomp.) (*ferrichloride*, m. p. 205°). Anisoylacetone and iretol yield similarly 5 : 7-*dihydroxy*-6 : 4′-*dimethoxy*-4-*methylflavylium chloride*, $+0·5H_2O$, (IV), m. p. 208° (decomp.) after darkening at 100—105° (*ferrichloride*, m. p. 180—181° with previous darkening), whilst anisoylacetone and antiarol afford 5 : 6 : 7 : 4′-*tetramethoxy*-4-*methylflavylium chloride*, m. p. 143—144° (decomp.) after darkening (*ferrichloride*, m. p. 176°). Demethylation of (III) and (IV) with a mixture of phenol and hydriodic acid gives 5 : 6 : 7 : 4′-*tetrahydroxy*-4-*methylflavylium iodide*, m. p. 290° (decomp.) after darkening at 278° (*chloride*, darkens at 200—270° without melting). Condensation of antiarolaldehyde and *p*-acetylanisole in acetic acid by hydrogen chloride gives 5 : 6 : 7 : 4′-*tetramethoxyflavylium chloride*, m. p. 145—146° (decomp.) (*ferrichloride*, m. p. 170°), which is demethylated by phenol and hydriodic acid to 5 : 6 : 7 : 4′-*tetrahydroxyflavylium iodide*. Conversion of this iodide into the chloride (scutellareinidin chloride) showed this substance to be identical with carajuretin hydrochloride. *Scutellareinidin chloride monomethyl ether* does not melt below 285°.

Condensation of iretol with *p*-anisyl β-hydroxyvinyl ketone gives 5 : 7-*dihydroxy*-6 : 4′-*dimethoxyflavylium chloride*, m. p. above 260°, which is also demethylated to carajuretin hydrochloride. Antiarolaldehyde and acetophenone yield 5 : 6 : 7-*trimethoxyflavylium chloride*, m. p. 124—125° (decomp.) (*ferrichloride*, m. p. 151°), which on demethylation affords 5 : 6 : 7-*trihydroxyflavylium chloride* (*baicaleinidin chloride*), decomp. 250—252° after darkening above 220° [*iodide*, m. p. 254° (decomp.) after sintering].

The dyeing properties of carajurin, carajurone, and carajuretin towards mordanted wool are recorded.

H. BURTON.

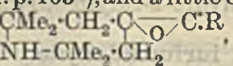
South African flowers. J. MOIR (J.S. African Chem. Inst., 1927, 10, 36—47).—The absorption spectra of dilute extracts of the colouring matter of various flowers were studied, using a modified direct-vision spectroscope. In order to find the pigment causing colour, the spectra of the oxonium salts of the following substances were examined: pelargonidin, cyanidin, delphinidin, myricetin, apigeninidin, and luteolinidin. Glucosides of pelargonidin were detected in Barberton daisy, brown nasturtium, scarlet salvia, and *Chelone barbata*. Other red flowers in which glucosides of other members of the class are regarded as contaminating the pelargonin or which are possibly glucosides of a methyl ether of pelargonidin are scarlet protea, bramble, eendagsbloem lily, and the red canna lily. Glucosides of cyanidin were found in scarlet zinnia, pink convolvulus, purple convolvulus, deep red Ards rose, pink hydrangea, blue hydrangea, crimson verbena, *Lychnis coronaria*, scarlet geum, puce-coloured hollyhock, and the anthers of the agapanthus lily. Glucosides of delphinidin are present in nearly all bright blue flowers.

Delphinin was detected in blue agapanthus lily, azure plumbago, blue jacaranda, scarlet pointsettia, royal-blue convolvulus, and common larkspur.

Petunin was found in the petunia, bramble, and habrothamnus. The yellow sunflower is coloured with a mixture of xanthophyll and quercitrin. The alkali-soluble pigment of sunflower is probably a quercetin glucoside. The common orange marigold probably contains glucosides of kæmpferol and myricetin. The brown Japanese sunflower probably contains lycopin and kæmpferol glucoside. Flowers yielding indefinite results were: the sulphur-yellow chrysanthemum, the yellow coreopsis, and the *Montbretia* lily. Every stage in the origin of flower colours can be followed by examining all the intermediate substances in concentrated sulphuric acid solution.

R. A. PRATT.

Pinacolin transformation in *N*-ring pinacones. L. ORTHNER (Annalen, 1927, 459, 217—233).—Ditertiary glycols which have one hydroxyl group attached to a piperidine ring are dehydrated, but not converted into pinacolins, by boiling with acids. This is probably due to the positive charge on the piperidinium ion inhibiting the formation of the carbonium ion through which the pinacolin transformation proceeds (cf. Meerwein, A., 1923, i, 324). Methyl 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine-4-carboxylate (cf. D.R.-PP., 90245, 91122), prepared from triacetonamine, is converted by magnesium ethyl bromide into 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-γ-*hydroxy*-γ-*amylpiperidine* (I), m. p. 68—69°, b. p. 131°/0·3 mm. (*picrate*, m. p. 135°), with some 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-α-*hydroxy*-α-*propylpiperidine*, m. p. 131·5° (*picrate*, m. p. 179—180°), and ethylene, and by magnesium iodide into 4-*hydroxy*-2 : 2 : 6 : 6-*tetramethyl*-4-β-*hydroxy*iso*propylpiperidine* (II), m. p. 120·5°, b. p. 132—133°/13 mm. (*picrate*, m. p. 185·5—186°). The pinacone (I) is converted by boiling 20% sulphuric acid into a mixture containing no ketonic substances, from which 2 : 2 : 6 : 6-*tetramethyl*-4-γ-Δ^{γ}-*pentenyl*-1 : 2 : 3 : 6-*tetrahydropyridine*, b. p. 109—110°/13 mm. (*picrate*, m. p. 136—137°); 2 : 2 : 6 : 6-*tetramethyl*-4-γ-Δ^{γ}-*pentenylpiperidine*, b. p. 110—112°/11 mm. (*picrate*, m. p. 163°), and a little of the *ethylene oxide* (III) (R=Et₂),

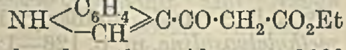


$$\begin{array}{l}CMe_2{\cdot}CH_2{\cdot}C\!\!-\!\!\!-\!O\!-\!\!-\!C{:}R \\ NH{-}CMe_2{\cdot}CH_2\end{array}$$

, m. p. 62·5° (*picrate*, m. p. 170·5°), are separated through the picrates. The oxide (III) forms the main product when (I) is boiled with 15% hydrochloric acid. Similarly, the glycol (II) affords with acids a mixture from which 2 : 2 : 6 : 6-*tetramethyl*-4-iso*propenyl*-1 : 2 : 3 : 6-*tetrahydropyridine picrate*, m. p. 179—180°, 2 : 2 : 6 : 6-*tetramethyl*-4-iso*propenylpiperidine picrate*, m. p. 253° [free *base* (IV) (?), m. p. 77—77·5°], and the *ethylene oxide* (III) ($R=Me_2$), m. p. 62° (*picrate*, m. p. 195—196°), are isolated. The constitution of the ethylene oxides (III) is established by their oxidation by chromic and sulphuric acids to $\alpha\alpha'\alpha'$-trimethyldiethylamine-$\alpha\beta$-dicarboxylic acid, identified as the *ethyl ester picrate*, m. p. 127—128°. This is also obtained in this way from 4-hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine-4-carboxylic acid, but the base (IV) gives an *ethyl ester picrate*, m. p. 193—194°.

H. E. F. Notton.

Syntheses by means of magnesylpyrroles. [II.] XI. α- and β-Ketonic acids. B. Oddo and A. Albanese (Gazzetta, 1927, 57, 827—835).—Ethoxalyl chloride reacts with magnesylindole to give *ethyl indolyl-3-glyoxylate*, (I), m. p. 186°, which is hydrolysed to the *acid*, m. p. 215° (decomp.) (*silver*, *lead*, *copper*, and *ferric* salts insoluble, *mercuric*, *barium*, *cobalt*, *nickel*, *cadmium*, and *manganese* salts soluble); this forms an *amide*, m. p. 248°, and on heating yields indole-3-aldehyde. With magnesylmethylindole, *ethyl 2-methylindolyl-3-glyoxylate* (II), m. p. 129·5°, is obtained; the *acid* has m. p. 186° (decomp.).

Ethmalonyl chloride (obtained from thionyl chloride and ethyl potassium malonate) reacts with magnesylpyrrole to give a mixture of *ethyl 3-acetylindole-ω-carboxylate*,  $NH{<}{\substack{C_6H_4\\ -CH}}{\geqslant}C{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ (III), m. p. 121°, hydrolysed to the *acid*, m. p. 192° (with decomposition to 3-acetylindole), and (probably) *ethyl 2-acetylindole-ω-carboxylate* (IV), m. p. 116°, hydrolysed to an *acid*, m. p. 315° (decomp.). (I) and (II) do not give silver derivatives with an ammoniacal silver nitrate solution; (III) and (IV) give a reaction, so that the former pair can probably assume an enolic and (?) quaternary basic form.

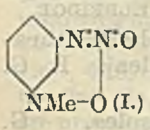
E. W. Wignall.

Oxidation of pyridine and the pyridine nucleus by sodium persulphate. J. Dorronsoro (Anal. Fís. Quím., 1927, 25, 409—410).—Pyridine and its derivatives are easily oxidised by sodium persulphate, as they are by potassium permanganate (cf. Delépine, A., 1927, 254). When pyridine was treated with 20% aqueous sodium persulphate in the amount required by the equation $2C_5H_5N+11O_2=10CO_2+2NH_3+2H_2O$, a small quantity of pyridine was recovered unchanged, and some nitric acid was found, formed by further oxidation of the nitrogen. α-Picoline behaved similarly, acetic acid being also formed.

R. K. Callow.

Nitroamines of the pyridine series; 3-nitroaminopyridine. A. E. Tschitschibabin and A. V. Kirssanov (Ber., 1927, 60, [*B*], 2433—2438).—3-Aminopyridine, dissolved in sulphuric acid (*d* 1·84), is converted by nitric acid (*d* 1·5) into *3-nitroaminopyridine*, decomp. 170—175° (*barium*, *potassium*, and *sodium* salts; *sulphate*). Unlike the corresponding compounds of the 2- and 4-series it does not suffer isomerisation when treated with acids, but (preferably under the influence of acetic anhydride in acetic acid) loses nitrous oxide and gives 3-hydroxypyridine. It is transformed by methyl sulphate into the *substance* (I), m. p. 189° after darkening at 185°. Reduction of 3-nitroaminopyridine by zinc dust in alkaline solution yields mainly 3-aminopyridine with small amounts of 3-hydrazinopyridine, identified as *benzaldehyde-3-pyridylhydrazone*, m. p. 163—165°. The isomerisation of 2-nitroaminopyridine by concentrated sulphuric acid is accompanied by the production of pyrid-2-one, which is obtained in 60% yield if acetic acid is used.

H. Wren.

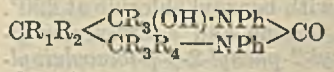


(I.)

Reaction of diazonium salts with hydroxymethylene*cyclo*hexanones and cyclic β-diketones. H. K. Sen and S. K. Ghosh (J. Indian Chem. Soc., 1927, 4, 477—491; cf. Coffey, A., 1923, i, 803).—2-Hydroxymethylene*cyclo*hexanone reacts with benzenediazonium chloride to give *cyclo*hexane-1 : 2-dionemonophenylhydrazone, m. p. 181—185° (osazone, m. p. 153—154°), which is transformed in boiling acetic acid to 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole, m. p. 168°. From the hydroxymethylene*cyclo*hexanone and the requisite diazonium chlorides there were prepared cyclo*hexane-1 : 2-dione*-p-*tolylhydrazone*, m. p. 190° (p-*tolylhydrazonephenylhydrazone*, m. p. 150° after sintering at 145°), and cyclo*hexane-1 : 2-dione*-p-*nitrophenylhydrazone*, m. p. 228—230° after darkening at 223° (p-*nitrophenylhydrazonephenylhydrazone*, m. p. 215—217°). The monohydrazones yield 1-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 194°, and 6-*nitro*-1-*keto*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 212° after sintering at 209°. 6-Methyl-2-hydroxymethylene*cyclo*hexanone and benzenediazonium chloride yield a *product*, sintering at 88°, becoming turbid and partly melting at 91°, and becoming clear at 131°, which is probably a mixture of two isomeric 6-methyl*cyclo*hexane-1 : 2-dionemonophenylhydrazones (*osazone*, m. p. 151—153°), and furnishes 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 171—173°. 6-*Methyl*cyclo*hexane*-1 : 2-*dione*-p-*tolylhydrazone* occurs in two modifications, m. p. 117—118° and 91—93° (p-*tolylhydrazone-phenylhydrazone*, m. p. 158—159°), and affords 1-*keto*-2 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 195°. 6-*Methyl*cyclo*hexane*-1 : 2-*dione*-β-*naphthylhydrazone*, m. p. 85—88°, yields 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthcarbazole*, m. p. 225° after blackening at 212°. 2-Acetyl*cyclo*hexanone with benzene- and toluene-*p*-diazonium chlorides yields cyclo*hexane*-1 : 2-*dione-acetylphenylhydrazone*, m. p. 159—161°, and -*acetyl*-p-*tolylhydrazone*, m. p. 151—153°. From 2-acetyl-6-methyl*cyclo*hexanone there are obtained the *acetylphenylhydrazone*, m. p. 137—140°, and the *acetyl*-p-*tolylhydrazone*, m. p. 117—120°, of 6-methyl*cyclo*hexane-1 : 2-dione. 2-Carbethoxy*cyclo*hexanone with benzene- and toluene-*p*-diazonium chlorides affords the *carbethoxyphenylhydrazone*, m. p. 90—92°, and the *carbethoxy*-p-*tolylhydrazone*, m. p. 97—99°, of *cyclo*hexane-1 : 2-dione.

H. Burton.

Action of the Grignard reagent on alkylbarbituric acids. A. W. Dox (J. Amer. Chem. Soc., 1927, 49, 3189—3190; cf. A., 1927, 1087).—In view of the results of Bauer (A., 1904, i, 417) and Houben (A., 1904, i, 302) on the formation of cyclic derivatives from a single carbonyl group and a Grignard reagent, the compounds to which the endo-ether structure was previously ascribed (*loc. cit.*) may, alternatively, have a structure analogous to that represented in the annexed formula.



$$CR_1R_2{<}{\substack{CR_3(OH){\cdot}NPh\\ CR_3R_4{-\!\!-}NPh}}{>}CO$$

F. G. Willson.

Mechanism of the oxidation of pyrazolines. R. LOCQUIN and R. HEILMANN (Compt. rend., 1927, **185**, 1477—1479; cf. 1925, i. 1185).—The products formed during the oxidation of 3-methyl-5-*iso*propylpyrazoline are 3-methyl-5-*iso*propylpyrazole, a mixture of the ketazines of *iso*butylideneacetone and *iso*heptanone, hydrolysed by sulphuric acid to hydrazine and the corresponding ketones, and high-boiling pyrazoline-like compounds. Similar results are obtained with 3-methyl-5-*iso*butylpyrazoline. The mechanism of the oxidation is discussed.

H. BURTON.

Reactions of hydrazines with hydroxymethylene-ketones and their derivatives. II. K. VON AUWERS and H. MAUSS (J. pr. Chem., 1927, [ii], **117**, 311—336; cf. A., 1927, 361).—*s*-Benzoylphenylhydrazine reacts with phenyl β-hydroxyvinyl ketone in ethereal solution to give 2-*benzoyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 155—155·5°, which is converted on long keeping into an *isomeride*, m. p. 188°. The substance of m. p. 155—155·5° is transformed into *s*-benzoylphenylhydrazine by boiling with alcoholic alkalis or by heating with glacial acetic acid and zinc dust; treatment with benzoyl chloride and pyridine affords *dibenzoyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 163—164°. Methylation yields 2-*benzoyl*-1-*phenyl*-1-β-*benzoylvinyl*-2-*methylhydrazine*, m. p. 158·5—159°, which is converted by hydrolysis into 2-benzoyl-1-phenyl-2-methylhydrazine, m. p. 135—136°. *as*-Benzoylphenylhydrazine reacts with phenyl β-hydroxyvinyl ketone to give β-*benzoylacetaldehydebenzoylphenylhydrazone*, m. p. 132—133°, which is converted into benzanilide by zinc dust and acetic acid and by benzoylation into 1 : 2-dibenzoyl-1-phenyl-2-benzoylvinylhydrazine (benzoyl derivative of the tautomeric form), m. p. 162·5—163°. By heating an alcoholic sodium hydroxide solution of the hydrazone, 4-*benzoyl*-1 : 5-*diphenylpyrazole*, m. p. 144—145°, identical with a specimen synthesised by heating 1 : 5-diphenylpyrazole with benzoyl chloride at 250°, is produced. β-p-*Toluoylacetaldehydebenzoylphenylhydrazone*, m. p. 132·5—134° (cf. A., 1926, 272), prepared from *as*-benzoylphenylhydrazine and *p*-tolyl β-hydroxyvinyl ketone, yields 4-p-*toluoyl*-1 : 5-*diphenylpyrazole*, m. p. 151—152°, which may also be prepared from *p*-toluoyl chloride and 1 : 5-diphenylpyrazole. 2-*Toluoyl*-1-*acetyl*-2-*phenylhydrazine*, m. p. 165—166°, from *s*-acetylphenylhydrazine and *p*-toluoyl chloride, affords as -p-*toluoylphenylhydrazine*, m. p. 80—82°, on boiling with 2*N*-sulphuric acid. The last-named condenses with phenyl β-hydroxyvinyl ketone to give, after treatment of the product with sodium hydroxide, 4-*benzoyl*-5-p-*toluoyl*-1-*phenylpyrazole*, m. p. 172—173°, which was also prepared by the alternative method. 1-*Phenyl*-2-β-p-*toluoylvinylhydrazine*, m. p. 124—125°, prepared from *p*-tolyl β-hydroxyvinyl ketone, yields on heating 5-p-*toluoyl*-1-*phenylpyrazole*, b. p. 220—240°, m. p. 61·5—62·5°, which may be converted into the 4-*benzoyl* derivative, m. p. 178·5°, by heating with benzoyl chloride at 220°. *p*-Tolyl β-hydroxyvinyl ketone and *s*-formylphenylhydrazine yield 1-*formyl*-2-*phenyl*-2-β-p-*toluoylvinylhydrazine*, m. p. 180·5°, which affords 3-*p*-toluoyl-1-phenylpyrazole, m. p. 95·5°, when heated with 2*N*-hydrochloric acid. The action of phenylhydrazine on p-*tolyl* β-*benzyloxyvinyl ketone*, m. p. 86—87°, yields 1-*phenyl*-1-β-p-*toluoylvinylhydrazine*, m. p. 172·5—173·5° (p-*nitrobenzylidene* derivative, m. p. 181·5°). 2-*Acetyl*-1-*phenyl*-1-β-*benzoylvinylhydrazine*, m. p. 169—170°, prepared from *s*-acetylphenylhydrazine and phenyl β-hydroxyvinyl ketone, yields a *methyl* derivative, m. p. 135·5—136·5°, which gives 1-acetyl-2-phenyl-1-methylhydrazine, m. p. 91—92°, and a *benzoyl* derivative, m. p. 161·5—162·5°. Phenyl β-hydroxyvinyl ketone and benzoylhydrazine react to afford 2-*benzoyl*-1-β-*benzoylvinylhydrazine*, m. p. 145—146°, which gives acetophenonebenzoylhydrazone on hydrolysis, and a *dimethyl* derivative, m. p. 147—148°.

