BRITISH CHEMICAL ABSTRACTS

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JULY, 1929.

General, Physical, and Inorganic Chemistry.

Amplifier for comparison of spectra. S. PIÑA DE RUBIES (Anal. Fís. Quím., 1929, 27, 48-56).-A method whereby the spectrum of a mineral may be projected simultaneously with those of its constituent elements is described. H. F. GILLBE.

-have been measured, using Illord special

Theory of coupling-widening of spectral lines. J. HOLTSMARK (Z. Physik, 1929, 54, 761-763).-From considerations of quantum mechanics the width of a spectral line is proportional to the square root of the density of the oscillators or resonators. The recently published work of Waibel on the cæsium principal series (this vol., 479) in which the square root law was found to be obeyed in all cases is shown to be in error as far as calculation of the width of lines is concerned. After correction the results agree with those of the present author. The small coupling width of emission lines found by Hasche, Pólányi, and Vogt (A., 1927, 396) is explained by the small coupling of the emitting resonators. A. J. MEE.

Emission lines in the spectrum of the solar corona. V. ZESSEVITSCH and V. NIKONOV (Nature, 1929, 123, 909-910).

Light-emission from atoms. D. G. BOURGIN and E. E. LIBMAN (Ann. Physik, 1929, [v], 1, 1096---1098).---A criticism of the work of Kleiber (this vol., 2). R. A. MORTON.

Physical criticism of Schrödinger's theory of Index in the state of the stat 687; this vol., 616) that the relative intensities of Stark components in hydrogen agree within experimental error with the new calculations by Schrödinger. Under precisely defined conditions, the pa-component ± 4 of the hydrogen line H_a is considerably more intense than the pa-component ± 3 . It is shown that the intensity ratios for the outer components of H_a , H_{β} , and H_{γ} obtained under the influence of electric adds are by no means constants characteristic of the hydrogen atom, since the values can vary over wide limits depending on the conditions of experiment. Considerable deviations from the Schrödinger values are obtained, and it is stated that the theory has not been confirmed.

II. For many reasons it is necessary to retain the idea of a strict correspondence between the amount of energy emitted and the frequency of the light, the relationship being definitely based on experience. Schrödinger's theory involves the breaking up of the elementary optical energy into any number of other frequencies, a view which cannot satisfactorily be reconciled with experience. Attempts to solve the difficulty are unconvincing.

SUBTATECHNIN

III. Schrödinger's theory is based on the assumption that a stationary state can be regarded as determined by characteristic vibrations of an electric charge distributed continuously over the space-field of the atom. Thus the electron of the hydrogen atom must have its mass distributed over the whole space of the atomic field (diameter of the order 5×10^{-9} cm.). The space occupied by the electrical charge of a free electron is very much smaller, and the idea of an "attenuated" electron is open to objection from the physical point of view. Schrödinger bases the equation for the stationary vibration state on the calculation of light emission from the damping of hypothetical oscillations, instead of an equation for the vibration state, which, in consequence of the damping by emission, shows a time change with respect to amplitude and energy. R. A. MORTON.

Spectrum of H₂. The bands analogous to the parhelium line spectrum. II, III, IV. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1929, A, 123, 466-488; 124, 50-68, 69-88; cf. this vol., 616).—II. The system with P strong, R weak ($3^{1}A \longrightarrow 2^{1}S$) is described. This system has no Q branches and the lines do not show the Zeeman effect, with the exception of $21420.70(3) = R(1)1' \longrightarrow$ 2". This appears to be a genuine abnormality. The same type of alternation of intensity is met with as same type of alternation of intensity is met with as in the other systems. The initial rotational levels present a curious oscillation in the second term difference both with m and n'. The three systems $3^{1}A \longrightarrow 2^{1}S(P > R)$, $3^{1}B \longrightarrow 2^{1}S(Q)$, and $3^{1}C \longrightarrow$ $2^{1}S(R > P)$ are compared. Five systems coming from electronic levels with principal quantum number 4, denoted by $4^{1}A \longrightarrow 2^{1}S$, $4^{1}B \longrightarrow 2^{1}S$, $4^{1}C \longrightarrow 2^{1}S$, $4^{1}X \longrightarrow 2^{1}S$, and $4^{1}E \longrightarrow 2^{1}S$, are described. Apart from some perturbations, these bands which come from 4' electronic levels all show the alternation in intensity which is so marked for all the other bands in this spectrum. The weight ratio of alternate states is found to be 3 to 1, as with the other systems, and the transitions are also governed by the same rules. The following values have been calculated: for neutral H_2 , the ionisation potential is 15.381 volts, and the heat of dissociation is 4.465 ± 0.04 volts; for

the hydrogen molecule ion, H_2^+ , the heat of dissociation is 2.50 volts, the vibration frequency at zero amplitude $(\omega_0)=2280$ wave numbers, and $x\omega_0=60$. These values are in excellent agreement with Burran's computations based on the wave mechanics (K. Danske Vid. selsk., Math-fys., 1927, 7, 14).

III. Descriptions are given of a number of band systems having P and R branches in which there is not so much disparity between the strengths of the two sets of branches as in the systems previously described. In these systems the rotational energy levels are remarkably close together compared with those of the bands previously described, the differences of the intervals increasing with m. A full account is given of the way in which the data for the rotational energy interval tables are obtained.

IV. Descriptions are given of the system ${}^{1}O \longrightarrow 2{}^{1}S(v_{e}=22814)$, the progression ${}^{1}Q=2{}^{1}S(v_{e}=21843)$, the progression starting from $4142 \cdot 801$ Å., and the progression $4097 \cdot 433$ Å. L. L. BIRCUMSHAW.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 103—108).—A more detailed account of work previously reported (cf. this vol., 479).

R. A. MORTON. Band systems in the molecular spectrum of hydrogen. I. Singlet system. II. Triplet system. W. FINKELNBURG and R. MECKE (Z. Physik, 1929, 54, 198—214, 597—631).—I. A discussion of the new measurements on the hydrogen band spectrum by Finkelnburg (this vol., 118), Gale, Monk, and Lee. Four band systems containing 383 lines are distinguished.

II. 825 lines in 60 bands have been classified and shown to belong to the triplet system of the hydrogen molecule. Nuclear vibration quantum numbers and moments of inertia can be derived for the terms 2^3S , 3^3P , 4^3P , and 3^3D . All the bands have the 2^3S -term as their common final term and, since this is also the initial term of the ultra-violet Lyman bands, the latter would appear to be given by the combination 1^1S-2^3S . The Balmer bands (α -, β -, γ -, δ -bands), described by Richardson as a triplet system, are shown to be singlet. Since most of the strongest lines of the spectrum have now been classified, such groups as H_2^+ and H_3 can play only a minor part in the emission (cf. this vol., 624).

E. B. ROBERTSON. Parahydrogen. K. F. BONHOEFFER and P. HARTECK (Naturwiss., 1929, 17, 321—322).—Parahydrogen melts and vaporises at lower temperatures than ordinary hydrogen. On the basis of m. p. 13.95° Abs., and b. p. 20.39° for ordinary hydrogen, parahydrogen shows pressures of 57.0 and 787 mm. as against 53.9 and 760 mm., whilst at 760 mm. the b. p. of parahydrogen is 20.26° Abs. The difference between the two forms arises from the smaller (0.65%) heat of vaporisation of the parahydrogen.

The α -system of the many-lined spectrum, emitted by normal hydrogen, has been compared with that from parahydrogen and striking intensity changes are observed. R. A. MORTON.

Variation of intensities in helium spectrum with pressure and electron velocity. (FRL.) M. G. PETERI and W. ELENBAAS (Z. Physik, 1929, 54, 92—98).—The relative intensities of the following helium lines have been measured, using Ilford special rapid panchromatic plates : (a) excited in a Geissler tube of 2.18 mm.^2 cross section by 1000 volts D.C., pressure 6.9 mm.; (b) excited in field-free space by electrons of known velocity, 60 volts, pressure 0.045 mm.: 6678, 5876, 5048, 5016, 4922, 4713, 4472, 4438, 4388, 4169, 4144, 4121, 4026, 3965, 3889 Å. It is found in all cases that at the lower pressure the lines are stronger. R. W. LUNT.

Variation of the intensities in the helium spectrum with the velocity of the exciting electrons. J. H. LEES and H. W. B. SKINNER (Nature, 1929, 123, 836).—For high exciting velocities the triplets vanish in intensity compared with the singlets, whilst for low exciting velocities the singlets are weak compared with the triplets. Further, whilst the light of the triplets is confined closely to the electron beam, the light from the singlets tends to spread away from it. A. A. ELDRIDGE.

Intensity measurements in the helium spectrum. D. BURGER (Z. Physik, 1929, 54, 643-655).-The intensity relationship for 56 helium lines has been measured, using a quartz spectrograph and Moll microphotometer. Only one line (3889 Å.) of the principal triplet series was included, but many lines of other series. The decrease of intensity appears to be greater in the principal singlet series than in the subordinate series; in all cases it is approximately equal to that found by Bongers (Diss., Utrecht, 1927) for the Balmer series. The ratio intensity/v⁴ for corresponding lines of the singlet and triplet systems of the subordinate series has been determined in many cases. For the lower terms it is found to be greater, and for higher terms less, than the expected value of 1:3. E. B. ROBERTSON.

New regularities in the band spectrum of helium. II. G. H. DIEKE, S. IMANISHI, and T. TAKAMINE (Z. Physik, 1929, 54, 826—843; cf. A., 1928, 677, 1295).—A series of new helium bands is investigated. They are mainly below 4500 Å. in wave-length. Those specially considered are the band complex 2p-2d, at λ 440 mµ; the bands of wave-length 378 mµ and 611 mµ, and the complex band λ 416 mµ. A. J. MEE.

Polarisation in the case of neon electron collision emission and the neon canal-ray emission. W. HANLE and B. QUARDER (Z. Physik, 1929, 54, 819—825).—An arrangement of apparatus is described for the polarisation of the emission due to electron collisions in neon at low pressures, and of the emission of the slow neon canal rays. Most of the lines showed partial polarisation, partly parallel with and partly perpendicular to the electron beam. As for mercury, with increasing velocity of the colliding electrons there was a decrease in the degree of polarisation. The optimum for most lines lies in the neighbourhood of 20—25 volts. The results are compared with those found for mercury, and show an agreement between analogous lines. The canal rays also show partial polarisation. The effect of a weak magnetic field on the lines is also investigated. The mercury triplet lines, 5460.7, 4358.3, and 4046.6 Å., were weakened. A. J. MEE.

Series in the krypton arc spectrum. W. GREMMER (Z. Physik, 1929, 54, 215—226).—The arc spectrum of krypton has been photographed and measured. Series have been found which correspond with the sp combination, using Paschen's notation, and the krypton spectrum has been shown to be of similar structure to those of neon and argon. 4s- and 9p-series of the 10p-term have been worked out, and these explain many lines of the spectrum.

E. B. ROBERTSON.

Spectroscopic method for the proof of the existence of unstable intermediate products in activated gases, and its application to active hydrogen, nitrogen, and oxygen. Z. BAY and W. STEINER (Z. physikal. Chem., 1929, B, 3, 149-161).-The method depends on the production of an emission spectrum from the activated gas by using highfrequency discharges with external electrodes, or electrodeless ring discharges. A method involving emission spectra is better than one using absorption spectra, because it is much more sensitive. The method can be used for the identification of intermediate products, and to follow the concentration changes of an intermediate product. The method is applied to active hydrogen, in which case the intermediate product is atomic hydrogen. The spectra of active nitrogen and oxygen obtained by this method were also investigated. Arc lines of nitrogen were shown to be present in the spectrum of the activated A. J. MEE. gas.

Electrodeless ring discharge with undamped excitation. H. STEINHÄUSSER (Z. Physik, 1929, 54, 788-797).-The conductivity and relative sparking potentials of air, oxygen, nitrogen, carbon dioxide, hydrogen, helium, neon, and argon were determined over a pressure range of 0-16 mm. by the electrodeless discharge method. The apparatus and method are described. A direct measurement of the sparking potential cannot be obtained by this means, but it is possible to find relative sparking potentials by finding the smallest current in the exciting coil that will bring about sparking. Curves are drawn for each gas showing (a) relative conductivity and (b) sparking current against pressure. It was found that the minimum sparking current coincided with the maximum value of the conductivity. For the "base" gases the sparking potential is reached at a lower pressure and has a greater value than in the case of the rare gases. The curves for both types of gas show maxima or minima, but in the case of the rare gases the maxima are not so sharp and extend over a wider pressure range. The effect of the life period of the electron is discussed. The life period of the electrons in the rare gases is longer than in the "base" gases, and this fact plays an important part in causing the difference between damped and undamped excitation. A. J. MEE.

Spectrum of doubly-ionised chlorine. K. MAJUMDAR and S. C. DEB (Indian J. Physics, 1929, 3, 445-450).—An extension of the work of Bowen (cf. A., 1928, 210). Thirty additional lines are classified, and are attributed to the transition $2M_2(M_3 \leftarrow N_2 \leftarrow N_3)$. N. M. BLIGH.

Spectra of As III and Sb III. P. PATTABHIRAMIAH and A. S. RAO (Indian J. Physics, 1929, 3, 437—444; cf. Rao and Narayan, A., 1928, 929).—Tables are given showing the relativity doublet law variations and a comparison of the term values in gallium-like and indium-like atoms. Forty-one lines of As III and 25 lines of Sb III are tabulated and classified; other combinations involving the characteristic difference 722 in arsenic and 1668 in antimony are also given.

N. M. BLIGH. Arc spectrum of silicon. A. Fowler (Proc. Roy. Soc., 1929, A, 123, 422-439).-The arc spectrum of silicon has been investigated with the vacuum grating spectrograph, the arc being passed in nitrogen at atmospheric pressure in order to extend the observations as far as possible to short wave-lengths and to minimise the introduction of lines of Si II. A catalogue of lines from 11231 to 1600 Å. is given, including many previously unrecorded lines in the Schumann region. Most of the deeper terms predicted by the Heisenberg-Hund theory have been identified, and several series of more than two members are available for the determination of term values. The term $3p^{3}P_{0}$, representing the lowest normal state of the Si 1 atom, is assigned the value 65765, representing an ionisation potential of 8.12 volts. Comparison is made between the triplets of Si I and P II, and except for the $3p^1$ terms, which are relatively much greater in P II than in Si I, the general expected similarity is found. L. L. BIRCUMSHAW.

Titanium band spectrum. A. CHRISTY (Nature, 1929, 123, 873—874).—Twenty bands, extending from 7990 to 6270 Å., have been assigned to a new resonance system. The frequencies of the heads of the new system are given by the expression : $14172 \cdot 2$, $14105 \cdot 8$, $14030 \cdot 8$, $+(862 \cdot 5n' - 3 \cdot 84n'^2) - (1003 \cdot 8n'' - 4 \cdot 61n''^2)$. A. A. ELDRIDGE.

Analysis of the arc and spark spectra of yttrium (Y1 and Y11). W. F. MEGGERS and H. N. RUSSELL (Bur. Stand. J. Res., 1929, 2, 733-769).--The available data for the arc and spark spectra of yttrium, including wave-length measurements, intensities, temperature classes, and Zeeman effects, have been collected and analysed. In the spectrum of doubly-ionised yttrium, Y III, the number of lines is relatively small, but they are characterised by an enormous difference in intensity between arc and spark lines. The series limit corresponds with an ionisation potential of 20.4 volts for the Y⁺⁺ atom. The spectrum of singly-ionised yttrium, Y II, shows a larger number of lines, which can be divided roughly into two classes. The strongest lines are formed by combinations of low energy states with the next higher or middle set. The second class is very much enhanced in passing from arc to spark. In the arc they are faint, but in the spark they are inclined to be hazy. This fact suggests that these high terms correspond with higher electron orbits and are therefore especially susceptible to Stark and pressure effects. The Y II spectrum parallels that of Sc II. A term table is given. The ionisation potential of singly-ionised yttrium is 12.3 volts. A term table is also given for the spectrum

of neutral yttrium, the ionisation potential being in this case 6.5 volts. The analyses given are supported by measurements of the Zeeman effect. All details of the three spectra are in agreement with Hund's correlation of spectral terms with electron configurations. The presence of yttrium in the sun is discussed. The evidence for the existence of both neutral and ionised yttrium is conclusive, but the two sets of lines behave very differently. It is shown that this behaviour is what would be expected of an element of moderate abundance and easy ionisation.

A. J. MEE.

Length of the spectral lines of a spark in relation to the concentration of the element. A. OCCHIALINI (Atti R. Accad. Lincei, 1929, [vii], 9, 573-577).-With increasing resistance in the circuit the length of lines produced in a nickel or lead-tin spark decreases, the decrease being rather greater in the latter than in the former case. With alloys containing between 0 and 8% Sn, the length of the tin line at 5800 Å. increases rapidly, the increase being more rapid the greater the capacity of the circuit. With alloys containing between 10 and 100% Pb the length of the lead line 5609 Å. increases approximately linearly with the lead content, the increase becoming less rapid the greater is the resistance F. G. TRYHORN. of the circuit.

Intensity of spectral lines. W. HANLE (Z. Physik, 1929, 54, 852—855).—It is usually assumed that the intensity ratio of spectral lines belonging to one term is constant. This is the case if the total radiation is considered, but if the collisions in one direction only are taken into account this ceases to be true. The intensities of two mercury lines, of wave-lengths 3663 Å. $(2^{3}P_{2}-3^{1}D_{2})$ and 3132 Å. $(2^{3}P_{1}-3^{1}D_{2})$ were compared parallel and perpendicular to the direction of electron collision, and it was shown that the intensity of the 3163 Å. line compared with that of the 3125 Å. line was 10% stronger parallel to the radiation than perpendicular to it. The same was found with the 5461 Å. mercury line. The mathematics of the problem is given for the ideal case of a rectilinear electron stream. A. J. MEE.

Excitation function of the mercury resonance line λ 2537 Å. W. HANLE (Z. Physik, 1929, 54, 848— 851).—Apparatus for the determination of the excitation function of the ultra-violet resonance line of mercury λ 2537 Å. is described. The light measurements were made with a photo-cell. The intensity of the line for excitation by electron collisions is found in relationship to the velocity of the exciting electrons. The sharing function increases linearly at first, reaching a maximum at a potential about 1.5 volts greater than the excitation potential, after which it falls. The results obtained agree within the experimental error with those of Bricout (A., 1927, 1125) using a different method. A. J. MEE.

Zeeman effect in the spectrum of ionised neon (Ne II). C. J. BAKKER (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 515-522).—The observed g values arising from the 3s and 3p electrons are compared with those calculated from Lande's formula; those of the 3s electron are normal, whilst certain anomalous values of the 3p electron correspond with

analogous terms in the A (II) spectrum which exhibit abnormal g values. H. F. GILLBE.

Second order Stark effect for H_{ν} . H. R. VON TRAUBENBERG and R. GEBAUER (Z. Physik, 1929, 54, 307—320).—The second order Stark effect for the fine components of H_{ν} has been determined by Stark's method, using fields up to 702,500 volts/cm. The components $\sigma 0$, $\sigma 3$, $\sigma 10$, $\sigma 13$, $\pi 15$, and $\pi 18$ are found to undergo a slight shift, which is proportional to the square of the field strength, towards the red. In no case do the results agree with Epstein's calculations based on the Bohr theory (Ann. Physik, 1916, [iv], 51, 184), but those for the middle component agree exactly with Schrödinger's theory. The higher components show systematic discrepancies from Schrödinger's theory, but the discrepancies decrease for lower pressures, so that they may be due to collisions. E. B. ROBERTSON.

Theories of the continuous X-spectrum and of the Compton effect. E. SEVIN (Compt. rend., 1929, 188, 1245—1246; cf. this vol., 483).—A comment on Décombe's deductions (this vol., 615). J. GRANT.

Change in resonance lines through multiple Compton effect. W. ORTHMANN (Z. Physik, 1929, 54, 767-778).—Mathematical. A. J. MEE.

Possible existence of important exceptions to the selection principle relative to the total quantum number. N-spectrum of thorium. J. THIBAUD (Compt. rend., 1929, 188, 1394—1396).— Bohr and Coster's values of the energy of the N-levels obtained by extrapolation of high-frequency spectrographic measurements give results for the electronic transitions N_{IV} — N_V and N_V — N_{VI-VII} in agreement with Thibaud and Soltan's experimental values (A., 1927, 1000) for the abnormal N-doublets of tantalum and tungsten, a difference of 1—3% being found for platinum and gold. Idei's values (this vol., 630) give closer agreement. Examination of the spectra of silver, palladium, bismuth, and thorium indicates that these levels alone among the outer levels are likely to violate the selection principle. J. GRANT.

Spectral relations between certain isoelectronic systems and sequences. II. Sc 1, Ti 11, V 111, Cr IV, and Mn V. H. E. WHITE (Physical Rev., 1929, [ii], 33, 672—683).—Previous work (cf. A., 1927, 601; this vol., 3) is extended to include the spectra of V 111, Cr IV, and Mn V, which closely resemble those of Sc I and Ti II, extrapolation from the known data of which have led to the identification of terms arising from the electron configurations $3d^3$, $3d^24s$, $3d^24p$, and $3d^24d$. The term values are tabulated for the three elements in each case. The Moscley diagram and the irregular doublet law are used to determine the positions of doublet and quadruplet levels and the location of the radiated frequencies. The respective ionisation potentials are approximately 29.6, 50.4, and 75.7 volts.

N. M. BLIGH.

Perturbations in molecules and the theory of predissociation and diffuse spectra. O. K. RIOE (Physical Rev., 1929, [ii], 33, 748-759).—When the discrete vibration rotation absorption bands connected with transitions to a final electronic state of a molecule overlap the continuous region for the transitions to another final state, some of the discrete bands may be diffuse, and the rotation lines broad. Using the methods of wave mechanics the width of the line is calculated directly in terms of the perturbation matrices. The total absorption over the width of the line is also found. N. M. BLIGH.

Space charge sheaths in positive-ray analysis. R. W. GURNEY and P. M. MORSE (Physical Rev., 1929, [ii], 33, 789—799).—It is shown that in the ionising chambers used for the positive-ray analysis of ionisation products a positive ion sheath is formed, and concentrates the applied field near the slit. The sheath thickness varies with the applied voltage, the electron current, and the pressure, and by making these variations the relative proportions of secondary and primary ions reaching the analyser collector can be changed. Curves are given for the sheath thickness and for the various ionic currents through the slit for several conditions in the chamber.

N. M. BLIGH.

Ionisation by collision in a uniform electric field. M. J. DRUYVESTEYN (Z. Physik, 1928, 52, 197-202).—Expressions are derived for the probability of ionisation by electron collisions in a gas under a uniform electric field; these may be used to derive the energy loss in "elastic" collisions when the electron density is accurately known.

R. W. LUNT.

Ionisation of potassium vapour. R. W. DITCH-BURN and F. L. ARNOT (Proc. Roy. Soc., 1929, A, 123, 516-536).-Experiments are described on the ionisation of potassium vapour by which it is possible to measure the m/e ratio for the ions produced. The apparatus employed is similar to that used by Smyth (A., 1924, ii, 85), and the ions are produced by three methods: (1) by photo-ionisation, (2) by electron impact, and (3) by the attachment of K+ ions from a Kunsman filament (cf. A., 1926, 218). The results are expressed by curves showing the ion current for different magnetic fields. The curve obtained with photo-ions is identical with that obtained with the Kunsman filament, except that it is slightly broader; the only ion present is K⁺. Important differences are found between the results for slow and fast electrons, probably due to the fact that the K_2^+ ion formed by the impact of 120-volt electrons is more highly excited than the K_2^+ ion formed by the impact of 35-volt electrons. With ions formed by attachment definitely stable and unstable K2+ ions are found. Estimates are given of the probabilities of ionisation by electron impact, of the formation of K⁺, and of the attachment of K⁺ to K. The lives of the unstable compounds are shown to be of the order of 10-6 sec. The results are considered in connexion with the band spectra of the alkali-metal molecules and other optical data. It is assumed that all the transitions of the K_2 and K_2^+ molecules are such that the moment of inertia increases and the heat of dissociation decreases on excitation.

L. L. BIRCUMSHAW. Latent carriers of electricity in the gaseous discharge. S. A. RATNER (Proc. Nat. Acad. Sci., 1929, 15, 318-323).—An investigation of the large ionisation currents observed inside the electrodes during some experiments on the discharge of electricity through gases, using special large hollow electrodes, is described. It is concluded that these currents are due to metastable atoms diffusing into the ionisation chamber and being present at a concentration higher than 10⁻⁵. The investigation throws some light on the phenomena observed behind a perforated cathode. N. M. BLIGH.

Increase of the sparking potential of a gas mixture by irradiation. F. M. PENNING (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 341-343). —See this vol., 114.

Method for determination of critical potentials and its application to mercury vapour. V. PAVLOV and (FRL.) N. SUEVA (Z. Physik, 1929, 54, 236-245).-It is shown that the relative number of slowly moving electrons in an electron beam traversing a dilute gas will exhibit maxima whenever the accelerating potential slightly exceeds a critical potential. The relative number of slowly moving electrons is given by the ratio $(I_{V}-I_{V+4V})/I_{V}$, where I_{V} is the electron current corresponding with a potential V at a given gas pressure. The smaller is the value of ΔV the more closely may maxima be detected; a value of 0.2 volt was chosen for the experiments in mercury vapour. In addition to the following critical potentials below the first resonance potential: $0.45, 0.65, 0.95, 1.20, 1.40, 1.65, 1.80, 2.00, \overline{2}.25, 2.60,$ 2.85, 3.10, 3.45, 3.6, 3.85, 4.15, and 4.40 volts, new critical potentials were observed at 5.25, 5.75, 6.05, 6.30, 7.10, 7.45, and 8.05 volts for which no corresponding spectral lines are known. R. W. LUNT.

Theory of the photo-electric effect. P. AUGER (Compt. rend., 1929, 188, 1287-1289).-Sommerfeld's formula expressing the probability of expulsion of a photo-electron in terms of the direction and speed of departure and the velocity of light ("Atombau und Spectrallinien," 1929) is in agreement with experimental results. J. GRANT.

Longitudinal distribution of photo-electrons. A. CARRELLI (Nature, 1929, 123, 836-837).

Variation of the photo-electric effect with temperature and determination of the long wavelength limit for tungsten. A. H. WARNER (Physical Rev., 1929, [ii], 33, 815–818).—The photoelectric current is plotted against temperature up to 1140° Abs. for carefully outgassed tungsten. A marked increase in sensitivity was found from 800° to 1000° Abs. The long wave-limit was found to be 2570 ± 50 Å., and was independent of temperature.

N. M. BLIGH.

Release of photo-electrons by X-rays from metallic reflectors at angles bordering on total reflexion. W. EHRENBERG and F. JENTZSCH (Z. Physik, 1929, 54, 227—235).—At total reflexion of X-rays from metallic mirrors, the number of photoelectrons emitted will be a minimum, thus furnishing a method of determination of the angle of total reflexion. Curves obtained from measurements on mirrors of steel, silver, and gold are given.

G. E. WENTWORTH.

Greatest speed of photo-electric electrons in the selective sensitivity range of potassium. H. TEICHMANN (Ann. Physik, 1929, [v], 1, 1069–1095).— The Einstein equation $eV = h(v - v_0)$ fixes the maximal velocity of the liberated electron. It is now shown that for the mercury lines 436, 405, 365.5, 313, 302, and 280 µµ, *i.e.*, over the region of selectivity, the greatest speeds observed agree well with the theoretical values. A method whereby gas-free electrodes can be obtained by volatilisation of metal in a high vacuum is described. R. A. MORTON.

Hydrogen ions as the reason for the occurrence of photo-electric spectral selectivity of potassium. R. FLEISCHER (Physikal. Z., 1929, **30**, 320—322).— Three different methods of sensitising potassium photo-electric cells indicate that potassium vapour plays an essential part in effecting the increased sensitivity. The vapour pressure of potassium at the ordinary temperature is insufficiently large for the effect to be realised. As a result of this treatment combination between potassium and the hydrogen present occurs readily, but it is not clear whether neutral hydrogen or H⁺ ions are responsible. The work of Suhrmann (cf. A., 1928, 1068) is therefore indecisive. R. A. MORTON.

Photo-electric effect with aluminium and its amalgams. A. SMITS and H. GERDING (Physikal. Z., 1929, 30, 322—325).—Measurements of the photoelectric effect with active and passive iron are open to criticism on the ground that adsorbed gases are present. Little progress seems possible in elucidating the physical difference between the active and passive states by photo-electric studies of iron. Aluminium and its amalgams present far less difficulty. It is found that an amalgam containing 0.26 at.-% Hg shows a photo-electric effect four or five times as great as that of pure aluminium. Even the threshold wave-length is altered. From this it is concluded that a change in the inner state of the aluminium has occurred. Earlier work on the influence of small quantities of mercury on the electromotive behaviour of aluminium yielded similar results. The work is interpreted to mean that passive aluminium is not in inner equilibrium, but is instead in a disturbed state deficient in ions and electrons. Traces of mercury set up the condition of inner equilibrium in the metal and the change involves an increase in the number of ions and electrons. This implies the observed increase in photo-electric effect.

R. A. MORTON.

Emission of positive ions from metals. H. B. WAHLIN (Nature, 1929, 123, 912).—When heated, copper, iron, nickel, and platinum give alkali ions only, whilst tungsten, molybdenum, and tantalum give ions of at. wt. in agreement with that of the emitting metal. A. A. ELDRIDGE.

Statistics of photons. I. I. PLACINTEANU (Ann. Sci. Univ. Jassy, 1929, 15, 359-362).—Mathematical.

Test for polarisation of electron waves by reflexion. C. J. DAVISSON and L. H. GERMER (Physical Rev., 1929, [ii], 33, 760-772; cf. A., 1928, 683, 1173).—Measurements were made of the intensity of an electron beam twice reflected from nickel crystal faces at bombarding potentials from 10 to 200 volts. Within this range five selectively reflected beams were observed and tested for polarisation by measuring the current received by a collector. No variation of the current is observed with variations of the planes of incidence of the two reflexions. It is concluded that electron waves are not polarised by reflexion (cf. Darwin, A., 1928, 1300). N. M. BLIGH.

Determination of the charge of positive thermions from measurements of shot effect. N. H. WILLIAMS and W. S. HUXFORD (Physical Rev., 1929, [ii], 33, 773—788).—The shot effect consists in fluctuations, which can be calculated on probability theory, taking place in the electron stream set up when electrons evaporating from a hot metal surface are attracted to a positively-charged electrode. A potassium—iron oxide mixture source of positive ions was used to investigate the shot effect of a space current of positive ions. Results indicate that the discharge may be properly controlled and temperature limited currents obtained, giving a value for the K⁺ ion equal in magnitude to the electron charge.

N. M. BLIGH.

Effect of external fields on the polarisation of the light in hydrogen canal rays. I. WALERSTEIN (Physical Rev., 1929, [ii], 33, 800—814).—It is found that the application of electric or magnetic fields to a canal ray in a high vacuum causes a periodic variation of the polarisation along the length of the beam. Curves showing polarisation ratio against the length of the canal ray are given for fields of varying intensities and parallel and perpendicular to the beam and to the line of vision. In some cases strong fields increase the number of changes in the polarisation in the length observed, and in other cases increase only the amplitude of the variation. N. M. BLIGE.

Isotope of oxygen of mass 17 in the earth's atmosphere. W. F. GIAUQUE and H. L. JOHNSTON (Nature, 1929, 123, S31).—Of 34 lines observed by Dieke and Babcock (unpublished), 27 are due to the alternate rotation levels of $O^{16}O^{18}$. Other lines are considered to originate from the molecule $O^{16}O^{17}$. Measurements of band spectra are regarded as being more trustworthy than those with the mass spectrograph. The maximum abundance of the $O^{16}O^{17}$ molecule is estimated to be 1 in 10^4 .

A. A. ELDRIDGE. Isotope of oxygen, mass 18. Interpretation of the atmospheric absorption bands. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 1436—1441).—The weak band in the atmospheric absorption bands for oxygen (cf. Mulliken, A., 1928, 1165) originates from oxygen molecules each consisting of an atom of mass 16 combined with an atom of mass 18. S. K. TWEEDY.

At. wt. of phosphorus. M. RITCHIE (Nature, 1929, 123, 838).—Determinations of the density and compressibility of phosphine give 30.97(9) and 30.98(2) for the at. wt. of phosphorus. A. A. ELDRIDGE.

Quantum mechanics of radioactive change. J. KUDAR (Z. Physik, 1929, 54, 297—299).—A continuation of a previous paper (*ibid.*, 53, 61) on the mathematical aspect of radioactivity.

G. E. WENTWORTH.

Energy changes in nuclear collisions. W. KUHN (Z. Physik, 1929, 52, 151-157).—Energy changes associated with collisions between rapid α -particles and atomic nuclei are discussed with reference to the possible changes which may take place in atoms in fixed stars. R. W. LUNT.

Actinium problem. G. ELSEN (Z. anorg. Chem., 1929, 180, 304—320).—An historical survey is given of the problem of the genesis of the actinium family of elements. All the known facts support the view that the actinium series is derived from a radioactive isotope of uranium, actino-uranium, which must have at. wt. >238. O. J. WALKER.