G. A. C. GOUGH.

Condensation of glyoxalines with formaldehyde. R. GRINDLEY and F. L. PYMAN (J.C.S., 1927, 3128—3136; cf. A., 1924, i, 1111).—4(5)-Bromoglyoxaline is converted by formaldehyde at 150° into 4(5)-*bromo*-5(4)-*hydroxymethylglyoxaline*, $+\frac{1}{2}H_2O$, m. p. 116—117° (all m. p. are corr.) [*hydrochloride*, m. p. 157° (decomp.); *picrate*, $+H_2O$, m. p. anhydrous 180°], which is reduced by hydriodic acid and phosphorus to 4(5)-methylglyoxaline. 1 : 4-Dimethylglyoxaline yields similarly 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline*, m. p. 126—127° (*hydrochloride*, m. p. 145°; *hydrogen oxalate*, m. p. 106—107°; *picrate*, m. p. 167—168°), which on reduction affords 1 : 4 : 5-trimethylglyoxaline. 1 : 5-Dimethylglyoxaline furnishes 1 : 5-*dimethyl*-2-*hydroxymethylglyoxaline*, $+\frac{1}{2}H_2O$, m. p. 126—127° (*picrate*, m. p. 174°), reduced to 1 : 2 : 5-*trimethylglyoxaline* (*picrate*, m. p. 208—209°; *chloroaurate*, m. p. 186—187°). 1 : 5-*Dimethyl*-4-*hydroxymethylglyoxaline* (*picrate*, m. p. 178—179°) is obtained by methylation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline and has m. p. 164—165°. 5-Chloro-1-methyl- and 1-methyl-glyoxaline yield the corresponding 2-hydroxymethyl derivatives (cf. Sarasin, A., 1923, i, 711; 1924, i, 1114; Sonn, Hotes, and Sieg, A., 1924, i, 877; 1925, i, 157). The nitroglyoxalines studied do not condense with formaldehyde. The above results show that glyoxalines containing a free imino-group yield 4(5)-hydroxymethyl derivatives, whilst *N*-methylglyoxalines yield either the 2- or 5-derivatives.

H. BURTON.

5 : 6 : 8-Trihydroxybenzo-1 : 10-naphthyridine, and its oxidation to 1 : 8-naphthyridine derivatives. E. SUCHARDA (Kosmos, 1920, 15 pp.; Chem. Zentr., 1927, i, 2831).—5 : 6 : 8-*Trihydroxybenzo*-1 : 10-*naphthyridine* (*sodium* derivative; *acetyl* derivative; *hydrochloride*), yellow, m. p. 348°, obtained by heating 2-aminopyridine-3-carboxylic acid and phloroglucinol at 210—220°, is oxidised by permanganate to 5-*hydroxy*-1 : 8-*naphthyridine*-6 : 7-*dicarboxylic acid*, light yellow, m. p. 304° (decomp.), which, when heated at 120° or boiled with 20% hydrochloric acid, affords 1 : 8-*naphthyridine*-6-*carboxylic acid*, white, m. p. 304° (decomp.). At 304°, both acids give 5-*hydroxy*-1 : 8-*naphthyridine*, white, m. p. 239°.

A. A. ELDRIDGE.

Manufacture of vat dyes of the [phen]anthraquinone series [complex carbazoles]. I. G. FARBENIND.—See B., 1928, 9.

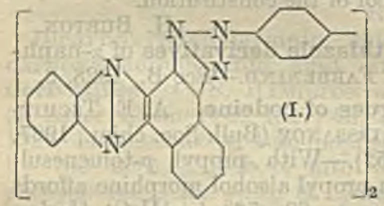
2-Aryl-αβ-naphtha-1 : 2 : 3-triazoles. G. CHARRIER and M. GALLOTTI (with J. M. CASALETTO,

L. Masciadri, and E. Greppi) (Gazzetta, 1927, **57**, 754—760).—By diazotising 2-*p*-aminophenyl-αβ-naphtha-1 : 2 : 3-triazole (A., 1924, i, 335), and treating the product with potassium iodide, the corresponding 2-p-*iodophenyl* compound, m. p. 218°, is obtained. When in the diazotisation concentrated solutions are used, the 2-*phenylnaphthatriazole*-p-*diazonium sulphate* can be isolated; when this is suspended in water and treated with potassium arsenite solution in the presence of copper powder, 2-*phenyl*-4 : 5-αβ-*naphtha*-1 : 2 : 3-*triazole*-4′-*arsinic acid* (decomp. before m. p.) is obtained, with a large proportion of the phenylnaphthatriazole itself.

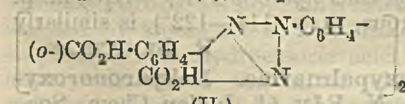
By the action of benzenediazonium chloride on 4-nitro-1-naphthylamine, 4-*nitro*-1-*amino*-2-*benzeneazonaphthalene*, m. p. 226°, is obtained, which on heating with copper in nitrobenzene yields 5-*nitro*-2-*phenyl*-αβ-*naphthatriazole*, m. p. 191°.

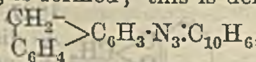
E. W. Wignall.

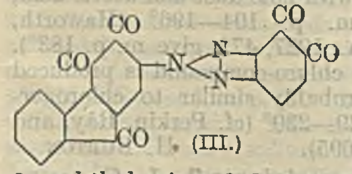
Polynuclear 1 : 2 : 3-triazoles and their oxidation products. G. Charrier and G. B. Crippa [with C. Pagani, E. Rovida, and C. Azimonti] (Gazzetta, 1927, **57**, 749—754).—The di-ψ-azimide, diphenylbisnaphthatriazole (Schmidt and Hagenböcker, A., 1921, i, 898), is oxidised by chromic acid to a *bis*-o-*quinone*, m. p. 390° (decomp.), which with phenylhydrazine yields a *bis*-(α-*hydroxy*-β-*benzeneazo*) derivative, m. p. 306°, and with *o*-phenylenediamine the *diphenazine* (I), m. p. above 435°.


(I.)

Oxidation of the original triazole by alkaline potassium permanganate yields the *tetracarboxylic acid* (II), m. p. 330°.


(II.)

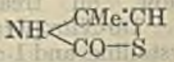
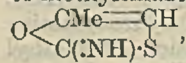
Similarly, 2-β-anthraquinonyl-αβ-naphthatriazole, m. p. 305°, obtained by dehydrogenating β-anthraquinonylazo-β-naphthylamine by copper powder in nitrobenzene, yields a *bis*-o-*quinone*, m. p. 350° (decomp.), an orange-red substantive dye to cotton. By the action of fluorene-2-diazonium sulphate on β-naphthylamine, 2-*fluoreneazo*-β-*naphthylamine*, decomp. from 360°, is formed; this is dehydrogenated to the *triazole*,  $\left.\begin{matrix}CH_2-\\ |\\ C_6H_4\end{matrix}\right>C_6H_3\cdot N_3{:}C_{10}H_6$, unchanged at 360°, which oxidises to the *keto-bis*-o-*quinone* (III), unchanged at 360°.


(III.)

E. W. Wignall.

Reaction of hydroxylamine with enol ethers and acetylenic ketones; new constitutionally unambiguous ***iso*****oxazole synthesis.** C. Weygand and E. Bauer [with W. Heynemann] (Annalen, 1927, **459**, 123—143).—Since it has been shown that the first stage in the formation of an *iso*oxazole from an unsaturated ketone and hydroxylamine may be either oximation or addition to the multiple linking (A., 1925, i, 1288), further evidence for the constitution of 3 : 5-disubstituted *iso*oxazoles is required (cf. Moureu, A., 1904, i, 95; Ruhemann and Watson, J.C.S., 1904, **85**, 1319; Jörlander, A., 1917, i, 222). This is afforded by their synthesis from chloroaldoximes (hydroxamic chlorides) and sodium arylacetylides in ethereal solution. Thus, ω-chloroanisaldoxime, m. p. 89—90° (cf. Rheinboldt, A., 1927, 245), and sodium phenylacetylide yield 5-phenyl-3-anisyl*iso*oxazole (I), m. p. 120—121°, whilst ω-chlorobenzaldoxime and sodium anisylacetylide yield 3-phenyl-5-anisyl*iso*oxazole (II), m. p. 127—128° (cf. Pond and Shoffstall, A., 1901, i, 35). When phenyl α-4-dimethoxystyryl ketone and hydroxylamine react in presence of acid or alkali, the compound (I) is obtained, but in neutral solution alkali-insoluble *phenyl α-hydroxylamino-4-methoxystyryl ketone* (III), m. p. 134°, is formed by addition of hydroxylamine to the double linking and elimination of methyl alcohol. This is precipitated by addition of water in an alkali-soluble enolic form which is converted by acids into the *iso*oxazole (I). Anisyl α-methoxystyryl ketone and hydroxylamine yield isomeride (I) in presence of hydrochloric acid, (II) in acetic acid or alkaline solution, and *anisyl α-hydroxylaminostyryl ketone*, m. p. 155—157°, in neutral solution. This resembles (III), being converted by acids into (II). When, however, (*a*) phenyl β-bromo-*p*-methoxystyryl ketone, (*b*) *p*-anisyl β-bromostyryl ketone, and the dibromides of (*c*) phenyl *p*-methoxystyryl ketone and (*d*) *p*-anisyl styryl ketone are treated with hydroxylamine and alkali, (*a*) and (*c*) yield (II), and (*b*) and (*d*), (I). This is attributed to the intermediate formation of a dimethylacetal oxime. Crude phenyl α-bromo-β-methoxy-β-anisylethyl ketone yields with hydroxylamine and alkali (II) and a little 4(?5)-hydroxy-3-phenyl-5-anisyl-4 : 5-dihydro*iso*oxazole (Jörlander, *loc. cit.*). By analogy, the products from phenyl α-methoxy-*p*-methylstyryl ketone and *p*-tolyl α-methoxystyryl ketone and this reagent are 5-*phenyl*-3-p-*tolyl*-, m. p. 125—126°, and 3-*phenyl*-5-p-*tolyl*-, m. p. 136—137°, -iso*oxazoles*, respectively. Benzoyl-*p*-anisylacetylene and hydroxylamine afford (*a*) with acetic acid or alkali the substance (I), (*b*) with hydrochloric acid (II), whilst p-*anisoylphenylacetylene*, m. p. 90—91°, from sodium phenylacetylide and anisoyl chloride gives (*a*) (II), (*b*) (I). Thus in (*a*) the reaction probably proceeds through a hydroxylamino-derivative similar to (III) and in (*b*) through an oxime.

H. E. F. Notton.

Hydroxythiazoles or thiazolones. A. Hantzsch [with H. Schwedler and H. Schwaneberg] (Ber., 1927, **60**, [*B*], 2537—2545).—Mainly a reply to Tcherniac (J.C.S., 1919, **115**, 1071).—Thiocyanoacetone is converted slowly by cold, rapidly by hot concentrated hydrochloric acid without resinification into methylthiazolone,  $NH\left<\begin{matrix}CMe{:}CH\\ \qquad|\\ CO-S\end{matrix}\right.$ (formerly considered to be hydroxymethylthiazole); under the influence of alkalis, even hydrogen carbonates, the production of the thiazolone is accompanied by extensive resinification. 2-Hydroxy-4-methylthiazole is very readily obtained by the action of methylxanthamide on chloroacetone; if, however, the hydrolysing action of the liberated hydrogen chloride is inhibited by the addition of potassium acetate and the use of alcohol is avoided, 4-*methoxy*-2-*methylthiazole*, b. p. 59—60°/18 mm. (additive *compound* with mercuric chloride, m. p. 123—124°), and, analogously, 4-*ethoxy*-2-*methylthiazole*, b. p. 71—72°/15 mm., are readily prepared. The methyl ether is also obtained by the action of diazomethane on methylthiazolone dissolved in alcohol, ether, chloroform, or benzene. It gives a *hydrochloride*, m. p. 78° with evolution of methyl chloride and production of methylthiazolone, thus differing from the isomeric *N*-ether *hydrochloride*, m. p. 109° with evolution of hydrogen chloride. Methylthiazolone and its *N*-methyl ether give additive *compounds* with mercuric chloride, m. p. about 180° (decomp.). This behaviour cannot be reconciled with Tcherniac's formulation of methylthiazolone as "methylrhodim,"  $O<\begin{matrix}CMe{=\!=}CH\\C(:NH)\cdot S\end{matrix}$, which could not give rise to *O*-ethers and the *N*-ethers of which must yield methylamine when hydrolysed. Contrary to Tcherniac's observation, homogeneous hydroxymethylthiazole and thiocyanoacetone are converted into methylthiazole (and resinous substances) when distilled with zinc dust. Comparison of hydroxymethylthiazole with its *O*- and *N*-ethers shows that it is to be regarded as methylthiazolone when solid. Optical analysis shows it to be a mixture of hydroxymethylthiazole and methylthiazolone in alcoholic solution, whereas in chloroform and, particularly, in benzene and ether the hydroxy-form appears present only in traces. Methylthiazolone dissolved in phosphoryl chloride is converted by a slight excess of phosphorus pentachloride in the presence of boiling ether into 5-*chloro*-4-*methylthiazol*-2-*one*, m. p. 140°, regarded by Tcherniac as "methylchlororhodim," which dissolves in solutions of alkali or sodium hydrogen carbonate and is precipitated unchanged from these solutions by immediate addition of acid. Boiling phosphoryl chloride transforms 4-methylthiazol-2-one into 2-chloro-4-methylthiazole, b. p. 164—165°, identical with the substance obtained by Tcherniac from thiocyanoacetone and hydrogen chloride. H. Wren.

Thiazoles. XIV. Synthesis of 2-*o*- and -*m*-aminophenyl-6-methylbenzthiazoles; new isomerides of dehydrothio-*p*-toluidine, and incidental compounds. M. T. Bogert and L. Smith (J. Amer. Chem. Soc., 1927, 49, 3135—3137; cf. A., 1927, 680).—Condensation of zinc 4-aminothio-*m*-tolyloxide with *m*-nitrobenzoyl chloride affords 1-m-*nitrophenyl*-5-*methylbenzthiazole*, yellow, m. p. 166°. The latter, on reduction with tin and hydrochloric acid, yields 1-m-*aminophenyl*-5-*methylbenzthiazole*, m. p. 181°, and this affords a *sulphonic acid*, dark brown, which is converted into a *dye*, analogous to chloramine-yellow, on treatment with alkaline hypochlorite. 1-o-*Nitrophenyl*-5-*methylbenzthiazole*, yellow, non-crystalline, and 1-o-*aminophenyl*-5-*methylbenzthiazole*, m. p. 137° (*acetyl* derivative, m. p. 150°), are obtained analogously, but sulphonation of the latter and subsequent treatment with hypochlorite does not yield a dye. F. G. Willson.

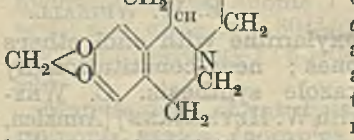
Benzidine rearrangement in heterocyclic series. I. P. K. Bose (J. Indian Chem. Soc., 1927, 4, 331—338).—Phenacyl bromide and phenylthiosemicarbazide react in alcohol to form 2-*phenylhydrazino*-4-*phenylthiazole*, m. p. 191° (*hydrobromide*; *acetyl* derivative, m. p. 161°). Boiling dilute hydrochloric acid converts the thiazole into 2-*amino*-4-*phenyl*-5-p-*aminophenylthiazole*, m. p. 193—194° [*dihydrochloride*, $+H_2O$, decomp. above 260°; *picrate*, m. p. 134—135° (decomp.); *chloroplatinate*; *diacetyl* derivative, m. p. 285—286°], due to a benzidine rearrangement (cf. Fargher and Pyman, J.C.S., 1919, **115**, 222; Pyman and Ravald, *ibid.*, 1920, **117**, 1426). 2-*Phenylhydrazino*-4-p-*tolylthiazole*, m. p. 186° (*hydrobromide*; *acetyl* derivative, m. p. 146°), yields similarly 2-*amino*-4-p-*tolyl*-5-p-*aminophenylthiazole*, m. p. 182° [*diacetyl* derivative, m. p. 290°; *dihydrochloride*; *chloroplatinate*; *picrate*, m. p. 215° (decomp.)]. 2-*Phenylhydrazino*-4-*methylthiazole*, m. p. 179° (*acetyl* derivative, m. p. 232°), yields 2-*amino*-4-*methyl*-5-p-*aminophenylthiazole*, m. p. 181° [*dihydrochloride*, $+2H_2O$, decomp. above 240°; *chloroplatinate*; *picrate*, m. p. 214° (decomp.); *benzylidene* derivative, m. p. 177°]. Oxidation of 2-*acetamido*-4-*methyl*-5-p-*acetamidophenylthiazole*, m. p. 292°, with potassium permanganate gives *p*-acetamidobenzoic acid, thus affording further proof of the constitution. H. Burton.

Manufacture of thiazole derivatives of α-naphthaquinone. I. G. Farbenind.—See B., 1928, 8.

Simple homologues of codeine. A. E. Tschitschibabin and A. Kirssanov (Bull. Soc. chim., 1927, [iv], 41, 1649—1652).—With propyl *p*-toluenesulphonate in boiling *n*-propyl alcohol morphine affords the n-*propyl ether*, m. p. 69—72° ($+\frac{1}{2}H_2O$) [*hydrochloride*, m. p. 146—153° (decomp.) ($+H_2O$, m. p. 111—114°)]. The n-*butyl ether hydrochloride*, $+H_2O$, m. p. 101—104° (anhydrous, m. p. 119—122°), is similarly prepared. R. Brightman.

Synthesis of oxypalmatine. Dehydro*nor*oxy-ψ-corydaline. J. N. Rây (J. Indian Chem. Soc., 1927, 4, 403—408).—Homoveratrylamine and meconinecarboxyl chloride react, giving *meconinecarboxy-β-veratrylethylamide*, m. p. 185°, which is converted by prolonged treatment with phosphorus oxychloride, followed by reduction with zinc dust and acetic acid, into oxypalmatine, m. p. 194—196° (Haworth, Koepfli, and Perkin, A., 1927, 472, give m. p. 183°). A small quantity of a chloro-compound is produced at the same time, probably similar to chloro*nor*oxyberberine, m. p. 229—230° (cf. Perkin, Rây, and Robinson, A., 1925, i, 695). H. Burton.

How do alkaloids originate? J. Gadamer (Festschr. A. Tschirch, 1926, 36—41; Chem. Zentr., 1927, i, 2558—2559).—A discussion. [With Wachsmuth.]—From *Corydalis cava* tops an *alkaloid*, to which the annexed formula is ascribed, has been obtained, and has been resolved by means of bromocamphorsulphonic acid. A. A. Eldridge.



Silicon organic compounds. I. Phenol esters of silicic acid. H. Jörg and J. Stetter

(J. pr. Chem., 1927, [ii], **117**, 305—310).—Silicon tetrachloride reacts with phenol (2 mols.) at 100° to give *dichlorodiphenoxysilicane*, b. p. 167—171°/13 mm., *chlorotriphenoxysilicane*, b. p. 229—230°/14 mm., and tetraphenoxysilicane, b. p. 280°/14 mm. In a similar manner *chlorotri*-p-*bromophenoxysilicane*, b. p. 310—320°/12 mm., *trichlorothiophenoxysilicane*, b. p. 110°/12 mm., and *tetra*-o-*methoxyphenoxysilicane*, b. p. 317—323°/12 mm., are prepared. By the interaction of magnesium phenyl bromide and dichlorodiphenoxysilicane in ethereal solution diphenylsilicanediol, m. p. 116° (cf. Martin, A., 1912, i, 1014), is prepared. Chlorotriphenoxysilicane yields similarly *triphenoxyphenylsilicane*, m. p. 40°, b. p. 250°/13 mm.

G. A. C. Gough.

Isomerism of *p*-hydroxyphenylarsinic acid. G. Gilta (Compt. rend., 1927, **184**, 1073—1075).—*p*-Hydroxyphenylarsinic acid, its 3-nitro-derivative, and its barium salt all occur in two different crystalline forms, which are regarded as possessing the benzenoid and quinonoid structure, respectively. The 3 : 5-dinitro-derivative of the acid is obtained in one form only. Isomerism analogous to the above is found in 4-hydroxy-3-methylphenylarsinic acid.

B. W. Anderson.

Dicarboxyphenylarsinic acids. II. 3 : 4-Dicarboxyphenylarsinic acid and some of its derivatives. C. S. Hamilton and V. C. Jelinek (J. Amer. Chem. Soc., 1927, **49**, 3165—3169; cf. A., 1926, 1162).—Methyl 4-aminophthalate is converted by the normal process into 3 : 4-*dicarbomethoxyphenylarsinic acid*, which is hydrolysed by absolute-alcoholic sodium ethoxide to the *tetrasodium* salt of 3 : 4-*dicarboxyphenylarsinic acid*, yellow, m. p. 180° (decomp.) (*trisodium* salt; *ethyl* ester), the latter being isolated by treatment of the *silver* salt in aqueous suspension with hydrochloric acid, and evaporation after removal of the silver chloride. The *acid anhydride* is obtained by heating the acid for 3 days under reduced pressure at 160° in presence of phosphorus pentoxide.

F. G. Willson.

Organo-antimony compounds. I. S. C. Niyogy (J. Indian Chem. Soc., 1927, **4**, 397—402).—2 : 6-*Di-iodo-4-nitroacetanilide*, m. p. 245—246°, is reduced by ammonium sulphide in alcoholic solution to 2 : 6-*di-iodo-4-aminoacetanilide* (*di-iodo-acetyl*-p-*phenylenediamine*), m. p. 247—248°, which is converted by the usual method into 3 : 5-*di-iodo-4-acetamidophenylstibinic acid* (*sodium* salt). Similarly, from 2 : 6-*dichloro-4-aminoacetanilide*, m. p. 209—210°, 2-*bromo-4-aminoacetanilide*, m. p. 120—121°, 2 : 6-*dibromo-4-aminoacetanilide*, m. p. 235—236°, and 2-*iodo-4-aminoacetanilide*, m. p. 134—135°, there were prepared the *sodium* salts of 3 : 5-*dichloro-4-acetamidophenyl*-, 3-*bromo-4-acetamidophenyl*-, 3:5-*dibromo-4-acetamidophenyl*-, and 3-*iodo-4-acetamidophenyl-stibinic acids*. 2-*Iodo-4-nitroacetanilide* has m. p. 138—139°.

H. Burton.

Derivatives of bismuth di- and tri-phenyl. S. Rozenblumóvna and S. Weil (Viadomosci farm., 1927, **54**, 25—28; Chem. Zentr., 1927, ii, 1251).—Diphenyliodobismuthine yielded bismuth triphenyl, not bismuth diphenyl; diphenylhalogenobismuthines, when treated in alcoholic solution with sodium hydroxide, yielded diphenylhydroxybismuthine (cf. Challenger and Allpress, J.C.S., 1921, **119**, 913).

A. A. Eldridge.

Hydrolysis of egg-albumin by pepsin in relation to the formation of diketopiperazines. A. Blanchetière (Compt. rend., 1927, **185**, 1321—1323; cf. A., 1927, 474).—Egg-albumin was hydrolysed at 45° in aqueous solutions containing 0·1N-hydrochloric acid, 0·1 g. of pepsin, and some toluene, for 1—82 days, and the diketopiperazine-nitrogen content was determined in each case. With raw albumin this figure decreased rapidly at first, reaching a constant value after 30 days. The reverse occurred with albumin previously denatured at 100°, an increase to a constant value being observed. The formation and hydrolysis of diketopiperazines indicated by these results is discussed.

B. W. Anderson.

Anhydrides of amino-acids from gelatin: hydrolysis by the method of Zelinski and Sadikov. N. Gavrilov and K. Lavrovski (Biochem. Z., 1927, **190**, 278—285).—From the solution obtained by heating gelatin in an autoclave with 1·5% sulphuric acid, *l*-prolylglycine anhydride and *l*-leucylglycine anhydride are isolated and together form 10% of the gelatin used.

P. W. Clutterbuck.

Hydrolysis of proteins by acids and alkalis. J. S. Jaitschnikov (Biochem. Z., 1927, **190**, 114—121).—The kinetics of the hydrolysis of 2 : 5-diketopiperazine, glycylglycine, peptone, and proteins (albumin, caseinogen, edestin, glutin, elastin, keratin, and silk) by varying concentrations of sodium hydroxide and hydrochloric acid at different temperatures have been determined. With the 2 : 5-diketopiperazine and the dipeptide the hydrolysis is a unimolecular reaction, whilst for peptones and proteins the formula of Schütz and Borisoff ($K=x/\sqrt{t}$, where K is the coefficient, x the amount of protein hydrolysed, and t the time) is applicable. The amount of hydrolysis has been measured by formol titration (Sørensen) after neutralisation.

A. Wormall.

Formation of metal–albumin compounds. A. Benedicenti and G. B. Bonino (Arch. sci. biol., 1926, **8**, 241—247; Chem. Zentr., 1927, i, 2521—2522).—The ratio of the *P.D.* between cobalt and egg-albumin treated with powdered cobalt to the temperature has a maximum value at the coagulation temperature of the protein. The effect of dilution with water and of variation in p_H around the isoelectric point was investigated.

A. A. Eldridge.

Protein–metal compounds. I. G. B. Bonino and M. Bottini. **II—IV.** G. B. Bonino and A. Grandi (Arch. sci. biol., 1926, **8**, 248—257, 258—276, 277—288, 289—292; Chem. Zentr., 1927, i, 2522—2523).—I. The potential of cobalt towards water is −0·708 volt, and towards a cobalt–protein solution of p_H 6·4 −0·648 volt.

II. With hydrogen-ion concentrations greater than that of the isoelectric point, the fixation of cobalt to gelatin and the decrease in the conductivity and viscosity are parallel.

III. Gelatin solutions (1%) of p_H 2—7 were treated with cobalt and placed in Malfitano's collodion sacs, the exterior liquid being 0·002N-cobalt chloride solution, and the p_H and total cobalt content were determined after 5—6 days. Parallel experiments were performed with gelatin solution against distilled water containing powdered cobalt, and also with exterior liquids of hydrogen-ion concentration greater than that of the isoelectric point, or N with respect to potassium chloride. In solutions of the same composition, qualitatively and quantitatively, values of ε in the relation $(1/\varepsilon)([\mathrm{Co}_{\mathrm{total}}]_2/[\mathrm{Co}_{\mathrm{total}}]_1)^{\frac{1}{2}} = ([\mathrm{Co}^{\cdot\cdot}]_2/[\mathrm{Co}^{\cdot\cdot}]_1)^{\frac{1}{2}}$ are highly concordant or identical. Increase of the total cobalt content is accompanied by decrease of the quotients $[\mathrm{H}^{\cdot}]_1/[\mathrm{H}^{\cdot}]_2$ and $\varepsilon([\mathrm{Co}_{\mathrm{total}}]_2/[\mathrm{Co}_{\mathrm{total}}]_1)^{\frac{1}{2}}$. If the metal–protein is brought into equilibrium with an acid solution, so that the p_H of the protein is less than 4·7, the values at equilibrium are less than unity.

IV. Varying quantities of sodium hydroxide were added to pure gelatin, and a portion was brought into equilibrium with cobalt. The conductivity increases at $p_H > 7$, and on further increase of p_H becomes zero, although combined cobalt is still present. It is supposed that at $p_H > 7$ tervalent cobalt is present in a complex form corresponding with the cobaltammines.

A. A. ELDRIDGE.

Combination of gelatin with organic bases. A. PETRUNKIN and M. PETRUNKIN (J. Gen. Physiol., 1927, 12, 101—110).—Alkaloids (atropine, strychnine, and quinine) and organic bases (guanidine and adrenaline) combine with gelatin on the basic side of the isoelectric point of the protein, but very little, if at all, on the acid side. W. O. KERMACK.

Irradiated proteins. II. Absorption in the ultra-violet of light-denatured serum-albumin. M. SPIEGEL-ADOLF and O. KRUMPEL (Biochem. Z., 1927, 190, 28—41).—Absorption spectra and curves have been determined for electrolyte-free serum-albumin solutions and for irradiated and non-irradiated serum-albumin in acid and alkaline solutions. The irradiated solutions show a stronger power of absorption for short waves in the region of 400 μμ to 267·5 μμ compared with the non-irradiated solutions, but there is no apparent displacement of the absorption maxima and minima. The absorption spectra of non-irradiated acid and alkaline serum-albumin solutions show slight differences only, whilst those of the irradiated solutions are practically identical. The results are discussed in relation to the absorption curves of the aromatic amino-acids and the behaviour of these acids on irradiation, and also in relation to the stronger absorption powers of 2 : 5-diketopiperazines compared with the corresponding dipeptides. A. WORMALL.

Separation of ovalbumin from conalbumin. H. WU and S. M. LING (Chinese J. Physiol., 1927, 1, 431—434).—A method is described for the separation of the ovalbumin from the conalbumin in egg-white based on the fact that ovalbumin undergoes coagulation by shaking whilst conalbumin does not. Of the total albumin of egg-white 10% is conalbumin.

E. A. LUNT.

Denaturation of proteins. V. Factors controlling coagulation of proteins by shaking. H. WU and S. M. LING (Chinese J. Physiol., 1927, 1, 407—430).—The conditions relating to the mechanical coagulation of solutions of egg-albumin, oxyhæmoglobin, and methæmoglobin have been investigated and show that, in contrast to the coagulation of albumin by alcohol, mechanical coagulation is not separable into the two stages of denaturation and agglutination. Whilst the rate of coagulation of hæmoglobin is increased by the addition of neutral alkali salts, the increase being approximately proportional to the concentration of the added salt, the coagulation of egg-albumin is not appreciably affected in this way. Non-electrolytes increase the rate of coagulation of both these substances. The p_H at which maximum coagulation takes place in the absence of electrolytes corresponds with the isoelectric point of the proteins examined, and the amount of coagulation is independent of the concentration of the protein solution used and is a linear function of time. No evidence of the liberation of any non-protein substance as a result of mechanical coagulation was obtained. It is concluded that mechanical coagulation is an irreversible surface reaction.

E. A. LUNT.

Determination of complex proteins by means of their "protein-error." R. GOIFFON and HAUDIQUET (Compt. rend. Soc. Biol., 1927, 97, 311—313; Chem. Zentr., 1927, ii, 1288).—Disturbance in colorimetric hydrogen-ion determinations caused by the presence of proteins (Sørensen's "protein-error") is employed for the determination of the proteins, by measuring (using a 0·02% solution of orange-IV) the increased buffer action of a solution on addition of a strong acid. A. A. ELDRIDGE.

Pregl's universal filling applied to macro-combustions. W. DAVIES (J.C.S., 1927, 3161—3162).—The universal filling devised by Pregl ("Die Quantitative Organische Mikroanalyse," 1923) for carbon and hydrogen determination has been successfully applied on a macro-scale. Details are given regarding the filling of the combustion tube and the special precautions to be taken in drying the lead peroxide asbestos plug. The lead peroxide in the combustion tube is heated by a hollow copper boiler, which itself is heated by *o*-dichlorobenzene. The procedure is normal, and representative analyses gave excellent results. R. A. PRATT.

Simultaneous determination of sulphur and chlorine in organic compounds. E. GEBAUER-FÜLNEGG and E. PETERTIL (Monatsh., 1927, 48, 619—625).—The method of Asbóth (A., 1896, ii, 448) for the determination of sulphur in organic compounds is adapted so that chlorine when also present may also be determined. The substance is heated with excess of sodium carbonate and sodium peroxide in a nickel crucible, which while still hot is plunged into water in a porcelain dish. The solution is acidified with nitric acid and is evaporated to dryness to render insoluble the silica which has been removed from the porcelain, and the sulphur in the soluble product is determined as barium sulphate. After the latter is precipitated, the solution is boiled with sodium sulphite and the chlorine determined as silver chloride.

E. W. WIGNALL.

Biochemistry.

Application of the oil turbine type of ultracentrifuge to the study of the stability region of carbon monoxide-hæmoglobin. T. SVEDBERG and J. B. NICHOLS (J. Amer. Chem. Soc., 1927, 49, 2920—2934).—Experiments with an oil turbine ultracentrifuge show that over the range p_H 6·0—7·56 the diffusion constant (0·071 cm.^{2}/day) and specific sedimentation velocity ($5{\cdot}46\times10^{-13}$ cm./sec.) of carbon monoxide–hæmoglobin are normal, whilst the mol. wt., 68,000, is normal from p_H 6·0 to p_H 9·05. At p_H 9·05, the carbon monoxide–hæmoglobin molecule appears to hold a unimolecular layer of water at its surface. F. G. WILLSON.

Metabolism of blood platelets. G. ENDRES and F. KUBOWITZ (Biochem. Z., 1927, 191, 395—397).—The respiration and anaërobic glycolysis of the platelets of human and dog's blood are determined and tabulated. P. W. CLUTTERBUCK.

Biological test for blood. W. WILLCOX (Analyst, 1928, 53, 2—5).—The value of the precipitin test is emphasised. The complement fixation test is regarded only as a confirmatory test. D. G. HEWER.

Technique of the precipitin test and its forensic value. G. R. LYNCH (Analyst, 1928, 53, 5—13).—For the detection of blood stains by the precipitin test it is necessary to prepare an antiserum (best from rabbits) capable of precipitin formation with at least a 1—5000 dilution of human serum in normal saline. The unknown extract is prepared by incubating the stained area in saline at 37°, testing for protein concentration, and diluting to give a concentration not greater than 1 in 1000, thus avoiding negative reactions due to zone reactions or false positive results from group reactions. The test is then made, either by layering, by dropping the antiserum on to the unknown extract, by running the antiserum down the side of the tube previously moistened with the unknown extract, or by Collés' tube method. The complete test requires 10 control tubes and is useful for the detection of occult blood in fæces and of the addition of egg-albumin to urine to simulate disease. It may also be used in cattle-maiming cases and is likely to find increased scope in food examination, for the blood of any animal may be immunised against a protein foreign to that animal. Difficulties due to group reactions of sera of closely-related animals may be overcome by the absorption method, by cross-immunisation, by dilution of the antiserum beyond the group reaction point, or by taking account of precipitation from similar dilutions of the antigen and related antigens. D. G. HEWER.

Use of blood-grouping reactions in forensic investigations. F. C. MARTLEY (Analyst, 1928, 53, 14—18).—Bloods may be divided into 4 groups according as to whether the blood-cells agglutinate when mixed with the sera or not. A blood may be placed in its correct group by mixing its corpuscles with sera of two known groups and observing presence or absence of clumping, and if necessary mixing the unknown serum with corpuscles from the known groups. Such tests are necessary before blood transfusion can be safely undertaken. Extent of agglutination varies within rather wide limits and is finite. Dried blood stains may be placed by using a known test serum of dilutions from 0·5, 0·25, down to 1 in 500 or 1000, and 1% agglutinable washed corpuscles added to an equal volume of each, and dilutions at which clumping occurs noted. The process is repeated with the same serum incubated with a piece of the same material free from stain, when clumping may not extend so far down the series. Incubation of the same serum with the blood stain is then carried out, when either the serum will cease to clump the test corpuscles or its power will be extinguished several places sooner than in the last test. D. G. HEWER.

Different sulphur contents of hæmoglobins from different sources. J. VALER (Biochem. Z., 1927, 190, 444—455).—A series of careful determinations of the sulphur and iron contents of recrystallised samples of the oxyhæmoglobin of the horse, ox, dog, and cat showed that whereas in cat and ox consistent values for the sulphur content could be obtained, this was not the case for horse, whilst with dog no sample contained the same amount of sulphur as any other, the preparation containing most having almost half as much again as that having least. With cat's oxyhæmoglobin, the minimal mol. wt. calculated from the iron content was 1690 and from the sulphur content 3299, *i.e.*, the iron and sulphur are in the proportion FeS_5. For ox blood, the proportions are FeS_3, and for horse, whilst several preparations correspond with the proportion FeS_3, others agree with Fe_2S_5. It is concluded that the supposed uniformity of samples of oxyhæmoglobin from different sources (previously concluded from identical iron determinations) does not exist.

P. W. CLUTTERBUCK.

Nature of the blood-sugar. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1927, 96, 414—416; Chem. Zentr., 1927, i, 2565).—Deproteinisation by zinc hydroxide in Hagedørn and Jensen's method for the determination of dextrose yields for the non-fermentable residue values which fluctuate around 0·23 g. per 1000. The non-fermentable residue is almost equally great in normal glycæmia for dogs, rabbits, and man, and is not augmented in hyperglycæmia. The origin of variations in the values obtained by various investigators is discussed.

A. A. ELDRIDGE.

Protein-blood-sugar. E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1927, 96, 417—421; Chem. Zentr., 1927, i, 2565).—The yeast method for the determination of blood-sugar reveals no so-called "protein-sugar," although traces, if present, could scarcely be detected. A. A. ELDRIDGE.

Ability of human blood to form lactic acid in presence of monosaccharides. A. ABRAHAM (Z. Klin. Med., 1926, 104, 609—618; Chem. Zentr., 1927, i, 2439).—The production of lactic acid by defibrinated human blood is increased in presence of dextrose, mannose, or (less markedly) lævulose.

A. A. ELDRIDGE.

Fermentation of dextrose in blood-plasma by yeast. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1927, **96**, 410—413; Chem. Zentr. 1927, i, 2562).—A mixture of 1 c.c. of serum or 0·2% oxalated blood, 1 c.c. of a suspension of fresh yeast (5 g.) in 0·9% sodium chloride solution (10 c.c.), and 8 c.c. of 0·9% sodium chloride solution is shaken for 30 min. at 38°, cooled, filtered, freed from protein with zinc hydroxide, and the dextrose determined by Hagedørn and Jensen's method. The autoreduction error is inconsiderable when the duration of the fermentation is brief. A. A. Eldridge.

Serum-globulin. L. Reiner (Biochem. Z., 1927, **191**, 158—174).—The precipitate corresponding with euglobulin may be prepared from sera by electrodialysis after repeated and thorough extraction with ether–alcohol. Euglobulin is not a lipoid–protein complex. By fractionation and purification, it changes in physical properties, particularly in solubility, becoming denatured in the process. The chief constituent of the globulin fraction is a protein practically insoluble in water and in physiological saline. By dialysis, the compound of globulin and protective colloid dissociates and the euglobulin precipitates. After the first precipitation, the precipitate still contains considerable amounts of protective colloid and it may still be dispersed as a cloudy solution in saline. After repeated precipitation, the protective colloid content and the dispersibility of the globulin decrease. The protective colloid also protects the globulin from the denaturing action of ether–alcohol. That the globulin has a wide isoelectric zone is evident from the course of the dissociation curve obtained by cataphoretic measurements, dissociation taking place at p_H 5·9 and between 4·6 and 4·1. Globulins with different isoelectric points could not be isolated. P. W. Clutterbuck.