Production of disintegration *H*-rays under the action of the α -radiation of polonium. C. PAVLOVSKI (Compt. rend., 1929, **188**, 1248—1250).— *H*-rays produced by disintegration of aluminium were demonstrated by the scintillation method and shown to be produced by α -radiation of polonium having a range of 3.9 or 2.4 cm. In general the results agree with those of Rutherford, who used α -rays of 4.9 cm. range. The maximum range of the H_{A1} particles is 48.2 cm. J. GRANT.

Disintegration of aluminium. C. PAVLOVSKI (Compt. rend., 1929, 188, 1334-1336; cf. preceding abstract).-Extrapolation of the curve relating the path of the α -particles with the maximum path of the H_{AI}-particles they expel, shows that the lower limit of the former is 1 cm. (cf. Schmidt, A., 1927, 494). Bothe's formula (A., 1928, 1302) for the maximum path of an H-particle which holds for nitrogen was not confirmed for aluminium, and it is inferred that the disintegration of the latter involves a more complicated mechanism. The curve relating the path of the a-particles and the relative number of H-particles indicates that the number of H_{AI} -particles increases rapidly for high-speed a-particles, but is in disagreement with the theoretical results of Gamow (this vol., 234). J. GRANT.

Rate of decay of polonium at different points in the U.S.S.R. L. N. BOGOJAVLENSKY (Nature, 1929, 123, 872).—The half-value period of polonium, kept for about 5 months in each of 18 Russian towns, varied between 125.6 days (Tiflis) and 181.6 days (Krasnodar), whilst the same specimens, after being kept for 5 months at Leningrad, gave values between 137.2 and 139.5 days. The phenomenon supports Perin's assumption of the existence of an external source of radiant energy which produces the radioactive decay of atoms. The greatest deviations occur at places with disturbed tectonics.

A. A. ELDRIDGE.

New fast β -radiation. D. SKOBELZYN (Z. Physik, 1929, 54, 686—702).—Six hundred Wilson chamber photographs of β -particles subjected to a magnetic field of 1500 gauss showed 32 almost straight tracks. Their length, slight curvature, and spatial distribution suggest identity with electrons scattered by the cosmic radiation. The Klein–Nishina relation is preferred to that of Dirac and Gordon for interpretation of absorption measurements, although predicted energy values no longer fit with "packing" values. Some of the observed tracks are multiple. The method of absorption measurements is discussed.

A. B. D. CASSIE.

Emanation method as an aid to chemical and physico-chemical investigations. O. HAHN (Naturwiss., 1929, 17, 295–296).—A summary. R. A. MORTON.

Electrical detection of single corpuscular rays. G. ORTNER and G. STETTER (Z. Physik, 1929, 54, 449-476).—The detection of corpuscular rays by means of thermionic valves is discussed. The essential details are a detector of high impedance and low grid current, a linear amplifier, and a thread galvanometer. The arrangement was used to examine the α -particles from radium-C. W. E. DOWNEY.

Absorption of high-frequency radiation. E. C. STONER (Phil. Mag., 1929, [vii], 7, 841-858).-The results of Ellis and Wooster (A., 1925, ii, 923; 1927, 606) on the β -rays and the heating effect of the γ -rays have been used in the determination of the intensities of the γ -rays of radium-B and -C. On the basis of these results it is shown that the number of impulses observed by Kovarik (A., 1924, ii, 447) is greater than the number of γ -ray quanta emitted by the disintegrating atoms. The results of Ahmad (A., 1924, ii, 440, 582; 1925, ii, 923) on the absorption of γ -rays are used to deduce γ -ray absorption coefficients and the values so obtained agree closely with those calculated from the formula of Klein and Nishina. Some apparently anomalous results of Ahmad are attributed to secondary scattering effects. The most penetrating cosmic radiation observed by Millikan and Cameron, having an absorption coefficient of 0.04 m.-1, has a wave-length, calculated from the Klein-Nishina formula, corresponding with the electron-proton annihilation wave-length. A. E. MITCHELL.

Existence of radioactive recoil ions of high mobility. L. L. LOEB and L. B. LOEB (Proc. Nat. Acad. Sci., 1929, 15, 305—310).—From experiments made using a Rutherford alternating-current method it is concluded that the existence of Erikson's highmobility radioactive recoil ions formed from recoil atoms of radium, thorium, and actinium emanations is very doubtful, and at present unconfirmed.

N. M. BLIGH.

Hydrogen-ion wave function. V. GUILLEMIN, jun., and C. ZENER (Proc. Nat. Acad. Sci., 1929, 15, 314—318).—Mathematical. N. M. BLIGH.

Why no hydrogen nuclei are emitted in radioactive changes. A. von GROSSE (Z. Physik, 1929, 54, 764—766).—Mathematical. Using Einstein's relativity relationship and Aston's curve (packing fractions plotted against at. wt.) it is shown that in consequence of the large packing fraction of the hydrogen nucleus it would be possible for it to be emitted only if there were a large absorption of energy. A. J. MEE.

Penetration of polonium into lead. (MLLE.) E. MONTEL (J. Phys. Radium, 1929, [vi], **10**, 78—80).— When a drop of a slightly acid solution containing a little polonium was placed on a thin lead plate, pressed down on a photographic plate, the polonium penetrated the lead. By using lead plates containing large crystals it is concluded, from the shape of the image, that the active material traverses the plate by passing between the crystals, the acid assisting by chemical action. J. L. BUCHAN.

Fine structure of the magnetic spectrum of the α -rays from thorium-C. S. ROSENBLUM (Compt. rend., 1929, 188, 1401—1403).—The Danysz focalisation method for the study of β -spectra has been applied to α -rays from thorium-C. Two very intense and almost coincident rays and two feebler isolated rays were observed in the magnetic spectrum for a field of 36,000 gauss. The results were independent of the nature and position of the radioactive source, of the degree of vacuum (0·1—0·001 mm.), and of the size of the slit. The velocities of the rays (thorium-C as unity) were 1·003, 0·975, and 0·961 for the weaker intense ray and for the two feeble rays, respectively. J. GRANT.

Action of metastable atoms of helium on a metal surface. M. L. E. OLIPHANT (Proc. Roy. Soc., 1929, A, 124, 228-242).—An apparatus is described for producing an intense beam of metastable helium atoms by the impact of positive ions at glancing incidence on the walls of a gas-free platinum canal. The excited ions are able to set free large numbers of electrons by collision with a metal target, by a process analogous to a collision of the second kind. By applying varying retarding potentials between the collecting cylinder and the target, the velocity distribution of the electrons has been investigated. Measurements with molybdenum, nickel, and magnesium targets indicate that the total number of electrons set free does not vary much with the surface, suggesting that every metastable atom gives rise to an electron. A fraction of the metastable atoms can be reflected from a metal surface, the amount of reflexion varying markedly with the gas condition of the surface and with the velocity of the original positive ions. Experiments are described which supply direct proof of the production of metastable atoms by glancing impact of positive ions on a metal surface. Some sputtering of the target is produced by the impact of the fast-moving neutral atoms, the kinetic energy of which is of the same order as that of the original beam of positive ions.

L. L. BIRCUMSHAW.

Reflexion of ultra-violet rays from metallic surfaces in relation of their microstructures. H. Kotô (Mem. Coll. Sci. Kyoto, 1929, 12, 81—96).— The intensity of reflexion for λ 3650 in the ultra-violet was determined for the following series of alloys: copper-silver, cadmium-bismuth, zinc-cadmium, copper-nickel, and magnesium-zinc. The intensity curves appear to be related to the equilibrium diagrams. There is a minimum in the intensity curve at a eutectic, except in the case of copper-silver; a maximum at a composition corresponding closely with a compound; and a break or maximum at the limit of solid solubility. These results are similar to those obtained by Chikashige (A., 1926, 896) using visible radiation. C. J. SMITHELLS.

Electronic theory of the ether and of light. A. VÉRONNET (Compt. rend., 1929, 188, 1380-1381).

Experimental test of the Maxwell velocity distribution law for electrons liberated from a glow cathode. A. DEMSKI (Physikal. Z., 1929, 30, 291-314).—Previous attempts to calculate the temperature of a glowing filament on the basis of the Maxwell velocity distribution law for liberated electrons have given discordant results, the values being mostly too high. The discrepancies have now been largely accounted for. The validity of the Maxwell law has been confirmed by using an alternating-current interrupter, although the condition of dynamic equilibrium required theoretically was not fulfilled. This method is not suitable for the measurement of temperature; the best method involves the use of a heated equipotential cathode without magnetic field. R. A. MORTON.

Perturbation theory in quantum mechanics. II. A. H. WILSON (Proc. Roy. Soc., 1929, A, 124, 176—188).—An extension of the theory previously developed (this vol., 363) to systems possessing both discrete and continuous spectra. The perturbation equations are derived in a somewhat more general form than has previously been given, those due to Born, Dirac (A., 1926, 1078), and Oppenheimer (A., 1928, 216) being particular cases obtained by different divisions of the Hamiltonian H into the parts H_0 , H_1 , $H_2(t)$. The necessary existence theorems are proved, and the validity of the perturbation theory is considered. L. BIRCUMSHAW.

Relativistic theory of an atom with many electrons. J. A. GAUNT (Proc. Roy. Soc., 1929, A, 124, 163-176).-Mathematical. The ordinary classification of multiplets and the selection and summation rules are derived from Dirac's relativistic equation, and it is shown that the selection rules are rigorous if there are no external fields, and that the rule " $\Delta \Sigma k$ is odd " is also rigorous, even in a uniform magnetic field. A practical consequence of this is that the O++ lines of nebular spectra, if correctly identified, can occur only in electric or non-uniform magnetic fields, since they have $\Delta \Sigma k = 0$. The classification of multiplets is discussed from the point of view of wave mechanics, spin effects being treated as small perturbations. The azimuthal quantum number l is defined, and the values of j appropriate to a multiplet of given l are deduced. The summation rule for the intensities in a multiplet is proved to a first approximation. L. L. BIRCUMSHAW.

Fall of a heavy gas in a light gas. Stability of ozone in the higher atmosphere. Y. ROCARD (Compt. rend., 1929, 188, 1336—1338).—A formula for the rate of fall of a globular mass of heavy gas in a lighter gas based on the kinetic theory has been deduced in terms of the mol. wt. of the gases, the radii of their molecules, Avogadro's number, and the gas equation constants. For ozone in nitrogen or hydrogen the rates of fall are 22 and 17 m./day, respectively. The conditions governing the stability of the layer of atmospheric ozone are discussed in the light of these results. J. GRANT.

Possible synthesis of elements in stars. R. D'E. ATKINSON and F. G. HOUTERMANS (Z. Physik, 1929, 54, 656—665).— α -Particles and protons have, according to Gamow, a calculable chance of entering any nucleus. Thermal velocities within a star are such that α -particles are unlikely to enter any nucleus, but protons may enter the lighter nuclei. The chance of formation, within a nucleus, of α -particles from protons is comparatively great. Energy due to packing may thus appear, and a new nucleus be formed. Synthesis of heavier nuclei presents more difficulties, but the Compton effect or spontaneous disintegration of light unstable nuclei may give velocities high enough for this possibility.

A. B. D. CASSIE. Synthesis of elements. II. G. I. POKROVSKI (Z. Physik, 1929, 54, 724-730).-An electron and a positively-charged nucleus may combine with a loss of mass the equivalent energy of which is radiated. This electron-proton system recoils with kinetic energy calculable in terms of the mass lost. When this kinetic energy is great enough two such systems of like charge, possessed of magnetic doublets, may approach so closely that magnetic forces bind them together. The magnetic moment is assumed, and the critical loss of mass required for binding, calculated for the lighter elements. Calculations agree favourably with Aston's results. The radius of the sphere in interstellar space effectively radiating this packing" energy to the earth is determined from Millikan and Cameron's results.

A. B. D. CASSIE. First- and second-order equations of the quantum theory. H. T. FLINT (Proc. Roy. Soc., 1929, A, 124, 143—150).—A solution is suggested for two difficulties raised by Dirac's treatment of the quantum theory of the electron (A., 1928, 344), and the nature of the invariance to be associated with the first-order equations is indicated. The phenomena are assumed to be five-dimensional, and are described by the introduction of two tensors containing an antisymmetric and a symmetric component. This procedure is, however, unsatisfactory from the point of view of the theory of physical unity.

L. L. BIRCUMSHAW. Translation of Dirac's theory of the electron into ordinary notation. E. MADELUNG (Z. Physik, 1929, 54, 303—306).—Mathematical. Dirac's theory is contained in a set of ordinary vector equations, which are established. The operational method is not required for solution of the central field problem. The equations established and Maxwell's have a surprising resemblance, which may lead to a better understanding of the interaction of matter and the electromagnetic field. A. B. D. CASSIE.

Tensor form of the wave-mechanics equation for an electron. H. MANDEL (Z. Physik, 1929, 54, 567-570).-Mathematical. W. E. DOWNEY.

Gravitation and the electron. H. WEYL (Proc. Nat. Acad. Sci., 1929, 15, 323—334).—Mathematical. The translation of Dirac's theory of the electron into general relativity is considered. N. M. BLIGH.

Possible geometrical explanation of the relativistic quantum theory. V. FOCK and D. IVANENKO (Z. Physik, 1929, 54, 798-802).--Mathematical. A geometrical explanation is given to Dirac's relationship. A. J. MEE.

Constitution of the solar atmosphere and identification of boron in the spots. S. B. NICHOLSON and N. G. PERRAKIS (J. Phys. Radium, 1929, [vi], **10**, 49-51).—Although the elements composing the atmosphere of the sun are chiefly those with low ionisation potentials, there are two exceptions: helium, with a high ionisation potential is present, but boron, the ionisation potential of which is low, is apparently absent. An examination of the band spectrum of sun spots, however, has shown the presence of 28 lines which have been identified with those of the spectrum of boron. J. L. BUCHAN.

Quantum-mechanical dispersion formula of normal atomic hydrogen. F. REICHE (Z. Physik, 1929, 53, 168—191).—Mathematical.

G. E. WENTWORTH.

New band system of carbon monoxide $(3^{1}S \rightarrow)$ 2¹P); the Angström band system. R. C. JOHN-SON and R. K. ASUNDI (Proc. Roy. Soc., 1929, A, 123,560-574; cf. Jasse, A., 1926, 452; Birge, A., 1927, 184).-Details are given of a new band system of carbon monoxide corresponding with the transition $3^1S \longrightarrow 2^1P$. Four bands have been observed, (0,0), (0,1), (0,2), and (0,3), with heads at 3680.05, 3893.19, 4125.02, and 4380.18 Å. The fine structure analysis of the (0,1), (0,2), and (0,3) bands has been determined, and it is found that the combination data obtained from this analysis fully supports the evidence that this system and the Ångström system have a common final state $2^{1}P$. The bands each have three branches of the P, Q, and R type, and are precisely similar to the Angström bands in structure. The nature of the electronic transition is confirmed by the fact that the lines $R(\frac{1}{2})$ and $Q(\frac{1}{2})$ are not observed. New experimental data are found in the case of the (0,0), (1,0), (0,4), and (0,5) Angström bands, and the combination data derived from these and from the new system, together with Hulthén's data (A., 1923, ii, 670), have been used to evaluate the constants of the $3^{1}S$, $2^{1}S$, and $2^{1}P$ levels of the CO molecule. An examination of the vibrational levels of the $2^{1}P$ state indicates that the perturbed level is n''=1 and not n''=0, as given by Birge (loc. cit.).

L. L. BIRCUMSHAW.

Frequencies characteristic of the carbonate group. C. SCHAEFER (Z. Physik, 1929, 54, 676– 678).—A criticism of Herzfeld's article ("Handbuch der Experimental-physik, VII"), particularly of the suggested harmonic relation between the double bands near 7μ and 14μ . A. B. D. CASSIE.

Quantum analysis of the blue-green bands of titanium oxide. A. CHRISTY (Physical Rev., 1929, [ii], 33, 701—729; cf. A., 1928, 1304).—The spectrum of the titanium bands is made up of a system in the blue-green and one in the yellow-red, both degrading to the red. The frequencies of all the heads in the blue-green region, and the frequencies of the lines and their combination differences for the (0,0), (0,1), and (1,0) bands are tabulated. Each band is composed of three R and three P branches. The combination principle is verified for about 90 lines, and quantum numbers are assigned. The moments of inertia of the TiO molecule are found to be 56.72×10^{-40} and 51.89×10^{-40} gm.cm.² for the initial and final states, and the initial and final state nuclear separations 1.693×10^{-8} and 1.619×10^{-8} cm., respectively. The triplet separation of the lines, although irregular, indicates a transition between two triplet levels, and is assumed to be ${}^{3}P - {}^{3}P$; *j* is found to be half integral. N. M. BLIGH.

Assignment of quantum numbers for electrons in molecules. III. Diatomic hydrides. R. S. MULLIKEN (Physical Rev., 1929, [ii], 33, 730—747; cf. this vol., 116; Hund, *ibid.*, 117).—A systematic survey is made of existing band spectrum data on energy levels of diatomic hydrides, and these data are interpreted in terms of theory. Quantum number assignments and multiplet separations are tabulated. Hund's new notation is explained and adopted. The formation of MH type molecules and the effects of the H on the M atom are discussed. Data are advanced as evidence that molecular stability is a matter of promotion energy rather than of valency linkings (Lewis and London). A simple explanation is given of observed multiplet widths in ²II and ³II states.

N. M. BLIGH.

Absorption of ultra-violet light by some purine derivatives and allied substances. L. MARCH-LEWSKI and J. WIERZUCHOWSKA (Bull. Acad. Polonaise, 1929, A, 65—79).—In aqueous solution guanine (in presence of sodium hydroxide) gives two absorption bands with maxima at 2460 and 2744 Å.; adenine sulphate, one band with maximum at 2606 Å.; uric acid, two bands. Allantoin, alloxan, alloxanthin, parabanic acid, and carbamide exhibit no selective absorption; barbituric acid gives one band with maximum at 2566 Å. but does not follow Beer's law. Diethylbarbituric acid shows no selective absorption but conforms to Beer's law.

A. I. VOGEL.

Absorption of light by some organic substances. L. MARCHLEWSKI and O. WYROBEK (Bull. Acad. Polonaise, 1929, A, 93—110).—The absorption spectra of solutions of some organic substances have been measured; all follow Beer's law. Pyridine in water gives three bands with maxima at 2620, 2570, and 2510 Å.; quinoline, four bands with maxima at 3135, 3060, 3000, and 2780 Å.; phenylacetic acid, three bands with maxima at 2645, 2580, and 2530 Å.; phenylglycollic and benzilic acids give absorption spectra similar to phenylacetic acid; menthone, two bands with maxima at 2890 and 2530 Å.; menthol, no absorption band; benzil, one band with maximum at 2590 Å.; tribromophenol, one band with maximum at 2690 Å., and benzyl alcohol, one band with maximum at 2570 Å. A. I. VOGEL.

Absorption of ultra-violet light by the methyld-glucosides. L. MARCHLEWSKI and J. MAYER (Bull. Acad. Polonaise, 1929, A, 111—118).—Pure α and β -methyl-d-glucosides do not cause selective absorption of light in the ultra-violet.

A. I. VOGEL.

Intensities of the mercury hydride bands. W. KAPUSCINSKI and J. E. EYMERS (Z. Physik, 1929, 54, 246—256).—The intensity distribution in nine of the mercury hydride bands has been investigated under various conditions of discharge. The results are discussed with reference to the theory of Hill and Van Vleck (A., 1928, 1076) and appear to deviate from it, in that the higher rotation states are too strongly represented. The heads of six of the bands have been measured, and an extension of Hulthén's tables (A., 1925, ii, 470; 1928, 1075) is given.

E. B. ROBERTSON. Intensity of γ -bands of nitric oxide. B. POGÁNY and R. SCHMID (Z. Physik, 1929, 54, 779– 787; cf. A., 1928, 930).—The nitric oxide γ -bands in the emission from the nitrogen afterglow were photographed and their intensities determined. Using the method due to Hill and Van Vlcck, the so-called effective temperature of the emission from the light sources used (vacuum arc and copper arc) was found. A. J. MEE.

Infra-red spectra of some halogen compounds. G. B. BONINO (Z. Physik, 1929, 54, 803-805).—In work by Pringsheim and Rosen on the Raman effect in organic liquids (A., 1928, 1307) it is shown that there is poor agreement between the wave-lengths of the infra-red bands and the Raman lines for compounds containing the C·H linking. It is now shown that if stricter methods are used the agreement is good for acetylene tetrachloride and dichloride, being even better in the latter case than in the former.

A. J. MEE.

Absorption bands in spectra of fixed stars. R. WILDT (Z. Physik, 1929, 54, 856—879).—By investigating the band spectra of stars the existence of certain molecules in stellar atmospheres can be proved. The spectra of oxides, carbon compounds, and hydrides are especially considered. The stability of chemical compounds in stellar atmospheres can be investigated also by the Nernst reaction isochore, and application is made of this method. A. J. MEE.

Fine structure of diffused rays at critical opalescence, with reference to the Cabannes-Daure effect. A. BOGROS and Y. ROCARD (J. Phys. Radium, 1929, [vi], 10, 72-77).—An apparatus is described for studying the fine structure of the diffused light produced by a mixture of water and phenol in the state of critical opalescence. No evidence of the Cabannes-Daure effect, the increase of the wave-length on diffusion, was observed. An explanation for this is advanced, and the probable cause of the Cabannes-Daure effect is discussed.

J. L. BUCHAN.

Molecular spectrum of ammonia. II. Double band at 10 μ . E. F. BARKER (Physical Rev., 1929, [ii], 33, 684—691; cf. Robertson and Fox, A., 1928, 1073; Stinchcomb and Barker, this vol., 488).— By means of a specially ruled grating the fine structure details of the ammonia absorption band from 8 to 14 μ was studied. Two narrow zero branches appear at 10.3 and 10.7 μ , with each of which is associated a positive and negative branch consisting of 10 or 12 lines. The double character is shown to be a consequence of the close proximity of the two equilibrium positions for the nitrogen atom, one on each side of the plane formed by the hydrogen atoms. The structure of the vibration-rotation band at 1.9 μ is discussed and the total intensities are tabulated.

N. M. BLIGH.

Pure rotation spectrum of ammonia. R. M. BADGER and C. H. CARTWRIGHT (Physical Rev., 1929, [ii], **33**, 692-700).—Improved experimental means for the study of absorption spectra in the extreme infra-red are described and applied to the study of the polyatomic molecule ammonia in the region 55— 130 μ . Six lines were observed; they belong to a pure rotation spectrum and are attributed to changes in the rotation energy of the molecule about an axis normal to the line of symmetry, j increasing by unity for the transitions. Results are shown to be in agreement with the predictions of wave mechanics. The moment of inertia of the molecule about the above axis is estimated as 2.77×10^{-40} g.cm.²

N. M. BLIGH.

Studies in photographic sensitivity. V. Effects of heat on the absorption spectrum and photo-electric conductivity of silver bromide, and their relation to the photographic action. 0. MASAKI (Mem. Coll. Sci. Kyoto, 1929, 12, 127-134; cf. B., 1929, 377) .-- The effect of temperature between 30° and 100° on the absorption spectra and photo-electric conductivities of silver halides was examined. The long-wave limit of absorption for silver bromide was shifted towards the red 1.1 A./1° rise in temperature, and similar results were obtained with silver chloride and iodide. The photo-electric conductivity of silver bromide decreased with rise in temperature, and the maximum shifted towards the red by about 1.4 Å./1°. It was previously observed that the sensitivity of certain photographic plates was increased and the maximum sensitivity shifted towards the red by rise in temperature, and a connexion between these phenomena is suggested.

C. J. SMITHELLS. Photoluminescence of liquids. S. J. VAVILOV and L. A. TUMMERMANN (Z. Physik, 1929, 54, 270— 276).—A study has been made of the blue luminescence obtained by ultra-violet irradiation, from a mercuryquartz lamp, of a number of colourless liquids, including organic compounds and solutions of mineral acids. The spectra for the same frequency of stimulation (400—560 mµ) are very similar. Other phenomena such as the extinction of the fluorescence, its polarisation and colour change with different irradiation have been investigated. It is concluded that the phenomenon discovered by Venkateswaran and Karl (this vol., 241) is another case of fluorescence.

G. E. WENTWORTH.

Duration of the phosphorescence of the I_2 , K_2 , Na₂, and Na resonance emission. H. H. HUPFELD (Z. Physik, 1929, 54, 484—497).—Gaviola's fluorometer (A., 1927, 712) was used to measure the duration of the phosphorescence of the iodine, potassium, and sodium band resonance emission as well as that of the *D*-line of sodium. For I_2 , $t=1\cdot10^{-8}\pm1\cdot10^{-9}$ sec.; for K_2 , $t=8\times10^{-9}\pm1\cdot5\times10^{-9}$ sec.; for Na₂, t= $75\times10^{-9}\pm1\cdot5\times10^{-9}$ sec.; for sodium *D*-line, t= $1\cdot5\times10^{-8}\pm0\cdot3\times10^{-8}$ sec. W. E. DOWNEY.

Polarisation phenomena in the gradual excitation of the fluoresence of mercury vapour. W. HANLE and E. F. RICHTER (Z. Physik, 1929, 54, 811-818).—The fluorescence of mercury vapour for the gradual excitation of the 2537 and 4047 Å. lines in particular was investigated. Nitrogen was added, a pressure of 1.5 mm. being used. The polarisation effects and intensity displacement of the 5461, 4358, and 4047 Å. lines are described and explained. The polarisation of the 4047 Å. line should be complete theoretically. This is not so in practice, the difference being ascribed to the effect of fine structure.

A. J. MEE.

Raman effect in alkali halides. C. SCHAEFER (Z. Physik, 1929, 54, 153—154).—A preliminary note stating that, as in the case of rock salt, no emission of the characteristic infra-frequency can be detected with lithium or sodium fluorides, and suggesting a possible theoretical basis for this. R. W. LUNT.

Raman effect in potassium carbonate solution. M. LEONTOVITSCH (Z. Physik, 1929, 54, 155—157).— Using exposures of 90 hrs., a satellite to the radiated lines 3126, 3132 Å. has been observed. This corresponds with an infra-red frequency, $\lambda=9.26 \mu$, and thus lies close to the frequency characteristic of calcite, $\lambda=9.13 \mu$. This frequency is therefore attributed to the CO₃ group. R. W. LUNT.

Raman effect by helium excitation. R. W. WOOD (Phil. Mag., 1929, [vii], 7, 858-868).-The method of using a mercury arc for the excitation of Raman lines previously described (A., 1928, 1306) has been improved so that cooling is effected by only a small quantity of absorbing medium. The mercury arc method of excitation is unsatisfactory in that it is incapable of providing truly monochromatic exciting radiation. This defect is not present when radiation from a helium discharge tube is used in conjunction with a filter of nickel oxide glass which transmits the 3888 A. line to almost its full intensity and the lines at 3965 and 4025 Å., with such feeble intensity as to give no Raman lines. The arrangement of the helium tube is described together with the method of preparing a standard scale from which the wavelengths of the infra-red absorption bands corresponding with the Raman lines can be read directly. The helium excitation apparatus has been used satisfactorily with liquids of b. p. 40°.

A. E. MITCHELL.

Raman effect. A. PETRIKALN and J. HOCHBERG (Z. physikal. Chem., 1929, B, 3, 217-228).-The Raman spectra of bromobenzene and pyridine resemble those of benzene and of chlorobenzene. The replacement of CH in the benzene nucleus by N does not alter the type of spectrum. With naphthalene the structure of the spectrum is quite different. Nitromethane gives a spectrum characteristic of methane derivatives, but with acetonitrile a different type of spectrum is obtained. The spectra of all the above substances have a Raman line characteristic of the C·H linking. This line is replaced by a strongly diffuse doublet in the Raman spectra of hexane and cyclohexane, which are closely similar to one another. The carbon disulphide spectrum shows only two lines. Diphenylmethane (in methyl alcohol) gave a very intense continuous spectrum, but no lines, and triphenylmethane (in ether) gave a few broad bands but also no lines. The corresponding infra-red bands have also been calculated from the observed frequency difference of the Raman lines. O. J. WALKER.

Raman spectra of solutions of some ionised substances. R. G. DICKINSON and R. T. DILLON (Proc. Nat. Acad. Sci., 1929, 15, 334-337).—Since there is a close agreement between the strongest lines of the Raman spectra of calcite and sodium nitrate solutions, and in order to obtain further comparable data the spectrum of the radiation scattered by solutions containing the ions CO_3 , CIO_3 , BrO_3 , IO_3 , SO_3 , HCO_3 , SO_4 , and CIO_4 was photographed. The assignment of exciting lines to shifted lines and the magnitudes of the frequency shifts with their estimated relative prominence are tabulated. The strong lines show a regularity, the magnitudes of the frequency changes are uninfluenced by the nature of the positive ion, and the frequency change corresponding with the strong line decreases with increase in atomic number of the central atom of the negative ion.

N. M. BLIGH. Raman effect in crystals. H. NISI (Proc. Imp. Acad. Tokyo, 1929, 5, 127–129).—The Raman spectra of quartz, topaz, and calcite have been determined. No Raman lines were found with fluorspar, contrary to the results of Landsberg and Mandelstam. The results for calcite confirm those of Wood, with the exception of a Raman line corresponding with an infra-red absorption band at 6.96μ . For topaz the mean differences between the exciting Hg lines and the Raman lines were 911 and 260 wave-numbers, corresponding with infra-red absorption bands at 11.0 and 38.5μ , respectively.

F. G. TRYHORN.

Change of the dielectric constant of a highly rarefied gas by means of electrons. L. BERG-MANN and W. DÜRING (Ann. Physik, 1929, [v], 1, 1041—1068).—The change in the dielectric constant of a highly rarefied gas in the presence of electrons has been measured by the second method of Drude. As the electron density increases the dielectric constant steadily decreases. The absolute values for the constant agree with theoretical requirements, as also does the course of the dispersion. R. A. MORTON.

Dielectric constant of some ionised gases. H. GUTTON (Compt. rend., 1929, 188, 1235—1237; cf. this vol., 228).—It is shown that the dielectric constant (K) of a gas may be obtained from the ionisation currents of the gases constituting the dielectrics of two condensers in series, one containing the ionised gas under test, and the other a gas of known properties (air). The equation $K=1+[0.278\times10^{10}N/(35\cdot5\times10^{10}N^{34}-\omega^2)]$ enables the number of electrons/c.c. of ionised gas (N) corresponding with resonance to be calculated for any pulsation ω . For $\lambda=248.7$ cm., $N=1.9\times10^8$. J. GRANT.

Dielectric constants of some metallic vapours. F. KRÜGER and F. MASKE (Physikal. Z., 1929, 30, 314—320).—The dielectric constant of mercury vapour at 312° and 10 cm. pressure is $\varepsilon = 1.000622$. At this pressure $\varepsilon = 1$ is proportional to the density; at the normal density at 0°, ε is calculated to be 1.0101. On the basis of the simple Maxwell relation $\varepsilon = n^2$ (*n*=refractive index) the value 1.00373 is obtained as against 1.0101. The lack of agreement makes it necessary to consider the rôle of characteristic frequencies of the kind postulated by the Ketteler-Helmholtz dispersion formula. Accepting Cuthbertson's dispersion data and using $\lambda = 2537$ Å. for an ultra-violet frequency it becomes necessary to assume the existence of selective absorption near 0.9 μ , and in view of uncertainties in the data, the band is placed as somewhere between 1 and 2 μ . If the value for the dielectric constant at a density 13.55 is calculated by extrapolation on the basis of the Clausius-Mosotti formula $(\varepsilon-1)(\varepsilon+2)1/d=$ constant the dielectric constant for liquid mercury becomes a negative quantity. Similarly, the introduction of the refractive index at λ_{∞} leads to a negative value, from which it is concluded that the extrapolation cannot be justified.

The dielectric constant of potassium vapour at 500° and 1 cm. of mercury is 1.00092, *i.e.*, 1.19 ± 0.04 at 0° and atmospheric pressure. From the dispersion data, $n^2=1.00252$, the discrepancy again pointing to the operation of infra-red frequencies. The dielectric constant of rubidium vapour was also studied, but the results were less satisfactory. R. A. MORTON.