Physico-chemical characteristics of normal and pathologically altered blood-serum. G. Lasch and J. Reitstötter (Biochem. Z., 1927, **190**, 84—94).—The methods employed previously (Reitstötter, A., 1921, ii, 176; 1923, i, 393) and the apparatus used are described fully, and it is considered that uniform, well-defined, and electrolyte-free protein fractions can be obtained in this way. The serum (*e.g.*, diphtheritic serum), contained in the centre portion of a cell which is divided into three chambers by two membranes, is freed from electrolytes and " extractive " substances (protein decomposition products) by electrodialysis. Euglobulin and a small fraction of the antitoxic substance are precipitated and are removed by centrifuging. The albumin and fatty substances which are still present can be removed by modifications of the process, and finally a water-clear solution, which contains the pseudoglobulin and the specific substance (antitoxin) associated with it, is obtained. The previous findings of Reitstötter (*loc. cit.*) on the sensitising action of protein fractions of normal and immune sera on ferric hydroxide sols, and the confirmatory experiments of Freundlich and Beck (A., 1926, 316), are discussed. A. Wormall.

Action of ultra-violet light on serum colloids. W. Gobel (Biochem. Z., 1927, **190**, 95—100).—Irradiation of human serum *in vitro* results in a lowering of the surface tension, but *in vivo* irradiation may lead to a rise or a fall. Subjects who have lived at high altitudes for a short period only (1—3 months) show a rise in the surface tension of the serum after irradiation, whilst those tested after a longer period (5—21 months) show a fall. This difference is probably due to an adaptation process, but no relationship between the type and the magnitude of the alteration in surface tension and the pigmentation of the irradiated skin can be observed. It is suggested that the results support the view that protein therapy and ray therapy have many common features and may be analogous. A. Wormall.

Loosely-combined copper and iron in blood-serum. O. Warburg and H. A. Krebs (Biochem. Z., 1927, **190**, 143—149).—The cysteine method for the determination of loosely-combined copper and iron in serum is described (cf. Warburg, A., 1927, 985). The values obtained for human serum give an average of $1·7\times10^{-3}$ mg. of copper and $0·7\times10^{-3}$ mg. of iron per c.c. of serum. Whereas the sera of the frog, dog, rabbit, guinea-pig, and rat contain about the same amount of copper as human serum, the sera of birds give lower values, although birds rendered anæmic by bleeding show an increase in serum-copper of three- to six-fold. The amount of loosely-bound iron in the sera of these different animals is generally greater than that in human serum. The loosely-bound copper of four different sera (horse and man) determined by this method is found to be equal to the total copper of the ashed serum. The copper content of the serum of rats which have received an intravenous injection of copper sulphate (0·5 mg. Cu per 160 g. rat) dissolved in physiological saline falls rapidly from its immediate high level and in about 6 hrs. has become normal. A. Wormall.

Chemical composition and properties of blood before and after food. I. Hydrogen-ion concentration of blood and its chloride, sugar, and calcium content. S. E. Sewerin. **II. Changes of the alkali reserve of the blood and of its chloride content during the digestion process.** G. W. Derwies and S. E. Sewerin (Biochem. Z., 1927, **190**, 326—329; 330—335).—I. Determinations of p_H on a number of rabbits after 1·5—2·5 days' fasting and on the same animals 3 hrs. after feeding with cabbage are tabulated and show that the blood is more acid during starvation. The chloride and calcium content of the blood is the same in the two conditions. The sugar content of the different rabbits varies greatly, but is higher in the fed than in the starving animals.

II. During digestion the alkaline reserve of the blood increases and the chloride content is only insignificantly changed, generally suggesting a slight rise. P. W. Clutterbuck.

Preservation of blood for chemical analysis by means of sodium fluoride. J. H. Roe, O. J. Irish, and J. I. Boyd (J. Biol. Chem., 1927, **75**, 685—695).—Under sterile conditions 1% of sodium fluoride will preserve blood for 10 days with respect to its content of non-protein nitrogen, uric acid, creatinine, sugar, and cholesterol; in the absence of aseptic precautions 2% of sodium fluoride is necessary to prevent marked changes in the blood. For the determination of carbamide by the urease method in blood preserved by fluoride, the blood must be diluted until the concentration of fluoride is 0·3% or less. C. R. Harington.

Simultaneous protease and residual nitrogen determination for blood. F. Himmerich (Biochem. Z., 1927, **191**, 74—82).—A micro-method for the simultaneous determination of protease and residual nitrogen of whole blood is described. Addition of sodium fluoride to hæmolysed blood in amount sufficient to act as antiseptic does not disturb the precipitation of protein and the action of blood-proteases. Shaking hæmolysed blood with chloroform accelerates the subsequent precipitation of protein with trichloroacetic acid, without having any effect on the residual nitrogen values obtained. The protein is also quantitatively precipitated by keeping for a long time with chloroform. Trichloroacetic acid is recommended as precipitant in protease determinations since it does not precipitate peptide nitrogen as do phosphotungstic acid and colloidal ferric hydroxide. P. W. Clutterbuck.

Gasometric nitrogen determination in small amounts of blood and urine by sodium hypobromite, using Borodin's apparatus. L. Solowjew (Biochem. Z., 1927, **190**, 199—216).—1—2 c.c. of urine or 0·3—1·0 c.c. of blood is heated with concentrated sulphuric acid and 30% hydrogen peroxide until the fluid is decolorised. The liquid is diluted with water to 30—50 c.c. and the ammonia in an aliquot portion (15—30 c.c.) is determined in the Borodin nitrometer by treatment with alkaline sodium hypobromite solution and measurement of the nitrogen evolved. The error under these conditions is less than ±3·0%. Solutions of sodium hypobromite which have been kept for some time give higher but more consistent results. The chief error is due to the liberation of small amounts of oxygen with the nitrogen, and when sodium hypobromite solution which has been kept for 2—5 days and then filtered is used, and the oxygen evolved in the determination removed by pyrogallol, the error is reduced to ±1—2·5% for quantities of nitrogen between 5 and 30 mg. A. Wormall.

Determination of minimal quantities of nicotine in blood. A. S. Sokolov and V. D. Lyubovtzeva (Trans. Sci. Chem. Pharm. Inst., 1923, No. 3, 69—77).—Blood (5 c.c.) is added to boiling water (25—30 c.c.) containing 2—3 drops of 10% acetic acid solution; 0·5 g. of sodium hydroxide and 4 g. of sodium chloride are added, and the mixture is distilled with steam. Nicotine (to 1 in 5×10^5) is determined in 150 c.c. of distillate (evaporated to 25 c.c.) with Lugol's solution.

Chemical Abstracts.

Formation of ammonia from cyanic acid. C. Artom (XII Int. Cong. Physiol., 1926, 9—10; Chem. Zentr., 1927, i, 2408).—The amount of ammonia formed when alkali cyanates at various p_H values are heated at 38° for 2—96 hrs. increases with rise of hydrogen-ion concentration, particularly between p_H 5 and 7. Cyanates may be present in the blood, and it may be possible to correlate spontaneous increase in the acidity of blood with extravascular and renal ammonia formation. A. A. Eldridge.

Determination of inorganic phosphorus in small amounts of blood. J. Warkany (Biochem. Z., 1927, **190**, 336—339).—The Briggs' modification of the Bell–Doisy method for the determination of phosphorus is adapted for micro-determinations, inorganic phosphorus being determined in 0·2 c.c. of serum. The method gives good agreement with the macro-method and is used for serum, serum of rachitic children, and for diluted serum after addition of known amounts of phosphate.

P. W. Clutterbuck.

Blood coagulation. H. de Waele (XII Int. Cong. Physiol., 1926, 165—166; Chem. Zentr., 1927, i, 2439).—The properties of fibrinogen and its compounds are described. Blood fibrinogen has solubility minima at p_H 4 and 7—9. Defatted fibrinogen does not coagulate. A. A. Eldridge.

Blood coagulation. XVI. Glycolysis in an artificial clotting mixture (fibrinogen+thrombin). XVII. Displacement of p_H during clotting. XVIII. Influence of hypo- and hyperpnea on clotting. B. Stuber and K. Lang (Biochem. Z., 1927, **191**, 374—377, 378—385, 386—394).—XVI. Whereas in the clotting of fibrinogen-serum or in the spontaneous clotting of whole blood and plasma a considerable amount of glycolysis occurs, the velocity of which is proportional to the clotting time, in the clotting of fibrinogen with the thrombin of Schmidt, no such glycolysis takes place, the difference being regarded as evidence of the artificial nature of this thrombin (cf. A., 1927, 68).

XVII. A double electrode is used to determine the changes of hydrogen-ion concentration in various clotting systems from the beginning of clotting at short intervals. During the clotting of both blood and milk, a displacement of the p_H to the alkaline side occurs.

XVIII. During hypo- and hyper-pnea, the clotting power of blood is greatly increased, glycolysis is considerably accelerated, and an increase in thrombocytes occurs. P. W. Clutterbuck.

Glycolysis and blood coagulation. B. Stuber and K. Lang (Verh. deut. Ges. inn. Med., 1926, 369—370; Chem. Zentr., 1927, i, 2439).—The glycolysis of blood rendered uncoagulable by oxalate, citrate, fluoride, etc. is subnormal. Coagulation of native plasma is associated with absorption of oxygen and production of carbon dioxide.

A. A. Eldridge.

Fibrinogen. R. Nordbö (Biochem. Z., 1927, **190**, 150—156).—From potentiometric titrations the isoelectric point of fibrinogen is found to be about p_H 5·5 and the acid-binding power in 0·85% sodium chloride solution is equal to 0·06 mg. of hydrogen chloride per mg. of fibrinogen. The flocculation zone differs with varying concentrations of fibrinogen and is broader with higher concentrations of the protein. A. Wormall.

Amount of fibrinogen and its relation to lability in plasma. K. Samson (Biochem. Z., 1927, **191**, 220—233).—The method of Leendertz (A., 1922, ii, 798) for the determination of fibrinogen gives results 15—20% lower than that of Starlinger (A., 1925, i, 716). In most cases the sinking velocity runs parallel to the determination of the amount of fibrinogen, the parallelism being least when the fibrinogen content is high. The method of Georgi (Klin. Woch., 1925, No. 43, 2053) for determination of the lability of the plasma by salting out with 26% sodium chloride and that of Gerloczy (Klin. Woch., 1922, No. 43) by inhibition of coagulation are based on quantitative processes and the parallelism with fibrinogen content is always clear. Refractometric determination of fibrinogen by salting out with sodium chloride is not possible. P. W. Clutterbuck.

Highly active anticoagulant from tissue. M. Doyon (XII Int. Cong. Physiol., 1926, 41; Chem. Zentr., 1927, i, 2566).—The filtrate from organs which had been incubated for months in sodium chloride solution was treated with alcohol, the precipitate redissolved in water and the constituents containing phosphorus precipitated at 100°. The nitrogenous, highly active substance was precipitated with acetic acid and alcohol, washed with alcohol and ether, and dried in a vacuum. A. A. Eldridge.

Composition of living organisms. I. Inorganic elements contained in cats. V. S. Sadikov and M. K. Shchegl'ska (Bull. Acad. Sci. U.R.S.S. [Russia], 1926, 1619—1646).—The animals were heated in an autoclave for 6 hrs. at 180—200°, and the product was resolved into an aqueous, an ethereal, an alcoholic, and a residual fraction. The percentage of carbon, hydrogen, and nitrogen in the aqueous fraction is identical for cats of all ages; chlorides, phosphates, and sulphates decrease with age, but the phosphorus content is constant. The carbon content of the ethereal fraction decreases somewhat with age. The carbon content of the alcoholic fraction increases with age; the nitrogen content is largest in old cats, and smallest in well-nourished cats. The residual fraction is chiefly inorganic; it is rather rich in phosphorus. Chemical Abstracts.

Composition of living organisms. II. Inorganic elements contained in frogs. V. S. Sadikov and R. A. Gutner (Bull. Acad. Sci. U.R.S.S. [Russia], 1927, 95—116; cf. preceding abstract).—Analytical data are given for frogs in various conditions of age and nourishment. Chemical Abstracts.

Influence of feeding on the quantitative composition of hens' eggs. E. F. Terroine and P. Belin (Bull. Soc. Chim. biol., 1927, **9**, 1074—1084).—The relative weights of white and yolk in eggs vary widely but independently of the food administered. The composition both of the white and of the yolk is very constant and independent of the food. In particular, the fatty substances remain constant whether or not fat is given in the food, provided ample carbohydrate is administered. W. O. Kermack.

Relation of the sterols to other substances of animal and plant origin. A. Windaus (Annal. Acad. Sci. Fennicæ, 1927, *A*, **29**, No. 24).—A summary of present knowledge of the sterols with special reference to their biological significance. G. A. C. Gough.

Cholesterol and nitrogen content of the cartilage at various ages and its significance in the physiology of age. M. Bürger (Verh. deutsch. Ges. inn. Med., 1926, 352—358; Chem. Zentr., 1927, i, 2662).—With increasing age, the cholesterol and nitrogen content and the dry matter of costal cartilage increase. A. A. Eldridge.

Characterisation of fats. P. Bamberger (Biochem. Z., 1927, **190**, 247—250).—The usual characteristic values (acid, saponification, Reichert–Meissl, Polenske, iodine) are expressed in such a way that from them an idea of the molecular composition of the fat can be obtained; *e.g.*, the number of c.c. of *N*-potassium hydroxide used for hydrolysis is found and gives the millimols. of fatty acid (free and esterified) in 1 g. of fat; the number of c.c. of *N*-sodium hydroxide needed to neutralise the free fatty acid in 1 g. of fat is found and gives the millimols. of free fatty acid in 1 g. of fat; the number of c.c. of 2*N*-iodine (2*N* since one double linking adds two iodine atoms) required for 1 g. of fat gives the new iodine value, etc. P. W. Clutterbuck.

Determination of the fat of animal organs. P. Bamberger (Biochem. Z., 1927, **190**, 251—260).—A method is described for determining the fat of organs, designed to eliminate possibility of change in its composition during the process, in which the carefully minced organ is dried in a vacuum at 80—90° for 10—12 hrs., most of the fat separated by continuous ether extraction of the powder for 6 hrs., and the rest obtained by transferring the residue to a collodion sac and treating in a special apparatus under sterile conditions with pepsin–hydrogen chloride for 6—8 days and then with trypsin (lipase-free) for 2—3 days with subsequent ether extraction of the residue after washing and drying in a vacuum. The fatty extracts are worked up in the usual way and the light petroleum extracts evaporated and dried, and the fat is weighed. The fat may be kept for months without change, out of contact with air and more particularly with light. P. W. Clutterbuck.

Glycerophosphatase of the central nervous system. Glycerophosphatase in men and animals. V. Vondráček (Biochem. Z., 1927, **191**, 88—94).—The enzyme is present in greatest amount in the cerebellum, less in the cerebrum, and least in the spinal cord in man. Comparative examination also in the case of rabbit, dog, ox, pig, and sheep shows also that the intensity of the action of phosphatase runs parallel neither to the phosphorus content nor to the phylogenetic development of the animal. P. W. Clutterbuck.

Mineral content of human skin. H. Brown (J. Biol. Chem., 1927, **75**, 789—794).—Figures are given for the concentrations of the inorganic constituents of human skin at various ages. C. R. Harington.

Fluorine content of teeth. F. Trebitsch (Biochem. Z., 1927, **191**, 234—240).—The method of Gabriel (A., 1893, ii, 81) is unsuitable for determination of fluorine in teeth. The fluorine content determined by the lanthanum method of Meyer and Schulz (A., 1925, ii, 598) is 0·29—0·59% of the dry weight. P. W. Clutterbuck.

Occurrence of trimethylamine oxide [in fish muscle]. F. A. Hoppe-Seyler and W. Schmidt (Z. Biol., 1927, **87**, 59—68).—Disintegrated muscle from various sea and river fish has been extracted with boiling water and the extract examined for trimethylamine oxide. This substance is more widely distributed than was previously thought and it has been isolated in appreciable amounts from the extracts of the sea fish, but in no case from the extracts of fresh-water fish. This difference is possibly due to differences in the food supply. No evidence has been obtained that spawning time or the season has any influence on the formation of this base.

A. Wormall.

γ-Butyrobetaine [in fish muscle]. F. A. Hoppe-Seyler and W. Schmidt (Z. Biol., 1927, **87**, 69—71).—γ-Butyrobetaine has been isolated from aqueous extracts of river-eel (*Anguilla vulgaris*), the yield of gold salt being 2·42 g. from 9·8 kg. of moist muscle. A. Wormall.

Sex differences of proteins in animals and plants. I. Sex differences of muscle- and serum-proteins. T. Tadokoro, M. Abe, and S. Watanabe (Proc. Imp. Acad. Tokyo, 1927, **3**, 543—546).—The ash and phosphorus contents of myosin and myogen, obtained from the muscles of various male and female animals, is appreciably greater in the female specimens. Titration of an alkaline solution of myosin and myogen (rotatory power lower for female specimen) with hydrochloric acid to determine the maximum point of the surface tension and turbidity of the solution shows that the female specimens require a smaller quantity of the acid. The free amino-nitrogen content of the female protein is also lower than that of the male. Arginine and lysine are in excess in the male protein, whilst histidine is in excess in the female.

Extension of the above work to male and female serum-globulin from different mammalian sources shows similar results. H. Burton.

Composition of the sexual organs. II. Amino-acids of the ovary of *Strongylocentrotus lividus* in various stages of the function cycle of the organ. G. Russo (Arch. sci. biol., 1926, **8**, 293—309; Chem. Zentr., 1927, i, 2662).—During development of the ovaries the protein-nitrogen increases, the non-protein-nitrogen remaining constant. The lysine increases and the histidine and cystine diminish. The amino-acids of the non-coagulable nitrogen increase during the development, but decrease at the beginning of the cycle.

A. A. Eldridge.

Composition of the sexual organs. III. Free and combined amino-acids in the testicles of *Bos taurus*. G. Russo (Boll. soc. biol. sperim., 1926, **1**, 210—212; Chem. Zentr., 1927, i, 2662; cf. preceding abstract).—A comparison of the composition of the testicles of the ox and the sea-urchin.

A. A. Eldridge.

Salivary secretions of blood-sucking insects in relation to blood-coagulation. L. Lloyd (Nature, 1928, **121**, 13).—A discussion of the action of coagulin and anti-coagulin. A. A. Eldridge.

Occurrence of acetaldehyde in cerebrospinal fluid. P. Thomas and E. Maftei (XII Int. Cong. Physiol., 1926, 158—159; Chem. Zentr., 1927, i, 2441).—Normal cerebrospinal fluid contains traces of acetaldehyde; larger quantities are observed in diabetes, paralysis, and dementia præcox.

A. A. Eldridge.

Effect of inanition on yield and composition of cow's milk. O. R. Overman and K. E. Wright (J. Agric. Res., 1927, **35**, 637—664).—Comparative data are given for the quantity and composition of the milk from 3 cows, giving a positive reaction to the tuberculin test, but otherwise in apparently good physical condition, during an inanition period of 5 days. As the period of inanition progresses the milk flow decreases together with the total fat, protein, lactose, and ash contents, whilst the percentages of fat, protein, and ash increase. There is a continual decrease in the specific gravity of the milk, and in the percentage of lactose. These changes were not so marked in one cow which was at the beginning of its lactation period, as in the other two which were in the later stages of lactation. E. A. Lunt.

Elimination of iodine in milk. W. Rasche (Z. Kinderheilk., 1926, **42**, 124—132; Chem. Zentr., 1927, i, 2441).—After ingestion by cows and goats of potassium iodide (0·5—1 g. 3—4 times at 48 hr. intervals), 11% of the iodine was recovered from the milk, irrespective of its volume or fat content.

A. A. Eldridge.

Amino-acid content of milk. F. Spirito (Pediatria riv., 1926, **34**, 921—929; Chem. Zentr., 1927, i, 2663).—Amino-acids were determined (mg. per 100 c.c.) as follows: cow's milk 10·17—14·68, asses' milk 16·03, goat's milk 10·53, human milk (3—4 months) 12·82, (9—12 months) 8·50, colostrum 17·48. A. A. Eldridge.

Creatinuria in children and its dependence on the thyroid gland. A. Palladin and E. Ssawron (Biochem. Z., 1927, **191**, 1—12).—Creatinuria, as found in children, also occurs in various other young mammals, but does not depend on the thyroid gland. Both creatine and creatinine are present in the urine of growing guinea-pigs, white mice, dogs (under 4—5 months), and rabbits (3—6 weeks). In young animals showing creatinuria, the creatine coefficient is greater than in adults. Extirpation of the thyroid gland in dogs during the period of creatinuria does not stop creatinuria, but results first in a transient decrease and after some time in a slightly lower creatinuria than in the control animals.

P. W. Clutterbuck.

Iodometric determination of homogentisic acid in urine. E. Metz (Biochem. Z., 1927, **190**, 261—264).—A method is described depending on the oxidation of the homogentisic acid in alkaline (hydrogen carbonate or borax) solution to the quinone by adding iodine until a blue colour is obtained with starch, and the reversion of the reaction on acidification with the setting free quantitatively of the amount of iodine used, with titration by thiosulphate.

P. W. Clutterbuck.

Conversion of Ronchèse's method for the determination of urinary uric acid into a micromethod. R. Danet (J. Pharm. Chim., 1927, [viii], 6, 405—407).—In a conical centrifuge tube are placed 10 c.c. of urine, 1·5 g. of ammonium chloride, and 1·5 c.c. of ammonia solution. After at least ½ hr., the liquid is centrifuged and decanted, the precipitate treated with 2 c.c. of Ronchèse's ammoniacal solution, and after centrifuging the liquid is decanted. The ammonium urate is treated with 30 c.c. of water, dissolved by means of a few drops of dilute acetic acid, treated with 2 c.c. of saturated sodium hydrogen carbonate solution, and titrated with 0·02*N*-iodine.

B. Fullman.

Serum-lipase, its determination by the stalagmometric method, significance, and clinical value. S. Katzenelbogen and H. Wohlers (Ann. méd., 1926, 20, 373—391; Chem. Zentr., 1927, i, 2557).—Rona and Michaelis' method was employed. Blood-serum gives velocity coefficients of 0·006—0·008; turbid serum gives higher values, but hæmolysis produces no change. The lipase titre falls in general cachexia. A. A. Eldridge.

Anæmia among troops in Bombay. P. N. Basu (Indian J. Med. Res., 1927, 15, 107—116).—The gastric juice was deficient in hydrochloric acid, and there is a slight diminution in blood-lipins. The ratio of neutral fat to free fatty acids in the fæces is 1 : 8·8 instead of 1 : 2·9. Chemical Abstracts.

Epidemic dropsy: its blood picture. C. Ray (Indian J. Med. Res., 1927, 15, 67—79).—Values (mg. per 100 c.c. of whole blood) were: total nitrogen 1400—2520, non-protein-nitrogen 22·4—42, urea 18—30, creatinine 1·2—1·4, uric acid 2·8—5·0, dextrose 95—135, chlorides 490—677, calcium 6·1—15, cholesterol 89—185. Chemical Abstracts.

Distribution of electrolytes in intestinal obstruction. D. W. Atchley and E. M. Benedict (J. Biol. Chem., 1927, 75, 697—702).—In intestinal obstruction there was observed in the blood-serum a decrease in total base, chlorides, and water, and an increase in carbonates, protein anions, phosphates, and sulphates; the last three account for the increase in undetermined acid observed by Gamble and Ross (A., 1925, i, 1352). The decrease of chlorides is due to their loss in the vomitus, the chlorine in the blood being replaced by phosphate and sulphate.

C. R. Harington.

Form of organic phosphorus in neoplasms. J. Enselme and [Mme.] J. Enselme (Bull. Soc. Chim. biol., 1927, 9, 1017—1026).—The phosphorus has been determined in normal and tumour tissue, by the method of Javillier and Allaire (A., 1925, i, 996). In cancerous tissue there is an increase of nucleic and of lipoid phosphorus. Radium treatment increases the lipoid phosphorus but decreases the nucleic phosphorus below the normal level.

W. O. Kermack.

Content in reduced glutathione of animal tissues during tuberculosis and various intoxications. P. Delore (Bull. Soc. Chim. biol., 1927, 9, 1070—1073).—The organs of tuberculous guinea-pigs and oxen contain the same quantity of reduced glutathione as do those of normal animals of the same species. Administration of phosphorus, arsenic, or of "novarsenobenzol" to a guinea-pig does not appreciably influence the content of its liver in reduced glutathione. W. O. Kermack.

Preparation and properties of glutathione. J. M. Johnson and C. Voegtlin (J. Biol. Chem., 1927, 75, 703—713).—A slight modification of the method of Hopkins (A., 1921, i, 635) is described by which 0·1 g. of reduced glutathione may be obtained from 1 kg. of baker's yeast. Copper, gold, and lead compounds of reduced glutathione have been prepared, in all of which the hydrogen of the thiol group appears to have been substituted by the metal; the yield of all these derivatives is small, owing, apparently, to oxidation of part of the glutathione with simultaneous reduction of the metallic salt employed. The criticism of Hopkins (A., 1927, 478) of the work of Hunter and Eagles (*ibid.*) is supported.

C. R. Harington.

Physiological study of glutathione by liver perfusion. R. Fabre and H. Simonnet (Compt. rend., 1927, 185, 1528—1530).—The amount of reduced glutathione found in Ringer's solution which has been perfused through the rabbit's liver for about 3 hrs. is remarkably small (5—8 mg. per 100 c.c.), whilst the liver loses all its glycogen. Destruction of the physico-chemical equilibrium of the cells, by circulation of water, or Ringer's solution containing 0·1% of potassium cyanide, or chloroform, causes the reduced glutathione of the liver to pass into the perfusate. H. Burton.

Relation of rate of growth to diet. II. L. B. Mendel and H. C. Cannon (J. Biol. Chem., 1927, 75, 779—787).—The conclusions of Osborne and Mendel (A., 1926, 1180), that the optimum rate of growth for rats at present accepted is too low, are supported by growth records of numerous animals in which daily increments of 3—5 g. were observed. These increments are comparable with those obtained on transferring an animal from a deficient to a complete diet, and with those observed by Evans (Harvey lectures, 1923—1924, 19, 212) to follow administration of pituitary extract to growing rats.

C. R. Harington.

Carbohydrate metabolism of the central nervous system. Glycogen and cerebroside content of the brain and the glycogen content of the heart in the normal condition and during deficiency of oxygen. Y. Kojima (Biochem. Z., 1927, 190, 379—387).—The glycogen content of the central nervous system and the cerebroside sugar content of rats are determined and, like the carbohydrate content of the heart, are shown to be very resistant during deficiency of oxygen. In 17 normal animals, the mean glycogen content of the brain was 0·2266% and of the heart 0·0829%, whilst in 7, kept in an atmosphere deficient in oxygen until symptoms supervened, they were respectively 0·2498 and 0·0816%. The heart and brain behave therefore differently from skeletal muscle.

P. W. Clutterbuck.

Absorption and utilisation of inulin in the white rat. M. G. Bodey, H. B. Lewis, and J. F. Huber (J. Biol. Chem., 1927, 75, 715—723).—Young white rats, on a basal carbohydrate-free diet, deposited considerable amounts of liver glycogen on addition of lævulose, and smaller but definite amounts after addition of inulin to the diet. C. R. HARINGTON.

Alimentary hyperglycæmia with lævulose feeding. F. KRONENBERGER and P. RADT (Biochem. Z., 1927, **190**, 161—167).—Lævulose (5—10 g.) has been administered to rabbits to determine whether the hyperglycæmia which is quickly produced after sugar administration is due to rapid absorption of the sugar or to a reflex stimulation of the liver by the sugar in the alimentary tract. Before, and after varying intervals following, the administration of lævulose, the total blood-sugar and the blood-lævulose have been determined, the latter by a modification of Selivanov's reaction and later by the diphenylamine method of van Creveld (Klin. Woch., 1927, 6, 697). The increases in total sugar and lævulose of the blood do not run parallel, although in some cases the amount of lævulose absorbed into the blood-stream is sufficient to account for the hyperglycæmia. In the majority of cases, however, evidence that hyperglycæmia may be produced by a reflex action is obtained. A. WORMALL.

Intermediary carbohydrate metabolism. IV. Reaction of normal dogs to continuous intravenous injection of dextrose. M. WIERZUCHOWSKI and H. GADOMSKA (Biochem. Z., 1927, **191**, 198—219; cf. A., 1926, 979; 1927, 790).—When dextrose is injected intravenously into dogs at the rate of 2 g. per kg. per hr., reaction may be "assimilative" (glycosuria approaches nil, blood-sugar 200 mg.-%) or "subassimilative" (glycosuria about 20% of the injected quantity, blood-sugar 300 mg.-%), or anything between these two extremes. In long experiments, deterioration of the power to assimilate dextrose was obtained in both types, but particularly in the assimilative type. The mean lactic acid content of the blood of a fasting dog is 15·7 mg.-%. By intravenous injection of sugar, the blood lactic acid follows a characteristic curve, increasing in the second and third hours by 6—28·7 mg.-% over the original values, the curve then either falling or remaining steady. The lactic acid values do not show differences with the different types of assimilation. Insulin injected during dextrose infusion generally has no effect on the blood lactic acid content, but when administered before dextrose injection affects the lactic acid values during the first hour after injection. P. W. CLUTTERBUCK.

Production of sugar from fat. Y. KOJIMA (Biochem. Z., 1927, **190**, 352—378).—When glycerol is added to the diet of rats rendered carbohydrate-free by feeding with peptone and thyroid tablets, sugar is formed from it. P. W. CLUTTERBUCK.

Utilisation of sodium *dl*-lactate administered intravenously. I. Excretion by kidneys and intestines. II. Changes in acid-base equilibrium. H. A. ABRAMSON and P. EGGLETON. **III. Glycogen synthesis by the liver. Blood-sugar. Oxygen consumption.** H. A. ABRAMSON, M. G. EGGLETON, and P. EGGLETON (J. Biol. Chem., 1927, **75**, 745—752, 753—761, 763—778).—I. After intravenous administration of sodium *dl*-lactate to fasting anæsthetised dogs in doses of 0·5—4·0 g. per kg., 7—40% of the *dl*-lactic acid was excreted in the urine within 3 hrs.; practically none was excreted into the intestine; the concentrating power of the kidney for lactic acid was about 10-fold.

II. Injection of sodium lactate was followed by an alkalosis, indicating utilisation of the lactic acid.

III. Injection of sodium lactate caused a slight fall in the blood-sugar, and in the glycogen in the liver (cf. Jansson and Jost, A., 1925, i, 1354; Elias and Schubert, A., 1919, i, 54); the oxygen consumption was but little increased; the rate of utilisation of lactic acid by dogs under these conditions was about 0·5 g. per kg. per hr.

C. R. HARINGTON.

Metabolism of alcohol in man. A. BORNSTEIN and A. LOEWY (Biochem. Z., 1927, **191**, 271—292).—The alcohol content of the blood of four persons, to whom 25—30 g. of alcohol was administered by mouth, increased within 30 min. from nil to 0·05—0·075% and then decreased, the blood becoming alcohol-free again after 4 hrs. The alcohol did not appear to have any specific dynamic action and the respiratory exchange was unaffected. If a large amount of carbohydrate in hourly doses for 7 hrs. was ingested before administration of alcohol, then, after taking alcohol, the R.Q. immediately began to fall, remained at this low level for 3 hrs., and then slowly increased. During these 3 hrs. the R.Q. remained unchanged in spite of the fact that the alcohol content of the blood decreased from 0·06 to 0·004%. Although no specific dynamic action was found on administration of alcohol either alone or after carbohydrate, yet a slight action was obtained when the two were administered simultaneously.

P. W. CLUTTERBUCK.

Active substances of striped muscle and the chemistry of muscular contraction. G. EMBDEN (Klin. Woch., 1927, 6, 628—631; Chem. Zentr., 1927, i, 2844).—Contraction of muscle is accompanied by liberation of ammonia, rapidly followed by recombination. Adenosinephosphoric acid and lactacidogen are considered active substances of striped muscle; their function is discussed. A. A. ELDRIDGE.

Heat measurements of the chemical reactions in muscle. O. MEYERHOF and J. SURANYI (Biochem. Z., 1927, **191**, 106—124).—The heat of hydrolysis of glycogen to reducing sugar, per 1 g. of sugar, amounts to 12—14 g.-cal. and the heat of esterification of glycogen with phosphate to 10—30 g.-cal., the amount being covered by the increase of acidity and the de-ionisation of muscle protein. The heat of conversion of hexosemono- into hexosediphosphoric acid is about 30 g.-cal., and this is explainable almost entirely in terms of increase of acidity. The heat of conversion of hexosediphosphate into lactic acid and phosphate is about 220 g.-cal. per g. of lactic acid. The average heat of breakdown of glycogen is 204 g.-cal., and deducting 25—30 g.-cal. for the increase in acidity, the heat of breakdown itself is 176 g.-cal. Finally, the hydrolysis of creatinephosphoric acid is 150—160 g.-cal. per g. of phosphoric acid. P. W. CLUTTERBUCK.

Can lactic acid disappear anaërobically from muscle? F. Lipmann (Biochem. Z., 1927, **191**, 442—449).—In presence of sodium fluoride, lactic acid never disappears anaërobically from minced muscle, the loss found by other authors being due to the methods used. P. W. Clutterbuck.

Ammonia content of and ammonia formation in muscle and its relationship to function and changes of condition. IV. W. Mozolowski and W. Lewiński (Biochem. Z., 1927, **190**, 388—398).—The formation of ammonia in frog's muscle depends on its size and on the time of the year, being much higher in the summer than in the winter. In the muscle of the intact normal frog the ammonia accumulated during work slowly decreases. Movement of the animal affects the resting value very considerably within 30—60 min. In nervous tissues, the ammonia content is not altered by mincing. In the curarised animal, stimulation of the nerves yields no increase of ammonia in the muscle, but direct stimulation gives the same result as in the non-curarised state. Sodium fluoride inhibits ammonia formation in muscle pulp, but in the intact muscle similar liberation of ammonia occurs as in mincing, heat rigor, or after caffeine. P. W. Clutterbuck.

Quantitative variations of urinary creatinine during muscular work and physical exercise. G. Carpentier and M. Brigaudet (Bull. Soc. Chim. biol., 1927, **9**, 1085—1094).—Physical exercise is followed promptly by an increase of creatinine in the urine and the amount of this increase does not appear to depend on the condition of training of the individual. W. O. Kermack.

Metabolism of nerves. III. Chemistry and intermediate processes. R. W. Gerard and O. Meyerhof (Biochem. Z., 1927, **191**, 125—146; cf. Amer. J. Physiol., 1927, **82**, 381; J. Physiol., 1927, **63**, 280).—Isolated resting nerve does not form lactic acid in oxygen, but does in nitrogen. The velocity of anaërobic lactic acid formation increases for the first 2 hrs. and then gradually falls away, amounting in the maximal period to 7·4 mg.-% per hr., and the total yield in 20 hrs. is 50—100 mg.-% at 25°. This decrease is caused by lack of carbohydrate. On suspending the nerve in Ringer's solution containing dextrose, the velocity remains constant at 12·5 mg.-% per hr. for more than 30 hrs., *i.e.*, a 60% increase over the maximal velocity without sugar. Accumulation of lactic acid does not itself inhibit glycolysis. On the other hand, lactic acid, once formed, does not disappear in oxygen. By stimulating in nitrogen, the formation of lactic acid is either not increased or only slightly. The total yield of lactic acid in sugar-free solutions corresponds approximately with the carbohydrate content of the nerves. Ammonia formation in resting nerves in oxygen is very small, in nitrogen is still smaller, but is considerably increased by stimulating the nerves in oxygen. The R.Q. of nerve at rest is 0·8 and is not affected by adding sugar, but increases to 1·0 on stimulating. Anaërobic formation of lactic acid is not inhibited by $4\times10^{-2}N$-potassium cyanide, but $2\times10^{-2}-1\times10^{-3}N$-potassium cyanide inhibits it to the extent of 80—90%. P. W. Clutterbuck.

Fat and lipin metabolism. VI. Rôle of the lungs in fat and lipin metabolism. S. Leites (Biochem. Z., 1927, **190**, 286—303).—Emulsions of olive oil and oleic acid injected into the jugular vein of normal dogs do not appear in the arterial blood as cholesterol or lecithin sols. After previous " blockade " with colloidal silver or colloidal ferric hydroxide, the injection of olive oil or fatty acid emulsions results in an increase of neutral fat or fatty acid in arterial blood. With parenteral injection of oleic acid or of sodium oleate, its retention in the lung is accompanied by an increase of cholesterol and of neutral fat in the arterial blood. In control experiments, the injection of oleic acid in the femoral artery does not bring about any increase in the cholesterol content of the blood of the femoral vein. With parenteral injection of lecithin sols, an increase of cholesterol and neutral fat is obtained in the arterial blood, along with the absorption in the lung. When (after " blockade ") the amount of fatty acid in the arterial blood is increased by retention of lecithin in the lung, the cholesterol content does not increase. By administration of olive oil by mouth, the neutral fat content of the arterial blood increases parallel to the retention of fatty acids in the lungs. These results support the assumption of cholesterol and neutral fat synthesis in the lungs from the absorbed oleic acid. In splenectomised dogs the cholesterol content of the arterial blood increases with enteral and parenteral injection of olive oil. By injection of cholesterol sols into the jugular vein an increase of neutral fat in the arterial blood is obtained which runs parallel to the retention of cholesterol in the lungs. P. W. Clutterbuck.

Fat metabolism. IX. Formation of acetone substances. R. Mancke and P. Serbescu (Z. Biol., 1927, **87**, 1—7; cf. A., 1927, 275).—Young pigs weighing about 35 kg. have been kept for 8—17 days on a purely fat diet and the amount of fat absorbed has been determined. No alterations in the blood-sugar or blood-lactic acid occurred and no acetone could be detected in the blood and urine. With a diet containing oleic acid only, with no antiketogenic glycerol present, and also with a diet consisting of oleic acid, olive oil, cod-liver oil, and butyric acid (as a ketogenic substance), similar results were obtained, and even in the latter case traces only of acetone were found in the urine. From these experiments it has been calculated that the pig is capable of oxidising completely per day nearly 2 g.-mol. of fatty acid which is not accompanied by antiketogenic substances. No evidence has been obtained that carbohydrate has been synthesised from fat in these experiments. A. Wormall.

Effect of administration of flesh on the respiratory exchange of rats after preliminary treatment in different ways, in respect to the function of the liver. T. Honda (Biochem. Z., 1927, **191**, 13—33).—After abundant administration of flesh and peptone to rats, further feeding with flesh shows a very decided specific dynamic action and this is even more pronounced when phloridzin is injected after several days' feeding. The effect is possibly due to a stimulated condition of the liver being set up during the preliminary treatment. P. W. Clutterbuck.

Effect of administration of flesh in respect to the preliminary condition of nutrition. T. Honda (Biochem. Z., 1927, **191**, 34—60).—The specific dynamic action of flesh, in rats, is considerably increased by previous administration of bread and milk. If a considerable amount of sucrose is added to this diet, the specific dynamic action of the flesh is even further increased. By feeding with fat, the specific dynamic action of flesh more or less disappears. P. W. Clutterbuck.

Nitrogen retention on feeding with ammonium salts. E. Schliephake (Biochem. Z., 1927, **190**, 59—66).—The nitrogen loss of guinea-pigs fed on a nitrogen-deficient diet is converted into a retention of nitrogen by the addition of ammonium chloride or citrate to the diet. The added ammonium salt has no significant influence on the total nitrogen, ammonia-nitrogen, or amino-nitrogen of the liver. A. Wormall.