Mol. vol. of organic groups in complex salts. Volume of o-phenylenediamine in its com-I. pounds with metallic salts. W. HIEBER and K. RIES (Z. anorg. Chem., 1929, 180, 225-234).-The densities of a series of compounds of o-phenylenediamine with the halides of cadmium, nickel, cobalt, and zinc, and with the sulphates of cobalt, nickel, copper, zinc, and cadmium have been determined at 25°, and the corresponding mol. vol. calculated. From these values the mol. vol. of o-phenylenediamine in each of these compounds is obtained and compared with that in the uncombined state. The mol. vol. of o-phenylenediamine is in general greater in its compounds and increases in the order chloride, bromide, iodide, but it depends also on the number of molecules of o-phenylenediamine present in the compound and on the temperature. The regularities found by Biltz (A., 1928, 697) for the mol. vol. of ammonia in its compounds with metallic salts do not apply in the case of the diamine. O. J. WALKER.

apply in the case of the diamine. O. J. WALKE. Dispersion of double refraction in quartz. T. H. HAVELOCK (Proc. Roy. Soc., 1929, Å, 124, 46—49).—The constant C in the relation for a uniaxial crystal, $(n_1^2-1)^{-1}-(n_2^2-1)^{-1}=C$, where n_1 is the ordinary and n_2 the extraordinary index (cf. *ibid.*, 1907, Å, 80, 28), has been recalculated for quartz for wave-lengths from 1852 to 21,719 Å., using the experimental data of Gifford (*ibid.*, 1902, Å, 70, 329) from 1852 to 7950 Å., and of Carvallo from 8320 to 21,719 Å. The mean value of C over the range 3961—8320 Å. is 0.014416, with a definite fall to about 0.01422 at the two extremes of the scale. Using this value of C in conjunction with the dispersion formula for the ordinary index proposed by Coode-Adams (A., 1928, 220), the calculated values of the double refraction are found to be in excellent agreement with the experimental values obtained by Harris (Phil. Mag., 1929, [vii], 7, 80) and by Gifford (*loc. cit.*). There is some indication that Harris's values for the short wave-lengths may be somewhat low. L. L. BIRCUMISHAW.

The tan $C \cdot H/T$ law of paramagnetic rotation of the plane of polarisation. W. SCHÜTZ (Z. Physik, 1929, 54, 731-735).—Mathematical.

Organic dipole-molecules with singly- and doubly-linked oxygen. K. L. Wolf (Z. physikal.

Chem., 1929, B, 3, 128-138) .- The part played by singly- and doubly-linked oxygen in determining the dipole moments of organic compounds is discussed. The assumption is made that singly-bound oxygen makes an angle of about 110° with the normal valency linking in the rest of the compound. It is shown that this assumption leads to correct values for the dipole moments of certain classes of compounds containing the hydroxyl or methoxyl groups. It also removes many difficulties previously experienced in calculating the dipole moments of benzene substitution products, and contradictions in the signs of the group moments disappear. Two possible linkings for the oxygen in the carbonyl group are discussed. In order to settle which occurs it is necessary to obtain experimentally the dipole moment of a cyclic saturated ketone. The results of experiments on the ultra-violet absorptions of cyclohexanone and menthone are used for this purpose. The value obtained for the dipole moment is about 2.75×10^{-18} , which is the same as for an aliphatic ketone. This is the result which would be expected if the oxygen of the carbonyl group were bound to the carbon by an ordinary double linking. The structure of the carboxyl group is also discussed. The relatively strong acid character of the hydroxyl group in the fatty acids is due to the effect of the carbonyl dipole on the hydroxyl group. A. J. MEE.

Expression for natural rotation [of light] corresponding with that for molecular refraction. K. L. WOLF and H. VOLKMANN (Z. physikal. Chem., 1929, B, 3, 139-148).—The expression obtained by Gans based on Born's theory, which has the same significance for natural rotation as the expression for specific refraction has for refraction is discussed. The formula is confirmed by the experiments of Wetterfors on bromocamphor in acetone (A., 1922, ii, 247). In order to test the Born-Gans theory on a somewhat wider basis, new determinations of the rotation, refractive indices, and densities of solutions of limonene in different solvents and for different concentrations were made. They provide a further confirmation of the theory. Deviations may be ascribed to the effect of the dipole moment of the solution and to molecular association, a fact which is confirmed by experiments on menthone and carvone and their solutions. In this connexion the dipole moment of menthone was determined and found to be 2.77×10^{-18} , whilst for limonene, in consequence of the small size of its moment, only the upper limit, 0.5×10-18, could be determined. The ultra-violet absorption curves of a 0.14M-solution of menthone in herane and absolute methyl alcohol are given.

A. J. MEE. Use of a magnetic field in the measurement of the forces tending to orient an anisotropic liquid in a thin, homogeneous layer. V. FREEDERICKSZ and V. ZOLINA (Amer. Electrochem. Soc., May 1929. Advance copy, 11 pp.).—The forces which cause the orientation of the "drops" of an anisotropic liquid in the form of a homogeneous layer have been investigated by balancing them against magnetic forces. It is concluded that the magnitude of the orienting forces depends only on the nature and condition of

the anisotropic liquid itself and is independent of the kind of glass on which the liquid rests and of the method of cleaning the glass surface, provided that cleaning is done carefully. For phenetole and anisaldazine the orienting force is found to vary as the reciprocal of the eighth power of the thickness of the liquid layer for magnetic fields between 4000 and 9000 gauss. Rise of temperature produces a small but definite decrease in the orienting force. H. J. T. ELLINGHAM.

Chemical and optical properties of the reactive organic groups. A. DADIEU (Z. Elektrochem., 1929, 35, 283—291).—A discussion on the relationships which subsist in various series of organic compounds between properties, such as dissociation constants, absorption spectra, and variations in reactivity and chemical constitution. H. T. S. BRITTON.

Kerr effect in viscous liquids due to radiofrequency oscillating field. S. C. SIRKAR (Indian J. Physics, 1929, **3**, 409–424).—The Kerr effect is reviewed theoretically and the method for its study in octyl, nonyl, and undecyl alcohols fully described. A restoration of light between crossed Nicols, differing entirely from the Kerr effect, was observed, and was most marked in the region of frequencies in which there is strong electric absorption, the liquid becoming translucent. The Kerr effect in undecyl alcohol became too small to be observed for an oscillating field of wave-length 114 cm., showing the existence of a time of relaxation lying between 10⁻⁸ and 10⁻⁹ sec. N. M. BLIGH.

Texture of drawn magnesium and zinc wire. E. SCHMID and G. WASSERMANN (Naturwiss., 1929, 17, 312—314).—With metals showing the facecentred cubic lattice, the central zone of the drawn wire shows the ordinary fibre structure. For the hexagonal metals magnesium and zinc the former exhibits a (centred or homogeneous) ring fibre structure, whilst zinc shows a spiral or double-cone fibre texture. The portions near the edge of the wire show simple conical structure in all cases.

R. A. MORTON.

Improvement (by heat treatment) of an aluminium alloy in respect of X-ray structure. [FRL.] VON GOLER and [FRL.] G. SACHS (Naturwiss., 1929, 17, 309-312).-An aluminium alloy containing 5% of copper has been studied in relation to physical properties, extension, etc., and parallel determinations of lattice constants have been made after heat treatment for definite times at various temperatures. The lattice constants show no change until the heat treatment has brought about a very considerable improvement in respect of cohesion. The lattice constant of the supersaturated mixed crystals after heat treatment is the same as that of the quenched alloy, indicating that the copper is completely " built R. A. MORTON. into" the lattice.

Plasticity. Deformation at low temperatures. M. PÓLÁNYI and E. SCHMID (Naturwiss., 1929, 17, 301-304).—Three kinds of plasticity are differentiated. Athermic plasticity occurs in crystals, *e.g.*, unicrystalline zinc and cadmium. The materials begin to give way under a tension 10⁻³ times the theoretical value, and a fall of temperature from BRITISH CHEMICAL ABSTRACTS .--- A.

300° to 20° Abs. causes only a 1:1.8 increase in the effective tension. It would appear that at the absolute zero such crystals would undergo plastic deformation under conditions not very different from those obtaining at the ordinary temperature. The extension curves for cadmium at S3° and 20° almost coincide, showing that the process of recovery is absent at these temperatures and the curve ceases to depend appreciably on temperature. Thermal plasticity, conditioned by heat motion, appears in amorphous substances like glass, pitch, and shellac. Deformation occurs under relatively small loads, the effect being a flow in the sense that an increase in the rate of deformation requires a considerable increase in the load. The effect depends greatly on temperature, and at absolute zero the plasticity might be expected to disappear, so that in the absence of cracks the theoretical cohesion of 10²-10³ kg./mm.² R. A. MORTON. should be observed.

Striking phenomenon with laminated mica crystals. H. W. ALBU and H. ZOCHER (Naturwiss., 1929, 17, 299—301).—Certain forms of mica in which the succession of laminæ result in almost total reflexion of direct rays, transmit quite freely with oblique incidence within an apparently quite small angular region. The emergent light is practically completely polarised. Viewed through a microscope the transmission is confined to a bright ring when the incident light is convergent. Mica is suggested as a "dark field filter" in microscopy.

R. A. MORTON.

Refractivity of gaseous compounds. G. W. BRINDLEY (Phil. Mag., 1929, [vii], 7, 891-897).-The apparently simple relationships between the refractivities of a number of gaseous compounds previously discussed (this vol., 380) are examined further. The following numerical relationships are shown to hold with fair accuracy for any given wavelength $(\mu-1)_{\text{HCl}}=4/7(\mu-1)_{\text{Cl}_{s}}, \quad (\mu-1)_{\text{CCl}_{s}}=16/7)\mu-1)_{\text{Cl}_{s}}, \quad (\mu-1)_{\text{HB}_{r}}=13/25(\mu-1)_{\text{Br}_{s}}, \text{ and } (\mu-1)_{\text{CCl}_{s}}=16/7)\mu-1/3(\mu-1)_{\text{Cl}_{s}}, \quad (\mu-1)_{\text{HB}_{r}}=13/25(\mu-1)_{\text{Br}_{s}}, \text{ and } (\mu-1)_{\text{CCl}_{s}}=16/7$ ing are either the ratios or multiples of the ratios of the numbers of M electrons in the molecules and it is shown that this is in general conformity with both the quantum and the electronic theories of dispersion. The difference between $(\mu-1)_{HCI}/(\mu-1)_{CI}$ and $(\mu-1)_{CI}$ $1_{\text{HBr}}/(\mu-1)_{\text{Bra}}$ is discussed and it is considered to be due to light absorption by bromine in the visible region of the spectrum. A. E. MITCHELL.

Quantum theory of gases and solutions. N. BARBULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 62-74; Chem. Zentr., 1928, ii, 2334).—The theory rests on the supposition that the translatory motion of molecules in the gaseous and liquid states is a vibratory movement of extremely small frequency. The mechanism of the increase of kinetic energy by absorption of heat radiation becomes a simple resonance phenomenon. A. A. ELDRIDGE.

Theoretical electronic explanation of organic compounds, especially benzene. M. ULMANN (Z. Elektrochem., 1929, 35, 268–274).—Theoretical. H. T. S. BRITTON.

Experimental test of the quantum theoretical dispersion formula. II. R. LADENBURG (Natur-

wiss., 1929, **17**, 296–299; cf. *ibid.*, 1926, **14**, 1208). —A review (cf. A., 1926, 994; 1928, 577, 1172). R. A. MORTON.

Liquid interference. H. MARK (Z. Physik, 1929, 54, 505-510).-Theoretical.

W. E. DOWNEY.

Co-ordination numbers. F. I. G. RAWLINS (Trans. Faraday Soc., 1929, 25, 283-285).—The quantity C.N. or the number of atoms or ions of a certain kind surrounding another atom at equal distances in the crystal lattice, and the inter-nuclear distance are discussed in relation to passage from crystalline to gaseous state, and some theoretical suggestions are made. The quantity C.N. is also found to be intimately associated with the degree of complexity of the infra-red spectra of crystals (cf. Tolksdorf, A., 1928, 565). N. M. BLIGH.

Electronic theory of valency. VII. Etch figures of sylvine. T. M. LOWRY and M. A. VERNON (Trans. Faraday Soc., 1929, 25, 286-291).-The possibility of a fine structure was investigated by etching sylvine crystals with a strong solution of potassium chloride. No evidence contrary or additional to that furnished by X-rays was obtained. The formation of ice is considered to be a polymerisation rather than an ionisation process. A network of single linkings is postulated also in the case of quartz and the anions of certain oxygenated crystalline salts. N. M. BLIGH.

Deflexion method for molecular beams. I. I. RABI (Z. Physik, 1929, 54, 190—197).—A modified form of molecular beam apparatus is described in which the deflexion produced in the stream is proportional to the strength of the magnetic field (and not as in earlier forms to the inhomogeneity), thereby greatly simplifying the technique. R. W. LUNT.

Experimental method for the measurement of molecular streams. H. MEYER (Z. Physik, 1928, 52, 235—248).—Experiments are described in which the momentum of gas molecules escaping through a narrow orifice is conveyed to a suspended quartz fibre system carrying a mirror. The deflexion of this system gives a measure of the momentum of the molecules and therefore of the number of molecules escaping through the orifice. R. W. LUNT.

Effective binding forces in polyatomic molecules. F. EBEL and E. BRETSCHER (Helv. Chim. Acta, 1929, 12, 443-449; cf. A., 1928, 485).-Two apparently opposed views regarding the nature of interatomic linkings are discussed: (1) that the magnitude of the force between two atoms in a molecule is a fundamental quantity characteristic of the particular atoms, and (2) that the force between two atoms depends on the constitution of the molecule, so that, for example, the magnitude of the C-C linking differs in ethane and in hexaphenylethane. Evidence for the latter view is obtained from an examination of the energy required to remove the sulphur atom in carbonyl sulphide. The values of the C-O and C-S linkings are 199.2 and 131.7 kg.-cals., respectively, when calculated by Fajans' method from the heats of formation of carbon dioxide and of carbon disulphide. From the heat of combustion

of carbonyl sulphide it can be shown that only 76.9 kg.-cals are required to remove the sulphur atom from that compound. The strength of the C-S linking in carbonyl sulphide is, therefore, apparently about half what it is in the disulphide. Similarly, the removal of a chlorine atom from carbonyl chloride requires only about half the amount of energy calculated for the C-Cl linking. The two views can, however, be reconciled. It is assumed that there is a spontaneous and periodic rearrangement of the interatomic forces in a molecule, so that the energy distribution in the molecule is continuously fluctuating between limiting states. The Fajans values of the atomic linkings represent the average distribution of the internal energy of the molecule, but in chemical reactions it is the extreme values of the binding forces which are effective. O. J. WALKER.

Mutual dependence of binding forces between atoms. F. EBEL and E. BRETSCHER (Helv. Chim. Acta, 1929, 12, 450-463).-According to the views put forward by the authors (cf. preceding abstract), the magnitude of the binding force between two atoms A and B should depend on the nature of any other atoms which are joined to A. A case in which this view can be tested experimentally is that of the P-O linking in the oxyfluoride and oxychloride of phosphorus. The value of this linking is 63.3 and 70.6 kg.-cals. in the oxychloride and oxyfluoride, respectively, as calculated from the heats of formation of these compounds from the corresponding phosphorus trihalide and oxygen. The replacement of chlorine by fluorine atoms therefore brings about a strengthening of the P-O linking, and not a loosening as would be expected from the older theories of organic chemistry. The heat of the reaction $PF_3 + 0.5O_2 = POF_3$ was measured and found to be 70.6 ± 1.0 kg.-cal., starting with the reactants in the gaseous state. A special form of gas calorimeter is described.

O. J. WALKER.

Relation between the influence of the elements on the polymorphism of iron and their place in the periodic system. F. WEVER (Naturwiss., 1929, 17, 304—309).—A definite periodic relation has been detected between the influence of an element on the polymorphic transformations of iron (from facecentred to body-centred cubic lattices) and its position in the periodic system. Similar relationships are probable for the properties of homogeneous mixed crystal series. R. A. MORTON.

Experimental determination of surface tension by the method of traction of discs. J. E. VER-SCHAFFELT (Bull. Acad. roy. Belg., 1928, [v], 14, 663-665).—A simplified process is described for calculating the results of determinations of surface tension (by measuring the force required to withdraw a disc from the liquid) from the formula given preriously (*ibid.*, 530), by a method of successive approximation. F. L. USHER.

Surface tension of sodium. F. E. POINDEXTER and (MISS) M. KERNAGHAN (Physical Rev., 1929, [ii], 33, 837—843).—Accurate experiments on molten sodium in a high vacuum, using a modified flat drop method gave values, corrected by Worthington's formula, of 206.4 and 199.5 dynes/cm. at 100° and 250°, respectively, for the surface tension of sodium. The molecules in liquid sodium are concluded to be polyatomic. N. M. BLIGH.

Emission of soft X-rays by different elements at high voltages. O. W. RICHARDSON and F. S. ROBERTSON (Proc. Roy. Soc., 1929, A., 124, 188-196).-Bymeans of the apparatus previously described (A., 1927, 804), an investigation has been made of the efficiency of 14 elements as emitters of soft X-rays at exciting voltages of about 2000, 4000, and 6000. Curves are plotted showing the relation of the ratio i_p/i_t to the atomic number, and are found to be of similar type to those previously obtained at lower voltages. Molybdenum maintains its position as the most efficient element over the whole range from 300 to 6000 volts. There is a remarkable change in the group of elements from chromium to copper; whereas at 300 volts chromium is the most and copper the least efficient of these elements, at the higher voltages this position is reversed. Similarly, in the middle of the fifth and sixth long periods, gold is much less efficient than platinum at low voltages, but at 6000 volts actually exceeds platinum. An indication of the same state of affairs is found for silver and palladium. Curves are also shown in which the values of i_p/i_t are plotted against the exciting voltage for each of the elements tested, and their individual peculiarities are discussed.

L. L. BIRCUMSHAW.

Absorption due to scattering of cathode rays. W. BOTHE (Z. Physik, 1929, 54, 161-178).—It is shown that the theory of multiple scattering suffices to account for the observed directional distribution of the scattering of an electron beam. In the case of aluminium the theory leads to an absorption coefficient in good agreement with the value found experimentally. G. E. WENTWORTH.

Continuous spectrum X-rays from thin targets. W. W. NICHOLAS (Bur. Stand. J. Res., 1929, 2, 837—870).—The high-frequency limit of the continuous spectrum from an infinitely thin target consists of a finite discontinuity. The energy distributions on a frequency scale are approximately horizontal, for gold and for aluminium, when $\psi=40^{\circ}$, 90°, and 140°, where ψ is the angle between measured X-rays and cathode stream. The intensities for these values of ψ are approximately 3:2:1, respectively. The bearings of these results on various theories of X-ray production are discussed and a structure for the moving electron is proposed which explains classically X-ray continuous spectrum phenomena. W. E. DOWNEY.

New integrating photometer for X-ray crystal reflexions, etc. W. T. ASTBURY (Proc. Roy. Soc., 1929, A, 123, 575—602).—The development of the new principle in photometry recently described (A., 1927, 912) had led to the design of an integrating photometer which is found by experiment to give correct measurements of the total intensity in X-ray crystal reflexions, and also seems capable of adaptation to the measurement of the integrated intensity of other types of radiation. The method uses a carbon print of a negative instead of the negative itself, and α -rays. By using the "stopping power" for

α-rays of a carbon tissue positive, ionisation is produced in an a-ray electroscope in direct proportion to the original X-ray intensity which formed the negative. Experimental tests of the integrating properties of the new instrument show that when a uniform radioactive deposit is covered with successive thicknesses of uniform carbon tissue, then, provided that the angle of emergence of the α -rays from the tissue does not exceed a certain limiting value defined by the "stop" in the base of the electroscope, the increase in ionisation recorded by the electroscope is directly proportional to the increase in X-ray intensity as represented by the thickness of the tissue. The applicability of the photometer to the measurement of the integrated intensity of any radiation the photographic density curve of which is approximately exponential is discussed, and it is shown how the instrument may be used for the measurement of α -, β -, and γ -rays, and also of visible light.

L. L. BIRCUMSHAW.

Determination of particle size by means of X-rays. R. BRILL (Z. Krist., 1928, 68, 387; Chem. Zentr., 1928, ii, 2620).—The methods of Scherrer and of Laue are discussed; calculation of particle size by the former method fails only for large particles, and for weakly absorbing substances. Preparations of iron of varying origin and treatment usually give fairly concordant values. A. A. ELDRIDGE.

X-Ray evidence for intermolecular forces in liquids. J. A. PRINS (Nature, 1929, 123, 908-909). -Whilst the principal halo of water lies at a diffraction angle corresponding with a spacing of about 3 Å., at the inner side of this halo the intensity is rather strong and approximately constant until an angle corresponding with a spacing of about 17 Å. is reached, when it diminishes rapidly and for still smaller angles approaches a limiting value. It appears that in the immediato neighbourhood of every molecule the mean density must be greater than at greater distances, indicating, in a dynamical sense, a "tendency to association " on account of the nature of the attractive intermolecular forces. Scattering inside the principal halo is observed also with liquids which are not usually regarded as "associating." A. A. ELDRIDGE.

X-Ray pattern of metallic crystals. G. B. DEODHAR (Nature, 1929, 123, 909).—Experiments with metal foils kept for about 20 yrs. at the ordinary temperature indicate that for silver and gold the lattice is the same, and is of the same magnitude, that these metals do not recover from the effects of the process by which the leaves are made (cf. Nishikawa and Asahara, Physical Rev., 1920), and that a thin metal leaf is to be regarded as an assemblage of metallic crystals. A. A. ELDRIDGE.

Intensity of total scattering of X-rays. I. WALLER and D. R. HARTREE (Proc. Roy. Soc., 1929, A, 124, 119—142).—Theoretical. Starting from Waller's general scattering formula (Z. Physik, 1928, 51, 213), an expression is deduced for the total scattering of the atoms in a gas; it is approximately valid if the frequency of the incident radiation is essentially higher than the K-absorption frequency of the atoms. This is first applied to the special case of the scattering by helium atoms, and it is then shown how approximate wave functions of required symmetry properties can be formed for an atom containing several electrons. The formula for the total scattering is evaluated for the case of argon and found to be in satisfactory agreement with Barrett's experimental results (A., 1928, 939). L. L. BIRCUMSHAW.

Spectroscopic measurements of M absorption levels for the elements uranium to tungsten. E. LINDBERG (Z. Physik, 1929, 54, 632—642).—The absorption edges M v, M iv, and M III have been determined for uranium, thorium, bismuth, lead, mercury, gold, platinum, and tungsten. Absorbing layers were metal deposits on aluminium foil, 0.5μ thick, or a powder of the element or its compound suspended in a celluloid film. The absorption levels M v, M iv, and M III, determined from previously known L III levels and L and M emission lines, are compared with those directly observed; a systematic deviation is noted. N levels are deduced from the M absorption and emission spectra. A. B. D. CASSIE.

X-Ray examination of highly-polymerised organic substances. E. OTT (Helv. Chim. Acta, 1929, **12**, 330—331).—A reply to the criticisms of Mie and Hengstenberg and of Staudinger and Signer (this vol., 49) of the author's previous paper (A., 1928, 465). The assumption that the elementary cell in highly-polymerised polyoxymethylene compounds contains one molecule is supported by X-ray as well as osmotic experiments. O. J. WALKER.

Diffraction of cathode rays by powdered crystals. T. MUTO and T. YAMAGUTI (Proc. Imp. Acad. Tokyo, 1929, 5, 122-124).-Celluloid and mica films were unsuccessfully tried as supports for powders for cathode-ray analysis. The effect produced by diffraction by the supporting film was superposed on that due to the substance with consequent blurring. Satisfactory results were obtained by using as a support a slice 40-50 µ in thickness of the pith of Tetrapanax papyrifer, K. Koch. Microscopic examin-ation showed that on this support the particles of the substance under examination adhered to the fibres. The most satisfactory support was strands of spider's web stretched on a metal frame, and dusted with the substance to be examined. The results for graphite and magnesium oxide obtained by cathoderay diffraction using such a support agreed closely with the X-ray measurements of these substances. F. G. TRYHORN.

Influence of temperature on the X-ray liquid haloes. V. I. VAIDYANATHAN (Indian J. Physics, 1929, 3, 391—398).—The X-ray diffraction haloes were studied at two temperatures of the order 30° and 140° for camphene, mesitylene, acetic acid, butyric acid, and ethyl alcohol, and the results were interpreted theoretically. These liquids, with the exception of camphene, show two haloes. With rise of temperature increase in the scattering at small angles was found, a contraction of the haloes and an increase in their diffuseness, a tendency for the separation between the inner and outer haloes to be effaced and for the inner one to become diffuse more quickly than the outer one. These effects are especially marked in the case of the last-mentioned three liquids, which are associated at ordinary and dissociated at higher temperatures. N. M. BLIGH.

Classical derivation of the Compton effect. C. V. RAMAN (Indian J. Physics, 1929, 3, 357-369).— By using an atomic model in which the electrons are regarded as a gas distributed in a spherical enclosure surrounding the nucleus, it is shown that a combination of statistical mechanics and classical wave theory leads directly to a quantitative theory of the Compton effect and an explanation of the known experimental facts. N. M. BLICH.

Fine structure absorption edges of metals and metalloids in the X-ray region. B. RAY and P. C. MAHANTI (Z. Physik, 1929, 54, 534-536).—The fine structure absorption edges of vanadium, chlorine, and sulphur in the X-ray region are discussed on the hypothesis of the existence of free electrons in metals. W. E. DOWNEY.

X-Ray analysis of the system chromiumnitrogen. Constitution of ferrochromium containing nitrogen. R. BLIX (Z. physikal. Chem., 1929. B. 3, 229-239).-X-Ray investigations by the powder method of preparations of chromium containing nitrogen in varying proportions, obtained by passing ammonia over chromium heated to 800°, show the existence of two intermediate phases. The first phase is homogeneous within a fairly wide interval of concentration round about 33 at.-% N, which corresponds with the formula Cr₂N. The chromium atoms are arranged in a hexagonal lattice with densest spherical packing, the nitrogen atoms probably being distributed at random in the hollow spaces of the lattice. The lattice constants increase with the nitrogen content from $a_1 = 2.747$ and $a_3 = 4.439$ Å. to the values 2.770 and 4.474 Å., respectively, the axial ratio remaining constant at 1.616. The second phase corresponds with the compound CrN and has the NaCl structure $(a=4\cdot140 \text{ Å}.; d_{calc}=6\cdot1, d_{obs}=5\cdot9)$. X-Ray examination of a ferrochromium alloy (60.3% Cr, 2.4% N, 0.7% Mn, 2% Si, and 0.21% C) indicates that the nitrogen is present mainly as the hexagonal Cr-N O. J. WALKER. phase.

Refractive indices and anomalous dispersion of soft X-rays in platinum, silver, calcite, and glass. E. DERSHEM (Physical Rev., 1929, [ii], 33, 659-671).-The refractive indices of several substances for homogeneous X-rays obtained by reflexion from a gypsum crystal were measured by the total reflexion method for the wave-length range 0.8-9.15 Å. Dispersion curves obtained by plotting $\delta = 1 - \mu$ against λ are given, and anomalous dispersion as shown by depressions in the curves is discussed in detail for each substance. The results fully reveal for the first time the type of anomalous dispersion occurring in the region of the K, L, and M absorption discontinuities. The form of the curve was independent of the sample used, but values of δ varied with film thickness and surface conditions.

N. M. BLIGH.

Compton modified line structure and its relation to the electron theory of solid bodies. J. W. M. DU MOND (Physical Rev., 1929, [ii], 33, 643-658; cf. this vol., 123).—The structure of the 3 c Compton line obtained with a special tube for a scattering angle of nearly 180° with a metallic beryllium scatterer is shown. Experimental line structure curves obtained by a photo-micrometric analysis of the spectra, and a general method of computing and normalising line structure curves are given. The relation between Compton line structure and electron velocity distribution according to various alternative assumptions is discussed. The evidence is in favour of the new wave-mechanical atom model and the new Sommerfeld theory of distribution of metallic electron velocities and of the degenerate gas state.

N. M. BLIGH.

Crystal structure and chemical constitution. V. M. GOLDSCHMIDT (Trans. Faraday Soc., 1929, 25, 253—283).—A lecture. N. M. BLIGH.

Chemical combination as an electrostatic phenomenon. V. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 210-216).— The stability of various types of crystal lattice for simple compounds is discussed on the basis of the work of Goldschmidt (A., 1927, 611).

S. I. LEVY.

Crystal structure of lithium chloride monohydrate. S. B. HENDRICKS (Z. Krist., 1927, 66, 297-302; Chem. Zentr., 1928, ii, 2621).—The unit cell, probably containing 1 mol., is tetragonal; d₀₀₁ 3.88, d₁₀₀ 3.81 Å. A. A. ELDRIDGE.

Calcium carbide lattice. C. HERMANN (Z. Krist., 1927, 66, 314—316; Chem. Zentr., 1928, ii, 2621—2622).—A lattice somewhat like the pyrite type is suggested. A. A. ELDRIDGE.

Structural relationships between pyroxene and amphibolite. B. GOSSNER (Zentr. Min. Geol., 1928, A, 340—341; Chem. Zentr., 1928, ii, 2341).— Comparison of the lattice constants indicates an isomorphism which is not exhibited in the external crystal morphology. A. A. ELDRIDGE.

Crystal habit of calcite from the minerogenetic point of view. G. KALB (Zentr. Min. Geol., 1928, A, 337-339; Chem. Zentr., 1928, ii, 2341).

Crystal structure of potassium chloroplatinate. F. J. EWING and L. PAULING (Z. Krist., 1928, 68, 223-230; Chem. Zentr., 1928, ii, 2432-2433).— Potassium chloroplatinate has d_{100} 9.73 Å.; μ 0.24 \pm 0.005 Å., and possesses the structure of potassium chlorostannate. A. A. ELDRIDGE.

Crystal structure of ethylammonium chlorostannate. R. W. G. WYCKOFF (Z. Krist., 1928, 68, 231—238; Chem. Zentr., 1928, ii, 2433).—Ethylammonium chlorostannate and chloroplatinate have, respectively, a_0 7.24, 7.13 Å., c_0 8.41, 8.53 Å. Parameters for the chlorine ions in the chlorostannate are u 0.16, v 0.17. The structure is the pyrochroite arrangement. A. A. ELDRIDGE.

Lattice constants of various fahl ores. F. MACHATSCHKI (Z. Krist., 1928, 68, 204—222; Chem. Zentr., 1928, ii, 2448).—All fahl ores are hexakistetrahedral, space-group T_a^s . The size of the unit cell varies about a 10.30 Å. according to the composition. Variations etc. are considered.

A. A. ELDRIDGE.

Structure of analcime. I. Space-group. J. W. GRUNER (Z. Krist., 1928, 68, 363-378; Chem. Zentr., 1928, ii, 2545).—The unit cell (cubic) has a 13.539 Å., and contains 16 mols. The lattice is body-centred; space-group probably O_h^{10} .

A. A. ELDRIDGE. Fine structure of brookite and the physical behaviour and changes of state of three natural forms of titanium dioxide. A. SCHRÖDER (Z. Krist., 1928, 67, 485—542; Chem. Zentr., 1928, ii, 2230).—The unit cell of brookite has a 9.136 ± 0.020 , $b 5.439\pm0.010$, $c 5.153\pm0.030$ Å.; the unit cell contains 8 mols. of TiO₂. A very slow change into rutile is postulated, and a study has been made of the effect of temperature on the physical properties of brookite. Dispersion and dilatation curves were obtained for anatase and rutile. Nigrin, which is also obtained by heating rutile at 700°, is not a new modification. A. A. ELDRIDGE.

Simple method of obtaining a single crystal of zinc with approximately any desired orientation of its principal axis. S. ITO (Mem. Coll. Sci. Kyoto, 1929, 12, 97—105).—A method of preparing single crystal sheets of zinc about $9 \times 7 \times 0.15$ cm. is described. A zinc sheet is supported in a thick asbestos box and heated until just molten. A small single crystal of known orientation is then placed in contact with one end of the sheet and the rate of cooling from this end is so controlled that a single crystal develops, the principal axis of which has the same orientation as that of the nucleus crystal. The orientation about the principal axis cannot be predetermined by this method. C. J. SMITHELLS.

Principles determining the structure of com-plex ionic crystals. L. PAULING (J. Amer. Chem. Soc., 1929, 51, 1010-1026).-The following five fundamental principles are enunciated which govern the structure of crystals containing only small cations (valency=z) with relatively large electric charges, and having crystal radii not exceeding about 0.8 Å., the anions being large, univalent, or bivalent, and not too highly deformable. (I) A co-ordinated polyhedron of anions is formed about each cation, the cationanion distance being determined by the radius sum and the co-ordination number (v) of the cation by the radius ratio (r). The minimum values of r are: tetrahedron, v=4, r=0.225; octahedron, v=6, r=0.414; cube, v=8, r=0.732. (II) In a stable co-ordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valency linkings (s, =z/v) reaching to it from the cations at the centres of the polyhedra of which it forms a corner. All crystals which have been investigated conform to this principle. (III) Shared edges, and particularly shared faces, decrease the stability of a co-ordinated structure; the effect is large for cations with large z and small v, and is especially large when r approaches the lower limit of stability of the polyhedron. (IV) In a crystal containing different cations those with large z and small v tend not to share polyhedron elements with each other. (V) The number of essentially different kinds of constituents in a crystal tends to be small. A method of estimating any distortion which may

occur in crystals is also given. The principles are used to predict the structures of cyanite, andalusite, and sillimanite. The principles require that no stable basic silicates of bivalent metals exist, and that in aluminium silicates of alkali metals there should be at least one aluminium ion for every alkali ion. The structures of aluminium silicates of bivalent metals which are simplest from the co-ordination point of view are shown to correspond with the formulæ $R^{H}_{3}Al_{2}Si_{3}O_{12}$ and $R^{H}_{3}Al_{2}Si_{6}O_{18}$, which include the garnets and beryl. S. K. TWEEDY.