Nitrogen distribution in the paunch of ruminants during feeding and starvation and its relationship to paunch infusoria. E. Mangold and C. Schmitt-Krahmer (Biochem. Z., 1927, **191**, 411—422).—The utilisation of micro-organisms as a source of protein in the nutrition of ruminants is investigated. The bacterial nitrogen is 10% of the total nitrogen of the paunch content of sheep receiving normal food. The paunch infusoria provide only a small part of the total paunch nitrogen. The total nitrogen of the paunch content in normally nourished sheep is 0·2—0·3%, and decreases quickly on starvation, amounting after 7 days to 0·05%. P. W. Clutterbuck.

Iron reserve. C. S. Williamson and H. N. Ets (Arch. Int. Med., 1927, **40**, 668—675).—Comparative experiments have been carried out on 126 rats to determine the effect on the iron reserve of a diet containing liver. Half the young animals were given a standard caseinogen diet, the other half received a similar diet with the caseinogen replaced by dried beef liver. The latter group after 3 months contained 141% more iron in the spleen and 57% more iron in the liver than the former group. That this iron can be used in the formation of hæmoglobin was shown by comparing the rates of hæmoglobin regeneration in each set of animals when anæmia induced by bleeding was followed by feeding both groups on the caseinogen diet. The former group showed no appreciable hæmoglobin regeneration in 28 days; the hæmoglobin concentration in the latter group was practically normal after the same period. E. A. Lunt.

Electromotive action of drugs as cause of their toxicity. II. Chemical nature of the tissue constituents which produce bioelectricity. III. Electromotive action of alkaloids on tissues compared with that on proteins, lipins, and "oils." R. Beutner (J. Pharm. Exp. Ther., 1927, **32**, 101—113, 115—120).—II. In support of the view that lipins play an important rôle in the phenomena of bioelectricity, it is found that the electromotive force of the system $0\cdot1M$-potassium chloride|lecithin|$x+$ is positive when x is a solution of propylamine hydrochloride, tetramethylammonium chloride, methylene-blue, rhodamine-$3B$, cocaine, or strychnine, and that the system $0\cdot1M$-potassium chloride|animal or plant tissue|x gives similar results. The effect of water, alcohol, and ether mixtures on the electrical potentials given by tissues also supports this conclusion. The results obtained by Höber (cf. A., 1925, ii, 131) with proteins are probably to be regarded as an effect of the water in the material.

III. The electromotive force of the system $0\cdot1M$-potassium chloride|R|$x+$ is positive in the sense indicated when x represents a solution of an alkaloidal salt and R represents a colloid and is very slightly positive or zero when R is lecithin, but is negative when R is an ordinary oil immiscible with water. When R represents a frog's muscle the system may be positive or negative according to the exact conditions, from which it appears that both types of material play a part in the electrical phenomena of tissues. W. O. Kermack.

Relationship between chemical reactivity and biological activity of iron compounds. L. Rosenfeld (Biochem. Z., 1927, **190**, 17—27).—The biological effects of oral administration to rabbits of a non-magnetic ferrosoferric carbonate which has a strong benzidine activity (with hydrogen peroxide) and a strongly magnetic iron oxide with a weak benzidine activity have been measured by determinations of the urinary C : N ratio. No increases in this ratio similar to those obtained with active iron oxide (Wada, A., 1926, 1057) have been observed. Thus neither the magnetic property nor the power to give the benzidine reaction is a measure of the biological activity or the therapeutic value of an iron compound. A. Wormall.

Hypoglycæmic action of ergotamine in diabetes. H. Moretti (Compt. rend. Soc. Biol., 1927, **97**, 320—324; Chem. Zentr., 1927, ii, 1278).—The mechanism of the hypoglycæmic action of ergotamin is discussed. A. A. Eldridge.

Hypoglycæmic properties of galegine sulphate. H. Simonnet and G. Tanret (Compt. rend., 1927, **185**, 1616—1617; cf. A., 1927, 991).—Galegine sulphate, in doses of the order of 4 mg./kg., causes a fall in the blood-sugar of both dogs and human beings in amounts varying up to 20%, a figure lower than that obtained by Müller and Reinwein (A., 1927, 1109). The same result is obtained with depancreatised dogs. J. W. Baker.

Effects of synthalin on metabolism. N. R. Blatherwick, M. Sahyun, and E. Hill (J. Biol. Chem., 1927, **75**, 671—683).—Administration of synthalin to rabbits by stomach tube caused no hypoglycæmia, but subcutaneous and intravenous injections produced this effect. Synthalin caused acute nephritis and damaged the liver in such a way as to interfere with the deamination of glycine after injection of the latter. The toxic effects of synthalin bear a general resemblance to those of hydrazine, and part of its power to reduce the blood-sugar apparently depends on the damage to the liver interfering with gluconeogenesis. C. R. Harington.

Physiology of the pyrimidines. L. R. Cerecedo (J. Biol. Chem., 1927, **75**, 661—670).—Uracil, thymine, and 4 : 5-dihydroxyhydrothymine, when administered to dogs, gave rise to increased excretion of carbamide; this indicates a possible similarity between the physiological oxidation of thymine and its oxidation *in vitro* (cf. Baudisch and Davidson, A., 1925, i, 1100). Cytosine and 5-methylcytosine were excreted partly unchanged, and partly as uracil and thymine, respectively. C. R. Harington.

Effect of some fractions of Liebig's meat-extract, obtained by the methods of Gulewitsch and Krimberg, on gastric secretion. A. Korchov (Biochem. Z., 1927, **190**, 188—198).—The carnosine fraction of meat extract, and carnosine itself, stimulate gastric secretion in dogs when injected subcutaneously or intravenously. The carnitine fraction has a similar action and the effect is proportional to the amount of carnitine present. The maximum rate of secretion occurs about the first half hour with intravenous and subcutaneous injections, but administration of either fraction *per os* produces a smaller effect, with a maximum rate of secretion 1½—2½ hrs. later. The stimulation is effected through the circulatory system. A. Wormall.

Comparative physiological action of phenylethanolamine. G. A. Alles (J. Pharm. Exp. Ther., 1927, **32**, 121—133).—β-Hydroxy-β-phenylethylamine is less toxic to guinea-pigs and has a more marked effect on the blood-pressure of rabbits than phenylethylamine. The conclusion of Barger and Dale (J. Physiol., 1910, **41**, 19) that the introduction of a hydroxyl group into the side-chain of phenylethylamine does not increase the activity unless there is at least one hydroxyl group in the nucleus does not appear to be true. W. O. Kermack.

Anomalies in the regulation of blood-sugar under Röntgen irradiation. J. Hisamoto and M. Takeshima (Okayama Ig. Zasshi, 1927, 39, 315—331).—Röntgen irradiation of rabbit's liver proportionally increases the blood-sugar when the liver-glycogen is high, and decreases it when the glycogen is low. Irradiation of the thorax or abdomen causes considerable variations in the blood-sugar. Irradiation of the liver of the normal fasting dog is followed by a persistent decrease in blood-sugar.
Chemical Abstracts.

Biochemistry of irradiation. VI. Influence of *X*-rays on the permeability of the surviving frog's skin. VII. Influence of *X*-rays on the composition of an artificially introduced peritoneal fluid. C. Kroetz (Biochem. Z., 1927, **191**, 250—262, 263—270; cf. A., 1925, i, 178; 1927, 589).—VI. *X*-Rays increase the permeability to chlorine and dextrose of the surviving skin of the frog (the mean increase is 198%), the effect being greater by irradiation of the membrane *in vivo* than *in vitro*. Irradiated sera and hæmoglobin solutions have no effect on the permeability to chlorine of unirradiated membranes.

VII. The globulin, amino-acid, and phosphate content of normal saline or Ringer's solution which has been introduced into the abdominal cavity of rabbits is greatly increased by irradiation of the abdomen with *X*-rays for some time. Since this increase is much greater than the increase of these substances in the blood, it is suggested that the permeability of the endothelial cells of the abdominal wall must become increased. P. W. Clutterbuck.

Biological effect of light. L. Pincussen (XII Int. Cong. Physiol., 1926, 134; Chem. Zentr., 1927, i, 2559).—The injurious or protective effect of alkali, alkaline-earth, or magnesium salts, and of halides and fatty acids, when dissolved in water in which tadpoles were exposed to radiation from a quartz lamp, was investigated. A. A. Eldridge.

Formation and constitution [and anti-tubercular action] of sodium aurosulphite. B. Oddo and Q. Mingoia.—See this vol., 140.

Chronic methyl alcohol poisoning. A. Leo (Biochem. Z., 1927, **191**, 423—438).—In dogs, it is possible in a short time to produce a tolerance to lethal doses of methyl alcohol, 1 litre of methyl alcohol being administered in 2 months. The excretion of formate in the urine decreases parallel with this increase in tolerance, but the decrease in excretion is not due to its increased combustion.
P. W. Clutterbuck.

Fatty degeneration of embryonic cells. G. Rosenfeld (Biochem. Z., 1927, **190**, 101—108).—Phloridzin, and in other cases phosphorus, have been administered to pregnant dogs, the dogs killed, and the fat contents of the livers of the mother and fœtal dogs determined. The livers of the fœtal dogs from the phloridzinised mother gave normal values for fat (mean value 2·91% of the dried weight), but with the phosphorus-treated dog the fat content of the fœtal liver was 3—4½ times the normal value. Similarly, the liver of a new-born dog to which small amounts of phloridzin were administered for 3 days had an abnormally high fat content. These increases in liver-fat are real and are not relative increases due to the disappearance of glycogen, and thus definite evidence of fat infiltration into embryonic livers has been obtained. The question of fat infiltration into embryonic and tumour cells is discussed.
A. Wormall.

Changes in oxygen capacity of the blood of rabbits following administration of nitrobenzene. B. B. Stimson (J. Biol. Chem., 1927, **75**, 741—744).—Following oral administration to rabbits of 0·1 c.c. per kg. of nitrobenzene, 2·2—14·7% of the total hæmoglobin was converted into a substance similar to but not identical with methæmoglobin.
C. R. Harington.

Multiphase action of potassium cyanide on the living cell. M. S. Resnitschenko (Biochem. Z., 1927, **191**, 345—354).—The amount of oxygen used by normal eggs of *Ascaris megalocephala* increases slowly in the first hour by 1·5% and in 16 hrs. by 22%, an increase related to the development of the egg. The respiration is only slightly decreased by concentrations of cyanide up to 2*M*, due to the physicochemical properties of the egg membrane, but with 3·2*M*-solutions, the eggs use 60% more oxygen ("paradox phase") in the first 30 min. after addition than in the same time before addition. The oxygen utilisation then falls fairly quickly and reaches a minimal value in 7—8 hrs. The amount of this minimal value is different for different concentrations of cyanide, the increased oxygen utilisation being directly proportional and the minimal oxygen usage inversely proportional to the cyanide concentration. Eggs placed in $3{\cdot}2M$-cyanide continue to use some oxygen up to the seventh day. The increased utilisation of oxygen is not conditioned by the reagent, but is due to reaction of the protoplasm itself.

P. W. Clutterbuck.

Zymosthenic action of mineral waters on liver catalase. A. Mougeot and V. Aubertot (Compt. rend. Soc. Biol., 1927, **96**, 399—400; Chem. Zentr., 1927, i, 2554).—Carbonated mineral waters activate the catalase in consequence of the bivalent ions, particularly in presence of calcium ions. Sulphur waters arrest the activity on account of the hydrogen sulphide content. The sulphate ion is antagonistic to the activating cations. A. A. Eldridge.

Endocrine glands and enzymes of the blood. I. Influence of potassium iodide, iodine, and "iodated albumin" on the catalase of the blood. O. A. Steppun and A. M. Timofeeva (Trans. Sci. Chem. Pharm. Inst., 1923, No. 3, 3—18).—Under the conditions employed, iodine and "iodated albumin," when added to rabbit's blood, decreased the catalase index (Bach); potassium iodide was without effect.

Chemical Abstracts.

Rôle of the catalase–anticatalase system in the animal organism. L. Stern and F. Battelli (XII Int. Cong. Physiol., 1926, 157; Chem. Zentr., 1927, i, 2554).—Catalase is often accompanied in animal tissues by anticatalase, the activity of which is concealed by the philocatalase. Anticatalase is active only in presence of oxygen or a hydrogen-acceptor; the optimal p_H is 6—7, and temperature 38—40°. A. A. Eldridge.

Decomposition of dextrose in the animal organism. A. Alekseev (Bull. Univ. Asie Cent., 1926, **10**, 39—49).—The presence of reductase and carboxylase in animal tissues was demonstrated by measurement of the carbon dioxide evolved in the reaction: $\mathrm{CHMe(OH){\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}CO_2H + CH_3{\cdot}CHO + CO_2}$. The activity of an extract is greatly diminished by boiling, but increased by addition of methylene-blue. The aqueous extract of ox liver and muscle is most active at p_H 7·0.

Chemical Abstracts.

Acceleration of sugar formation in the excised frog's liver by destruction of its structure. E. J. Lesser (Biochem. Z., 1927, **191**, 175—180).—The amount of sugar found in the frog's liver, which has been ground after washing out with buffer solution at p_H 7·5 for removal of blood-diastase, is always about 4·5 times as high as the sugar content of the intact liver. The view of Bang (A., 1913, i, 552, 553, 1267) that this is due to the greater action of blood-diastase in the ground material is incorrect, and his inability to show that disintegration of structure was responsible for the increase in sugar is explained by the fact that the intact and ground lobes of liver were not examined under comparable conditions (cf. A., 1913, i, 931).

P. W. Clutterbuck.

Partial hydrolysis of populin to saligenin and benzoylglucose by an enzyme in taka-diastase. T. Kitasato (Biochem. Z., 1927, **190**, 109—113).—Populin (monobenzoylsalicin) is hydrolysed by an enzyme of taka-diastase into saligenin and a *benzoylglucose* which appears to differ from the natural compound (vacciniin). Some free benzoic acid and dextrose are also formed by partial hydrolysis of the benzoylglucose and the last-named has not been obtained pure. A. Wormall.

Biochemical synthesis of β-5-bromosalicylglucoside. Attempt to synthesise β-3 : 5-dichlorosalicylglucoside. P. Delauney (Compt. rend., 1927, **185**, 1530—1532; cf. A., 1927, 174).—5-Bromosaligenol and dextrose, dissolved in aqueous acetone, are treated with emulsin, when β-5-bromosalicylglucoside (lævorotatory) is formed. Using 3 : 5-dichlorosaligenol, the initial rotation shows a large increase during 15 days, presumably due to the formation of the glucoside. H. Burton.

Reversibility of enzyme action. I. B. Suzuki and T. Maruyama (Proc. Imp. Acad. Tokyo, 1927, **3**, 533—535).—A solution of β-glucosidase has no action on maltose or α-methylglucoside. With β-methylglucoside a reducing sugar is produced. *iso*Maltose develops an increased reducing power, whilst *iso*maltosazone develops a slight reducing action after 3 days. A concentrated dextrose solution shows a decrease in its reducing power when treated with β-glucosidase, owing to the formation of *iso*maltose (cf. Armstrong, A., 1906, i, 127), isolated after removal of the dextrose with *S. marxianus* as the osazone, m. p. 155°. H. Burton.

Extraction of amygdalin and emulsin from bitter almond cake. M. Bridel and (Mlle.) M. Desmarest (Compt. rend., 1927, **185**, 1514—1515).—Details are given for the extraction of amygdalin by 70% alcohol, and emulsin by water, from the same material. The emulsin preparation contains also β-glucosidase, lactase, and invertase. H. Burton.

Enzymic liberation of methyl alcohol from pectin by an enzyme of tobacco. C. Neuberg and M. Kobel (Biochem. Z., 1927, **190**, 232—240).—Autolysis of tobacco leaves results in the liberation of 60% of the loosely-combined methyl alcohol, which presumably comes from the pectin-like constituents of the leaves (cf. A., 1927, 385). A pectase solution can be obtained by pressing fresh tobacco leaves, and keeping the juice for 24 hrs. under chloroform, followed by filtration. The enzyme in the filtrate can be purified by precipitating with alcohol and dissolving in water, and these solutions, as well as the impure filtrates, have a very powerful pectase activity; the optimum p_H for the coagulation of solutions of lemon pectin is about 5·5, which is the p_H of the natural juice. This coagulation of lemon pectin by tobacco-leaf extracts is accompanied by an almost complete liberation of methyl alcohol, since 80—90% of the pectic methyl alcohol is liberated in less than 1 hr. Heated extracts of tobacco leaves have no action on pectin. A. Wormall.

Arsenate activation and the specificity of phosphatase. C. Neuberg and J. Leibowitz

(Biochem. Z., 1927, **191**, 460—465).—The effect of arsenate on the hydrolysis of zymodiphosphate by yeast in presence of chloroform and toluene is investigated under conditions which exclude fermentation. Very great acceleration of hydrolysis is obtained, the phosphatase action being increased five times. Arsenate also activates taka-phosphatase in its action on hexosediphosphate. Kidney phosphatase, although indifferent to small concentration of arsenate, is inhibited by the higher concentrations which activate yeast. Many organisms possess two specifically different phosphatases. Kidney phosphatase acts differently from the muscle enzyme.

P. W. CLUTTERBUCK.

Decomposition of zymodiphosphate by means of animal phosphatase to hexosemonophosphoric ester. C. NEUBERG and J. LEIBOWITZ (Biochem. Z., 1927, **191**, 456—459).—Magnesium hexosediphosphate is treated with the clear maceration juice of horse kidney and the monophosphate isolated as the barium salt; yield 30%.

P. W. CLUTTERBUCK.

Action of suprarenal tissue on lecithin. H. C. W. VINES (Endocrinol., 1927, **11**, 224—228).—The lipolysis of lecithin by suprarenal tissue in a saline medium at p_H 7·4 and 37° is increased in the presence of cholesterol. Choline is probably attacked. The side-chain of the adrenaline molecule may be derived from choline. CHEMICAL ABSTRACTS.

Adsorption of urease by cholesterol. M. JACOBY (Biochem. Z., 1927, **190**, 157—160).—Cholesterol adsorbs urease from solution (cf. Jacoby and Shimizu, A., 1922, i, 481). The activity of the adsorbed enzyme is greatly increased by the addition of " auxo-bodies " (potassium cyanide) and is decreased when the adsorption precipitate is washed with a phosphate solution of p_H 9·18. A. WORMALL.

Comparative sensitiveness of the active and inactive forms of enzymes to ultra-violet rays and to heat. E. F. TERROINE and R. BONNET (Bull. Soc. Chem. biol., 1927, **9**, 982—1000).—The amylases of the dog's pancreatic fluid and of the gastro-intestinal juice of *Helix pomatia* and intestinal invertase are more easily destroyed by the action of ultra-violet rays when they are activated by the presence of sodium chloride. Pepsin, lipase, and trypsin, on the other hand, are not more sensitive to the action of these rays when activated by their respective co-enzymes, hydrochloric acid, or sodium chloride, bile salts, and enterokinase. Pepsin and snail amylase are, but pancreatic amylase, lipase, trypsin, and intestinal invertase are not more sensitive to heat when activated. W. O. KERMACK.