Determination of parameters in crystal structure by means of Fourier series. W. L. BRAGG (Proc. Roy. Soc., 1929, A, 123, 537-559).-Previous work on the Fourier representation of the results of X-ray analysis is discussed (cf. Allison and Duane, A., 1925, ii, 930; Havighurst, A., 1926, 995). In Havighurst's calculations, although a triple Fourier series in x, y, z is used, the density is calculated only for a series of points along a chosen line in a crystal. The present paper describes more extensive evaluations of the series, in that the density is calculated for values of two variables. The values of F(hkl) are measured for all crystal directions round a given zone; e.g., if the zone is the a axis, the values of F(0kl) are used. A Fourier series is formed in which these values appear as coefficients, the variables being the co-ordinates y and z. Values of y and zare taken at convenient intervals and the Fourier series is summed for every pair of co-ordinates. The result is a table of figures indicating the distribution of scattering matter in the unit cell, as projected on the face (100). This is done for the a, b, and c axes as zones in turn, leading to projections of the unit cell on the (100), (010), and (001) faces. The projections enable the atomic parameters to be measured and the number of electrons in each atom to be counted. The series is applied to the crystal diopside, (CaMgSiO₃)₂, which has already been analysed by another method (Warren and Bragg, Z. Krist., 1928, 69, 167), and the two sets of 14 parameters, found by the two methods, agree to within 0.5%. The numbers of atomic electrons in the projections are approximately : Ca 16.5, Mg 12.5, Si 11.5, O 8.5-9. The oxygen does not appear to be an ion O^{-2} with 10 electrons. The groups of F values used for any projection may be conveniently described as the "weights" attached to a network of points on a central section of Ewald's reciprocal lattice (Z. Krist., L. L. BIRCUMSHAW. 1921, 56, 129).

Crystal structure of gallium. F. M. JAEGER, P. TERPSTRA, and H. G. K. WESTENBRINK (Z. Krist., 1927, 66, 195—216; Chem. Zentr., 1928, ii, 2620).—Gallium, m. p. 30.2° , on rapid crystallisation gives bipyramidal crystals; on slow growth they tend to be tabular. Crystals obtained from the supercooled liquid were ditetragonal-bipyramidal, a:c=1.16753. The space-group is probably $D_{4^{\circ}}^{*}$; the smallest separation of two gallium atoms is 2.56 Å. A. A. ELDRIDGE.

Crystal lattice of Fe₄N. R. BRILL (Z. Krist., 1928, 68, 379—384; Chem. Zentr., 1928, ii, 2621).— An iron catalyst used for the synthesis of ammonia and containing 5% N was cubic, with lattice constant 3.80 Å. The presence of the compound Fe_4N with 1 mol. in the unit cell is postulated.

A. A. ELDRIDGE. **X-Ray study of the binary systems of iron with** phosphorus, arsenic, antimony, and bismuth. G. Hägg (Z. Krist., 1928, 68, 470-472; Chem. Zentr., 1928, ii, 2620-2621).—The compound Fe₃P is tetragonal (sub-group of C_4^h), body-centred, with 8 mols. in the unit cell. The symmetry of Fe₂P is a sub-group of D_{6h} . FeAs has a rhombic unit cell. The system iron-antimony forms mixed crystals between 63.5 and 65.5% Sb. FeSb₂ is rhombic; the unit cell contains 2 mols.; space-group apparently V_{12}^{h2} . A. A. ELDRIDGE.

Atomic distances in mixed crystals of gold and copper. A. E. VAN ARKEL and J. BASART (Z. Krist., 1928, 68, 475—476; Chem. Zentr., 1928, ii, 2621).— Values for a complete series, the members varying by 10 at.-%, are tabulated. The differences are proportional to the fifth power of the mixture ratio.

A. A. ELDRIDGE.

Arrangement of minute crystals in electrolytically deposited bismuth and antimony. I, II. H. HIRATA (Elec. Rev. Japan, 1928, 16, 651—656, 761—767).—Small current densities and low electrolyte concentrations favour regular arrangement of the minute crystals of bismuth. The orientation of the crystals when arranged in fibres or in single pointed crystals was examined. CHEMICAL ABSTRACTS.

Crystal form of boleite. B. GOSSNER (Amer. Min., 1928, 13, 580–582).—Boleite is cubic, a 15.6 Å., with 32 mols. in the unit cell.

CHEMICAL ABSTRACTS.

Atomic spacing in gypsum. S. VON FRIESEN (Z. Physik, 1929, 54, 679-685).—Precision measurements of the grating constant for gypsum show this to be independent of the specimen.

A. B. D. CASSIE. Structure of boracite. J. W. GRUNER (Amer. J. Sci., 1929, [v], 17, 453-460).—The unit cell of boracite is a base-centred orthorhombic prism, $a_0=b_0=16.97$ Å., $c_0=12.00$ Å. : there are eight molecules to the unit cell. The probable formula is $Mg_6Cl_2B_{14}O_{26}$. The space-group is either $C_{4\pi}^*$ or $C_{2\pi}^*$, the former being the more probable.

C. W. GIBBY.

Crystalline hydrated aluminium hydroxide of von Bonsdorff. II. R. FRICKE (Z. anorg. Chem., 1929, 179, 287—292; cf. A., 1928, 1199).—The relatively slight differences existing between the X-ray diagrams of bayerite-a and bayerite-b indicate that the latter resembles hydrargillite to a greater extent than does the former. H. F. GILLBE.

New determination of the lattice constants of KF, CsCl, and BaF₂. E. BROCH, I. OFTEDAL, and A. PLEST (Z. physikal. Chem., 1929, B, 3, 209—214).— The lattice constants of carefully purified samples of the above substances were determined by the powder method, using magnesium oxide and silver as reference substances. The following mean values of a were obtained: KF 5.333, CsCl 4.113, and BaF₂ 6.184 Å. The corresponding values of d_{calc} are 2.5283, 3.9905, and 4.8943, and of d_{obs} , 2.5053 \pm 0.0005, 3.988 \pm 0.004, and 4.893 \pm 0.009. O. J. WALKER. Crystal structure of strontium. A. J. KING (Proc. Nat. Acad. Sci., 1929, **15**, 337–338).—A more accurate determination by means of powder spectrograms (cf. Simon and Vohsen, A., 1928, 694) confirmed a face-centred cubic structure and gave the values $6\cdot075\pm0\cdot004$ Å. for the unit cube edge, $4\cdot295$ Å. for the distance between strontium atoms and d_{cnlc} , 2.58. N. M. BLIGH.

Atomic arrangement in the silicates. W. L. BRAGG (Trans. Faraday Soc., 1929, 25, 291-314).-A general survey of the structures of silicates analysed by X-ray methods is given. Data are examined and a structure is illustrated for the following minerals: beryl, phenacite, olivine, monticellite, norbergite, chondrodite, humite, clinohumite, zircon, topaz, staurolite, cyanite, sillimanite, mullite, andalusite, and diopside, as well as for the garnet series. A method of determining the position of atoms by means of a two-dimensional Fourier series is illustrated and compared with a method based on calculated and observed strengths of diffraction. The nature of the SiO₄ group and the general features of silicate structures are summarised. N. M. BLIGH.

Structure of the AX₄ group. A. M. TAYLOR (Trans. Faraday Soc., 1929, 25, 314—316).—Measurements of the infra-red spectra of some substances of the AX₄ type are tabulated, and it is shown that generally two vibration frequencies are present. Their bearing on inter-atomic forces and the relations between atoms in a chemical radical is discussed. Evidence indicates that the atoms of the group are linked by semi-polar linkings. Shared electrons appear to be more effective in screening the oxygen atoms than in screening the central atom.

N. M. BLIGH.

Fine structure of felspars. E. SCHIEBOLD (Trans. Faraday Soc., 1929, 25, 316—320).—X-Ray crystal analysis indicates that the felspars have similar crystalline structures. Crystallographic data for various felspars are tabulated, and the monoclinic felspars are referred to a four-fold primary basecentred unit from which is deduced a double primary unit into which the corresponding unit of the triclinic felspars would pass by a simple deformation. The structures, effects of replacements of different metallic atoms, and pseudocubic character of the substances are discussed in detail. An attempt is made to deduce details of the atomic arrangements in felspars from radiograms. N. M. BLIGH.

Constitution and structure of ultramarine. F. M. JAEGER (Trans. Faraday Soc., 1929, 25, 320-345).—The general preparation and characteristics of the ultramarines or sodium aluminosilicates are described. Some substituents are replaceable, as in the case of the permutites, and investigations are described of their relations with certain natural minerals such as sodalite, hauyene, and nosean, analogous to the permutites. The results of the substitution of silver in silver ultramarine by the alkali metals are tabulated and plotted; tables of powder-spectrogram and rotation-spectrogram data are given for a number of ultramarines and related compounds, and deductions therefrom on the structure of the substances are made and discussed in detail. The causes of their colours is also considered. It is concluded that data are not yet sufficient for the structure problem to be finally settled and that much analytical work on substitution compounds is necessary. N. M. BLIGH.

X-Ray diffraction in liquid alloys of sodium and potassium. K. BANERJEE (Indian J. Physics, 1929, **3**, 399–408).—The X-ray diffraction haloes produced by alloys of varying compositions were studied, and interpreted with the help of the theory of X-ray diffraction in liquids and aqueous solutions. The effect is found to be additive as regards that due to the liquid compound Na₂K and that due to the excess of either metal dissolved in this compound. The halo for Na₂K indicates that the atoms of this compound are placed at the apices of a triangle.

N. M. BLIGH.

Corrosion of a crystal of dolomite by an active isotropic liquid. L. ROYER (Compt. rend., 1929, 188, 1303—1305).—According to the author's deductions (this vol., 631) the corrosion of a dolomite crystal by an inactive organic liquid is in accord with the existence of the elements of symmetry Λ^3C only. Active organic acids, however, produce effects indicating a ternary Λ^3 axis as the only element of symmetry and characterise the crystal as a ternary tetartohedral. It is concluded that although the true symmetry of dolomite is ternary parahemihedral, it may assume a tetartohedral form in an active medium. J. GRANT.

Mechanical model of an asymmetric carbon atom. H. G. TANNER (J. Physical Chem., 1929, 33, 755—759).—A description is given of the construction and functioning of a mechanical model of an asymmetric carbon atom, the analogy being based on the postulate that electrodynamical asymmetry of the four valency linkings of the carbon atom is responsible for optical activity. Rotational polarisation can be imitated with the model as well as preferential transmission of one of two species of circularly polarised waves.

L. S. THEOBALD.

Crystal structure of solid methane. J. C. MCLENNAN and W. G. PLUMMER (Phil. Mag., 1929, [vii], 7, 761—764),—The crystal structure of solid methane at temperatures between -190° and -255° has been examined by the X-ray powder method. The results indicate the occurrence of a face-centred cube of edge 6.35 Å., having 4 mols. per unit cell. The space-group of the carbon atoms is either T^2 or T_d^2 . There is no evidence of the occurrence of a pyramidal structure. A. E. MITCHELL.

Hydrocarbon model. A. MüLLER (Trans. Faraday Soc., 1929, 25, 347–348).—A model is constructed for the hydrocarbon $C_{29}H_{60}$ previously examined (cf. A., 1928, 1176). N. M. BLIGH.

Structure of the carbon chain in hydrocarbons C_nH_{2n} . J. HENGSTENBERG (Z. Krist., 1928, 67, 583—594; Chem. Zentr., 1928, ii, 2221).—Penta-triacontane has a 7.43, b (perpendicular) 4.97 Å.; d 0.942, whence the unit cell contains 2 mols. The CH₂ group in the C direction occupies 1.27 Å. Paraffins of high mol. wt. yield diagrams due to a simple CH₂-lattice. Assuming rhombic symmetry, the space-group is probably V_1^{16} . Zig-zag chains, in

which the carbon atoms are 1.52 Å. apart, are postulated. A. A. ELDRIDGE.

X-Ray evidence on the structure of the benzene nucleus. (MRS.) K. LONSDALE (Trans. Faraday Soc., 1929, 25, 352—366).—An historical survey of X-ray work on carbon, benzene, and benzene derivatives is given. A number of questions on the structure and size of the benzene nucleus and of its component atoms are listed, and it is shown that some of these have been partly or wholly answered by means of a complete crystalline analysis of hexamethylbenzene (cf. this vol., 17). The fate of the fourth valency linking and the relationship of the aromatic to the aliphatic carbon atom are discussed in the light of recent theoretical X-ray work.

N. M. BLIGH.

Structure of the benzene ring in hexamethylbenzene. (MISS) K. LONSDALE (Proc. Roy. Soc., 1929, A, 123, 494-515).-One of the chief difficulties encountered hitherto in the study of the benzene nucleus has been that the unit cell of the various crystalline derivatives examined invariably contained more than one molecule, and so far no aromatic substance has had a simple enough structure for the positions of the separate atoms to be found without any previous hypotheses as to the shape or size of the molecule. Hexamethylbenzene, however, avoids this difficulty; the unit cell is triclinic and contains one molecule only. The prisms have been examined by the ionisation spectrometer using a Coolidge tube with a molybdenum anticathode. The dimensions of the cell are a=9.010, b=8.926, c=5.344 Å.; $\alpha=44^{\circ}27'$, $\beta = 116^{\circ} 43', \gamma = 119^{\circ} 34'; a:b:c=1.0095:1:0.5987.$ The space-group is either C_1^1 or C_1^1 , the molecule being either asymmetrical or centro-symmetrical; probably the latter, on analogy with benzene, hexachlorobenzene, and hexabromobenzene. The crystal is easily deformed by slipping about any of the crystallographic axes. The structure factors have been calculated for a large number of planes from the observed intensities and are found to obey the following rules : (1) the factors in the [001] zone repeat themselves closely throughout the series of planes $(100) \rightarrow (010)$, $(010) \longrightarrow (110)$, and $(110) \longrightarrow (100)$. This clearly indicates a hexagonal arrangement of atoms in the [001] zone. (2) The factors are almost independent of the last index l, which shows that the carbon atoms at least must all lie within 0.1 Å. of the (001) cleavage plane. It is deduced from the relative values of the factors that a unique structure can be assigned to the molecule, which exists in the crystal as a separate entity and has a hexagonal form. Thus the X-ray evidence supplies a definite proof that the chemist's conception of the benzene ring is a true representation of the facts. The puckered or "diamond " type of ring and the more compact model proposed by Morse (A., 1928, 222) are shown to be wholly inadmissible. Only a plane ring can account both qualitatively and quantitatively for the hexagonal structure of the [001] zone, for the lack of dependence on l, and for the relative values of the structure factors observed for (001) and a large number

of other planes. The diameter of the aromatic

carbon atom is 1.42 ± 0.03 Å., *i.e.*, the ring is similar

in structure and in dimensions to that occurring in graphite. Three of the valencies of the aromatic carbon atom are co-planar, the ring itself and all the side-chain carbon atoms lying in one plane. The methyl group does not scatter like a single atom, but in scattering power is heavily weighted at the end nearer to the benzene ring. L. L. BIRCUMSHAW.

Crystal class of pentaerythritol. E. ERNST (Z. Krist., 1928, 68, 139—151; Chem. Zentr., 1928, ii, 2221).—The class has not yet been determined, despite detailed morphological and optical investigations. A. A. ELDRIDGE.

Lauric acid. R. BRILL and K. H. MEYER (Z. Krist., 1928, 67, 570—582; Chem. Zentr., 1928, ii, 2221).—The unit cell, in which a 9.76 and b 4.98 Å. are at a right angle; d 27.5 Å.; $\sin \beta 0.750$, whence the c axis is 36.9 Å., contains four molecules, since d=1.020. The space-group is C_{2h}^{1} or C_{2h}^{2} . A spiral structure of the chain is not possible; the crystal contains bi-molecules with the like ends one against another. A. A. ELDRIDGE.

Long spacings of fatty acids. S. H. PIPER (Trans. Faraday Soc., 1929, 25, 348—351).—Although the method is of limited scope, an X-ray investigation of long-chain compounds can be made by measuring the spacings and intensities of reflexion from a set of widely-spaced planes which are characteristic of the length of the chain. Some equimolar mixtures of acids having odd and even numbers of carbon atoms give photographs similar to those from pure acids, and sometimes have the spacings of pure acids. These mixtures both in spacings and m. p. show alterations resembling those of the pure odd and even acids.

N. M. BLIGH. Nature of dextrin, gelatin, and sodium oleate solutions as revealed by X-ray diffraction. P. KRISHNAMURTI (Indian J. Physics, 1929, **3**, 307— 329).—An extension of previous work (cf. this vol., 236) to colloidal solutions. Dextrin and gelatin gave patterns similar to those of the sugars, and in dilute solutions both gave rise to gaseous scattering from which the mol. wts. were calculated as approximately 600 and 3000, respectively. Sodium oleate showed a separate ring just below the water ring, of approximately the same size as for the powder, explained as due to large groups of molecules. The powder patterns of gelatin and starch also showed at very small angles a fairly intense ring not previously observed.

N. M. BLIGH.

X-Ray diffraction in liquid mixtures. P. KRISHNAMURTI (Indian J. Physics, 1929, 3, 331— 355; cf. preceding abstract).—The pattern for a mixture was, in general, found not to be a superposition of those due to its components. For phenol, timethylcarbinol, and piperidine the rings due to the two components exist separately in the mixture pattern; for glycerol, ethyl alcohol, and lactic acid only one ring is observed, the water ring having contracted and the liquid ring expanded. For pyridine solutions the pyridine ring has expanded slightly, the water ring being unchanged. Butyric acid solutions gave only one broad ring. The last two liquids thus form a transition between the previous two groups, the difference between which is suggested as being due to the difference in the attractive forces between similar and dissimilar molecules in the mixtures. In the case of non-aqueous systems, a mixture of methyl salicylate and o-nitrobenzaldehyde gave a pattern almost the same as that for either liquid, results being similar for aniline and cyclohexane. In the case of cyclohexane and methyl salicylate a different pattern was given for the mixture. N. M. BLIGH.

X-Ray diffraction in liquids of the terpene series. V. I. VAIDYANATHAN (Indian J. Physics, 1929, 3, 371-389).--Using CuKa radiations, the series. haloes of 21 liquids were examined, and the results explained on the assumption that the X-ray diffraction peaks in liquids occur at wave-lengths corresponding with the mean molecular distances between them. In some cases a less distinct inner halo was observed. The molecular diameters obtained were, for the longchain olefinic terpenes, geraniol, linalol, rhodinol, citral, and citronellal 4.95 Å.; for terpineol, 5.08 Å.; for menthone, carvone, and thujone, 5.35 Å.; for the cyclic C₁₀H₁₆ terpenes, terpinene, d-limonene, d(l)-limonene, d- α -phellandrene, sylvestrene, camphene, and d- and l-pinene, values increasing from 5.44 to 6.02 Å.; for the sesquiterpenes, cadinene, inene, caryophyllene, and cedrene, 7 Å., approximately. The last four showed an exterior diffuse halo. The values were in general found to increase gradually and to be approximately constant in each class. Densities were calculated. N. M. BLIGH.

Magnetostriction and the phenomena of the Curie point. R. H. FOWLER and P. KAPITZA (Proc. Roy. Soc., 1929, A, 124, 1-15).-Magnetostriction must be related to the change of length at the Curie point in exactly the same way as Weiss's thermomagnetic effects are related to the change of specific heat at the Curie point. From a revision of Heisenberg's calculation of the partition function for a magnetised crystal (A., 1928, 1300), and a theoretical examination of the size of the crystal as a function of the magnetisation, it is shown that the phenomena of the Curie point and magnetostriction will both fit satisfactorily into Heisenberg's theory. An explanation is suggested for the origin of these changes of L. L. BIRCUMSHAW. sign.

Rôle of conductivity electrons in ferromagnetism. J. DORFMAN and R. JAANUS (Z. Physik, 1929, 54, 277-288).—An investigation is made (cf. this vol., 127) of the position of the elementary magnet in the case of metallic nickel. It may be either the electron bound to the positive ion of the metal or the "free" conductivity electron. At the Curie point the jump of the specific heat of the conductivity electron is only slightly greater than the corresponding change, per atom, of the metal. Hence the electron bound to the positive metallic ion plays no important part in ferromagnetic processes, the seat of the elementary magnet being the conductivity electron. G. E. WENTWORTH.

Rôle of conductivity electrons in ferromagnetism. J. DORFMAN and I. KIKOIN (Z. Physik, 1929, 54, 289—296; cf. preceding abstract).—The fact that the conductivity electron plays the part of the elementary magnet in ferromagnetic processes has led to the possibility of calculation of the magnetic spin moment of the conductivity electron, which is found, within an accuracy of 5%, to be a Bohr magneton. G. E. WENTWORTH.

Hall effect in very intense magnetic fields. A. MAZZARI (Nuovo Cim., 1928, 5, 215-223; Chem. Zentr., 1928, ii, 2226-2227).

Paramagnetic susceptibility of quinquevalent vanadium ion. N. PERRAKIS (Amer. Electrochem. Soc., May, 1929. Advance copy, 5 pp.).—The paramagnetic susceptibilities of ammonium and sodium vanadates and of two forms of vanadium pentoxide are independent of temperature over the range 17— 77°. To the molar susceptibilities of these compounds estimated corrections for the diamagnetism of the rest of the molecule are applied, and the mean value of 44×10^{-6} is obtained for the susceptibility of the quinquevalent vanadium ion. The difference between this value and data for metallic vanadium obtained by Honda and by Owen is discussed.

H. J. T. ELLINGHAM.

Magnetic moment of the complex ions of the iron group. P. WEISS (Amer. Electrochem. Soc., May, 1929. Advance copy, 4 pp.).—The magnetic moments of the simple ions of the iron group, with minor exceptions, depend only on the number of electrons in the ion, in accordance with Kossel's displacement law, but for complex ions containing these metals the magnetic moment is either equal to that of the normal ion of the same valency or to that of a normal ion the effective atomic number of which is greater by 4 units. The significance of this relation is discussed. H. J. T. ELLINGHAM.

Two Curie points, ferromagnetic and paramagnetic. R. FORRER (Compt. rend., 1929, 188, 1242—1244).—A study of the thermal variation of an almost rectangular hysteresis cycle of nickel shows that the two Curie points determine two different coexistent regions, a hysteresis region extending to the paramagnetic Curie point, and a region of spontaneous orientation below the ferromagnetic point. The former point is always higher than the latter by about 15—40°. Ferromagnetism can exist only below both points, whilst paramagnetism is limited solely by the upper. J. GRANT.

Magnetic properties of iron sesquioxide and some ferrites above their Curie point ; conservation of the paramagnetism constant in these compounds. (MLLE.) A. SERRES (Compt. rend., 1929, 188, 1239—1241).—The mean value of $28.17 \times$ 10^{-6} /g. (error 0.3%) was obtained for the susceptibility of iron at 700-750° from measurements on pure ferrous and ferric oxide, and the fact that this value falls between the extreme values obtained by other workers for γ -iron indicates that the paramagnetism of the latter is conserved in combination. The reciprocal of the susceptibility of magnesium, copper, lead, and nickel ferrites corrected for the paramagnetism of the sesquioxide $(\chi 1573 \times 10^{-6})$ is a linear function of temperature up to 750°, but slight changes in direction of the lines in all cases except that of lead confirm the hypothesis of the superposition of a

constant and variable paramagnetic constant (cf. Forestier and Chaudron, A., 1927, 11).

J. GRANT.

Ferromagnetic properties of ferrites. (MLLE.) S. VEIL (Compt. rend., 1929, 188, 1293-1294).—The author's experiments (this vol., 248) on the precipitation of a ferric salt by sodium hydroxide in the presence of a bivalent salt of the same anion have been extended to copper, and the same results obtained in the cold. If, however, the hydroxides were suspended in warm water they changed from para- to ferro-magnetic, although when iron was replaced by nickel or cobalt the differences between the relative coefficients of magnetisation of the calcined precipitates prepared in the cold and in the warm were far less marked. J. GRANT.

Variation of the piezo-electric constant of quartz with temperature. A. ANDREEV, V. FRÉEDERICKSZ, and I. KAZARNIRVSKY (Z. Physik, 1929, 54, 477—483).—The piezo-electric modulus, d_{11} , of quartz between 15° and 500° has been measured by the method of electrical oscillations. The modulus, d_{11} , depends only slightly on temperature, a result which is at variance with that obtained by the electrostatic method. Piezo-electric oscillations have been observed up to 575°. W. E. DOWNEY.

Atomic theory of ferro-magnetism. N. AKULOV (Z. Physik, 1929, 54, 582-587).—Theoretical. W. E. DOWNEY.

Electromagnetic theory of Maxwell-Lorentz and the molecular diffusion of light. J. CABANNES and Y. ROCARD (J. Phys. Radium, 1929, [vi], 10, 52-71).—Theoretical. A study of the undulatory and quantum theories of light with special reference to the Raman effect. J. L. BUCHAN.

Magnetostriction in bismuth. E. VAN ATREL (Bull. Acad. roy. Belg., 1928, [v], 15, 148-149).-A claim for priority against Schulze (cf. A., 1928, 1314). F. L. USHER.

Law of magnetisation of solid crystals. Resolution of the Faraday effect into two effects of different origin. Diamagnetic and paramagnetic rotation of the plane of polarisation. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 536—549).— Measurements have been made at very low temperatures (about 2° Abs.) of the variation of the magnetic rotatory power with intensity of the field. The law governing the relationship between rotation and field intensity, which below about 4.2° Abs. is no longer linear, is independent of the wave-length, and its significance for molecular physics is discussed. H. F. GILLBE.

Coercivity and mechanical hardness. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1929, 54, 1-15).—Experiments are described to show that, in a number of alloys of the metals iron and nickel with aluminium, copper, and chromium, no simple relationship can be traced between coercivity and mechanical hardness. R. W. LUNT.

Theory of the plasticity of metals. H. SHÔJI (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 180-186).—In a previous paper the plasticity, P. of a metal was shown to be represented by P = $(1/w_0)(dv/dw)$, where dv/dw is the final velocity of elongation per unit length, caused by a load wo exceeding the elastic limit. It is now proposed that dv/dw and w_0 represent two different constants of plasticity, and the values of plasticity for a number of metals are recalculated using the previous data.

C. J. SMITHELLS. Dehydration of benzene. J. J. MANLEY (Nature, 1929, 123, 907) .- Determinations of the refractivity of benzene in the presence of phosphorus pentoxide during about 6 months were plotted against the time; the resulting curve consists of two distinct smooth portions having different directional values. It is concluded that the first limb represents the rate of removal of mechanically admixed water, whilst the second measures the rate of withdrawal of water in actual combination with benzene. It thus appears that benzene forms one or more hydrates, a view which is supported by the observation that the specific volume of benzene in the presence of phosphorus pentoxide depends on the temperature to which the benzene has been exposed immediately before the determination is carried out. Within certain limits of temperature the drying power of anhydrous benzene is greater than that of phosphorus A. A. ELDRIDGE. pentoxide.

Physical properties of platinum. A. T. GRI-GORIEV (Z. anorg. Chem., 1929, 178, 213-218).-See A., 1928, 941.

Determination of mol. wts. in the vapour state from vapour-pressure and evaporation data. E. W. WASHBURN (U.S. Bur. Stand. Res. Pap., 1929, No. 53).-The determination of the vapour pressure of a substance by measuring the amount required to saturate, by aspiration, a known volume of an indifferent gas, is chiefly open to error in the measurement of the gas volumes, quantities which have large temperature coefficients. By using a reference substance of known mol. wt. the measurement of these gas volumes is eliminated. The possible errors due to pressure, temperature, and saturation measure-F. J. WILKINS. ments are considered.

Electrical conductance method for determining liquefaction temperatures of solids. E. W. WASHBURN and E. R. SMITH (Bur. Stand. J. Res., 1929, 2, 787-791).-When a solid or mixture of solids behaves as an electrical insulator below its m. p., but conducts as soon as the liquid phase appears, it will be easy to determine this temperature by noting where the change in conductance occurs. The method will be especially useful where only a small quantity of the substance is available, and will be trustworthy where other methods fail. The apparatus and method used are described. The eutectic temperatures of several substances were found. The transition temperature of Na₂SO₄,10H₂O \longrightarrow Na₂SO₄ was found to be 32.33° (usually accepted value, 32.384°), and of

 $Na_2CrO_4, 10H_2O \longrightarrow Na_2CrO_4, 6H_2O,$

19.51° (usually accepted value, 19.525°).

A. J. MEE.

Temperature-conductivity curves of solid salts. II. Halides of potassium and thallium. T. E. PHIPPS and E. G. PARTRIDGE (J. Amer. Chem. Soc., 1929, 51, 1331-1345).—The conductivities, *κ*, of solid potassium and thallium halides have been investigated. Log \varkappa is a linear function of 1/T, although for the potassium salts the graph is two intersecting straight lines (cf. Phipps and others, A., 1926, 231). The graph for thallous iodide is also two straight lines, relatively slightly inclined, owing to a change of crystal form. In polar lattices only the positive ion conducts at lower temperatures; both ions conduct at high temperatures (cf. A., 1928, 1192). The "heats of liberation," H, of the ions are calculated from the graphs; they represent the minimum energy an ion must possess in order to be able to partake in the conduction process. H for the potassium ion exceeds that for the sodium ion in the same halide salt; the values for thallium are smaller than those for sodium except in the iodide. In the sodium and potassium halides, H appears to be proportional to the m. p. of the salts.

S. K. TWEEDY.

Table of electrochemical equivalents. G. A. Roush (Amer. Electrochem. Soc., May, 1929. Advance copy, 11 pp.).-Electrochemical equivalents of the elements calculated on the basis of the 1929 at. wts. and expressed in mg. per coulomb, g. per amp.-hr., lb. per amp.-hr., and the corresponding reciprocals, are tabulated. H. J. T. ELLINGHAM.

Experiments on the conductivity of ionic crystals. Effect of tempering, treatment with water, and plasticising. F. QUITTNER and A. SMEKAL (Z. physikal. Chem., 1929, B, 3, 162-165). -The results of experiments on the conductivity of ionic crystals are summarised and discussed. The dependence of conductivity phenomena on the loose structure of the crystal is shown. The effect of heating the crystals at 400°, and then cooling, is described; conductivity is increased by this treatment. By treating the crystals with water, there is still an effect on the conductivity even after they have been carefully dried. The inner structure of the crystal must therefore be altered by this treatment. Experiments on the plastic deformation of crystals were first carried out with natural sylvine. The resulting effect on the conductivity can be ascribed to changes in the structure of the crystal, a fact which can be verified independently by coloration experiments with the radiation from radium.

A. J. MEE.

A. J. MEE. Intensity gauge for supersonic radiation in liquids. W. T. RICHARDS (Proc. Nat. Acad. Sci., 1929, 15, 310—314).—High-frequency sound waves of high intensity have been applied to chemical phenomena (cf. Richards and Loomis, A., 1928, 141). The differentiate of a backtonic intensity. 141). The difficulties of absolute intensity measurements are discussed, and a gauge of the ear-trumpet type which is capable of giving reproducible values is described. N. M. BLIGH.

Transmissibility of thin metal foils for longwave infra-red radiation, and their electrical conductivity. H. MURMANN (Z. Physik, 1929, 54, 741-760).-A formula for the transmissibility of plane parallel metallic plates for long-wave infra-red radiation is derived from Maxwell's theory. According to this formula the transmissibility should 754

be independent of the wave-length and dependent only on the product of the thickness and electrical conductivity of the foil. Experiments were carried out to test this. The transmissibilities relative to a plain celluloid sheet in the spectral range $6.7-108 \mu$ were determined. It is shown that in agreement with the theory the transmissibility is independent of wave-length. In order to test its dependence on thickness and electrical conductivity the resistances of the foils were determined. The transmissibility was found to be dependent on the product of thickness and electrical conductivity. For antimony and silver, two modifications with different conductivities were shown to exist.

A. J. MEE.

Results of the wave-mechanics calculation of the temperature relationship of the electrical resistance of pure metals. G. Borelius (Z. Physik, 1929, 54, 806-810).-By applying work on X-rays to the scattering of de Broglie waves, formulæ for the effect of temperature on the resistance of pure metals have been derived by Houston (A., 1928, 695), Frenkel and Mirolubov (A., 1928, 933), and Bloch (this vol., 247). Without entering very far into the theory and underlying assumptions, a critical examination of these formulæ is made. None agrees entirely with the experimental results. The best equation put forward to connect temperature with the resistance of pure metals was the empirical formula of Grüneisen (Physikal. Z., 1918, 19, 282). For low temperatures this gives the resistances proportional to T^4 , where T is the absolute temperature. Houston gives the resistance proportional to T^2 , and Frenkel and Mirolubov, and Bloch give it proportional to T^3 . Actually Grüneisen's formula deviates from the truth at lowest temperatures. A. J. MEE.

Optical characters of copper halides. M. HAASE (Z. Krist., 1928, 68, 82-86; Chem. Zentr., 1928, ii, 2329).—The refractive indices of cuprous chloride, bromide, and iodide between 535 and 700 $\mu\mu$ have been measured, and the molecular volumes and molecular refractions for the *D*-line determined. Values increase regularly from chloride to iodide.

A. A. ELDRIDGE.

Optical properties of some salts of gluconic acid. G. L. KEENAN and S. M. WEISBERG (J. Physical Chem., 1929, 33, 791–794).—Optical data for the gluconates of ammonium, potassium, sodium, barium, and lead, and for the gluconic γ -lactone are recorded together with the interference figures and values of 2E. The double refraction is strong, except in the case of the lead salt, which is only moderate.

L. S. THEOBALD.

B. p. of magnesium, calcium, strontium, barium, and lithium. H. HARTMANN and R. SCHNEIDER (Z. anorg. Chem., 1929, 180, 275–283; cf. Ruff and Hartmann, A., 1924, ii, 481).—The b. p. of the above metals have been determined at various pressures by direct measurement of the temperature of the condensing metallic vapour. From the temperature-pressure diagram the following values are obtained for the b. p. at 760 mm. : magnesium $1380\pm5^{\circ}$, calcium $1712\pm5^{\circ}$, strontium $1639\pm5^{\circ}$, barium $1810\pm10^{\circ}$, and lithium $1609\pm5^{\circ}$. From these values the heat of evaporation, conventional chemical constant, Trouton's constant, and critical temperature are calculated. The irregular sequence of the b. p. in the alkaline earth-metal series corresponds with the irregular variations of the crystal structure of these metals. O. J. WALKER.

[Specific heats of] solid elements. W. HERZ (Z. anorg. Chem., 1929, 180, 284-286).—The entropy at the ordinary temperature (S) and the specific heat (s) of solid elements satisfy the relationship $Ss_{\frac{1}{2}}=k$, where k is about 5. Since a similar relationship, $SL^{\frac{1}{2}}=k'$, holds for the heat of evaporation per g. (L), the expression $(L/s)^{\frac{1}{2}}=$ constant can be derived.

O. J. WALKER. Thermochemical studies in the acetylene series. P. LANDRIEU and F. BAYLOCQ (Bull. Soc. chim., 1929, [iv], 45, 217-225; cf. A., 1914, ii, 30). -The heats of combustion of n-amylacetylene and n-hexylacetylene have been determined by improved methods (A., 1923, ii, 535; 1925, 427) with the object of obtaining an accurate value for the heat of saturation of the acetylenic linking. The following constants are given : n-amylacetylene, b. p. 99– 100°/763 mm., m. p. -81 to -80°, d_0° 0.7505, d_0^∞ 0.7338, n_0^∞ 1.4086; n-hexylacetylene, b. p. 124–125°/763 mm. m. p. -80 to -79° , d_0° 0.7667, d_{20}° 0.7470, $n_D^{\circ\circ}$ 1.4172. Although the pressure of oxygen in the bomb some-times reached 45 kg./cm.², combustion was never complete, and a correction was applied for the residual carbon (less than 2 mg.). The molecular heats of combustion at constant volume (Q_r) and constant pressure (Q_p) are: *n*-amylacetylene, Q_v 1092 kg.-cals., Q_p 1093.5 kg.-cals.; *n*-hexylacetylene, Q_v 1243.5 kg.-cals., Q_p 1245.5 kg.-cals. The heats of saturation, obtained by using the accepted data for n-heptane and n-octane, are respectively 58.8 kg.-cals. and 58.7 kg.-cals. F. L. USHER.

M. p. of palladium. C. O. FAIRCHILD, W. H. HOOVER, and M. F. PETERS (Bur. Stand. J. Res., 1929, 2, 931-962).-The m. p. of palladium has been determined by measuring with an optical pyrometer the ratio of brightness of the red light ($\lambda = 6258$ Å.) emitted by black bodies at the m. p. of palladium and gold, respectively. The crucible method was shown to be more trustworthy than the wire method. The result obtained by the crucible method, when substituted in Wien's or Planck's equation, gives the m. p. of palladium as 1556.6° with an uncertainty of 1°. In the computations C_2 was taken as 1.432 cm. deg. and the m. p. of gold as 1063°. The average of this result and those of six previous determinations is $1553^{\circ}\pm0.7^{\circ}$. The uncertainty in C_2 is estimated as 0.002, and in the m. p. of gold as 0.5° ; it is concluded that the uncertainty in the value of the m. p. of palladium on the centigrade thermodynamic scale is approximately 2°. If 1063° is the m. p. of gold, the m. p. of palladium is 1553°.

W. E. DOWNEY.

Entropy of gases in irreversible processes. D. ENSKOG (Z. Physik, 1929, 54, 498-504).--Mathematical. W. E. DOWNEY.

Coefficient of cubical expansion of liquids and critical temperature. V. N. THATTE (Phil. Mag., 1929, [vii], 7, 887-891).-In the application of van der Waals' equation to the liquid state it is assumed that the term a/v^2 is large compared with the external pressure p, i.e., $a/v^2 \simeq RT/(v-b)$. It is also assumed that the ratio of the volume of the liquid occupied by the molecules to the total volume of the liquid is practically constant for liquids under the ordinary temperatures and pressures; hence, taking 1/R as proportional to the critical temperature T_c the coefficient of cubical expansion of the liquid C = $1/(kT_c-2T)$. k has been found from the known values of C and T_c for a number of liquids to be 2.5. The equation is similar to that deduced by Davies (A., 1912, ii, 426) from Mathias's law and Guldberg's density calculations, but the results obtained from it are in closer agreement with the accepted values. A. E. MITCHELL.

Vaporisation under the influence of an electric field. E. H. GREIBACH (Physical Rev., 1929, [ii], 33, 844—850).—The effect of a non-uniform electric field on the vaporisation of a solid is shown to consist in a minute increase in the heat of vaporisation and a decrease in the rate of evaporation. In the case of a metal filament, expressions are obtained for the density of the saturated vapour, the increase of heat of vaporisation, and the ratio of apparent to normal rate of evaporation. Comparison of the last result with experimental data is inconclusive.

N. M. BLIGH.

Heat of decomposition of azoimide. W. A. ROTH and F. MULLER (Ber., 1929, 62, [B], 1188-1194).—Attempts are described to deduce the heat of decomposition of homogeneous liquid azoimide by subtracting from the heats of combustion of phenyl azide and ethyl azidoacetate the "heat values" of the inset groups C₆H₄ and CH·CO₂Et. The minimal value of 67 kg.-cal. is thus obtained, whereas 53 kg.cal. is calculated from Berthelot's observations for dilute solution. Ethyl azidoacetate burns quantitatively and the heat of combustion is independent of the age (4511-4512 g.-cal./g.), whereas phenyl azide almost always yields a certain amount of soot and its heat of combustion diminishes with age so regularly that the value for the fresh material can be calculated by extrapolation. The heat of formation of phenyl azide is about 70 kg.-cal. more negative than that of benzene, whereas that of ethyl azidoacetate is about 77 kg.-cal. smaller than that of ethyl acetate.

The production of unusually large quantities of nitric acid during the combustion of azido- and diazocompounds is discussed from the point of view of energy. A primary elimination of $2N_2$ from 2 mols. of azido-compound would liberate more than twice as much heat as is required for the fission of the quantity of nitrogen and oxygen into atoms from which the observed excess of nitric acid could be produced. H. WREN.

Thermal expansion of tantalum. P. HIDNERT (Bur. Stand. J. Res., 1929, 2, 887–896).—Three samples of worked and annealed tantalum have been examined over the range -198° and $+500^{\circ}$. Worked tantalum was found to expand to practically the same degree as annealed tantalum. Between 20° and 500° the

expansion may be expressed by the equation $L_t = L_o[1+(6\cdot59t+0\cdot00008t^2)10^{-6}]$. The coefficient increases slightly with rise of temperature.

W. E. DOWNEY.

Heat capacity of hydrogen iodide from 15° Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and R. WIEBE (J. Amer. Chem. Soc., 1929, 51, 1441—1449).—Experiments previously described (A., 1928, 228, 1083) are repeated with hydrogen iodide. As in the case of hydrogen bromide, two regions of high heat capacity occur in the solid state, apparently due to internal molecular transitions. The molal heat of fusion is 686.3 g.-cal. at the m. p. (222.31° Abs.) and that of evaporation, 4724 g.-cal. at the b. p. (237.75° Abs.). The "observed" molal entropy at the b. p. is 47.8 g.-cal./1°, in agreement with the value calculated from spectroscopic data. S. K. TWEEDY.

Critical temperature measurements on carbon dioxide in small capillaries. H. T. KENNEDY (J. Amer. Chem. Soc., 1929, 51, 1360—1366).—The critical temperatures of carbon dioxide as measured in capillary tubes of varying diameter down to 0.004 mm. is 30.96°, independent of the size of the tube. S. K. TWEEDY.

Time variation of thermodynamic processes. N. VON RASCHEVSKY (Z. Physik, 1929, 54, 736— 737).—Thermodynamics deals with a system the processes of which do not vary with time. The progress of entropy and free energy near this equilibrium state is followed formally, by two differential equations. A. B. D. CASSIE.

Thermodynamics of solutions. V. FISHER (Z. Physik, 1929, 54, 715-723).—A general equation satisfied by usual thermodynamical parameters specifying a solution is deduced from equality of the thermodynamic potential for the pure solute and for the solute in solution. Appropriate simplifying assumptions give, (i) the law of partial pressure for a gaseous mixture, (ii) van't Hoff's laws and other equations for dilute liquid solutions. (ii) is applied to solutions of sucrose and calcium ferrocyanide in water. A. B. D. CASSIE.

Semi-empirical vapour-pressure formula. V. KIREJEV (Z. Elektrochem., 1929, 35, 217-220).-The author has derived the formula $(a(1\cdot 10-\tau)/\tau)d\tau =$ $(1-\pi/\pi)d\pi$, in which $a=L_b/RT_b(1\cdot10-\tau_b)$ (T=absolute temperature, $T_c=$ critical temperature, $T_b=$ b. p., P= pressure, $P_e=$ critical pressure, $L_b=$ latent heat of vaporisation at T_b , and $\tau=T/T_c$ and $\pi=P/P_c$) connecting vapour pressures, greater than about 0.3 atm., over a range of temperatures up to $\tau=0.85$. A method of evaluating the integration constant of the expression in its integrated form, together with tables of appropriate data, are given. The expression is based on: (i) the Clausius-Clapeyron equation, (ii) a vapour-pressure formula obtained by Nernst ("Theoretische Chemie," 8-10 ed., p. 313), and (iii) an empirical formula which the author has found to connect the change in the heat of vaporisation with that of temperature.

H. T. S. BRITTON.

Shrinkage of glass threads during heating. I. SAWAI and Y. UEDA (Z. anorg. Chem., 1929, 180, 287-303; cf. A., 1928, 1085).---Using a soda-lime glass, measurements have been made of the changes in length on heating of glass threads of various diameters between 0.031 and 0.316 mm. As in the case of lead borate glasses, a contraction was found to occur at two temperatures. The first shrinkage disappears, however, by a preliminary heating at 500°. The temperature at which shrinkage commences is greatly dependent on the diameter of the thread, the load placed on it, and the rate of heating. From the shrinkage measurements the surface tension and viscosity of the glass thread can be calculated. The theoretical significance of the shrinkage temperature is discussed. O. J. WALKER.

Determination of internal friction of metals, especially mercury. F. SAUERWALD and W. RADECKER (Z. Physik, 1929, 54, 844—847).—A number of experimental results are cited on the basis of which it is concluded that the values for the internal friction of mercury previously obtained must be correct within experimental error. A slip of any large dimensions cannot occur at the walls of the vessel. The value of the Hagenbach correction is discussed. A. J. MEE.

Gaseous effusion at high temperatures. F. R. BICHOWSKY and C. W. WILSON (Physical Rev., 1929, [ii], 33, 851—859).—A method of investigating the effusion of gases through a small orifice is described, and applied to helium for the range of temperature $1000-2100^{\circ}$ Abs., and of pressure 0.2-0.8 mm. The kinetics of the problem is discussed. The effusion was found to follow Knudsen's formula. Correcting for viscosity and slip effects, the pressure varies with the absolute temperature when the rate of flow is constant. The apparatus thus serves as a gas thermometer. Experiments with hydrogen at high temperatures were inconclusive owing to the presence of atomic hydrogen. N. M. BLIGH.

Azeotropism in binary systems containing an acid. M. LECAT (Ann. Soc. Sci. Bruxelles, 1929, 49, B, ii, 28-47).-Azeotropic data already published for binary systems containing one acid component are grouped systematically and reviewed. The general conclusion is that the azeotropic lowering, δ , for a given difference Δ between the b. p. of the components, diminishes rapidly with increasing mol. wt. of the acid, the degree of molecular association varying inversely with the mol. wt. For formic acid mixtures, the azeotropic lowering satisfies the equation $\delta = 20 - 0.589 \Delta + 0.0045 \Delta^2 - 0.0000024 \Delta^3$; for acetic acid, the equation becomes $\delta = 10 - 0.61\Delta + 0.0134\Delta^2$ $0.00011\Delta^3$. For propionic, butyric, and isovaleric acids one equation is approximately valid, viz., $\delta = 7 - 0.562\Delta + 0.0185\Delta^2 + 0.000233\Delta^3$. The curves for benzoic and phenylacetic acids lie between those for acetic and propionic acid; δ_0 (*i.e.*, for $\Delta=0$) is about 8.7. H. F. GILLBE.

Binary azeotropes. XIII. M. LECAT (Ann. Soc. Sci. Bruxelles, 1929, 49, B, ii, 17-27; cf. this vol., 255).—A further list is given of 167 positive azeotropes, 21 eutectics, and 2 negative azeotropes, together with 10 euzeotropes having approximately rectilinear isobars, 29 with isobars convex to the concentration axis, 8 with concave isobars, and 14 other azeotropes. H. F. GILLBE.

Alloys of gold and platinum. A. T. GRIGORIEV (Z. anorg. Chem., 1929, 178, 97-107).—See A., 1928, 955.

X-Ray study of the internal transformation of silver-zinc alloys. A. ROUX and J. COURNOT (Compt. rend., 1929, 188, 1399—1401).—The X-ray spectrum (A., 1928, 851) of an annealed silver-zinc alloy (30·23% Zn) is formed by juxtaposition of the spectra of the constituents, whilst that of the tempered alloy has characteristics only of the principal constituent. Deformation may be due to precipitation of the minor constituent. The authors' micrographic observations and general theory of tempering and recovery (loc. cit.) are confirmed. J. GRANT.

Critical solution temperature phenomena in the ternary system phenol-thymol-water. (Miss) K. W. WILCOX and C. R. BAILEY (J. Physical Chem., 1929, 33, 705-708).-The ternary system phenolthymol-water has been investigated at 15°, 65°, 200°, and 250°, and the ternary diagram is reproduced. At 250°, the curve obtained is a critical saturation curve typical of the addition of a third substance soluble in one only of the partly miscible liquids; at 120°, the curve is of the type characteristic of the addition of a substance soluble to a considerable extent in both liquids. Thus, at high temperatures phenol reduces the solubility of thymol in water, and at low temperatures increases it. At the ordinary temperature, a mixture of equal weights of water and thymol can be rendered homogeneous by the addition of nearly twice the weight of phenol.

L. S. THEOBALD.

Solubility of silicon in hydrofluoric acid. C. BEDEL (Compt. rend., 1929, 188, 1255—1257).— Solutions of silicon (89-96%) containing silica, traces of iron and aluminium, zinc, lead, silver, or magnesium in hydrofluoric acid of concentration corresponding with HF,2H₂O were concentrated by evaporation. The rate of dissolution rises to a maximum (1.25%/hr.)when the concentration of acid is 14% and then decreases to a minimum (0.3%/hr.) for 40% acid, after which it again increases. It is independent of the size of the particles and is far greater for silicon crystallised from silver than for that obtained by other methods. J. GRANT.

Conditions of solubility of silicon in hydrofluoric acid. C. BEDEL (Compt. rend., 1929, 188, 1294—1296; cf. preceding abstract).—The solubility of silicon in hydrofluoric acid is increased in the presence of oxidising agents (including air) and is influenced by the E.M.F. between the silicon and metallic impurities. In 30% acid silicon is electronegative to platinum, silver, and copper, and electropositive to lead, iron, zinc, magnesium, and aluminium. J. GRANT.

Life history of adsorbed atoms and ions. J. A. BECKER (Amer. Electrochem. Soc., May, 1929. Advance copy. 21 pp.).—The condition of adsorbed atoms and ions is discussed in the light of recent experimental work (cf. A., 1926, 988; 1928, 1303). From the way in which the electron work function of a surface is altered by adsorbed particles it is possible to calculate the ratio of adsorbed ions to adsorbed atoms. The fields due to adsorbed ions can exert appreciable forces on other adsorbed ions or atoms at distances of 10 or more atomic diameters, so that the possibility of evaporation of an adsorbed particle is greatly affected by the presence of neighbouring particles. Within a cortain range of temperature the adsorbed particles migrate over the surface as a two-dimensional gas and may move over distances of several thousand atom diameters before evaporating. H. J. T. ELLINGHAM.

Sorption of gases by minerals. I. Heulandite and chabazite. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1929, 4, 96—103).—Heulandite dehydrated at 350° absorbs ammonia fairly rapidly at 25°, the total amount taken up being approximately equivalent to the water lost on dehydration; ethylene and carbon dioxide are not appreciably absorbed. Dehydrated chabazite takes up carbon dioxide and ammonia very rapidly, and ethylene rather slowly. R. CUTHILL.

Adsorption [in gases]. II. W. KALBERER and C. SCHUSTER (Z. physikal. Chem., 1929, A, 141, 270-296; cf. this vol., 132).-The heats of adsorption of various gases (argon, carbon dioxide, nitrogen, ethylene) by silicic acid gels have been measured directly and compared with those deduced from the adsorption isotherms, from which information can also be obtained regarding the magnitude and properties of the adsorbing surface. In particular the steep rise of the first part of the carbon dioxide isotherm points to inhomogeneity of the surface, i.e., to " active centres," and evidence is adduced in favour of condensation in fine capillaries. A close connexion is shown to exist between the heat of adsorption and the volume of the adsorbed layer, expressed as the product of the area of the adsorbing surface and the mean amplitude of vibration of the adsorbed molecules at right angles to the surface; this volume (Adsorptionsraum) increases as the heat of adsorption decreases. The surface structure of silicic acid gel is in an extremely labile condition unless it has been strongly heated, and its area is approximately 10⁶ cm.² per From an examination of the isotherms it is shown that the differential heat of adsorption should increase with fall of temperature, and this has been confirmed experimentally for carbon dioxide at high pressures, where the surface is not so labile. The heat of adsorption increases with increasing surface density of the adsorbed molecules, and is largely dependent on the previous history (heating, progressive extraction of gas, etc.) of the absorbent, particularly at low

F. L. USHER.

Adsorption of water, ethyl alcohol, ethyl acetate, and acetic acid vapours by tungstic and zirconium oxides; bearing on heterogeneous catalysis. J. N. PEARCE and M. J. RICE (J. Physical Chem., 1929, 33, 692—704).—A continuation of previous work (A., 1925, ii, 381) in which thoria and alumina were the adsorbents. Comparison with the present results, obtained at 99.4° , shows that for unit volume of adsorbent the adsorption of water vapour

pressures.

decreases in the order thorium, aluminium, tungsten, and zirconium oxides, which is also the order of the dehydrating power of these oxides towards alcohol. With ethyl acetate the order is reversed. It is inferred that in catalysed esterification the vapours of alcohol and acetic acid must be adsorbed simultaneously and that the catalytic effect increases as the adsorbing power for water vapour decreases.

L. S. THEOBALD.

Adsorption from aqueous solutions by silica. F. E. BARTELL and Y. Fu (J. Physical Chem., 1929, 33, 676-687).-The adsorption of various organic and inorganic acids, bases, and salts from aqueous solution by pure dehydrated silica, prepared from silicon tetrachloride by the method of Ebler and Fellner (A., 1911, ii, 723), has been investigated. Inorganic bases are preferentially adsorbed in the order lithium > sodium > potassium > ammonium hydroxides, the order being the same as that of the hydration of ions and being due probably to the hydrophilic nature of silica. The commoner inorganic acids are not adsorbed, but organic acids are slightly adsorbed in amounts which decrease as a homologous series is ascended, e.g., formic>acetic> propionic>butyric acids. The greatest adsorption is obtained with salicylic and benzoic acids. The adsorption from aqueous salt solutions is hydrolytic, the base being adsorbed in all cases, and with the sodium salts of organic acids adsorption increases as an homologous series is ascended. An equilibrium exists between the base adsorbed and the acid in solution, the extent of the former being controlled by the hydrogen-ion concentration of the solution. This probably accounts for the greater adsorption of salts of organic acids than of inorganic salts. Data for the adsorption of benzoic acid by silica from solutions in carbon tetrachloride and benzene support the conclusion of Patrick and Jones (A., 1925, ii, 193) that greater adsorption corresponds with lower solubility of the solute adsorbed in the solvent. The degree of adsorption is also influenced by solidliquid interfacial tension relationships, greater adsorption being obtained with the solvent which has the lower adhesion tension with the adsorbent (cf. A., 1923, ii, 464). L. S. THEOBALD.

Adsorption of electrolytes by crystal faces. (MLLE.) L. DE BROUCKERE (Bull. Acad. roy. Belg., 1928, [v], 15, 170-184; cf. A., 1928, 831).-Experiments on the adsorption of chlorides by crystalline barium sulphate have been extended to cadmium, mercuric, lead, and lanthanum chlorides and previous results have been confirmed. The same results are obtained from whichever side the equilibrium is approached and whatever the analytical methods employed, and they are quite reproducible. Anions and cations are adsorbed in equivalent amounts. Comparison of the adsorption isotherms shows that the valency of the cation is unimportant, but that at saturation the isotherms are in the order of decreasing at. wt. of the cation. The isotherms agree with Freundlich's formula at low concentrations only. No analogy between the coagulation of colloidal solutions by electrolytes and the adsorption of electrolytes by crystal surfaces is apparent. Calculations of the quantity of electrolyte adsorbed per unit surface at saturation support the idea of a film of unimolecular thickness on the crystal. F. L. USHER.

Adsorption phenomena of silver iodide. II. A. OBRUTSCHEVA (Biochem. Z., 1929, 207, 25— 27; cf. A., 1927, 617).—Further experiments show that the position of the point of maximum adsorption depends, not only on the nature of the adsorbent and of the adsorbed substance, but also on the concentration of the solution of the latter, The theoretical treatment previously given requires to be modified in view of the greater complexity now found to exist in the process. W. MCCARTNEY.

Electric charge of [solid] silver iodide in saturated solutions of silver iodide. E. LANGE and P. W. CRANE (Z. physikal. Chem., 1929, A, 141, 225-248).-It is shown on thermodynamical grounds that a preferential adsorption of iodide ions is to be expected when solid silver iodide is in contact with its saturated aqueous solution. Measurements of the electrokinetic potential of silver iodide have been made with a differential endosmometer in which, by using a P.D. varying from 600 to 8000 volts, separate determinations could be completed in 30 sec. When the precipitate was formed from solutions containing excess of silver ions the potential was at first always more positive than when iodine ions were in excess, but after 80 washings the difference was reduced to 1 millivolt, whence it is inferred that no difference would be found in a perfectly washed precipitate. The electrokinetic potential of the substance in its saturated solution is -0.004 ± 0.001 volt at 20°. Figures are given showing the variation of this potential with concentration of silver ion. The isoelectric point lies at a concentration of about 4×10^{-6} N-silver nitrate, above which the potential becomes positive. Similar measurements with silver bromide in its saturated solution gave a value of -0.0015 volt. The negative potential of the solid against its own solution is considered to be due to adsorption of the halogen ion, the stronger adsorption of iodine compared with bromine ions being ascribed to its greater deformability. Peculiarities in the behaviour of silver iodide, such as the unequal stabilising power of silver and iodine ions, and the ready formation of complex anions, receive a simple explanation in the displacement of the isoelectric point to the silver side of the equivalence point.

F. L. USHER.

Significance of the adsorption of ions by colloid particles in coagulation by electrolytes. H. FREUNDLICH, K. JOACHIMSOHN, and G. ETTISCH (Z. physikal. Chem., 1929, A, 141, 249—269).—The connexion between ionic adsorption and coagulation is shown to be less simple than was assumed in Freundlich's original theory. According to this the coagulation values for different ions correspond with their adsorption measured in equivalents, and the observed discrepancies cannot be ascribed to experimental errors. A new series of experiments with definitely hydrophobic sols (arsenious sulphide, gold) is described, in which the coagulation values for ions of different valency have been redetermined. The amounts of different cations adsorbed at this point

have been determined by sensitive potentiometric and colorimetric methods and found to be not only not equivalent, but even of different orders of magnitude. It is considered that the space distribution of ions round a colloidal particle is very specific and that the thickness of the double layer varies considerably; e.g., with colloidal gold the area occupied by electrolyte in the case of powerful ions with a small coagulation value is less than the total surface area of the gold and there is no ground for assuming a double layer thicker than unimolecular, whereas in the case of univalent ions the area is much greater and the adsorption layer consequently thicker. It is suggested that the lowering of the electrokinetic potential to a critical value need not be effected by adsorption of equivalent amounts of the oppositely charged ion, but may depend on the distribution of cations and anions on the surface of the particles. The amounts of hydrogen ion displaced when different cations are adsorbed have been measured and found to be of the same order of magnitude for all. It is confirmed that the coagulation value for univalent ions rises with dilution of the sol. The quantities of different cations adsorbed at the coagulation concentration by arsenious sulphide, in milli-equivalents per g., are : Na^{*} 5.80, H^{*} 4.28, Ba^{**} 0.21, Zn^{**} 1.50, Ni^{**} 1.22, In^{***} 0.56, Fe^{***} 0.37, Th^{****} 0.27, "neufuchsin" 0.08, methylene-blue 0.13. F. L. USHER.

Capillarity. XI. Diffusion and concentration alterations in capillaries. K. SCHULTZE (Kolloid-Z., 1929, 48, 15—25).—The difficulties and sources of error in the measurement of the rise of salt solutions in capillaries of different dimensions are discussed. E. S. HEDGES.

Drop-weight method for the measurement of surface tension. A. FERGUSON (J. Sci. Instr., 1929, 6, 163—167).—A discussion of the equation $mg = 2\pi r\gamma$ used by Quincke in the absolute determination of surface tension by the drop-weight method. Edwards' work (B., 1929, 400) is criticised. C. W. GIBBY.

Measurement of the interfacial tension of oils. J. C. EDWARDS (J. Sci. Instr., 1929, 6, 167–168).— A reply to Ferguson (cf. preceding abstract).

C. W. GIBBY.

Change in the surface tension of some solutions of univalent chlorides with time. E. O. SEITZ (Ann. Physik, 1929, [v], 1, 1099-1108).-Klein-mann's technique (A., 1926, 900) has been applied to potassium, lithium, and hydrogen chlorides. The alkali chlorides show with increasing concentration a linear increase in the static surface tension at constant temperature, whilst the acid exhibits a linear decrease in the surface tension α . In both cases the change of α with the temperature is -0.015 per degree. The effect of time is given by the relation $\delta \alpha = \Delta \alpha \cdot e^{-\alpha t}$, $\delta \alpha$ being the excess over the static value at any time, $\Delta \alpha$ that at t=0, and 1/a being the time occupied for $\delta \alpha$ to fall to the eth part. Taking $1/\alpha$ as τ , it is found that τ_0/τ (τ_0 being the value for pure water) shows a variation with concentration which is almost exactly in agreement with the variation of the Kohlrausch degree of dissociation Λ/Λ_{∞} . This applies to the alkali salts at constant temperature, but not to hydrogen chloride in which τ and τ_0 are not very

different. As the temperature rises, the concentration being constant τ decreases linearly. The temperature coefficient of $-d\tau/\tau$ varies from 0.017 (hydrogen chloride) to 0.027 (lithium chloride).

R. A. MORTON.

Kinetic phenomena at metallic surfaces. G. VON HEVESY and M. BILTZ (Z. physikal. Chem., 1929, B, 3, 271-281).-If a metal is dipped into a solution containing ions of the metal there is a transfer between the ions in the solution and the atoms of the metal. The transfer effect can be followed by a radioactive method. The kinetics of the change are investigated, the metals being both in the massive and the colloidal form. In the first instance the transfer between massive lead and lead ions was investigated, in one case active lead foil and inactive lead ions being used, and in the second inactive lead foil and active ions. The transfer is practically the same for both methods. The transfer between colloidal lead and lead ions was then determined. With lead sols there is no reversibility. In this case there is a considerable adsorption of lead ions on the colloidal particles. The velocity of transfer between adsorbed ions and ions in the solution is very small. The transfer between massive copper and silver ions is considered, together with the reverse case. The velocity of the change is greater and the effect of adsorption is less marked. A large proportion of the copper goes into solution as the univalent ion.

A. J. MEE.

Determination of the thickness of a film of oleic acid in the saturation state on water and of the saturation pressure of this film. F. EMIR (Compt. rend., 1929, 188, 1284—1286).—The solubility of a film of oleic acid is greater on water than on 0.05N-hydrochloric acid and increases with the superficial density and with rise of temperature. The saturated film on water or acid has a thickness of 23 Å., a value in close agreement with that found by X-ray spectrography and which is independent of temperature (15—30°). The saturation pressure, which is 30.9 dynes/cm.² at 15° and increases with rise of temperature (cf. Marcelin, A., 1926, 120), seems to vary with the origin of the acid.

J. GRANT.

Molecular sieve membranes. L. MICHAELIS (5th Coll. Symp. Mon., 1928, 135—148).—A strong molecular sieve filter is obtained by allowing a solution of collodion to evaporate on a mercury surface. A method for determining the "fineness" of such a sieve is described, and relative values for various materials are recorded. The diameter of the pores is probably of the order of magnitude of single molecules. Relative velocities of diffusion through membranes separating water from 0.1M-solutions are : methyl alcohol 9.2, ethyl alcohol 3.0, propyl alcohol 1.0, carbamide 1.0, butyl alcohol 0.8, glycerol 0.22, chloral hydrate 0.11, monochlorohydrin 0.067, dextrose 0. NH₃ diffuses much more rapidly than NH₄. The diffusion of electrolytes is extremely slow. With potassium chloride against sodium nitrate, diffusion of cations appears to proceed by "exchange," the anions diffusing but slightly, if at all. The valency of the anions has little influence.

CHEMICAL ABSTRACTS.

Osmosis of ternary liquids. General considerations. IX. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 254-263).—Theoretical. A continuation of the discussion (this vol., 392) of the influence of the composition of the liquids and the nature of the membrane on the direction of diffusion. F. J. WILKINS.

Osmotic vapour-pressure. I. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 264–271).—Theoretical. A consideration of the relation between water vapour pressure and osmotic water vapour pressure and the influence of the latter on membrane diffusion.

F. J. WILKINS. Effect of electrolytes on electro-endosmosis through wood membranes. A. J. STAMM (5th Coll. Symp. Mon., 1928, 361—368).—Dilute alkali solutions increase, and dilute acid solutions decrease, the rate of electro-endosmosis through wood membranes. Concentrated acids and bases permanently reduce the rate. Aqueous salt solutions show the normal effect of salts with anions and cations of different valency on negatively-charged membranes. Tervalent and quadrivalent cations cause a reversal of the direction of flow and of the sign of the contact potential. Multivalent anions increase the rate of flow and the negative contact potential.

CHEMICAL ABSTRACTS.

Preparation of colloidon membranes. J. BÖESEKEN and O. MEYER (Rec. trav. chim., 1929, 48, 504—507).—Membranes which are capable of effecting the osmotic separation of dextrins from sugars may be prepared by precipitating copper ferrocyanide in a collodion membrane.

H. F. GILLBE.

Influence of solvent on rotatory dispersion. A. L. T. MOESVELD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 344—355).—The rotatory dispersion of bornyl acetate in the liquid state, or when dissolved in various solvents, can be expressed by a one-term Drude equation. The values of the constant k of this equation have been determined for a set of six solvents and their binary combinations. The variations in its value are interpreted in terms of a deformation of solute molecules.

F. J. WILKINS.

Cryoscopic determinations of the molecular equilibria of resorcinol in aqueous solutions of sodium chloride. F. BOURION and C. TUTTLE (Compt. rend., 1929, 188, 1496-1498).-Solutions of resorcinol in 0.5M- or 1.225M-sodium chloride solutions show evidence of equilibria between simple and double or triple molecules for concentrations of resorcinol up to 0.625 and above 0.875, respectively. The cryoscopic constant, which is higher than for potassium chloride or aqueous solutions (this vol., 648), increases with the concentration of sodium chloride. Apparent contradictions to the author's thermodynamic treatment of such solutions (loc. cit.) are due to adsorption of water by the ions or molecules of the dissolved salt. J. GRANT.

Change of volume on neutralisation. J. J. SASLAVSKY, E. G. STANDEL, and V. V. TOVAROV (Z. anorg. Chem., 1929, 180, 241-251).—The change of

volume on mixing solutions of acids and bases of various concentrations in different proportions has been measured for the following systems : potassium hydroxide-acetic acid, sodium hydroxide-acetic acid, -nitric acid, -sulphuric acid, ammonia-nitric acid. In most cases there is an increase in volume on neutralisation, the maximum change in volume corresponding with the neutral salt formation. With ammonia solutions there is a contraction in volume on neutralisation. Curves are given in which the percentage of alkali in the solution is plotted against the volume of the solution after mixing. In the case of the alkali-monobasic acid systems these curves show a sharp maximum at the point corresponding with complete neutralisation, and the two branches of the curve are symmetrical with respect to this point. The curvature of these two branches increases with the concentration of the solutions which are mixed. On mixing very concentrated solutions of alkali and acetic acid there is actually an initial contraction in volume. In the case of sulphuric acid the hydrogen sulphate stage of neutralisation is clearly O. J. WALKER. shown on the curve.