Proteolytic activity of pancreatic extracts. I. A. SMORODINCEV and A. N. ADOVA (Bull. Acad. Sci. U.R.S.S. [Russia], 1926, **20**, 1491—1502).—Dog's pancreatic juice, obtained by Pavlov's method, is 1·5—2 times as active as the best tryptic preparations; the proteolytic activity of the latter is weakened by treatment involved in Wittich's, and in Fränkel's modification of Danilevski's method. Wittich's preparation is 10 times as active as Danilevski's. Treatment of aqueous pancreatic extracts with phosphoric acid and milk of lime reduces the proteolytic activity by nearly 50%. Prolonged evaporation of extracts in a vacuum causes reduction of proteolytic activity by 14%. Filtration of aqueous glycerol pancreatic extract through paper leaves a residue which possesses considerable digestive properties; the filtrate yields with alcohol a precipitate which is easily soluble in alkalis and possesses a high proteolytic activity, whereas the residual liquid has no proteolytic properties. CHEMICAL ABSTRACTS.

Determination of protease and p_H optimum. A. N. ADOVA (XII Int. Cong. Physiol., 1926, 4—5; Chem. Zentr., 1927, i, 2457).—In Gross' method, the p_H of the medium deviates from the optimum value for pepsin and caseinogen. In the determination of α-proteases by Mett and Fuld's method, and in that of β-proteases by Gross and Robertson's method, the protein is prepared in nearly optimal medium.

A. A. ELDRIDGE.

Pepsin. H. ELBLINGER and C. FUNK (Biochem. Z., 1927, **191**, 186—197).—Aqueous pepsin solutions are very unstable, being inactivated by too great dilution and by shaking with air. Addition of alcohol or acetone in presence of mineral acids converts pepsin into an insoluble compound from which it cannot be regenerated. Pepsin can be precipitated from concentrated solutions by picrates etc. (cf. Funk, this vol., 208) and by this method it may be concentrated 2—5 times. Pepsin gives two fractions, either of which has only feeble activity but recombined has the original peptic power. The view that these precipitates are compounds and not adsorbates is favoured by the greater stability and by the fact that many reagents give only inactive precipitates. The solubility of the sodium and barium salts and the insolubility of the heavy metal salts possibly indicate the presence of acidic groups in the pepsin molecule.

P. W. CLUTTERBUCK.

Action of tyrosinase on phenols. Classification of oxidases. C. E. M. PUGH and H. S. RAPER (Biochem. J., 1927, **21**, 1370—1383).—Anilino-*o*-quinones produced by the action of tyrosinase on several phenols in presence of aniline have been isolated. From phenol or pyrocatechol dianilino-*o*-benzoquinone was obtained, whilst in the case of *m*-cresol, *p*-cresol, or homocatechol dianilinohomoquinoneanil was produced. The *o*-quinones are therefore produced by the enzyme from the phenols, but owing to their transient existence they can be isolated only when removed from the sphere of action. Peroxidase and hydrogen peroxide, acting on pyrocatechol or homocatechol, also produce *o*-quinones. Further evidence indicating the formation of *o*-quinones is offered by the isolation of a sulphinic acid derivative of *o*-benzoquinone by the action of tyrosinase on pyrocatechol in presence of benzenesulphinic acid.

The isolated anilinoquinones have been identified by synthesis. 4 : 5-Dianilino-*o*-benzoquinone, m. p. 193·5° (cf. Kehrmann and Cordone, A., 1913, i, 1396), was prepared by treating an ethereal solution of *o*-benzoquinone with aniline in water. *Dianilinohomoquinoneanil*, $C_{25}H_{21}ON_3$, brownish-red, m. p. 202·5°, was obtained by treating homoquinone with aniline in water or by oxidising homocatechol with silver oxide in glacial acetic acid in presence of aniline.

Not all phenolic substances which are attacked by tyrosinase give rise to anilinoquinones when the enzyme acts on them in the presence of aniline, but *m*- and *p*-methoxyhydroxybenzenes do so. Tyrosine and pyrogallol, although oxidised by the enzyme, do not yield anilino-compounds under these conditions.

Homoquinone deaminates glycine in the same manner as does *o*-benzoquinone (cf. Happold and Raper, A., 1925, i, 474; Robinson and McCance, *ibid.*, 745). The oxygen absorbed during the oxidation by tyrosinase of several phenols has been measured and indications have been obtained with those phenols giving rise to anilinoquinones that, in absence of aniline, some further reaction involving oxidation occurs beyond formation of the *o*-quinone. The "direct oxidase" theory of Bach and Chodat is criticised in the light of the above results, and a new classification of oxidases into aërobic and anaërobic oxidases is suggested. S. S. Zilva.

Purification of rennin. H. Lüers and J. Bader (Biochem. Z., 1927, **190**, 122—142).—Rennin preparations have been purified by the application of adsorption methods involving the use of alumina and kaolin as adsorbents and a phosphate buffer of p_H 6·97 for elution. The most active preparation obtained has an activity of 1 in $16·44 \times 10^6$ calculated on the dry weight, compared with values of 1 in 20,000 to 1 in 100,000 for commercial rennet preparations. The salt-free dried substance contains 0·687% of nitrogen, gives weak biuret and xanthoproteic reactions, and negative ninhydrin and Millon's tests. The preparation does not reduce Fehling's solution either before or after hydrolysis with hydrochloric acid. The rennin and peptic activities of the preparation do not run parallel throughout the process of purification, but the differences are not significant enough to prove that the two enzymes are different. A. Wormall.

Biological sugar degradation. H. von Euler, K. Myrbäck, and R. Nilsson (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 3).—Dried yeast, free from co-zymase, has little action on an aqueous solution of acetaldehyde containing a phosphate buffer (p_H 6·12), but rapidly attacks it when co-zymase is added. Dried *B. casei* ε behaves similarly to co-zymase-free yeast. The extracts of the muscle and the liver of the rat decolorise methylene-blue at p_H 8·3 in aqueous solution and more rapidly if solutions of glycogen, zymophosphate, or sodium succinate are added. G. A. C. Gough.

Influence of colloids on fermentation. R. Grieg-Smith (Proc. Linn. Soc. N.S. Wales, 1927, **52**, ii, 17—24).—Fermentation, but not inversion, of sucrose by heated yeast is accelerated by mineral colloids, which adsorb the invertase of normal yeast. Fermentation of dextrose by normal yeast is accelerated by fuller's earth. Small quantities of agar depress, and large quantities accelerate, the fermentation of invert-sugar. Chemical Abstracts.

Modifications produced in the course of alcoholic fermentation by the action of an oscillating electromagnetic field on the yeast. II. E. Benedetti (Atti R. Accad. Lincei, 1927, [vi], 6, 331—335; cf. A., 1927, 1221).—Fermentation of dextrose solution containing inorganic nutrient materials is accelerated considerably if the yeast used is previously exposed to the action of an oscillating electromagnetic field of 272·7 kilocycles for 35—40 min., and slightly if the frequency is 400 or 500. The fermentation is, however, retarded if the frequency is as high as 1200. T. H. Pope.

Apparatus for graphic registration of fermentation. G. Joachimoglu (Biochem. Z., 1927, **190**, 399—401). P. W. Clutterbuck.

Partial dephosphorylation of hexosediphosphoric acid by yeast. C. Neuberg and J. Leibowitz (Biochem. Z., 1927, **191**, 450—455).—Magnesium hexosediphosphate is treated with bottom yeast and the hexosemonophosphate isolated as the barium salt; yield 17% of theory.

P. W. Clutterbuck.

Structure of hexosephosphoric esters and methylglyoxal from their spectrographic behaviour. C. Neuberg and S. A. Schou (Biochem. Z., 1927, **191**, 466—471).—The spectrographic behaviour of magnesium hexosediphosphate, calcium hexosemonophosphate (Neuberg's), and barium hexosemonophosphate (Robison's) is investigated. All these esters show, besides general absorption, an absorption band with a maximum at about 2630 Å., the position of which corresponds with the absorption maximum of acetone. The molecular extinction coefficient ε is 10—100 times as high for the sugar phosphoric esters as for the free sugars. For methylglyoxal, absorption began at 3200 A. and attained a maximum at 2780 Å. (ε=13·2). At shorter wave-lengths, the absorption decreases and shows a minimum at 2415 Å. (ε=2·7) followed by a further increase in the extreme ultra-violet. The course of absorption corresponded entirely with that of aliphatic substances which contain only one carbonyl group, as is seen by comparison with the absorption of propaldehyde. It is therefore suggested that one carbonyl group of methylglyoxal, probably the ketone group, is hydrated, its absorption effect being thus lost. P. W. Clutterbuck.

Supposed separation of methylglyoxal in alcoholic fermentation. C. Neuberg and M. Kobel (Biochem. Z., 1927, **191**, 472—477).—It was not found possible to isolate any methylglyoxal by means of semicarbazide during alcoholic fermentation, the sparingly soluble substance obtained being shown to be hydrazodicarbonamide, resulting from decomposition of semicarbazide itself.

P. W. Clutterbuck.

Carbohydrate and fat metabolism of yeast. IV. Nature of the phospholipins. C. G. Daubney and I. S. Maclean (Biochem. J., 1927, **21**, 373—385).—The total amount of ether-soluble substances in yeast increases to five times its original amount and that of the phospholipins to three times its original value after incubation in dextrose–phosphate medium. The lipin fraction was investigated in the following way. Pressed yeast was grown in a sugar–phosphate medium for 28 hrs., while a current of air was blown through the solution. After collecting the yeast, it was ground with sand and extracted with alcohol. The ethereal solution of this extract was then precipitated with acetone. The lecithin–kephalin ratio of the lipin fraction (the precipitate) was examined by hydrolysing, removing the fatty acids by extraction, and determining the total and amino-nitrogen. The examination of the degree of unsaturation by determining the iodine value and by bromination of the acids of the ether–soluble lead salts of the lipin fraction established the presence of oleic acid only. Palmitic acid was also present. From the quantitative data obtained, it is computed that yeast kephalin is a mixture of 82% of dioleylkephalin and 18% of oleylpalmitylkephalin, and the lecithin a mixture of 75% of oleylpalmityl-lecithin and 25% of dioleyl-lecithin.

The analysis of the acetone-soluble fraction of the alcoholic extract of the yeast revealed the presence of dibromostearic and tetrabromostearic acids, from which the existence of oleic and linoleic acids in the original fat is deduced. Palmitic acid was also isolated. The unsaponifiable fraction consisted of about 50% of sterols, including ergosterol and some unidentified compounds. S. S. Zilva.

Sulphur metabolism of yeast. H. Sugata and F. C. Koch (Plant Physiol., 1926, **1**, 337—347).—Sulphate is the form of sulphur most available to yeast; it is converted into yeast-protein, and probably partly into cystine. Cystine, cysteine, and hydrogen sulphide stimulate yeast growth at low, and retard it at higher, concentrations. Cystine is converted partly into yeast protoplasm and partly into sulphate. Chemical Abstracts.

Phytochemical reduction by bacteria. C. Neuberg and E. Simon (Biochem. Z., 1927, **190**, 226—231).—*p*-Xyloquinone is reduced practically quantitatively to *p*-xyloquinol and valeraldehyde to amyl alcohol (yield 73%) by *B. coli* which is fermenting a nutrient solution containing dextrose, whilst sodium thiosulphate with *B. lactis aërogenes* yields hydrogen sulphide, but only to the extent of 1—2%. The high yields in the first two cases indicate that the reduction is a true hydrogenation and is not a dismutation process in which two molecules of substrate are concerned. A. Wormall.

Action of *B. lactis aërogenes* and *B. coli* on hexosemonophosphoric acid. N. Kageura (Biochem. Z., 1927, **190**, 181—187).—*B. lactis aërogenes* and *B. coli* produce appreciable amounts of lactic acid from the sodium and calcium salts of the hexosemonophosphoric acid prepared by the method of Neuberg and Leibowitz (A., 1927, 993). The yield of lactic acid is always less than the theoretical amount calculated from the amount of inorganic phosphate liberated. A. Wormall.

Formation of succinic acid by fermentation of sugars by *B. coli*. A. I. Virtanen (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 26).—Anaërobic fermentation of dextrose by a strain of *B. coli* isolated from fæces, in an atmosphere of carbon dioxide, yielded after 18 days about 39·1% of lactic acid, 19·8% of succinic acid, 11·0% of acetic acid, and 4·8% of formic acid. In a similar way aërobic fermentation yields after 24 days 34·0% of lactic acid, 20·6% of succinic acid, 11·3% of acetic acid, and 1·1% of formic acid. It is suggested that dextrose breaks down in two ways during this fermentation: first to succinic acid and acetaldehyde (which gives alcohol and acetic acid) and second through a hexosephosphate to methylglyoxal, which in turn gives lactic acid, acetaldehyde, and formic acid (see also A., 1927, 701). G. A. C. Gough.

Applications of the polarographic method. M. Shikata.—See this vol., 136.

Fission of sugar by *Bacillus propionicus*. K. Maurer (Biochem. Z., 1927, **191**, 83—87).—The result of Virtanen (Soc. sci. Ferm., 1923, **1**, 36; 1925, **2**, 20) that by the fermentation of sugar with *B. propionicus* there are produced by a subsidiary reaction acetaldehyde and succinic acid, was not confirmed. P. W. Clutterbuck.

Influence of active and inactive serum on the bacterial formation of nitrite. O. Weltmann, O. Bsteh, and K. Neumayer (Z. Hyg. Infekt.-Krankh., 1927, **107**, 126—129; Chem. Zentr., 1927, i, 2440).—Bacterial reduction of nitrate to nitrite is arrested by serum diluted with physiological sodium chloride solution. Inactive serum has no inhibitory effect. A. A. Eldridge.

Alcohol-soluble specific substances of *Bacillus diphtheriæ* and of *Streptothrix*. J. Freund (J. Immunol., 1927, **13**, 161—169).—The alcohol-soluble specific substance of *B. diphtheriæ* contains 5·6—5·7% N; after hydrolysis the biuret reaction is negative and the ninhydrin reaction positive. It is probably not of protein nature. An alcohol-soluble specific substance was present in a *Streptothrix* strain, but not in *B. xerosis*, *Trichophyton*, *Actinomyces*, or yeast. Chemical Abstracts.

Urea-splitting bacterium in the human intestinal tract. J. V. Cooke and H. R. Keith (J. Bact., 1927, **13**, 315—319).—" *B. ammoniagenes* " is exceptionally active in producing ammonia from urea. Chemical Abstracts.

Formation of indigotin from indole by soil bacteria. P. H. H. Gray (Proc. Roy. Soc., 1927, B, **102**, 263—280).—A soil organism, *Pseudomonas indoloxidans*, has been isolated, which will oxidise indole to indigotin. It is probable that the oxidation does not take place within the organism but is brought about in the surrounding medium by an exo-enzyme which diffuses from the growth. The organism cannot use indole as a sole source of energy, but given a source of carbon and no nitrogen other than indole it can oxidise indole to indigotin. A high ratio of carbon to hydrogen in the energy source favours indigotin formation.

Mycobacterium globerulum and *Micrococcus piltonensis* produce small amounts of indigotin on indole agar only. E. A. Lunt.

Antiseptic action of phenol and *p*-chlorophenol in solvents with different dielectric constants. W. E. Engelhardt (Biochem. Z., 1927, **190**, 217—225).—The antiseptic action against *Staphylococcus aureus* and anthrax spores of phenol dissolved in different solvents shows no relationship to the dielectric constant of the solvent, but *p*-chlorophenol has an antiseptic action in solvents of high dielectric constant only (water, glycerol, and nitrobenzene). This difference between phenol and *p*-chlorophenol cannot be explained on the basis of lipoid-solubility, but is attributed to the greater dissociation of *p*-chlorophenol. These results support the hypothesis of Hellenbrand and Joachimoglu (A., 1925, i, 466) that dissociated substances have an antiseptic action which is related to the degree of dissociation, and therefore to the dielectric constant, of the solvent. A. WORMALL.

Amount of carbohydrate in antitubercular vaccine B.C.G. of Calmette and Guérin. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1027, 9, 1095—1096).—*B. tuberculosis* bovine type when boiled with sulphuric acid yields 22·6% of its weight as hexose and pentose (calculated as dextrose), of which 11% is pentose (calculated as arabinose). The corresponding figures for the bacillus prepared for use as a vaccine by Calmette and Guérin's process are 26·8 and 9·6%, respectively. W. O. KERMACK.

Influence of electrolytes on the phenomena of agglutination. M. PIETTRE and A. CHRÉTIEN (Compt. rend., 1927, 185, 1319—1321).—Dilute solutions of sodium chloride and similar electrolytes exert little influence on the agglutination of paratyphoid bacilli. Maximum agglutination of these bacilli, cultivated in peptone water, is obtained in faintly acid solution, whilst, if the peptone water also contains dextrose, the fermentation of which produces an acid reaction, maximum agglutination is observed in faintly alkaline solution. Chemical neutrality of the bacillary substance is the most favourable condition for its combination with agglutinin.

B. W. ANDERSON.

Insulin-like substances in higher plants and micro-organisms. P. E. SIMOLA (Annal. Acad. Sci. Fennicæ, 1927, *A*, 29, No. 15).—Extraction of potatoes, rhubarb leaves, yeast, and bacteria (*B. casei* ε and *B. subtilis*) with alcohol containing hydrochloric acid (but not with aqueous acids) yields insulin-like substances, which may also be obtained by the extraction of a mixture of the cells and picric acid with acetone. Whilst the crude products sometimes exert hyperglycæmic action, the purified extracts all produce hypoglycæmia, a state which is often accompanied by considerable toxic symptoms when the extracts are purified by the picrate method.

G. A. C. GOUGH.

Structure-fixation of dextrose and its significance in the fate of dextrose. O. LOEWI (Naturwiss., 1927, 15, 93—94; Chem. Zentr., 1927, i, 2565—2566).—Human erythrocytes in sodium fluoride plasma fix dextrose, which is not attacked, but in serum the same erythrocytes convert a portion into lactic acid. The effect of insulin is to make greater quantities of dextrose available for decomposition by causing greater fixation. In diabetic plasma the dextrose-fixing power is reduced by a thermostable, dialysable substance, which can be extracted from the dialysate with alcohol; it appears in blood when excess of insulin is given. A. A. ELDRIDGE.

Distribution of reducing substances between blood-plasma and striped muscle. Effect of insulin. B. S. CUENCA (Biochem. Z., 1927, 190, 1—16).—The reducing substances have been determined (as dextrose) in blood-plasma and voluntary muscle of starved and fed mice and the effect on these values of injection of insulin, dextrose, and adrenaline has been noted. The ratio, reducing substances in 100 g. of muscle to reducing substances in 100 c.c. of blood-plasma, is 0·72±0·05 for mice previously starved for 18 hrs. and 0·77±0·06 for fed mice. The plasma-sugar figures 5 min. after intravenous injection of a 10% solution of dextrose (0·2 g. of dextrose per 100 g. weight) are 551 mg. (as dextrose) per 100 c.c. for the starved mouse, 477 mg. for the insulin-treated starved mouse, and 453 mg. for the fed mouse. The corresponding distribution coefficients (muscle-sugar/plasma-sugar) are 0·28, 0·26, and 0·48, respectively, and normal coefficients are attained after more than 30 min., in 10 min., and in 23 min., respectively. These results are interpreted as indicating that the sugar penetrates into the muscle most rapidly with the insulin mouse and least with the starved mouse, and it is suggested that the number of open muscle capillaries is greatest in the former case and least with the starved animal. A. WORMALL.

Action of insulin on dextrose *in vitro*. T. J. C. COMBES (Compt. rend, Soc. Biol., 1927, 97, 268—270; Chem. Zentr., 1927, ii, 1278). No action was detected.

A. A. ELDRIDGE.

Insulin reactions. L. FOSHAY (Arch. Int. Med., 1927, 40, 661—667).—Data are given for the serum and corpuscular dextrose in the blood in the case of five diabetic patients on insulin treatment. In all cases the insulin reaction occurred where the corpuscular dextrose concentration was low, even although the serum-dextrose concentration was high, thus showing that the whole blood-sugar concentration bears no relation to the occurrence of insulin reactions. The author believes that the insulin reaction is due to a lack of available dextrose in the cells of the fixed tissues and regards the corpuscular dextrose concentration as an index of this quantity. E. A. LUNT.