Electrostriction by dissolved dipole molecules. G. JUNG (Z. physikal. Chem., 1929, B, 3, 204—208).— Mathematical. The electrostriction effect in solutions, due to dissolved particles which are electrically neutral dipoles is of the same order of magnitude as that due to ions. O. J. WALKER.

Dispersoidal synthesis of gold by means of alkaline formaldehyde solutions. P. P. von WEIMARN (Japan. J. Chem., 1929, 3, 165-215).-The paper summarises the results of many years' work on the production of gold sols, the experimental details of which have been published elsewhere. The influence of purity of the reagents in the preparation of red gold sols by reduction with formaldehyde is discussed : the only effect of increasing purity is to increase the concentration to which the red sols can be evaporated before they become blue. In several respects, the author's views are opposed to those of Zsigmondy. It is concluded that a large proportion of the work on dispersoidal gold synthesis should be repeated, not only quantitatively but qualitatively, that it is not possible to accept "coagulation values" obtained up to the present time, and that the identification of the synthesis of colloidal gold with spontaneous crystallisation is erroneous. E. S. HEDGES.

Preparation of colloidal bismuth and arsenic soluble in water. A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 269–274).—Colloidal bismuth and arsenic soluble in water were prepared from bismuth oxychloride and arsenic trichloride, respectively, by means of an acetic acid solution of "Paal's liquid" (A., 1902, i, 653, ii, 500). The colloids were purified by centrifuging, brought into solution by means of a 20% solution of sodium hydroxide, and evaporated to dryness on a water-bath. Both are powders, the bismuth colloid containing 17.9% of metal, the arsenic colloid 23–27% of metal. Both are negatively charged. A. FREIMAN.

Tartaric acid method for synthesis of electronegative sols. III. Adsorption of sodium

tartrate and succinate by aluminium hydroxide. A. DUMANSKI and A. JAKOVLEV (J. Russ. Phys. Chem. Soc., 1929, 61, 151–157, and Kolloid-Z., 1929, 48, 151–145).—See A., 1928, 1321.

Tartaric acid method for the synthesis of electronegative sols. V. Sulphide sols. A. DUMANSKI and A. BUNTIN (J. Russ. Phys. Chem. Soc., 1929, 61, 279-314).-Sols of lead, tin, ferric, and nickel sulphides have been prepared by the tartarie acid method, either from solutions of tartrates of the corresponding metals and hydrogen sulphide or from solutions of salts in tartaric acid and hydrogen sulphide. The conditions governing the formation of the sulphide sols, e.g., concentrations of starting materials etc., were also investigated. In the case of lead and tin sulphides the stability, density, relative viscosity, cataphoretic velocity, and behaviour towards alkalis, acids, and salts were also determined. It was found that there is no adsorption, peptisation, or chemical reaction between sodium tartrate and the sulphides. A. FREIMAN.

Tartaric acid method of preparing negativelycharged sols. V. Physico-chemical properties of tartaric acid tungsten colloids. A. DUMANSKI and S. I. DIJATSCHKOVSKI (Kolloid-Z., 1929, 48, 49—57).—Measurements of the density, viscosity, angle of rotation, and conductivity of solutions prepared by mixing equivalent solutions of sodium tungstate and tartaric acid are recorded. An examination has been made of systems containing different ratios of tartaric acid to tungstate : colloidal solutions are readily obtained and some of the products have been analysed. The colloid solutions examined gelatinise and exhibit thixotropy. The gels also exhibit photochemical sensitivity. The complexes are hydrolysed by dilution. E. S. HEDGES.

Desiccation of colloidal solutions of alumina and chromium oxide. P. BARY and J. V. RUBIO (Anal. Fís. Quím., 1929, 27, 273-284).—A more detailed account of work already published (this vol., 392).

Coalescence of an unfilterable precipitate of barium sulphate. H. M. TRIMBLE (Proc. Oklahoma Acad. Sci., Univ. Ok. Bull., 1928, [ii], No. 409, Studies Ser., No. 29, 197).—Large particles do not grow at the expense of smaller ones; aggregation of particles is followed by cementation. CHEMICAL ABSTRACTS.

Changes in physico-chemical properties in the region between colloid and molecular disperse solutions. I. Wo. OSTWALD and A. QUAST (Kolloid-Z., 1929, 48, 83-95).-Measurements have been made of the diffusion coefficients of a number of dyes (night-blue, crystal-violet, new-fuchsin, brilliantgreen, Congo-red, benzopurpurin, nerol, and sulphonecyanin) in mixtures of water and alcohol of varying composition, and from the results the relative sizes of particles of the dyes have been calculated by Einstein's equation. In all cases, the maximum degree of dispersion is obtained when mixtures of medium composition (40-60% of alcohol) are used as solvent. The radius of the particles may vary with the composition of the solvent mixture to the extent of E. S. HEDGES. 1:100.000 A JAODCORD

Influence of electrolytes on the viscosity of colloids. N. R. DHAR and S. GHOSH (Kolloid-Z., 1929, 48, 43-49).-Measurements on more than 30 sols show that the viscosity of the sols is reduced by the addition of small quantities of electrolytes, and it is held that such a decrease in viscosity occurs whenever ions with the same charge as the sol are preferentially adsorbed. Conversely, viscosity rises with the purity of the sol and it is shown experimentally that sols of chromium hydroxide and of zirconium hydroxide are more viscous with increasing purity: the viscosity of a zirconium hydroxide sol was reduced to one half by addition of a 1% solution of zirconium oxychloride. The experiments support the authors' contention that the viscosity is the smaller the higher is the charge and that the uncharged material is more strongly hydrated than the charged sol. The conclusion is reached that the stability of a hydrophilic or hydrophobic sol is not connected with its degree of hydration. E. S. HEDGES.

Lyophilic colloids. II. Casein sol. H. R. KRUYT and H. LIER (Koll.-Chem. Beih., 1929, 28, 407-450; cf. this vol., 136).-Measurements of the viscosity of solutions of purified casein in acids and in alkalis have been carried out and Poiseuille's law was found to be valid for all the solutions used. Measurements of relative viscosity were made with sols of casein of different concentration in presence of varying concentrations of bases, the hydrogen-ion concentrations of the sols being measured also. A viscosity maximum was observed at $p_{\rm H}$ 11.5, in agreement with the view that casein does not form a true solution, but contains polymolecular particles, of which only the surface molecules react. At a con-stant hydrogen-ion concentration, the increase in relative viscosity is parallel to the colloid concentration. In acid solution, sols of casein have a viscosity maximum at $p_{\rm fl} 2.6$. The acid sol is less stable than the basic sol. The addition of neutral electrolytes causes a decrease in viscosity, the valency of the cation being important in the alkaline sols and that of the anion being important in the acid sols. Observations on the flocculation of both the acid and basic sols show that these behave like typical suspensoid colloids. The alkaline sols are dehydrated in the usual way by alcohol and acetone, but the acid sols are not dehydrated under these conditions. The isoelectric point of casein lies between $p_{\rm ff}$ 3.5 and 6.5. Only electrolytes of the type of sodium hydroxide and hydrochloric acid are able to peptise casein powder.

E. S. HEDGES. Osmometer for the measurement of the osmotic pressure of colloids. A. GRIGAUT and BOUTROUX (J. Chim. phys., 1929, 26, 224-228).— An apparatus is described by which osmotic pressures of hydrosols may be measured accurately up to a pressure equal to 60 cm. of water. Two hemispherical cells are separated by a semi-permeable diaphragm, and from the glass walls of the cells two horizontal glass capillary tubes protrude perpendicularly to the diaphragm. A tap is inserted in one of these tubes. The hydrosol is placed in the cell which can be closed by the tap, whilst the cell on the opposite side of the diaphragm contains the ultra-filtrate of the sol. Diffusion of the ultra-filtrate is allowed to occur through the diaphragm for some hours into the hydrosol while the tap in the capillary tube is kept closed; on opening the tap the diaphragm regains its initial condition and the water which has passed through it causes a displacement of the meniscus in the capillary tube. The pressure can be calculated from the increase in volume, or it may be measured directly on opening the tap by means of a pressure gauge connected to the end of the capillary tube.

H. T. S. BRITTON. General colloid chemistry. XXIV. Colloid salt conductivity and colloid ion mobility. E. VALKÓ and N. WEINGARTEN (Kolloid-Z., 1929, 48, 1-10).—The application of Hittorf's method of measuring ionic mobility to the study of colloid systems is discussed. Measurements have been made of the decrease in mobility of the colloid ions of an aluminium hydroxide sol when the chlorine ion is replaced by the sulphate ion, and a comparison with the decrease in conductivity is given. The colloid ions present in an aluminium hydroxide sol have a greater mobility when the sol is diluted. Reproducible sols, which can be characterised by electrochemical methods, have been prepared by incomplete precipitation of a solution of aluminium chloride by E. S. HEDGES. silver oxide.

Macroscopic method of determining the cataphoretic velocity of colloidal particles. A. E. ALEEV and A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 275—277).—One of the conditions limiting the applicability of the macroscopic method (Gerasimov, A., 1927, 726) of determining the cataphoretic velocity of colloidal particles has been investigated. A. FREIMAN.

Kinetics of coagulation of colloids of the second order. K. JABECZYNSKI and H. JASZCZOŁTÓWNA (Bull. Soc. chim., 1929, [iv], 45, 202–206).—See this vol., 506.

Influence of stirring on the rate of coagulation of colloids. K. JABŁCZYNSKI and (MLLE.) G. SZAMES (Bull. Soc. chim., 1929, [iv], 45, 206-210; cf. A., 1925, ii, 35).-The rate of coagulation of ferric oxide hydrosols by potassium chloride at the ordinary temperature has been followed spectrophotometrically at different rates of stirring. Both dialysed and undialysed sols were studied, and were aged for 6 months before use. Immediately after mixing with the electrolyte stirring increases the normal rate of coagulation, but afterwards diminishes it, the latter effect being more marked as the rate of stirring is increased. Diluting the sol tends to neutralise the effects of the stirring; whilst in the case of the undialysed sol, in which the ratio Fe: Cl was 1:0.22, the initial stage of acceleration was not observed, probably on account of its short duration. It is considered that this initial acceleration is due to the increased frequency of collisions between the primary particles, and the subsequent retardation to mechanical disruption of the larger aggregates produced during the first stage. The usual mathematical expression for the rate of coagulation cannot be applied when the liquid is stirred. F. L. USHER.

Mechanical coagulation of goethite sol. H. FREUNDLICH and S. LOEBMANN (Koll.-Chem. Beih., 1929, 28, 391-406).—The observation by Freundlich and Kroch (A., 1927, 18) that sols of goethite (prepared from iron carbonyl and hydrogen peroxide) are coagulated by mechanical agitation has been developed into a quantitative investigation, and the results have been compared with the similar mechanical coagulation of cupric oxide sols. With both sols the coagulation velocity is independent of the number of particles in the sol and of the volume of liquid stirred, whilst a quadratic relation exists between coagulation velocity and rate of stirring. Only a definite number of particles are coagulated by stirring a goethite sol, the rest remaining unaltered in the sol. A number of attempts at explanation of mechanical coagulation are shown to be improbable and the most likely explanation is that coagulation takes place at the surface of the solution, where a certain orderly arrangement of particles may exist: mechanical agitation effects a constant change of surface. The surface concerned need not be the sol-air interface, and experiments have shown that the effect is produced at any surface provided by a medium of low dielectric constant, whether it be a gas (e.g., air), a liquid (e.g., benzene), or a solid (e.g., powdered quartz). The effect of alcohols on the mechanical coagulation of goethite has also been examined. Propyl alcohol at low concentrations aids the coagulation, but has the reverse effect at higher concentrations : isoamyl alcohol favours coagulation at all concentrations, and methyl alcohol tends to prevent coagulation at all concentrations. The influence of electrolytes at small concentrations under the threshold value for coagulation is diminished and the amount of sol remaining uncoagulated is increased. Anions of high valency are particularly active in this respect. E. S. HEDGES.

Flocculation of arsenious sulphide sols by thorium chloride. A. BOUTARIC and C. SEMELET (J. Chim. phys., 1929, 26, 195-204).-The following experiments are described : (1) Equal volumes of an arsenious sulphide sol were each mixed with water and solutions of thorium chloride of varying concentrations, such that the final volumes of the mixtures were the same and their thorium chloride contents equal. The mixtures which had been prepared from the more concentrated thorium chloride solutions flocculated in less time than did those in which more dilute solutions had been used. (2) Arsenious sulphide sols of the same concentration were mixed with equal volumes of thorium chloride solutions of varying concentration and the times taken by the mixtures to flocculate were observed. By plotting the logarithms of the concentrations of the thorium chloride solutions against the reciprocals of the times required, it was found possible to ascertain the concentration of thorium chloride below which coagulation could not be effected. (3) Equal volumes of thorium chloride solutions of the same concentration and of arsenious sulphide sols of varying concentrations were mixed and allowed to flocculate. The data show that the times required increases with the concentration of the colloid. (4) Sols having particles of different size (an orange-coloured sol containing fine grains is obtained by passing a rapid flow of hydrogen sulphide through an arsenious acid solution, whereas a yellow, coarse-grained sol is produced with a slow supply) were investigated as in (2) and show that a smaller minimum concentration of thorium chloride is required for the flocculation of the coarse-grained sol as compared with the fine-grained sol. By employing the same concentration of thorium chloride less time was required to flocculate the former. (5) The time taken by a sol to flocculate under the influence of a given concentration of thorium chloride increases rapidly with rise of temperature. (6) Arsenious acid in the sulphide sol exerts a protecting influence against thorium chloride. (7) An excess of hydrogen sulphide in the sols reduces their stability towards thorium chloride. (8) Methyl alcohol, ethyl alcohol, and acetone each exercises a protective action on the sols against thorium chloride, whilst sucrose appears H. T. S. BRITTON. to be without effect.

Effect of multivalent cations on some colloidchemical properties of kaolin. I. I. SHUKOV and M. N. SOKOLOVA (Kolloid-Z., 1929, 48, 71-78).-An investigation has been made of the relation between the stability of kaolin suspensions and electrolyte adsorption and capillary electric phenomena. Two kinds of kaolin (Gluchov and Gluchovetz) were employed and the electrolytes used were ferric chloride and thorium nitrate. In all cases the adsorption follows an anomalous course : the adsorption curve of thorium nitrate on Gluchov kaolin reaches a maximum and then continues as a straight line, but in the other cases the adsorption curve falls subsequently. These anomalies are believed to be due to the change in the degree of hydrolysis of the salt at different concentrations. The adsorption of both electrolytes is stronger by Gluchov than by Gluchovetz kaolin, in accordance with the higher negative charge and greater stability of the former. The sign of the charge is reversed with excess of the electrolytes, Gluchov kaolin requiring the higher concentration, and the concentration required is the same for both electrolytes when expressed in terms of normality. Gradual addition of ferric chloride to a Gluchovetz kaolin suspension causes a decrease in stability until the isoelectric point is reached, after which the reversed sol is stabilised. With Gluchov kaolin a second zone of decreasing stability is realised. Measurements of filtration velocity of suspensions of both kinds of kaolin show that the velocity is greater E. S. HEDGES. the smaller the stability.

Peptisation of dyes by neutral salts. W. OSTWALD (Ber., 1929, 62, [B], 1194—1196).—The blue-black precipitate of the free dye acid of Congored is insoluble in water but dissolves to red solutions in about 0.5N-potassium chloride or magnesium chloride. The effect is even more marked when the blue sol is used which forms red or yellowish-red solutions with neutral chlorides, iodides, bromides, chlorates, nitrates, sulphates, etc. of uni- and multivalent cations in concentration less than N. Ammonium chloride, nitrate, and sulphate do not exhibit this behaviour. In more concentrated salt solutions precipitation occurs. H. WREN.

Relations between electrokinetic migration velocity, peptisation, and stability of coarsely disperse systems. A. von Buzágh (Kolloid.-Z., 1929, 48, 33-43).-Measurements of cataphoretic migration velocity have been carried out with suspensions of animal charcoal in picric acid solutions and with suspensions of kaolin and of bentonite in solutions of sodium hydroxide, using different concentrations of the electrolyte as peptiser and varying amounts of the solid phase. In each case, the migration velocity for a constant amount of solid phase rises at first with increasing concentration of the electrolyte, reaches a maximum, and then falls. similar curve with a single maximum is obtained when a constant concentration of peptising agent is used and the migration velocity is plotted against the amount of solid phase. The similarity in the two curves is to be expected on the assumption that a definite electrical charge on the particles is necessary for peptisation and that this charge is related to a definite adsorbed amount of the peptising agent, for with small amounts of solid phase the relative amount of adsorbed electrolyte is too high, whilst with large amounts of solid phase there is insufficient electrolyte to stabilise the particles. The maximal value of migration velocity is practically the same, in agreement with the theory, whether obtained by varying the amount of the peptising agent or of the solid phase. A maximum is also observed in the curve connecting the degree of peptisation (i.e., the ratio of peptised material to the total solid phase) with the amount of solid phase, the maximum corresponding with the maximum of electrical charge. In pure water, the migration velocity is independent of the amount of solid phase, and the degree of peptisation is constant for small amounts of solid phase, but later falls with increasing amounts of solid phase. E. S. HEDGES.

Kinetic studies in the system colloidal ferric hydroxide-hydrochloric acid-water. E. HEY-MANN (Kolloid-Z., 1929, 48, 25-33).-The ageing of solutions of ferric chloride has been followed by making conductivity determinations. The ageing is due to the slow condensation of the primary particles of hydrolysis product to form particles of ferric hydroxide of colloidal dimensions, and it was found that direct addition of ferric hydroxide to the system accelerates considerably the ageing process. Alumin-ium hydroxide does not exert this effect. The formation of the colloidal particles from the primary hydrolysis product is an autocatalytic process. The dissolution of the particles of ferric hydroxide by hydrochloric acid does not follow a unimolecular course and it is suggested that the reaction does not occur on the surface of the particles only. The ageing of solutions of sodium aluminate also is accelerated by the addition of aluminium hydroxide. E. S. HEDGES.

Thixotropy of dispersions of small concentration. I. E. A. HAUSER (Kolloid-Z., 1929, 48, 57-62).—The influence of the dimensions of the containing vessel, the volume, and the concentration on the thixotropy of natural bentonite suspensions is discussed. The destruction of the thixotropic properties of bentonite by dialysis and the possibility of the thixotropy reappearing after addition of electrolytes are also discussed. An ultramicroscopic investigation of dialysed bentonite suspensions of low concentrations has shown that through the addition of increasing quantities of electrolytes, first the translation and then the rotation component of the Brownian movement is stopped. Further addition of electrolyte causes aggregation of the particles and finally flocculation. E. S. HEDGES.

Syneresis. S. LIEPATOV (Kolloid-Z., 1929, 48, 62-63).—Polemical. Kuhn (this vol., 137) has misunderstood the author's results, some of the misunderstanding being due to misprints, which are now rectified. E. S. HEDGES.

Syneresis. A. KUHN (Kolloid-Z., 1929, 48, 63).— A reply to Liepatov (preceding). E. S. HEDGES.

Mol. wt. of cellulose. K. HESS (Rec. trav. chim., 1929, 48, 489–491).—The applicability of the mass action law to the cuprammonium-cellulose system expresses the kinetic individuality of the $C_6H_{10}O_5$ group, in contradiction to MacGillavry's assumption (this vol., 262). H. F. GILLBE.

Mol. wt. of cellulose. D. MACGILLAVRY (Rec. trav. chim., 1929, 48, 492–493).—The optical behaviour of cellulose in cuprammonium solutions is explicable on the assumption of equivalent glucose residues, without having regard to the molecular size. Conversely, the latter cannot be determined from the optical behaviour. H. F. GILLBE.

Orientation and pseudo-crystallisation phenomena resulting from the action of stretching in colloidal gels. J. J. TRILLAT (Compt. rend., 1929, 188, 1246-1248).—The X-ray examination of stretched films of cellulose, cellulose nitrate, and cellulose acetate affords evidence of molecular anisotropy as the stretching increases, the mean degree of molecular oscillation about the direction of stretch decreasing with increasing strain. Under high strains the diagrams are analogous to those of the corresponding crystalline substance, and it would seem that passage from the gel state occurs in stages, the final condition being that of pseudo-crystallisation in which the molecules occupy the same positions as in the crystal lattice but are not in perfect alignment. Modification of chemical properties may result as a consequence of change in orientation of active groups. J. GRANT.

Magnetisation coefficient and structure of solutions of gelatin. M. FALLOT (Compt. rend., 1929, 188, 1498—1500).—The magnetisation coefficient of gelatin at 19° increases linearly with concentration (0-1.5%), but there is a sharp change in the direction of the line at the concentration (0.8%) corresponding with the maximum dielectric constant observed by Marinesco (this vol., 646). The magnetic and electric axes of the dipoles are probably perpendicular to one another. J. GRANT.

Physico-chemical properties of pineapple-stem colloids. C. P. SIDERIS (Plant. Physiol., 1928, 3, 309-321).—Two proteins and a carbohydrate were identified in the expressed fluid, and their colloidal behaviour with solutions of sodium chloride and hydroxide, respectively, was examined. It is suggested that the carbohydrate colloid has a hollow spherical structure, the shell being formed of aggregated micelles held together by electrostatic forces. Protein colloids may have similar structures, the carboxyl groups projecting inwards and the aminogroups outwards, or *vice versa*, according as the $p_{\rm H}$ of the solution is on the acid or alkaline side, respectively, of the isoelectric point.

CHEMICAL ABSTRACTS.

Qualitative reaction of protein. I. Reaction of acid in the acetic acid-sodium chloride test. S. OGATA (Hokkaido J. Med., 1928, 6, 26-36).—The amount of sodium chloride necessary to precipitate gelatin from aqueous solution decreases to a constant value, dependent on the gelatin concentration if below 3%, when acetic acid is added. In solutions more acid than $p_{\rm H}$ 9.6 the action of sodium chloride is not affected. CHEMICAL ABSTRACTS.

Action of sodium chloride on collargol. G. S. VOZDVISCHENSKI and A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 193—196).—Increase in the amount of albuminous matter present is found to decrease the protective action of sodium chloride on collargol, and this is more pronounced for nondialysed collargol or non-dialysed solutions of albumin than for the dialysed substances. Dilution increases the effectiveness of sodium chloride and this action is also more pronounced in the case of non-dialysed samples. On dialysis an adsorptionally very sensitive portion of the albuminous matter passes out through the membrane. A. FREIMAN.

Theory of vegetable tanning. IV. Separation into two liquid phases in systems hydrophyllic colloid-water-polyphenol. H. G. B. DE JONG (Rec. trav. chim., 1929, 48, 494-503).-Dehydration of a gelatin sol at the isoelectric point by resorcinol occurs only between certain concentration limits of the latter. Over the same range, a fluid coagulum is produced, and if the mixture is kept for a time it separates into two layers, the one which is richer in gelatin containing the greater proportion of resorcinol. The separation process commences with a micro-separation of the resorcinol solution at the surface of the gelatin particles, followed by coalescence when conditions become favourable. A similar type of separation in gelatin sols has been observed with a number of phenols, with chebulic acid, digalloylglucose, and tannin, and also in agar and starch sols in presence of tannin. H. F. GILLBE.

Layered sedimentation of suspensions of erythrocytes. V. DUCCESCHI (Kolloid-Z., 1929, 48, 78—79).—When the blood of various animals is added to the extent of 3-5% to a 1% solution of sodium chloride or Ringer's solution, the easily coagulable part settles in the course of 2—3 hrs. and the red corpuscles remain suspended for 24—48 hrs. During this time, the suspension of corpuscles frequently assumes a periodic structure, sedimentation taking place in layers. An explanation is not given.

E. S. HEDGES. Chemistry of body processes. Nature of the action between gelatin and electrolytes. A. L. FERGUSON (5th Coll. Symp. Mon., 1928, 159–178).– A discussion. CHEMICAL ABSTRACTS.

Double refraction of stretched rubber, W. C. VAN GEEL and J. G. EYMERS (Z. physikal. Chem., 1929, B, 3, 240-246).-Two samples of rubber have been examined : (a) an unvulcanised plastic rubber and (b) an elastic rubber obtained by drying pure latex. In the case of the plastic rubber the double refraction is a linear function of the tension except with low tensions, where the rubber still has elastic properties. With elastic rubber much higher values of the tension are reached before the relationship becomes linear, and a formula is given which expresses the variation of double refraction with tension up to the limiting tension at which proportionality commences. At this limiting tension the extension of the rubber is 70%, which appears to be a characteristic magnitude for pure rubber. O. J. WALKER.

Absolute zero of internal energy and entropy, and the corresponding inertness of matter. R. D. KLEEMAN (Science, 1928, 68, 235–236; cf. A., 1928, 1187).—The first and second differential coefficients with respect to temperature of the internal energy, pressure, and volume of a condensed substance at 0° Abs. either at constant volume or pressure or under its own vapour pressure are equal to zero. The inertness to changes in temperature possessed by matter at 0° Abs. indicates that at this temperature an atom differs considerably in its nature in virtue of a change in electronic configuration. A further proof that at 0° Abs. the internal heat of evaporation is zero is given. L. S. THEOBALD.

Chemical combination as an electrostatic phenomenon. VI. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 224—228).—A mathematical discussion of recent attempts to deduce theoretically dissociation energies, heats of formation, and other intramolecular quantities. S. I. LEVY.

Recent views on electrolytes. N. BJERRUM (Ber., 1929, 62, [B], 1091-1103).—A lecture.

H. WREN.

Equilibrium constant in double decompositions in aqueous solution. (MME.) LEMAR-CHAND and LEMARCHAND (Compt. rend., 1929, 188, 1289—1291).—The heat of reaction (10610 g.-cal.) for the double decomposition of barium chloride and sulphuric acid which is calculated from the equilibrium constants at 18° and 100° (this vol., 266) by means of the integrated van 't Hoff equation is in close agreement with thermochemical determinations (10100 g.-cal.). J. GRANT.

Equilibrium, phosphoric acid-hydrogen fluoride-monofluophosphoric acid-water. W. LANGE (Ber., 1929, 62, [B], 1084—1088; cf. this vol., 662).— Weighed quantities of phosphoric acid and hydrogen fluoride are preserved at 20° in a platinum crucible with a tightly fitting lid. The mixture is poured into dilute potassium hydroxide solution at -10° in quantity sufficient for complete neutralisation and unchanged phosphoric acid is precipitated as silver phosphate. The incidence of the equilibrium $H_3PO_4+HF \Longrightarrow H_2PO_3F+H_2O$ is established, but the dependence of the reaction on the concentration of water can be explained only by the assumption that undissociated molecules, which are present in the concentrated acid but disappear on dilution with water, are involved. H. WREN.

Polarity of halogens in solutions of pyridinium and allied dichloroiodides. T. H. READE (J.C.S., 1929, 853-863). — Pyridinium, phenyltrimethyl-ammonium, and allied dichloroiodides dissolve in water to form solutions which are rich in hydrogen ions, chlorine ions, and hypoiodous acid. Molecular chlorine and iodide ions are absent, but molecular iodine is present as a decomposition product of hypoiodous acid. Unless treated with a reducing agent or some other special reagent, the solution does not immediately give a blue coloration with starch, but does so after some hours. A similar behaviour is observed with dichloroiodides dissolved in solutions of sodium chloride or hydrochloric acid. The tendency of dichloroiodides to ionise is retarded by the addition of a large excess of chlorine ions or hydrogen ions, the former having the greater effect. The rate of formation of hypoiodous acid has been determined and is taken as a measure of the degree of dissociation of the dichloroiodides. In 0.001M-solution, the dichloroiodides behave like double salts which contain a highly reactive, positively-charged iodine atom, which forms hypoiodous acid by combination with the hydroxyl ion of water. Hypoiodous acid behaves similarly towards phenolic substances and aromatic amines. E. S. HEDGES.

Dissociation constant of glutimic acid. V. ZAFOUK (Z. Zuckerind. Cechoslov., 1929, 53, 465– 468).—From measurements of the electrical conductance of solutions of the sodium salt of glutimic acid at 25°, a mean value of 5.9×10^{-4} was found for the dissociation constant. The values calculated fell gradually from 5.93×10^{-4} in M/16 solution to $5.25 \times$ 10^{-4} for M/1024 solution. From measurements of hydrogen-ion concentration in mixed solutions of glutimic acid and its sodium salt, values for the dissociation constant between 6.25×10^{-4} and 3.40×10^{-4} for M/75 and M/1000 solutions, respectively, were obtained. F. G. TRYHORN.

Isomerism of the oximes. XXXIV. Dissociation constants of isomeric oximes and their influence on the production of the isomerides in alkaline solution. O. L. BRADY and N. M. CHOKSHI (J.C.S., 1929, 946—951).—Measurements of the dissociation constants of a number of oximes are given. Where there is little difference between the dissociation constants of two stereoisomeric oximes, both forms are produced on oximating the aldehyde or ketone in alkaline solution. The relation between the dissociation constants and the configuration of the isomerides is considered for the case of the ketoximes. If the analogy of the cinnamic acids be accepted, the results favour the old as against the new configurations of the ketoximes, but the analogy seems doubtful in view of the evidence in favour of the new configurations. E. S. HEDGES.

Determination of the alkali-fixing capacity of the most important sugars. P. HIRSCH and R. SCHLAGS (Z. physikal. Chem., 1929, A, 141, 387412).—The acid properties of sugars are so feeble that the usual methods of determining dissociation constants are not trustworthy. The conductometric method of Hirsch (cf. A., 1926, 700) is applicable, using the formula $c=100\Delta\kappa/\Lambda_{\text{NaOH}}-\Lambda_{\text{NaX}}$, where c is the concentration of the alkali-sugar compound (NaX), $\Delta \kappa$ is the decrease in conductivity, and A the equivalent conductivity of the compound indicated. Sugar introduced into a solution of sodium hydroxide causes a decrease in conductivity due to the formation of a sodium-sugar salt. This decrease is accurately measurable and reproducible. Λ_{NaOH} was directly measured and it was assumed that sugar molecules have no influence on it. Λ_{NaX} must be obtained indirectly, since the salt is hydrolysed. To do this the conductivity of the solution of sugar and sugar salt with excess alkali was found directly, and the concentration of free alkali was determined potentiometrically on the basis of separate experiments conducted in the presence of different concentrations of various salts. The conductivity due to this free alkali could thus be calculated, and hence that of the sugar salt. Since the concentration of the latter is known from the difference in concentration of the free alkali at the beginning and end of the experiment, the equivalent conductivity could be calculated. By plotting the amount of alkali combined with 1 g.-mol. of sugar against the $p_{\rm H}$ of the liquid it was found that all the sugars investigated contain more than one acid group per molecule. The simplest assumption compatible with the experimental results is that the sugars are dibasic, and on this basis the dissociation constants of dextrose, lævulose, maltose, sucrose, and lactose have been calculated from Hirsch's formula. The experiments are not consistent with the enolisation theory of Michaelis as an explanation of the acid nature of sugars. By plotting the decrease in conductivity obtained on adding increasing amounts of sugar to a given concentration of alkali against concentration of sugar straight-line curves are obtained, from which the concentration of sugar solutions can be found quickly and accurately by determining the decrease in conductivity and reading off from the curves. F. L. USHER.

Activity coefficients of certain acid-base indicators. J. SENDROY, jun., and A. B. HASTINGS (J. Biol. Chem., 1929, 82, 197-246).-Extensive series of comparative electrometric determinations of the hydrogen-ion activity and colorimetric determinations have been made with solutions of several indicators of the phenolsulphonephthalein class in presence of neutral salts and of buffer mixtures. The indicators were found to behave like other weak acids in that the value of pK' is dependent on the total ionic strength of the solution, the quantitative connexion being expressed by the equation of Debye and Hückel. The relationship is influenced in a subsidiary degree by other factors such as the specific interionic effects of individual ions. The colorimetric determination of p_{aH} with the aid of bicolour standards is discussed in the light of these results.

C. R. HARINGTON.

Effect of salts on weak electrolytes. III. Interaction of certain weak electrolytes. H. S. SIMMS (J. Physical Chem., 1929, 33, 745-754; cf. A., 1928, 1093, 1326) .- The inactivation of one weak electrolyte by another has been investigated by an examination of the effect of glycine on the dissociation index (pK_{2}) of phosphoric acid. The presence of glycine lowers this value, the effect being decreased by the addition of magnesium or sodium chloride. With increasing amounts of glycine, this effect reaches a maximum and then decreases, indicating that neutral glycine inactivates the HPO₄" ion. The formula $k=c_{a}f/(1-f)$ can be applied, where c_{a} is the concentration of glycine and 1-f is the fraction of HPO₄" inactivated by glycine. Sodium monohydrogen phosphate, as is to be expected, increases the pK_2' of glycine, an effect which is also produced by the sulphate ion. At an ionic strength $\mu = 0.2$, sodium oxalate, succinate, and citrate give curves parallel to that of the phosphate in their tendency to increase the pK_{2} of glycine, but at $\mu=0.01$ these salts tend to decrease the dissociation index in the order oxalate> succinate>citrate>phosphate>sulphate. This order does not correspond with the size of the ions or with the distances between the charges. Analogous effects are obtained with succinimide when these salts are added. L. S. THEOBALD.

New kind of dehydration. D. BALAREV (Kolloid-Z., 1929, 48, 63—70).—Previous work on the dehydration of gypsum is reviewed and shown to be contradictory. Some new experiments are described and these lead to the conclusion that the process of dehydration is a combination of two independent processes. The term "hemihydratic" is applied to this new form of dehydration. The apparently contradictory results of different investigators are explained on this view. E. S. HEDGES.

Equilibrium diagram of the cadmium-antimony system. T. MURAKAMI and T. SHINAGAWA (J. Study Met., 1928, 5, 283-296).-When the fused mass is rapidly cooled the β -phase, belonging to the metastable system, appears; on further cooling this is converted into the γ -phase of the stable system. When the cooling is slow, the y-phase is formed directly. The β-phase is a solid solution containing the compound Cd₂Sb₂ and forms a eutectic (395°, 54% Sb) with cadmium. It is present in the range 40-45% Sb, and is converted into the γ -phase, a solid solution containing the compound CdSb (eutectics with cadmium and antimony) at 250°. The solid solubility limits of cadmium in antimony are 0.15% at the eutectic temperature and less than 0.1% at the ordinary temperature; the solubility of antimony in cadmium is less than 0.1% at either temperature.

CHEMICAL ABSTRACTS. Action of gas on metals. II. The systems

chromium-nitrogen and manganese-nitrogen. G. VALENSI (J. Chim. phys., 1929, 26, 202-218; cf. this vol., 664).—Measurements of the dissociation pressures under isobaric conditions, viz., under 760 mm., show that in the case of chromium the solid phase contains about 29% N between 500° and 870°; 27% between 930° and 970°—this amount corresponds with CrN—and 12.6% between 1030° and 1200°. In the case of manganese the solid phase contains 15.4% N at 390°, and 6% at 1050°.

Chromium isotherms between 810° and 920° have ranges of constant pressures, which are probably the dissociation pressures of chromium nitride at the respective temperatures. No such constant pressure range occurs in the manganese isotherms. The dissociation pressure of chromium nitride can be calculated from the expression log_e p=96.144 log_e T+88,444/T-750.61. H. T. S. BRITTON.

Ceramics of refractory substances. III. System ZrO_2 -ThO₂. O. RUFF, F. EBERT, and H. WOITINEK (Z. anorg. Chem., 1929, 180, 252-256; cf. this vol., 650).—When zirconium and thorium dioxides are heated together in the solid state there is no change in the lattices of the two oxides up to 2400°, but at 2600° formation of mixed crystals begins. From cooled liquid mixtures of the two oxides two series of mixed crystals are obtained ($a=5\cdot20$ and $5\cdot51$ Å.). The m. p. of zirconium oxide is gradually increased by the addition of thorium oxide, and extrapolation gives a value of $3050^{\circ}\pm25^{\circ}$ for the m. p. of the latter oxide. The presence of a lower oxide of thorium due to thermal decomposition or reduction could not be established. O. J. WALKER.

Binary system carbamide-ammonium nitrate. Molecular association in each component. W.J. Howells (J.C.S., 1929, 910-915) .- The equilibrium curve for the binary system ammonium nitrate-carbamide consists of two branches and exhibits a eutectic point at 44.7° and 47% of carbamide. The ammonium nitrate exhibits a transition point at 126°. Compound formation between these two substances does not occur at the temperatures involved. For dilute solutions, the molecular depression per 100 g. of carbamide is approximately 215. In molten carbamide, ammonium nitrate has an association factor approaching 2, and acctamide has an association factor approaching 3. For dilute solutions in molten ammonium nitrate, the molecular depression is about 221 per 100 g. In this solvent, water, carbamide, and lithium nitrate are all normal or nearly so, but sodium nitrate and acetamide are slightly associated. Potassium nitrate causes a sub-normal depression of the f. p., partly due to separation with the solvent in the form of mixed crystals. Calcium nitrate is slightly associated and ammonium chloride strongly associated in molten ammonium nitrate.

E. S. HEDGES.

Solubility in the gaseous phase, especially in the system $NH_3(liq.)-NH_3(gas)-H_2(gas)-N_2(gas)$. H. L. CUPPLES (J. Amer. Chem. Soc., 1929, 51, 1026—1033) —A "solubility effect" may be defined as a change in activity of one component caused by the presence of other components. No solubility effects are involved in the Poynting effect. Activity calculations for the system $NH_3(liq.) NH_3(gas)-H_2(g)-N_2(g.)$ at pressures up to 600 atm. and temperatures between -40° and 20° yield results for the percentage of ammonia formed from the free gases which agree substantially with the experimental results of Larson and Black (A., 1925, ii, 501, 852). There is no indication of a solubility effect of the gas phase for ammonia vapour. S. K. TWEEDY.

Thermal equilibrium between ethylene, iodine, and ethylene di-iodide. R. B. MOONEY and E. B.
LUDLAM (Proc. Roy. Soc. Edin., 1929, 49, 160-169) .--The dissociation pressures corresponding with the coexistence of ethylene di-iodide and iodine as solid phase have been measured over the range 11-65°. The vapour pressures of ethylene di-iodide in the absence of dissociation have also been determined between 16° and 33° and the results indicate a molecular latent heat of vaporisation of 15,700 g.-cal. Using the data obtained, together with Baxter's values for the vapour pressure of iodine, the equilibrium constant K of the reaction $C_2H_4+I_2 \Longrightarrow C_2H_4I_2$ has been calculated for a series of temperatures. It is found that the relationship between log K and 1/T is not linear. The divergence from linearity is ascribed to the lowering of the vapour pressure of iodine by adsorbed ethylene F. J. WILKINS. and ethylene di-iodide.

Thermal behaviour of phenols. II. The thermodynamics and the mechanism of the thermal decomposition of phenol and its homologues. A. HAGEMANN (Z. angew. Chem., 1929, 42, 503—508).—The behaviour of phenol and m-cresol during hydrogenation and in contact with hot catalysts (thermal decomposition) has been studied thermodynamically and the equilibria represented by equations. The results agree closely with those found experimentally. A. R. POWELL.

Aqueous solutions of copper and ferrous sulphates. F. K. CAMERON and H. D. CROCKFORD (J. Physical Chem., 1929, 33, 709—716).—At 30°, the solubility of copper sulphate in water is depressed by sulphuric acid. Copper and ferrous sulphates mutually depress the solubility of each other in water, and the presence of sulphuric acid augments the depression. With regard to the two solid phases in contact with copper sulphate, ferrous sulphate, sulphuric acid, and water it is suggested that one consists of copper sulphate pentahydrate and the other of a solid solution of ferrous sulphate, sulphuric acid, and water. The brick-red salt $CuSO_4$, $FeSO_4$, $2H_2O$ described by Etard (A., 1879, 104) could not be prepared.

L. S. THEOBALD.

System sodium iodate, sodium chloride, water. H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1929, [v], 17, 424—430).—Isotherms for this system have been determined at 35°, 25°, 15°, and 0°. The solid phases which occur are NaCl; NaCl,2H₂O; NaIO₃,H₂O; NaIO₃,5H₂O; and a double salt 2NaIO₃,3NaCl,10H₂O. The solid phases at the characteristic temperatures are: NaCl; NaIO₃,H₂O, and double salt (24·6°); NaIO₃,5H₂O; NaIO₃,H₂O, and double salt (6·8°); NaIO₃,5H₂O; NaCl, and double salt (0·04°). The temary eutectic temperatures are : ice, double salt, NaCl,2H₂O ($-21\cdot18^{\circ}$); ice, double salt, NaIO₃,5H₂O ($-16\cdot8^{\circ}$ to -17°). C. W. GIBBY.

Equilibria between water, the nitrates, and the subhates of sodium and of potassium. E. CORNEC, H. KROMBACH, and A. SPACK (Compt. rend., 1929, 188, 1250—1253).—These equilibria have been studied between -2° and 90° and the results obtained represented schematically for ten temperature ranges. Darapskite (Na₂SO₄, NaNO₃, H₂O) is present between 10° and 74°, whilst glaserite appears at 90° but not at -2° , at which temperature a saturated solution of the four salts is obtained. Glauber's salt is present

below 32.4°. Hamid's conclusions (A., 1926, 245, 246) that a triple salt exists at 25° and that sodium nitrate and glascrite cannot coexist were not confirmed. J. GRANT.

Systems Al(NO₃)₂-Fe(NO₃)₃-H₂O and KNO₃-Fe(NO₃)₃-H₂O at 0° and at 40°. G. MALQUORI (Atti R. Accad. Lincei, 1929, [vi], 9, 569-572).—In contact with solutions containing $37\cdot81-12\cdot33\%$ of aluminium nitrate the stable solid phase at 0° is Al(NO₃)₃,9H₂O. The phases Al(NO₃)₃,9H₂O and Fe(NO₃)₃,9H₂O are coexistent with a solution of composition 11.02% Al(NO₃)₃, 25.09% Fe(NO₃)₃, 63·89% H₂O. For solutions containing less than 11.02% of aluminium nitrate the stable phase is Fe(NO₃)₃,9H₂O. At 40° the invariant system corresponds with 17.12% Al(NO₃)₃, 32.69% Fe(NO₃)₃, 50·19% H₂O, the stable phases being the same as at the lower temperature. In the second system at 0° an invariant point corresponds with 38.55% Fe(NO₃)₃, 3.92% KNO₃, 57.53% H₂O, the stable phases being KNO₃ and Fe(NO₃)₃,9H₂O. No invariant point occurs in this system at 40°.

F. G. TRYHORN.

Isotherms at 20° of the systems $La(NO_3)_3$ -Mn $(NO_3)_2$ -H₂O, $La(NO_3)_3$ -Mg $(NO_3)_2$ -H₂O, and Mn $(NO_3)_2$ -Mg $(NO_3)_2$ -H₂O. C. DI CAPUA (Gazzetta, 1929, 59, 164—169).—An examination of these isotherms for the presence of double salts yielded negative results. Saturated solutions at 20° of the nitrates of lanthanum, manganese, and magnesium contain respectively 60·13, 56·81, and 43·68% of the salts. F. G. TRYHORN.

Individuality of heats of dilution of strong electrolytes. E. LANGE and J. MEIXNER (Naturwiss., 1929, 17, 273).—Preliminary. The integral heats of dilution V_c of uni-univalent strong electrolytes, even for concentrations below 0.01N, show definite differences, e.g., LiF>KF, LiF>LiBr, KF> KCl>KNO₃, KCl>CsCl, whilst the probable ionic diameters a show differences in the reverse order, Li⁺<K⁺<Cs⁺; F⁻<Cl⁻<Br⁻<NO₃⁻. For lithium fluoride and calcium sulphate V_c is greater than would be expected from the limiting law in the Debye-Hückel theory (a=0). It is shown that it is unnecessary to assume negative a value for positive deviations. R. A. MORTON.

Transference number of barium chloride as a function of the concentration. G. JONES and M. DOLE (J. Amer. Chem. Soc., 1929, 51, 1073-1091).--The Hittorf transport numbers, t, for barium chloride were determined over a hundred-fold concentration range in an improved apparatus of the Washburn type. The quantity 1/(1+t) is accurately a linear function of \sqrt{c} , the actual relationship being (i) t+1= $A/(1+B\sqrt{c})$, where A=1.4476 and B=0.07010. Previous determinations of transport numbers over large concentration ranges have all been effected by means of the E.M.F. method and the results do not conform with (i). E.M.F. of cells of the type Ag, AgCl/BaCl, (0.05M)/BaCl₂(c)/AgCl, Ag were, therefore, determined at 25°, where c varies between 0.001 and 1.0M, but the potentials found agreed almost exactly with those of Lucasse (A., 1925, ii, 399). The erroneous transport numbers calculated by this author from his E.M.F. results are attributed therefore to

the complicated graphical procedure which he was compelled to use. An analytical method of computation is given. Lucasse's data for cells without liquid junctions yield the following equation for the mean activity coefficients of the ions of barium chloride at 25° (cf. Hückel, A., 1925, ii, 513): (ii) log $f-0.15266c=-1.734\sqrt{c/(1+2.2318\sqrt{c})}$. Combination of (ii) with (i) yields a relationship between a (activity) and c, which permits an integration of the fundamental thermodynamic equation (iii) $dE=-(3RT/2F)td \ln a$. When treated in this way Lucasse's data give A=1.4372 and B=0.05409 in (i). Combination of the authors' E.M.F. data with Lucasse's data gives A=1.4500 and B=0.07135in (i). The analytical method, however, is regarded as the more trustworthy. S. K. TWEEDY.

Mobility of the hydrogen ion and the electrical conductivity of the halogen hydracids. (MLLE.) M. DE HLASKO (J. Chim. phys., 1929, 26, 125-148).-The electrical conductivities of aqueous solutions of hydrochloric, hydrobromic, hydriodic, bromic, and iodic acids have been measured at 25°. Values higher than those generally accepted have been obtained for the equivalent conductivities of hydrochloric, hydrobromic, and hydriodic acids at infinite dilution, being 431.5, 433.7, and 432.3, respectively. The mobility of the hydrogen ion is found to be 355.1. The densities and viscosities of the solutions used have been measured. The conductivities of aqueous solutions of bromic and iodic acids were calculated from the data for solutions of hydrobromic and hydriodic acids saturated respectively with bromine and iodine. Iodic acid is stronger than bromic acid. The constant for the hydrolysis of bromine in accordance with $2Br_2+H_2O = HBr_3+$ HBrO, in solutions saturated with bromine, can be calculated with the aid of the law of mass action. C. W. GIBBY.

Relation between electrical conductivity of solutions and their vapour pressure. T. DALH-BLOM (Teknisk Tidskr., 1928, 58, Kemi, 76—79; Chem. Zentr., 1928, ii, 2706—2707).—The expression $k \log p_0/p+rC=nF$, where C is the conductivity, p_0 and p are the vapour pressures of the solvent and salt solution of concentration n, respectively, and k, r, and F are constants, is derived. Hence $12.45\Delta t + rC=nF$, where Δt is the depression of the f. p. A theoretical explanation is offered.

A. A. ELDRIDGE.

Number of water and alcohol molecules associated with the silver ion. G. C. SCHMIDT and M. KELLER (Z. physikal. Chem., 1929, A, 141, 331-342).— The general question of the number of solvent molecules associated with ions is critically discussed. The presence of at least a few silver ions in alcoholic and aqueous solutions of silver nitrate is inferred from the fact that a current passes on the application of the smallest E.M.F. It has been shown by means of cryoscopic and conductivity experiments that both ammonia and pyridine when added to such solutions give rise to a complex ion AgX_2 , which is more soluble in alcohol than in water. Further addition does not result in the binding of more ammonia or pyridine. The transference numbers of these com-

plex silver ions have been determined and compared with those of the silver ion in both alcoholic and aqueous solutions of silver nitrate. The conclusion reached is that there are on the average two solvent molecules associated with the silver ion, assuming that the volumes occupied by the molecules of ammonia and water are in the ratio 94/85 as found by Grimm. Measurements of the conductivity when increasing amounts of ammonia and pyridine are added to dilute aqueous solutions of silver nitrate point to an equilibrium $Ag(NH_3)_2 \Longrightarrow Ag(H_2O)_n$. In aqueous solutions there appears to be an equilibrium between the ions $Ag(H_2O)_2$, $Ag(H_2O)$, and Ag, and similarly for the alcoholic solution. F. L. USHER.

Electrochemistry of the system AlBr₃-KBr in benzene. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1585-1592).-See this vol., 144.

Electrochemistry of solutions of phosphorus pentachloride in bromine. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1505-1512).—See this vol., 144.

Single potential of the copper electrode. E. NEWBERY (J. Amer. Chem. Soc., 1929, 51, 1315– 1322).—The varying values which have been recorded for the potential of the copper electrode are attributed to the rapid formation of a thin film of basic salts, and a method is described whereby the potential may be ascertained before this film has had time to form. The single potentials of pure copper and of twophase copper amalgam are found experimentally to be identical, whence, from the work of Nielsen and Brown (A., 1927, 1144), the standard potential of copper referred to the normal hydrogen electrode is 0.3502 volt. S. K. TWEEDY.

Single potential of the nickel electrode. E. NEWBERY (J. Amer. Chem. Soc., 1929, 51, 1429-1436).-The potential of nickel in a solution of its ions is uninfluenced by the purity of the nickel salt and by metallic impurities or gaseous oxygen in the electrode, but it is very much affected by the physical state of the electrode surface and by the presence of gaseous hydrogen. The electrode appears to react somewhat with the electrolyte. The potential was investigated by observations on a cell of the type Ni|NiSO40.5M|Hg2SO4|Hg, special precautions and technique being adopted. For each abrading material used to polish the electrode there is a definite limiting potential. Constant and reproducible values are obtained only when the nickel is treated anodically with a small current density insufficient to produce passivity. It is suggested that two allotropes of nickel exist, one, preponderating in amorphous nickel, having a potential of 0.45 volt or more (referred to N-hydrogen electrode) and the other a potential of 0.05 volt or less; the equilibrium of these allotropes in ordinary nickel accounts for the third observed potential, 0.17 volt. This hypothesis also affords an explanation of the retardation phenomena observed during the electrolytic deposition of nickel and of the electrodeposition of polished nickel. It is probable that the true reversible potential of a metal giving rise to hydrated ions cannot be directly determined. S. K. TWEEDY.

Electrolytic potentials of some metals. L. BOUCHET (Compt. rend., 1929, 188, 1237-1239).--The electrolytic potentials of magnesium, zinc, hydrogen, copper, and silver are -1.766, -1.052, -0.281, 0.041, and 0.502, respectively, compared with the N-calomel electrode at 18-24°. Slight variations with the salt used were obtained in the case of zinc.

J. GRANT.

Calcium amalgam electrode in dilute aqueous solutions. R. J. FOSBINDER (J. Amer. Chem. Soc., 1929. 51, 1345-1356).-The activity coefficients of calcium chloride up to 3.3M were determined from E.M.F. measurements on cells of the type : Ag $AgCl[CaCl_{o}(c)]Ca$ amalgam[CaCl_{o}(0.0099M)]AgCl[Ag], the results, up to 1M, being in agreement with those of Lucasse (A., 1925, ii, 399). An apparatus suitable for determining the activity coefficients of calcium ions, including a dropping calcium amalgam electrode, is described, and used for determining the said coefficients from 0.01 to 0.001 M in calcium sulphate, lactate, hydroxide, chloride, and acetate solutions at about 25°. The results are in approximate agreement with the requirements of the Debye-Hückel theory. Addition of electrolyte or protein lowers the potential of the calcium amalgam electrode. Experiments on dog's blood show that the electrode is useless for determining calcium-ion activity in any solution containing cations other than calcium. Proteins probably form a skin over the electrode, thus hindering the establishment of true electrochemical equilibrium.

S. K. TWEEDY.

Potential of inert electrodes in solutions of sulphurous acid and its behaviour as an oxidising and reducing agent. A. A. Noves and H. H. STEINOUR (J. Amer. Chem. Soc., 1929, 51, 1409-1428).—Experiments relating to the potential E of a platinised platinum electrode in solutions containing sulphite and hydrogen ions (cf. Carter and James, A., 1925, ii, 134) are described. Under quiet conditions E is fairly constant, but on prolonged agitation of the solution it becomes more negative and then gradually increases to the quiet-state value. A combination of catalytic and adsorption effects at the electrode is the possible explanation. The potential is not accidental; at 25° it is given empirically by $-0.37-0.0296 \log [H^{-}]^{4/3}$. It is due to sulphurous acid and some decomposition product of this acid. It is independent of the initial condition of the electrode and is scarcely affected by the presence of sulphuric, hydrochloric, and dithionic acids. The aforesaid decomposition product is probably hyposulphurous acid (H2S2O4, which the authors, in accordance with a systematic nomenclature which they propose for certain sulphur acids, rename "dithionous acid "), and the nearly constant value of E is said to be due to the rate of production of this acid from sulphurous acid, being equal to the rate at which it spontaneously decomposes. Addition of sulphur has no influence on E at low temperatures, but at higher temperatures it may affect the potential because of the accelerated rate of decomposition of the hyposulphurous acid. The potential is complicated by the presence of oxygen, since this latter assists the decomposition of the hyposulphurous acid. A quantitative interpretation of the chemical

behaviour of sulphurous acid is given, and the free energy changes of several ionic reactions involving sulphur acids are calculated. S. K. TWEEDY.

Electromotive behaviour of aluminium and its amalgams. R. MÜLLER (Z. Elektrochem., 1929, 35, 240—249).—The potentials set up between aluminium and aluminium amalgams, respectively, and nonaqueous solutions containing aluminium bromide have been investigated by comparing them with the potentials of certain silver comparison electrodes. In one case, the liquid phase consisted of fused aluminium bromide and potassium bromide, whilst in another, aluminium bromide was dissolved in pyridine. The data show that the potential of aluminium and its amalgams with regard to a particular solution is the same and is independent of the composition of the amalgam.

Several experiments were made to ascertain the decomposition potentials of aluimnium and bromine from non-aqueous solutions, using either platinum or mercury as cathode. H. T. S. BRITTON.

Behaviour of the antimony electrode in buffered and unbuffered solutions. V. G. LAVA and E. D. HEMEDES (Philippine Agric., 1928, 17, 337—349).—Antimony electrodes, which are recommended for sugar solutions but not for soils, were tested in buffer solutions of potassium dihydrogen phosphate and sodium hydroxide and in mixtures of 0.01N-sodium hydroxide and 0.01N-hydrochloric acid at 26—29°; the $p_{\rm H}$ is given by $E=0.052\pm0.057$ $p_{\rm H}$.

CHEMICAL ABSTRACTS.

Influence of the solvent on the E.M.F. of silver halide cells. I. Water-ethyl alcohol mixtures. A. S. AFANASIEV (Z. Elektrochem., 1929, **35**, 220-222, and J. Russ. Phys-Chem. Soc., 1929, **61**, 613-618).—Measurements were made of the E.M.F. of cells of the type Ag|AgCl,KCl|KBr,AgBr|Ag in the half-elements of which various solvent media, consisting of mixtures of water and ethyl alcohol in differing proportions, were used. The E.M.F. found were in good agreement with those obtained by calculation, using Brodsky's formula (A., 1926, 688) which he developed for the E.M.F. of similar mercurous halide concentration cells containing various nonaqueous solvents. H. T. S. BRITTON.

Oxidation-reduction. XIV. Equilibrium potentials of sodium 2:6-dibromobenzenoneindophenol-2'- and -3'-sulphonates, 2:6:2'-trichlorobenzenoneindophenol, and 2:6-dimethylbenzenoneindophenol. W.L. HALL, P.W. PREISLER, and B. COHEN (U.S. Public Health Rep., Suppl. 71, 1928, 26 pp.).—The equilibrium potentials and dissociation constants of the four compounds mentioned in the title have been determined at 30° by methods previously described (cf. A., 1923, ii, 726; 1924, ii, 597). Deflexions in the $E'_0 - p_{\rm ff}$ curves (where E'_0 is the potential corresponding with an equimolecular mixture of oxidant and reductant) denote detectable dissociation, and when the change in slope $(-dE/dp_{\rm fl})$ is negative, the dissociation causing the change is assigned to the reductant : when the change is positive, dissociation is attributed to the oxidant. The first three of the above compounds occupy positions on the extreme electropositive side (*i.e.*, most easily reducible) of the indophenol series. The effect of

substituting sulpho-, chloro-, and methyl groups is discussed, and a list of 13 useful oxidation-reduction indicators is given together with values of E'_0 at $p_{\rm fl}$ 5.0—9.0 and 30°. H. BURTON.

Polarographic studies with the dropping mercury cathode. I. Amphoterity of ferrous hydroxide. B. SCHRAGER (Coll. Czech. Chem. Comm., 1929, 1, 275—281).—Measurements with the polarograph show that ferrous hydroxide dissolves slightly in aqueous solutions of sodium hydroxide, owing to the reaction $Fe(OH)_2 + OH' \longrightarrow Fe(OH)'_3$, the ratio $[Fe(OH)_3'/[OH']$ having the value 5×10^{-5} . From the value for the deposition potential of ferrous iron in the solution, the value of the product $[Fe''][OH']^2$ is calculated to be 7×10^{-13} . Cobaltous and manganous hydroxides also show acidic properties. R. CUTHILL.

Tervalent chromium. (MME.) N. DEMASSIEUX and J. HEYROVSKY (J. Chim. phys., 1929, 26, 219-223) .- Polarisation curves obtained with the " polarograph " during the electrolysis of tervalent chromium salt solutions of different concentrations, in which the dropping mercury electrode is used, are described, and the inflexions are attributed to either $Cr^{\dots} \rightarrow$ Cr'' + F or $Cr'' \longrightarrow Cr + 3F$. The curves are stated to show that the less hydrated chromium ions in the green salts (according to Werner's theory) are reduced and discharged at potentials which are more positive than those at which the more hydrated chromium ions in the violet salts become reduced. This is true of the chloride and sulphate solutions, although with the latter the abnormally great displacements of the potentials at which reduction occurs indicate that the complexity of the ions varies with dilution in passing from the green to the violet form. The potentials at which reduction occurs in potassium and rubidium chrome alum solutions are coincident, and indicate, it is believed, the progressive dissociation of the anion complexes. The constitution of chrome alums is compared with that of simple salts. No reduction occurs in alkaline chromium hydroxide solutions, which is regarded as proof of the colloidal nature of the hydroxide, in contrast with solutions of zincates and plumbites in which reduction has H. T. S. BRITTON. been observed.

Influence of glycine on the electrical conductivity of salt solutions. T. MURAYASU (Hokkaido J. Med., 1928, 6, 328—336).—The reduction of the conductivities of 0.5M-solutions on the addition of glycine diminishes in the order : hydrogen chloride, sodium chloride, cobalt nitrate, sodium carbonate, calcium chloride, potassium dichromate, barium chloride, aluminium chloride, ammonium chloride; with ferric chloride, chromic chloride, zinc sulphate, copper sulphate, magnesium sulphate, potassium ferrocyanide there is an increase in conductivity which diminishes in the order given.

CHEMICAL ABSTRACTS.

Anodic behaviour of aluminium. W. J. MÜLLER and K. KONOPICKY (Z. physikal. Chem., 1929, 141, 343—377; cf. A., 1928, 247).—The theories hitherto advanced to explain the anodic passivity and valve action of aluminium electrodes are critically examined. Measurements have been made of the

rate of decrease of the current under a constant P.D. and Meserve's observation, that after the lapse of a certain time this is inversely proportional to the square of the current strength, has been confirmed. It is therefore improbable that the action is due to the formation of a protective film of oxygen, which according to the authors' results can occur only if the aluminium is made chemically passive. The gas evolved at an aluminium anode has been examined and shown to contain a varying quantity of hydrogen, a result in agreement with the theory that the anodic passivity is due to a layer of hydroxide, since aluminium even when highly anodically polarised is still chemically active and capable of liberating hydrogen from the electrolyte. The oxygen produced is not formed at the surface of the metal but on the skin of hydroxide covering it. It has further been shown that the hydroxide layer is the seat of both resistance and capacity, and it cannot therefore be assumed that the latter is due to a film of oxygen. The dissipation of the charge in a formed anode follows the normal course of the discharge of a condenser through a resistance as long as the electrolyte is approximately neutral. The conclusion reached is that, as an anode, aluminium becomes covered with a gelatinous layer of hydroxide which must be negatively charged and consequently pressed against the metal, whilst the electrolyte is expressed from the pores of this gel by cataphoresis. The reverse process occurs when the aluminium becomes the cathode. An expression based on this view has been deduced giving a relation between current strength and time which is in complete agreement with the experimental results. F. L. USHER.

Application of reduced equations to chemical reactions. W. SWIENTOSLAWSKI and J. G. ZAWIDZKI (Rocz. Chem., 1929, 9, 246—265).—Curves expressing the velocity of chemical reactions are plotted using the reduced co-ordinates x' and τ , where τ is the time necessary for the reaction of a definite fraction (x'=1/n=1/4, 1/2, or 3/4) of the substrate. Using these co-ordinates, the initial concentration of substrates and the velocity coefficient are eliminated from the velocity equation, so that one single curve is obtained for all equations of the same order for a given value of n. The value of this simplification for the investigation of the problems of kinetics is discussed. R. TRUSZKOWSKI.

Ignition of combustible gas with three-part spark. T. TERADA, K. YUMOTO, and R. YAMAMOTO (Proc. Imp. Acad. Tokyo, 1929, 5, 125-126).-The three-part spark is a special type of long spark produced when a spark gap is charged up gradually by a statical machine, when the ratio of the gap to the diameter of the spherical electrodes is greater than 2, and the potential of the positive electrode is lowered by earthing, or by a needle-point leakage. The spark is tripartite, the positive and negative parts being smooth and continuous, whilst the centre is split and of greater luminosity. Ignition of coal gas occurs easily in the positive or negative portions of the spark, but the character of the spark is altered during the process. Minimum frequency of ignition was found at the junctions of the positive and negative portions with the middle of the spark. A maximum occurs at a point slightly to the negative side of the centre of the spark. Frequency of ignition approaches 100% at the surface of the negative electrode, and falls nearly to zero at the positive surface.

F. G. TRYHORN.

Ignition temperatures of mixtures of carbon monoxide and air. M. PRETTRE and P. LAFFITTE (Compt. rend., 1929, 188, 1403—1405).—The authors' method (this vol., 271) shows that the ignition temperature of air containing 10-40% of carbon monoxide is approximately 655°, but that it rises rapidly for higher concentrations. The higher is the temperature of the mixture the greater are its limits of inflammability. Traces of residual burnt gases do not affect the results as in the case of hydrogen (*loc. cit.*), but water vapour and traces of hydrogen lower the ignition temperature, the latter to an extent increasing with its concentration (*e.g.*, 80° for 0-005 part). J. GRANT.

Photographic investigation of flame movements in carbon monoxide-oxygen explosions. W. A. BONE and R. P. FRASER (Phil. Trans., 1929, A, 228, 197-234).—A camera for photographing explosion waves is described. The film is fixed to the periphery of a wheel 6" in diameter, which can be driven by a friction drive at any speed between 30 and 12,000 r.p.m. The flame velocity in mixtures of carbon monoxide and oxygen is diminished by intensive drying, but the mixture could still be ignited after 240 days' drying. The effects of intensive drying can be overcome by applying an electric field throughout the duration of the explosion. There is always an induction period when feeble sources of ignition are used. With condenser discharges the general flame speed is not greatly accelerated by considerable increases in spark intensity, but combustion was retarded when violent flame oscillations were set up by very heavy sparks. The flame oscillations are held to be due either to repeated reflexions of the two opposite compression waves from the ends of the explosion tube or else to compression of unburnt gas in front of the flame and/or contraction of the burnt gas behind it. Flame speeds may be raised by "shock waves " from one uniform rate to another by abrupt steps. C. W. GIBBY.

Role of electrical carriers in the explosion of combustible gases mixed with air. F. HABER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 11, 162-170).—The deformation of the explosion zone and the effect on the velocity of transmission of ignition produced by the passage of explosive mixtures with air through the continuous field of a redge-shaped condenser have been studied. The deformation is not a general property of flame and occurs only in gas mixtures which are good conductors. It diminishes when the continuous field is replaced by an alternating field of high frequency. From the results obtained with mixtures of various gases with air it is concluded that uncharged radicals and not electrical particles are responsible for the process of combustion and especially for the velocity of propagation of ignition. The uncharged radicals are produced with less expenditure of energy than the charged, and only in the case of the groupings C·C and possibly CH, which possess low excitation potentials, is the ionisation potential low enough to bring about in an air flame an appreciable fission into ions and electrons. The essential source of ionisation is the chemical energy of the elementary processes of combustion. L. S. THEOBALD.

Unimolecular reactions. D. G. BOURGIN (Proc. Nat. Acad. Sci., 1929, 15, 357-362).—The new quantum mechanics is applied to the study of unimolecular reactions, with special reference to the N2O5 molecule, and the problem is shown to be closely allied to that of thermionic emission and radioactive disintegration. A particular mode of decomposition described by the severing of a certain linking is considered and an intermediate region in which the energy exceeds the dissociation energy is assumed. The molecular motion is described by a Schrödinger wave equation and an expression for the reaction velocity is finally obtained in which the parameters may be determined from band spectra data as well as from reaction rate experiments. A means is provided for estimating the equilibrium point of the unimolecular decomposition. N. M. BLIGH.

Oxidation of iodide ion by persulphate ion. I. Effect of tri-iodide ion formation on the reaction velocity. E. JETTE and C. V. KING (J. Amer. Chem. Soc., 1929, 51, 1034—1047).—The kinetics of the reaction $2KI+K_2S_2O_8=2K_2SO_4+I_2$ have been studied. The results indicate that the tri-iodide ion reacts with the persulphate ion, and at a rate which is approximately one half of that of the iodide ion (cf. Kiss and Zombory, A., 1927, 632, etc. which work is criticised), so that the observed velocity is the sum of the velocities of two reactions. The tri-iodide ion probably does not act as a catalyst for the main reaction. S. K. TWEEDY.