Glycæmia, glycogen, and insulin action with decapsulated rats. A. ARTUNDO (Compt. rend. Soc. Biol., 1927, 97, 411—413; Chem. Zentr., 1927, ii, 1278).—Resistance or sensitivity towards insulin cannot be ascribed only to glycogen changes.

A. A. ELDRIDGE.

Effect of insulin on the decomposition of pyruvic acid in mammalian muscle. E. TOENNIESSEN (Verh. deut. Ges. inn. Med., 1926, 454—456; Chem. Zentr., 1927, i, 2445).—The decomposition of pyruvic acid to acetic acid by the abdominal muscles of the rabbit, suspended in Ringer solution of p_H 6·8—7·3, is almost completely inhibited by the addition of small quantities of insulin; with larger quantities, the pyruvic acid disappears by synthesis of carbohydrate.

A. A. ELDRIDGE.

Influence of insulin on phosphorus metabolism. Z. KOŁODZIEJSKA and K. FUNK (Med. dośw. spol., 1926, 6, 83—90; Chem. Zentr., 1927, i, 2564).—Insulin appears to have no influence on the phosphorus elimination or content of rats. A. A. ELDRIDGE.

Influence of nickel and cobalt on the hypoglycæmic action of insulin in the rabbit. M. Labbé, Roubeau, and F. Nepreux (Compt. rend., 1927, **185**, 1532—1534).—Traces of nickel and cobalt salts prolong the hypoglycæmic effect of insulin (cf. Bertrand and Mâchebœuf, A., 1926, 869).

H. Burton.

Antagonism of insulin and "thyreodin" in carbohydrate metabolism. M. Rosenberg (Klin. Wochschr., 1927, 6, 631—634; Chem. Zentr., 1927, i, 2841).—In diabetes, insulin and "thyreodin" are antagonistic. Glycosuria in non-diabetics is not markedly affected by insulin. A. A. Eldridge.

Influence of the thyroid hormone on protein metabolism. L. Lichtwitz and L. Conitzer (Z. ges. exp. Med., 1927, **56**, 527—534; Chem. Zentr., 1927, ii, 1277).—Loss of weight following treatment of myxœdema with "thyreodin" is not simply correlated with loss of nitrogen. The negative nitrogen-balance is due to the removal of the supply-protein, and is accompanied by a reduction of the plasma-protein. A. A. Eldridge.

Methylating function of the thyroid. B. Stuber and F. Stern (Biochem. Z., 1927, **191**, 363—373).—Further work (see A., 1924, i, 239) on the methylation of guanidineacetic acid to creatine shows that in dogs, rabbits, and cats this methylation is a specific function of the thyroid and is not shared by either the pituitary or the sex glands. Methylation of pyridine in dogs, however, proceeds quite independently of these glands. P. W. Clutterbuck.

Female sexual hormones. Bencan, C. Champy, and T. Keller (Compt. rend. Soc. Biol., 1927, **97**, 229—232; Chem. Zentr., 1927, ii, 1277).—The placenta contains the hormone of the follicles and the hormone of the corpus luteum; thus the secretion of sexual hormones is not confined to a definite class of histological elements. A. A. Eldridge.

Blood-gases and their relations to the internal secretions of animals kept on a diet deficient in vitamin-*A* and -*B*. E. Miyake (Fol. endocrinol. japon., 1926, **2**, 23—24, 593—641).

Chemical Abstracts.

Avitaminosis and metabolism. A. Palladin (XII Int. Cong. Physiol., 1926, 123—124; Chem. Zentr., 1927, i, 2443).—Metabolic disturbances due to avitaminosis and hunger, respectively, are distinct; the differences observed are described.

A. A. Eldridge.

Glutathione and avitaminosis-*B* in the pigeon. L. Randoin and R. Fabre (Bull. Soc. Chim. biol., 1927, **9**, 1027—1069).—Various tissue extracts from pigeons have been titrated with iodine, using as end-point (1) ammonium nitroprusside to determine the free sulphydryl groups (G) and (2) a starch reagent to determine the total power of the tissue to reduce iodine (G_1). The G values of the various organs of pigeons decrease as the result of starvation simultaneously with the decrease in body temperature. Pigeons on a diet deficient in vitamin-*B* show a decrease of G in the skeletal and heart muscles after the tenth or fifteenth day. With normal pigeons the ratio G_1/G remains comparatively constant, being 1·65 for the pectoral muscle, 1·77 for the leg muscles, 1·92 for the heart muscle, 1·49 for the liver, and 1·38 for the blood. When the pigeons are deprived of vitamin-*B* the ratios for the skeletal and heart muscles markedly increase. During starvation the ratios for the muscles also increase, but to a smaller extent. The increase in G_1/G occasioned by lack of vitamin-*B* results partly from the decrease of the free sulphydryl groups in the tissues, G, and partly from the simultaneous increase in reducing substances other than those containing the sulphydryl group.

W. O. Kermack.

Vitamin-*B*. C. Funk (XII Int. Cong. Physiol., 1926, 58; Chem. Zentr., 1927, i, 2443).—A mixture of naphthol-yellow-*S* and silver picrate precipitates the greater part of vitamin-*B*, most of the other nitrogenous substances remaining in solution. Vitamin-*B* appears to be separable into two fractions.

A. A. Eldridge.

Chemical composition of the bones of scorbutic guinea-pigs. E. Brouwer (Biochem. Z., 1927, **190**, 402—410).—The bones (tibia) of guinea-pigs fed on a diet free from vitamin-*C* contain 10% less calcium and phosphorus and 19% less dry substance (but the ratio CaO/P_2O_5 is unchanged) than those of animals on practically the same diet to which is added 1—2 g. of fresh grass per day. A similar result is obtained by adding 0·5 g. of cod-liver oil daily. The brittleness of scorbutic bones is caused less by the deficiency of calcium and phosphorus than by changes in microscopic structure.

P. W. Clutterbuck.

Isolation of the antirachitic factor from irradiated cholesterol. I. I. Nitzescu and G. Popoviciu (XII Int. Cong. Physiol., 1926, 118; Chem. Zentr., 1927, i, 2443).—Concentration of the antirachitic factor can be effected with alcohol.

A. A. Eldridge.

Reproductive failure of white rats on synthetic diets. U. Suzuki, W. Nakahara, and N. Hashimoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 143—151).—White rats fed on a synthetic diet of meat protein, sucrose, starch, mineral salts, oryzanin, and biosterin proved sterile. The addition of cholesterol or synthetic triolein to the diet, or the ultra-violet irradiation of the rats, did not affect this condition, which is attributed to absence of vitamin-*E* in the diet. E. A. Lunt.

Food requirements of the growing rat. II. Effect of variation in proportion and quality of recognised nutrients. L. S. Palmer and C. Kennedy (J. Biol. Chem., 1927, **75**, 619—657).—Young rats were kept, out of access to their fæces, on a basal diet of dextrin, purified caseinogen, butter fat, agar, salts, and wheat embryo extract, which, according to views at present accepted, should have been sufficient for normal growth; the growth obtained was, however, always less than that obtainable on a full natural diet. The deficiency was not affected by increasing the supplies of any known vitamin. Improved growth was obtained by addition to the diet of fat-free wheat embryo, or of commercial lactose, or by substitution of a crude animal protein for the purified caseinogen. The effect of the wheat embryo was not due to vitamin-*B*, since yeast had no influence on growth. Butter fat of summer origin gave better results than that obtained in winter. It appears therefore that hitherto unrecognised factors essential to growth may have been associated with the lactose and the crude proteins which gave good results.

C. R. HARINGTON.

Vitamin "D_m" [bios] in fermentation vinegar. A. JANKE and H. LACROIX (Biochem. Z., 1927, **190**, 67—74).—The growth factor responsible for the stimulation of yeast growth is present in fermentation vinegar but not in vinegar essence, and that present in the former is derived from the metabolism of the acetic acid bacteria. The growth factor is resistant to heat and can be adsorbed by fuller's earth, from which it is eluted with 1% ammonia. No activation of the growth of yeast by this growth factor occurs in the absence of the salt solution used. A. WORMALL.

Respiration and fermentation in green plants. II. Metabolism of phanerogams. L. GENEVOIS (Biochem. Z., 1927, **191**, 147—157; cf. A., 1927, 905).—Measurements of the respiratory and fermentative activities of the parts of plants (*Lathyrus odorata*, *Caltha palustris*, *Aquilegia vulgaris*, *Elodea canadensis*, etc.) at different stages of growth are described and an attempt is made to trace a connexion between the amount of their metabolism and their condition of growth and development, and to compare these activities in plant and animal cells. Fermentation is increased during the growth of the embryo, but both respiration and fermentation decrease with increasing age. Both respiration and fermentation are also equally high during the formation of seed. Whereas there is no difference in fermentation in the intact and the minced seeds, respiration increases considerably on mincing, the oxygen supply being, in the intact seed, insufficient to attain maximal respiration. The sensitivity to cyanide of the respiration of embryos decreases with age. The respiration of older embryos, however, can be increased with sugar, and this increased respiration is then inhibited, in the same way as the high respiration of the younger embryos, by cyanide. P. W. CLUTTERBUCK.

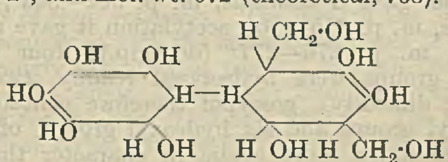
Formation of pigments in plants. H. SCHMALFUSS and H. BARTHMEYER [with H. BRANDES] (Biochem. Z., 1927, **190**, 424—432).—The conditions for darkening of the fruit-cases of the horse-chestnut, of the pulp of apples and pears, and of the tissues of many fungi correspond with those for the pods of the broom (*Sarothamnus scoparius*, Wimm.). With the Sarothamnus type, the scratched part reacts more acid and darkens under the influence of atmospheric oxygen in 30 min. at 20°. This type is different from the bean type (*Vicia faba*, L.) in that, with the latter, the scratched part becomes more acid but does not darken in 30 min. but only slowly on keeping. In the intact bean pod, formation of melanin is but little affected by the concentration of oxygen, chromogen, and acidity within wide limits, but is greatly affected by concentration of enzyme. The formation of melanin is inhibited by various secondary products present, but darkening may be artificially brought about by treating with ammonia, chloroform, and ether, crushing, and drying. P. W. CLUTTERBUCK.

I. Assimilation of formaldehyde. II. Enzymic condensation of formaldehyde to sugar. J. BODNÁR, L. E. RÓTH, and C. BERNAUER (Biochem. Z., 1927, **190**, 304—325).—The changes of dry substance and sugar contents of leaves of *Tropæolum majus* when grown in normal air and in atmospheres containing formaldehyde, acetaldehyde, and toluene, in presence and in absence of sunlight, are determined. The dry substance and sugar contents of the formaldehyde-treated leaves are greater than that of the control and of the original leaves, the leaves therefore having synthesised sugar from formaldehyde. No starch could be detected in leaves grown in formaldehyde with the exclusion of light and it is assumed that formaldehyde inhibits the condensation of sugar to starch. Acetaldehyde, however, cannot increase the dry substance and sugar contents of the leaves, but both acetaldehyde and toluene are injurious to respiration. P. W. CLUTTERBUCK.

Anthocyanins in the pigment of Isabella grapes. R. J. ANDERSON and F. P. NABENHAUER (N.Y. Agric. Exp. Sta. Tech. Bull., 1926, No. 123, 1—13). —The pigment is a monoglucoside, $C_{23}H_{25}O_{12}Cl,4H_2O$, apparently identical with œnin. Œnidin chloride is 3 : 5 : 7-trihydroxy - 2 - (4 - hydroxy - 3 : 5-dimethoxyphenyl)benzopyrylium chloride.

CHEMICAL ABSTRACTS.

Bergenin. I. V. S. SADIKOV and R. GUTHNER (Biochem. Z., 1927, 190, 340—351).—The "glucoside" bergenin, extracted in 1850 by Garreau from Siberian saxifrage (*Bergenia Siberica*) and renamed bergenitol by Morelle (A., 1882, 159), on account of its resemblance to mannitol, is re-examined. By extraction with cold (0—5°) water (Morelle extracted at 80°) a crystalline sample of bergenin was obtained the prismatic angle of which was 88° 45′ (Morelle's bergenitol, 91° 15′), which showed the phenomenon of double m. p. at 138° and 230° (Morelle's bergenitol, 130° and 230°), the mol. wt., 348, and the analytical composition of which agreed with the formula $C_{14}H_{20}O_{10}$ (Morelle's bergenitol, $C_8H_{12}O_6$). Two samples of this bergenin had rotations α_D +47·2°, +51·3°, whereas Morelle's bergenin had α_D −51·36°. This bergenin contained two methoxy-groups and when heated with sodium acetate and acetic anhydride gave a deca-acetyl derivative, $C_{14}H_{10}(OAc)_{10}$, m. p. 192·5—193·5°, α_D +25·2°, and mol. wt. 672 (theoretical, 768). Bergenin is not hydrolysed by heating with 5% sulphuric or hydrochloric acid and is not a glucoside. The above formula is suggested and discussed.



P. W. CLUTTERBUCK.

Preparation of sinigrin. H. HÉRISSEY and R. BOIVIN (Bull. Soc. Chim. biol., 1927, 9, 947—949).—Black mustard seed (1 kg.) is extracted for 20 min. with boiling acetone (10 litres containing 2·5 litres of water). The mixture is cooled and filtered and the filtrate is distilled until the residue is reduced to about 2 litres, which, after being separated from oil and filtered, is fermented by fresh baker's yeast for 2—3 days. The product is neutralised by adding calcium carbonate to the hot solution, filtered, and concentrated under reduced pressure to a syrup which is taken up in 85% alcohol (3 litres). After 24 hrs. the alcoholic solution is filtered and concentrated under reduced pressure. The residue is extracted with boiling 95% alcohol (300 c.c.), kept for 24 hrs., filtered, and seeded, when almost pure sinigrin slowly crystallises. The extraction of the residue is repeated six or seven times. The yield is 11—12 g.

W. O. Kermack.

Chemical nature of the sulphur-containing glucoside of *Alliaria officinalis*. H. Hérissey and R. Boivin (Bull. Soc. Chim. biol., 1927, 9, 950—952).—By the use of the authors' method (cf. preceding abstract) for the separation of sinigrin 1·4 g. of this compound have been isolated from 400 g. of seeds of *A. officinalis*. W. O. Kermack.

Cortex of *Byrsonima crassifolia*. G. Heyl and H. Heil (Festschr. A. Tschirch, 1926, 62—71; Chem. Zentr., 1927, i, 2668).—The cortex of *Byrsonima crassifolia* contains *byrsonimol*, $C_{29}H_{52}O$, m. p. 197·5°, $[\alpha]$ +96·94° (*acetyl* derivative, m. p. 242°; *benzoyl* derivative, m. p. 232°), giving in concentrated sulphuric acid a yellow solution becoming brown on addition of acetic anhydride or reddish-yellow to dull red when warmed. The substance, when treated with acetic anhydride and (dropwise) with concentrated sulphuric acid, gives a deep violet-red solution. These and other colour reactions are given by naturally occurring higher alcohols of the character of phytosterols. A. A. Eldridge.

Gossypol. I. Preparation and properties. E. P. Clark (J. Biol. Chem., 1927, 75, 725—739).—Gossypol was obtained from cotton seed as the acetate by the method of Carruth (A., 1918, i, 266), freed from acetic acid, and crystallised from a mixture of ether and light petroleum; it had the formula $C_{30}H_{30}O_8$, mol. wt. 572, m. p. 214° (decomp.); on titration with potassium hydroxide it neutralised 2 molecules of the latter. On treatment in ethereal solution with acetic acid it yielded the *substance* $C_{30}H_{30}O_8,AcOH$, m. p. 189—190° (decomp.), which was decomposed by water; on heating at 215° it lost $2H_2O$ to give *anhydrogossypol*, m. p. 268° (softening at 229—230°). Gossypol gave a *dianilide*, m. p. 302—303°, and a *dioxime*, m. p. 315°; on acetylation it gave a *hexa-acetate*, m. p. 276—277° (decomp.); four of the acetyl groups were hydrolysed readily, two with greater difficulty; gossypol therefore contains two carbonyl groups and six hydroxyl groups, of which two are much more acidic in character than the remainder. C. R. Harington.

Isolation of the physiologically active principles contained in the leaves of the ombú (*Phytolacca dioica*). F. Reichert (Anal. Asoc. Quím. Argentina, 1927, 15, 221—224).—Physiologically active solutions were obtained by extraction of dried leaves of the ombú with water and alcohol. By precipitation of the aqueous extract with lead acetate and afterwards with basic lead acetate, decomposition of the lead compounds by hydrogen sulphide, and precipitation with alcohol, four fractions were obtained which gave the characteristic reactions of saponins. Three of these were toxic, causing hæmolysis. R. K. Callow.

Utilisation by *Aspergillus niger* of gein, the eugenol-yielding glucoside of the roots of *Geum urbanum*. H. Hérissey (Bull. Soc. Chim. biol., 1927, 9, 943—946, and J. Pharm. Chim., 1928, [viii], 7, 5—8; cf. A., 1925, i, 487, 1383).—The growth of *A. niger* on a culture medium, the sucrose of which has been replaced by gein, is inhibited considerably when the medium is acid, and almost entirely when it is non-acid. W. O. Kermack.

Nitrogen nutrition of moulds. Assimilation of urea-nitrogen. D. Bach (Compt. rend., 1927, 185, 1309—1310).—Of 24 species of *Mucorinæ* grown in liquid media containing urea as the only source of nitrogen, only 6 developed normally.

B. W. Anderson.

Plant growth-promoting substances, hydrogen-ion concentration, and the reproduction of *Lemna*. N. A. Clark (Plant Physiol., 1926, 1, 273—279).—The rate of reproduction of *Lemna major* is increased when the hydrogen-ion concentration is kept uniform and the amount of bacterial growth diminished. The optimum p_H probably varies with the composition of the culture solution.

Chemical Abstracts.

Ultrafiltration of small amounts of liquid by means of the centrifuge. A. Tóth (Biochem. Z., 1927, 191, 355—362).—A method is described for carrying out ultrafiltration experiments using the centrifuge, with amounts of liquid up to 5—6 c.c. Collodion solutions in acetic acid are better than in ether-alcohol for ultrafiltration purposes, since the latter dry too readily, and a thicker membrane is required for the same filtration with the centrifuge than with the water-pump. The preparations of a viscose solution and of a viscose membrane are described and the permeability of the membrane is tested against a series of colloids.

P. W. Clutterbuck.

Use of Stolte's ashing method in micro-analysis. C. Egg and K. Klinke (Biochem. Z., 1927, 191, 439—441).—Stolte's method (A., 1911, ii, 946) of ashing, which avoids loss of alkali chlorides, is shown to be trustworthy. P. W. Clutterbuck.

Reagents for the chemical fractionation of biologically active raw material. C. Funk (Biochem. Z., 1927, 191, 181—185).—A general method is described for attempting the fractionation of trypsin, pepsin, pituitrin, vitamins-*B* and -*C*, and insulin by the use of various reagents, such as the sodium, barium, lead, silver, and mercury salts of picric acid and to a less extent of picrolonic and flavianic acids, the salts being more specific than the free acids and scarcely affecting the activity of the material.

P. W. Clutterbuck.

Precipitation of magnesium ions by tropæolin-*OO* and the use of this reaction for its colorimetric determination. J. Zahradníček.—See this vol., 145.