Oxidation of iodide ion by persulphate ion. II. Effect of removing the products of the reaction on the reaction velocity. C. V. KING and E. JETTE (J. Amer. Chem. Soc., 1929, 51, 1048-1057).-The results previously obtained (preceding abstract) were confirmed and found to hold for higher concentrations also. The confirmation was effected by conducting experiments in which the iodine was removed either by means of organic solvents or by reaction with sodium hydroxide. The reaction was also studied in presence of neutral salts (nitrates of magnesium, calcium, sodium, and barium; sulphates of calcium and potassium). Removal of the sulphate ion (as barium or calcium sulphate) probably does not increase the velocity of the main reaction. The equilibrium constant of the reaction $I_2+I' = I_3'$ in 0.1M-potassium nitrate solution was also determined. S. K. TWEEDY.

Kinetics of oxidation of organic compounds by bromine. II. Action of bromine on formic acid. E. JÓSEFOWICZ (Rocz. Chem., 1929, 9, 309– 325).—The velocity of reaction between dilute aqueous solutions of bromine and formic acid is expressed approximately by the equation $dx/dt=k(a-x)^2/2x$, where a is the initial concentration of formic acid

and x that of hydrogen bromide at time t. The value of k diminishes progressively. The velocity equation in the presence of excess of hydrogen bromide is $dx/dt = \hat{k}(a-x)^2/(c+2x)$, c being the initial concentration of hydrogen bromide. In the presence of excess of hydrogen chloride or nitric acid, dx/dt = $k(a-x)^2/(0.75c+2x)$. The addition of bromides, chlorides, or nitrates has little influence on the reaction velocity, which is, however, considerably accelerated by the addition of sodium sulphate, which increases the $p_{\rm H}$ of the solution. The velocity of this reaction is unaffected by light. Its temperature coefficient for the interval 20-30° is 2.26. The reaction takes place between bromide and formate ions. The retardation of reaction by hydrogen bromide is due partly to diminution of dissociation of formic acid owing to hydrogen ions and partly to combination of bromide ions with molecules to yield inactive tribromide ions. R. TRUSZKOWSKI.

Concentration of sugar and rate of hydrolysis in an acid medium. H. COLIN and A. CHAUDUN (Compt. rend., 1929, **188**, 1291–1292; cf. A., 1925, i, 233).—The ratio k_{40}/k_5 for the hydrolysis of sucrose (loc. cit.) which decreases with the concentration of acid (for hydrochloric, sulphuric, oxalic, or acetic acid) may be less than unity at high dilutions and bears no simple quantitative relation to the $p_{\rm H}$ value. The arbitrary nature of Moran and Lewis' correction for the volume of water liberated on hydrolysis (loc. cit.) is indicated. J. GRANT.

Decomposition of sodium sulphate. (MLLE.) G. MARCHAL (Bull. Soc. chim., 1929, [iv], 45, 225— 228).—The rate of decomposition of sodium sulphate has been studied by heating the anhydrous substance in a resistance furnace in a stream of dry nitrogen, the amount of change being ascertained from the loss of weight. By heating alone at 1300° the loss of weight was 4.23% in 4 hrs. Admixture of silica or of alumina greatly increased the initial rate of decomposition, the loss of weight after the first hour being 14.14% for silica and 22.03% for alumina, using equimolecular proportions in each case. The reaction can be utilised for the preparation of alumina in a pure state from minerals containing it.

F. L. USHER.

Reactions [and corrosion phenomena] at high pressures. E. BERL.—See B., 1929, 419.

Oxidation of iron and steel at high temperatures. L. B. PFEIL.—See B., 1929, 437.

Effect of cold-working on corrosion of iron and steel. H. ENDÔ.—See B., 1929, 437.

Corrosion of steel by acid solutions. H. ENDÔ. —See B., 1929, 437.

Corrosion of aluminium. J. CALVET.—See B., 1929, 438.

Corrosion of aluminium alloys. QUILLARD and BASCOU.—See B., 1929, 477.

Application of the logistic function to experimental data. L. J. REED and J. BERKSON (J. Physical Chem., 1929, 33, 760-779).—Mathematical. In view of the erroneous conceptions which exist concerning this function, the basic properties of the equation are reviewed. Applications to autocatalytic reactions, bimolecular reactions, and to oxidation and reduction potentials are discussed.

L. S. THEOBALD.

Catalysis of the reaction between persulphate and iodine ions. II. Velocity of ionic reactions. A. von KISS (Rec. trav. chim., 1929, 48, 508—516).— The results originally obtained (A., 1927, 632) have been confirmed, and an error in Saal's calculation (A., 1928, 484) is demonstrated. Measurements have been made of the velocity of the reaction between the ferric and iodide ions in dilute solution.

H. F. GILLBE. Autocatalytic decomposition of thiosulphuric II. K. JABŁCZYNSKI and S. FRENKENBERG acid. (Bull. Soc. chim., 1929, [iv], 45, 210-217; cf. A., 1926, 913).—The influence of sulphur nuclei, of "sulfidale" (a medicinal preparation of finely divided sulphur), and of mastic on the rate of decomposition of thiosulphuric acid solutions has been studied by measuring the opacity of acidified solutions of sodium thiosulphate, gum arabic being present in all cases. The addition of sulphur nuclei, obtained by dialysing a reaction mixture left over from a previous experiment, caused the time of half change (t) to decrease. The difference between the values of t without and with sulphur nuclei is nearly proportional to the quantity of nuclei added. When this quantity is very large the reaction ceases to be autocatalytic and becomes unimolecular, the sulphur as it is produced being deposited on the nuclei already present, and no fresh nuclei being formed. "Sulfidale," in which the sulphur particles have an average diameter of 1.54 µ, and a colloidal suspension of mastic also exert an accelerating influence on the reaction, and to about an equal extent, but the period of induction is longer than when colloidal sulphur is added. It is considered that the colloidal sulphur liberated during the reaction acts by destroying the condition of supersaturation, whereas "sulfidale" and mastic behave at first like indifferent solids, becoming catalytically active only after they have adsorbed a sufficient quantity of colloidal sulphur.

F. L. USHER.

Reaction kinetics of heterogeneous catalysis. W. FRANKENBURGER (Z. Elektrochem., 1929, 35, 278–283).—A theoretical discussion of the mechanism of the various stages, their temperature coefficients and reaction orders, of decompositions occurring at the surfaces of catalysts. H. T. S. BRITTON.

Decomposition reactions during catalytic hydrogenation in presence of nickel. Rôle of the catalyst in heterogeneous catalysis. A. A. BALANDIN (Z. physikal. Chem., 1929, B, 3, 167—194). —From an examination of a large amount of experimental data on the catalytic hydrogenation of organic compounds in presence of nickel (cf. Senderens) it is shown that there is a definite order in which the various atomic groups are eliminated from the original molecule (compounds involving only the six elements hydrogen, carbon, nitrogen, oxygen, chlorine, and bromine are considered). The linkings which are most easily broken are not those which are most unstable in the free molecule. The ease with which a particular atom or group of atoms is eliminated from the molecule depends on its affinity towards the catalyst, which acts by weakening the linking between that atomic group and the rest of the molecule. The nature of the catalyst is therefore an important factor. This view is illustrated also by means of a number of other reactions which are catalysed by nickel, e.g., dehydrogenation of hydrocarbons, amines, and alcohols, hydrogenation of double linkings, dehydration of alcohols, and many condensation reactions. O. J. WALKER.

Promoter action of copper and copper oxide on the reaction $2H_2 + O_2 = 2H_2O$. I. Oxidation velocity of copper. II. Reduction of cupric oxide. III. Autocatalysis in the heterogeneous system. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1928, 31, 300-306, 399-406, 407-410.)-I. The velocity of oxidation of copper in the atmosphere of oxygen at 0.12 mm. was investigated. The surface of the bulb of a mercury thermometer was covered with the thin layer of copper. Through the bulb a thin glass capillary spiral tube was passed, and sealed at its ends to the wall of the bulb. This capillary tube carried in it an electrically heated spiral of platinum wire $(10 \text{ cm.} \times 0.1 \text{ mm.})$. Thus the mercury in the bulb, together with the thin layer of copper on it, could be heated to any desired temperature. The reaction velocity was determined by the change of pressure, which was measured by means of the McLeod manometer. The velocity of oxidation increased with time, according to the equation -dp/dt =kpt, where p and t are the pressure and time, respectively. This increase was thought to be caused by the catalytic action of copper oxide, which was formed by the reaction, the action taking place at the copper-copper oxide interface. After some time, the velocity of oxidation decreased, owing to the decrease in the surface of copper and in the pressure of oxygen. The relation between the velocity of oxidation and temperature was given by the equation $\log k = -3823/T + 5.5$, where k and T are the velocity coefficient and absolute temperature, respectively.

II. The reduction of cupric oxide by hydrogen is autocatalytic even above 200°. The reaction is retarded by the presence of water vapour. When hydrogen is passed over cupric oxide the weight of the latter increases at first and then decreases. This initial increase in weight is due to surface adsorption of water vapour. By measuring the decrease in pressure and condensing the water vapour formed by liquid air, the velocity of reduction was found to be given by the equation $-dp/dt = kpt/(p_0-p)$, where P_0 and p were the initial pressure of hydrogen and the pressure at the time t, respectively. The velocity coefficient k at T° Abs. is given by: $\log k = -5257/T + 7.38$.

III. The autocatalysis in the heterogeneous reaction can be easily explained by Volmer's nucleus theory, but it still remains doubtful whether all autocatalytic actions in a heterogeneous system are due to the removal of the difficulty of the formation of nuclei. There are two possibilities, namely, (1) facilitation of the rate of the molecular change, and (2) the removal of the difficulty of nucleus formation. Y. NAGAI.

Catalytic action of some compounds containing iron. H. VON EULER, H. NILSSON, and D. RUNEHJELM (Svensk Kem. Tidskr., 1929, 41, 85-92).—The catalase activity of hæmin and of certain allied compounds on solutions of hydrogen peroxide (0.008-0.009M) has been determined and the constant K = k/[millimol. Fe] calculated, where k is the velocity coefficient of the reaction and (millimol.Fe) the concentration in millimols. per litre of the ironcontaining compound under examination. The values found are for hæmin K=0.06, for pyratin, C30H28O4N4FeCl (prepared by heating hæmin with resorcinol at 180–190°) K=0.8, mesohæmin K=1.1-1.7, and deuterohæmin K=1.0. The buffers used appear to influence the values of the constants. All these substances bring about the oxidation of reduced phenolphthalein by hydrogen peroxide, their activities being approximately proportional to 100, 1000, 125, and 200, respectively. W. O. KERMACK.

Catalytic reduction of carbon monoxide under normal pressure. I. Investigation of catalytic activity of metals by means of heating curves. II. Investigation of effect of foreign substances on catalytic activity of cobalt by means of heating curves. S. KODAMA (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 277–283, 284–287).-I. The catalytic effect on the reduction of carbon monoxide with hydrogen of metals obtained by reduction of their oxides has been examined at temperatures up to 450° by means of heating curves. Copper reduced at 180° has no action. Nickel brings about the formation of hydrocarbons, whilst cobalt causes separation of carbon in addition. With cobalt, but not with nickel, the catalytic activity depends on the temperature at which the metallic oxide was reduced. Iron is oxidised with separation of carbon, and no hydrocarbons are formed. Cobalt, nickel, and the oxidised iron decompose pure carbon monoxide.

II. If the cobalt is charged with thoria, no carbon separates, but hydrocarbons are still formed. Charging with copper has a similar effect, but the activity of this catalyst is rather less. Aluminium oxide and manganous oxide have a deleterious influence on the activity, and potassium carbonate favours the separation of carbon. R. CUTHILL.

Nature of carbon produced by catalytic decomposition of carbon monoxide with iron. T. WATANABE (Bull. Inst. Phys. Chem. Res., Japan, 1929, 8, 288—292).—The carbon produced by the catalytic decomposition of carbon monoxide proves, from X-ray examination, to be of a graphitic nature. The higher is the temperature of its formation, the more does it approximate to the normal structure of graphite, the smaller is its adsorptive power, and the higher its density. R. CUTHILL.

Thermal decomposition of methane. I. Decomposition in silica bulbs. G. C. HOLLIDAY and H. C. EXELL (J.C.S., 1929, 1066-1074).—The decomposition of methane on silica at temperatures between 800° and 1200° has been studied. Extremely slow decomposition follows a very rapid initial one, and a practically stable mixture is obtained containing more methane than is present at true equilibrium. The lower is the initial pressure the greater is the final amount of decomposition. Hydrogen added initially behaves in the same way as that produced in the reaction. It is considered that the retardation is due to preferential adsorption of hydrogen, protecting the surface. Similar results were obtained with porcelain; no retardation was observed with a nickel catalyst. The effect of temperature on the false equilibrium is analogous to that on a true equilibrium. Ethane gave the same false equilibrium mixture as methane. C. W. GIBBY.

Kinetics of the catalytic dehydrogenation of decahydronaphthalene. N. D. ZELINSKI and A. A. BALANDIN (Bull. Acad. Sci. U.S.S.R., 1929, No. 1, 29-52) .- The degree of dehydrogenation of decahydronaphthalene was determined by measuring the volume at N.T.P. of hydrogen evolved on passing a known volatilised quantity of decahydronaphthalene over a layer of a suitable catalyst heated in an electric furnace. The catalysts used were platinised charcoal (30% Pt), platinum-black (30%) on asbestos, and nickelised asbestos (72% Ni). In the case of platinised charcoal it was found that dehydrogenation is almost complete (99%) at 333° and that it is much more effective than platinum-black on asbestos. The same method was used for investigating the dehydrogenation of cyclohexane using platinised charcoal, genation of cyclohexane using platinised charcoal, palladised asbestos, and nickelised asbestos as cata-lysts and the dehydrogenation of piperidine using platinised asbestos and palladised asbestos as cata-lyst. By using Arrhenius' relation $k=k_0e^{-Q/RT}$, values of k_0 and Q for dehydrogenation of decahydro-naphthalene are obtained as follows : using platinised charcoal $k_0=7\cdot128\times10^{10}$, Q=18890 g.-cals., using platinum-black on asbestos $k_0=2\cdot202\times10^{10}$, Q=18990g.-cals., and using nickelised asbestos $k_0=3\cdot63\times10^4$, Q=9990 g.-cals. For the dehydrogenation of cyclo-hexane using platinised charcoal $k_0=1\cdot12\times10^9$, Q=hexane using platinised charcoal $k_0 = 1.12 \times 10^9$, Q =18040 g. cals., using palladised asbestos $k_0 = 5.754 \times 10^7$, 18040 g.-cals., using paradised aspestos $k_0 = 0.704 \times 10^4$, Q = 15300 g.-cals., and using nickelised asbestos $k_0 = 1.143 \times 10^2$, Q = 9710 g.-cals. From the data of Zelinski and Pavlov (A., 1923, i, 767) for the use of platinised asbestos, $k_0 = 1.122 \times 10^9$, Q = 18040 g.-cals. Dehydrogenation of piperidine using platinised asbestos gives $k_0 = 5.00 \times 10^6$, Q = 19930 g.-cals., and by using palladised asbestos $k_0 = 6.026 \times 10^8$, Q = 16250 g.-cals. From these results the authors conclude that the energy of activation (Q) as well as the temperature the energy of activation (Q) as well as the temperature coefficient of the reaction velocity (k_0) are independent of the nature of the catalysed substance and depend only on the catalyst used. By plotting the reciprocal of the temperature against the logarithm of the percentage of hydrogen evolved they obtain, instead of straight lines, lines bent upwards at a temperature of abour 270° and explain this as being due to a much larger decomposition of the hydrocarbon with a consequent formation of a thin, invisible layer of carbon on the catalyst, the catalytic activity of which is therefore lowered. Different experiments at temperatures below 270° give in all cases the same volumes of hydrogen, whilst by heating at temperatures above 270° and subsequently determining the volume of hydrogen evolved on dehydrogenation at temperatures below 270° the volume of hydrogen evolved is less.

The authors also investigated the effect of addition of pure naphthalene on the dehydrogenation of deca. hydronaphthalene and of the addition of benzene on the dehydrogenation of cyclohexane. The effect was measured by determining the volume at N.T.P. of hydrogen evolved and also by the increase in density and of the refractive index of the different mixtures. They conclude that the effects of addition of one of the products of the reaction are rather complicated and that the effects of adsorption are of the greatest importance. A. FREIMAN.

Topochemical reactions. V. KOHLSCHÜTTER (Helv. Chim. Acta, 1929, **12**, 512—529).—A lecture, giving a general account of topochemical reactions, *i.e.*, reactions which are localised at a particular point in a reacting system, as distinct from reactions which take place throughout a homogeneous gaseous or liquid phase. The process of crystallisation is dealt with in particular. O. J. WALKER.

Electrolysis of [solutions of electrolytes in] water with alternating current. A. CANAUD (Compt. rend., 1929, 188, 1397—1398).—The volumes of hydrogen evolved during the electrolysis of 0.001*M*aqueous solutions of electrolytes with electrolytic iron electrodes, by an alternating current of 50 cycles at 110 volts, have been redetermined under more refined conditions (cf. A., 1928, 489). The volume decreases slightly with increase in mobility of the cations for the non-hydrolysable sulphates, and is high and low in the presence of hydrogen and hydroxyl ions, respectively. The electrodes are attacked in the former case, but not in the latter. J. GRANT.

Alkaline electrolytic iron. S. J. LLOYD.-See B., 1929, 438.

Electrochemical corrosion of painted or lacquered steel. A. R. Evans.—See B., 1929, 437.

Electrolytic formation of sodium arsenate. 0. Essin (Z. Elektrochem., 1929, 35, 234-240).-On electrolysis of an alkaline solution of arsenious oxide, containing 80.5 g. of oxide and 100.6 g. of sodium hydroxide per litre, between iron electrodes in a cell without a diaphragm, with a C.D. of both anode and cathode equal to 0.03 amp./cm.², about 50% of the oxide underwent oxidation at the anode, whilst about 12% became reduced at the cathode. This was prevented by interposing a diaphragm between the electrodes and using sodium hydroxide solution as catholyte. A solid crust of sodium arsenate appeared around the anode through the anolyte becoming supersaturated when certain concentrations of electrolyte were employed. A series of experiments was performed in a diaphragm cell with an electrolyte containing about 70 g. of arsenious oxide and 87.5 g. of sodium hydroxide per litre, with anode C.D. ranging from 0.003 to 0.03 amp./cm.² and with equal current concentrations. The yields of arsenate varied from 0 to 100%, the maximum corresponding with each C.D. being indicated by the liberation of oxygen at the anode. H. T. S. BRITTON.

Electrodeposition of chromium from aqueous solutions of chromic acid. J. ROUDNICK (Z. Elektrochem., 1929, 35, 249-254).—Experiments were carried out to ascertain the conditions under

which a constant ratio of tervalent chromium to sexavalent chromium could be obtained during the electrodeposition of chromium from a 20% solution of chromic acid in which an amount of sodium sulphate equal to 0.2% of that of the chromic anhydride was dissolved. Copper was used as cathode, and as anode either lead or platinum was employed. The electrode reactions were investigated partly by analysing the gases evolved. Anodic oxidation of the tervalent chromium produced at the cathode was greater at a lead anode than at a platinum anode. The platinum anode became coated with a greenishyellow diaphragm, composed of both tervalent and sexavalent chromium oxides, which was not attacked by dilute hydrochloric acid or sodium hydroxide solution. An increase in the deposit of chromium by increasing the tervalent chromium content of the electrolyte could not be obtained.

H. T. S. BRITTON.

Theory of the electrodeposition of chromium from aqueous chromic acid solutions. III. E. MÜLLER and J. STSCHERBAKOV (Z. Elektrochem., 1929, 35, 222-234).-Solutions of pure chromic acid alone and also together with various proportions of sulphate ion, introduced in the form of sodium sulphate, were electrolysed, using either a bright platinum wire as cathode or a copper plate on which electrolytic chromium had been deposited. The equilibrium potential of the cathode was measured before electrolysis, whilst during the passage of the current the potentials assumed with varying currents were found, and they were determined again one minute after the current had been switched off. Despite the strong oxidising action of chromic acid, it appears that when it is absolutely pure it cannot be reduced electrolytically, but may be reduced in the presence of sulphate ions. The results obtained are considered to point to the formation of an invisible, non-conducting film over the cathode. The layer is formed by the reduction of the chromic acid, has fine pores, and contains sulphate-ions. The difference in the behaviour of bright platinum and chromium cathodes is discussed on the basis of the H. T. S. BRITTON. theory.

Electrolytic copper obtained from electrolytes containing gelatin. Determination of watercontent. Hygroscopic and catalytic properties. C. MARIE and P. JACQUET (J. Chim. phys., 1929, 26, 189-194).-Marie and Buffat (A., 1927, 840) found that the deposits formed on the cathode in the electrolysis of copper sulphate solutions containing gelatin were contaminated with gelatin and copper suphate. The present experiments deal principally with the water contents of rapidly dried deposits; these are proportional to the excess in the weights of the cathodic deposits over those calculated for pure copper from the voltameter readings. They were equal to the sum of the normal water contents of the constituents, gelatin and hydrated copper sulphate comprising the extra amounts. Difficulty was experienced in obtaining concordant results of the water contents by drying the deposits in a current of hydrogen owing to the catalytic action, which was promoted by the exceedingly fine and porous copper deposits, between the hydrogen and the small amount of oxygen which it contained as impurity.

H. T. S. BRITTON.

Cause of periodic phenomena in electrolysis. E. S. HEDGES (J.C.S., 1929, 1028—1038).—The anodic dissolution of copper in hydrochloric acid has been studied, using a rotating anode. The frequency of the periods is independent of current density over a certain range, and above that falls almost linearly with increasing current density. The frequency is independent of the rate of dissolution of the metal, and directly proportional to the speed of rotation. Evidence has been obtained showing that a critical concentration of chloride ions is necessary before the anode film can be dissolved. The author's theory of anodic polarisation is amplified. C. W. GIBBY.

Electrosynthesis of hydrocarbons. L. BERMEJO and L. BLAS (Anal. Fis. Quim., 1929, 27, 228-235) .--Peroxides are formed at the anode during the electrolysis of sodium benzoate, but no diphenyl is formed. On the other hand, no peroxides can be recognised at the anode during the electrolysis of acetates, and the formation of hydrocarbons does not appear to be a result of anodic oxidation (cf. Fairweather and Walker, A., 1927, 119). A quantitative yield of ethane is obtained by the electrolysis of saturated zinc acetate solution with platinum electrodes at 15° with a current density of 1 amp. per cm.² In the electrolysis of lead acetates it is found that the tetra-acetate is formed only in anhydrous acetic acid solution. Aqueous acid or neutral solutions yield at the anode lead peroxide, formed by decomposition of the tetra-acetate. Alkaline solutions of basic lead acetate yield at the anode lead sesquioxide, formed by oxidation of the basic acetate. No ethane is formed in these cases. R. K. CALLOW.

Electrolysis of ammonium acetate and ammonium hexoate. F. FICHTER and W. LINDENMAIER (Helv. Chim. Acta, 1929, 12, 559-572).-The electrolysis of ammonium acetate in an aqueous solution containing free acetic acid with a platinum anode gives an approximately 90% yield of ethane and a small amount of acetamide, the yield of which can be increased by cooling the anode. It is suggested that the acetamide is formed by the action of free ammonia, resulting from hydrolysis of ammonium carbonate or acetate, on the primarily formed acetyl peroxide: $(CH_3 \cdot CO_2)_2 + NH_3 = CH_3 \cdot CO_2OH +$ CH3 CO·NH2. Similarly, hexoamide is obtained by the electrolysis of ammonium hexoate. When an ammoniacal solution of ammonium acetate is electrolysed with a platinum-iridium anode a dark brown resinous condensation product is formed, which is soluble in water and insoluble in alcohol. In addition, methyl alcohol and formaldehyde are found in the solution. With a graphite anode very small amounts of methylamine are formed, probably by the action of free ammonia on the peracetic acid : $CH_3 \cdot CO_2OH +$ $NH_3 = MeNH_2 + CO_2 + \hat{H}_2O$. In support of this view it was found that the explosion of acetyl peracid in an atmosphere of ammonia also produces small quantities of methylamine. Carbamide is always formed during the electrolysis of ammonium acetate solutions. This is due to a secondary reaction, the ammonium carbonate which is first formed being converted into carbamide at the anode.

O. J. WALKER.

Electrolytic reduction of benzoic acid. F. SOMLÓ (Z. Elektrochem., 1929, **35**, 264—265).—The supposition of Baur and Müller (A., 1928, 490) that the oil having the empirical formula C_0H_8O was cyclohexenone obtained by the cathodic reduction of benzoic acid is adversely criticised, on the grounds that no such product was prepared by Mettler (A., 1906, i, 851) in the electrolytic reduction of phthalic acid under similar conditions. H. T. S. BRITTON.

Electrolysis in gels. I. P. HAPPEL, R. E. LIESEGANG, and O. MASTBAUM (Kolloid-Z., 1929, 48, 80-82).—When a layer of gelatin containing sodium chloride and litmus is electrolysed between two platinum wires, the region round the cathode becomes coloured blue, whilst the anodic region develops a red colour. While the current is flowing these regions are not circular, diffusion of the hydrogen and hydroxyl ions taking place most readily along the axis joining the two poles. The coloured regions become circular when the current is interrupted.

E. S. HEDGES.

Test of the radiation hypothesis of chemical reaction. W. URE and R. C. TOLMAN (J. Amer. Chem. Soc., 1929, 51, 974–983).—The rate of racemisation of *d*-pinene in the liquid state at temperatures (near the b. p.) at which the thermal reaction is just appreciable is uninfluenced by infra-red radiation up to 3μ , the density of which has been largely increased over that prevailing in a hohlraum at the reacting temperature of the pinene. Mayer's experiments (A., 1928, 140) do not prove the ineffectiveness of radiation up to 13μ . S. K. TWEEDY.

Light- and dark-reactions involving reversible and consecutive reactions. R. WEGSCHEIDER (Monatsh., 1929, 51, 285-324; cf. A., 1923, ii, 49).--The theory of photochemical processes of the type $M \Longrightarrow M', M' \longrightarrow X$, where M' is an activated intermediate product formed under the influence of light in accordance with the law of photochemical equivalence, and M is the only molecular species which absorbs light, has been investigated mathematically by the methods of the classical kinetic theory. The intensity of the light proves to enter into the equation for the rate of formation of X not as the first power but as a power which gradually diminishes to zero as the intensity increases. It appears probable, however, that the total absorption from the start of the reaction until M is exhausted is independent of the intensity. The number of quanta absorbed per mol. of X formed will vary considerably during the course of the reaction, so that the figures determined over a selected interval are more or less fortuitous. Only if the second reaction is unimolecular and the first reaction irreversible will the quantum number approximate to unity. The concentration of M' does not remain constant during the reaction, as some have assumed in order to account for photochemical reactions the velocity of which is proportional to the square root of the intensity of the light, e.g., the formation of hydrogen bromide from its elements (cf. Skrabal, A., 1927, 188). Nevertheless, the square

root law may be explained if the activation reaction is unimolecular and the reverse reaction bimolecular, provided that the ratio of the square of the concentration of M' to the concentration of M remains sensibly constant during the reaction, although not necessarily equal to the equilibrium constant. With favourable values of the velocity coefficients, this condition is, indeed, fulfilled during a large portion of the reaction period. R. CUTHILL.

Rôle of the walls of the vessel in the photochemical reaction H_2+Cl_2 . A. TRIFONOV (Z. physikal. Chem., 1929, B, 3, 195—203).—Velocity measurements have been made of the photochemical formation of hydrochloric acid in cylindrical vessels of different dimensions. At low pressures (about 10 mm.) the quantum yield is proportional to the square of the diameter of the vessel. This is ascribed to the cessation of the chain reactions $H_2+Cl=$ $HCl+H, H+Cl_2=HCl+Cl$ at the walls of the vessel due to adsorption of hydrogen and chlorine atoms. With increase of pressure the formation of hydrochloric acid becomes independent of the dimensions of the vessel. O. J. WALKER.

Budde effect in bromine and chlorine. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1929, 51, 1395—1399).—The Budde effect for bromine and chlorine undergoes no change when these halogens are purified and dried (cf. Brown and Chapman, A., 1928, 469). Hydrogen readily reduces pyrex glass at the temperature of the softening point of the latter. S. K. TWEEDY.

Effect of pressure on the photochemical formation of hydrogen bromide. I. W. Jost and G. JUNG (Z. physikal. Chem., 1929, B, 3, 83– 94).—According to a formula worked out on the assumption of triple collisions, the reaction velocity of the photochemical formation of hydrogen bromide should depend on the total pressure. Experiments of Bodenstein and Lütkemeyer (A., 1925, ii, 218), do not indicate this. Experiments and apparatus to test the validity of the equation are described, and it is found that the reaction velocity is inversely proportional to the square root of the total pressure.

A. J. MEE.

Effect of pressure on the photochemical formation of hydrogen bromide. II. W. JOST (Z. physikal. Chem., 1929, B, 3, 95-127) .- The photochemical formation of hydrogen bromide is studied especially from the points of view of dependence on pressure, the walls of the vessel, and the wave-length of light used. An apparatus which can be used for this and similar purposes is described, The velocity of formation was measured over a large pressure range and with light of the continuous spectrum and of the wave-length of absorption of bromine. The velocity of formation in the continuous and band spectra is almost the same. The accurate kinetics of the reaction are derived mathematically, equations found in the previous paper (cf. preceding abstract) being developed and extended. The activated bromine atoms formed primarily in the light affect the reaction like inactive atoms and become deactivated before entering into the reaction. The walls exert a characteristic effect on the reaction velocity comparable with that observed by Bodenstein, Lehner, and Wagner for carbonyl chloride. The velocity coefficients for the part reactions are calculated.

A. J. MEE.

Radio-chemical synthesis of ammonia. E. PONSAERTS (Bull. Soc. Chim. Belg., 1929, 38, 110— 120).—The value of the ratio of the number of molecules of ammonia formed to the number of ion pairs produced when mixtures of nitrogen and hydrogen are exposed to radon rises rapidly as the partial pressure of nitrogen is increased, to a maximum value of 0.32 at 25%. It remains steady until the nitrogen partial pressure reaches 75%, after which it decreases rapidly again. Doubling the total gas pressure or raising the temperature by 20° has no marked influence on the maximum value of the ratio.

Nitrogen under the influence of radon reacts with mercury to form a brown solid which is possibly a mercury nitride. F. J. WILKINS.

Influence of the variation of intensity [of light] on the velocity of the decomposition of ferric thiocyanate and the bleaching of neocyanine and some other photochemical reactions. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 197—205).—From experiments with a 1000-watt gas-filled tungsten lamp it is shown that the velocities of the decomposition of ferric thioeyanate, of the bleaching of neocyanine, and of the reactions between chromic acid and citric and tartaric acids are proportional to the square root of the intensity of the incident radiation, whereas the velocities of the reactions between lactic and chromic acids and between iodine and sodium lactate and tartrate are directly proportional to the intensity of the radiation. A. R. POWELL.

Reaction of excited mercury with oxygen. Addendum. A. J. LEIPUNSKI and A. W. SAGULIN (Z. physikal. Chem., 1929, B, 3, 215-216).—Tables of time and pressure values omitted from the original paper (this vol., 155) are given. O. J. WALKER.

Photochemical reaction between dextrose and hydrogen peroxide in acid medium with tungstic acid sol as photocatalyst. I. J. C. GHOSH and J. MURHERJEE (J. Indian Chem. Soc., 1929, 6, 231-238).—The rate of oxidation of dextrose by hydrogen peroxide in presence of tungstic acid sol (prepared from sodium tungstate and an excess of hydrochloric acid) is almost negligible in the dark, but exposure to radiations in the immediate ultra-violet $(330-400 \,\mu\mu)$ causes a rapid increase. Oxidation of 1 mol. of dextrose corresponds with the decomposition of 1 mol. of hydrogen peroxide. A study of the change shows that the reaction velocity is unimolecular with respect to the peroxide, and the velocity coefficient raries inversely as the square root of the concentration of free hydrochloric acid for the same concentration of tungstic acid, increases slightly with increased dextrose concentration, and with increased sodium tungstate concentration first increases, passes through a maximum, and then diminishes rapidly. The results are discussed assuming that adsorption of hydrogen-ions and peroxide molecules on the tungstic acid sol occurs, with subsequent activation of the peroxide. H. BURTON.

Effect of short-wave radiation on proteins. M. SPIEGEL-ADOLF (Klin. Woch., 1928, 7, 1592—1596; Chem. Zentr., 1928, ii, 2483).—Seralbumin, serum, other blood proteins, and egg-albumin, when exposed to ultra-violet light, undergo an increase of absorption in a certain wave-length range in the ultra-violet. Addition of alkali or acid increases the effect, but addition of acid to non-irradiated protein produces a shift of the absorption towards the shorter wavelengths. Preparations irradiated by radium show increased absorption towards the shorter wavelengths. A. A. ELDRIDGE.

High-pressure syntheses of carbonates and silicates. W. EITEL and W. SKALIKS (Naturwiss., 1929, 17, 316—319).—A progress report on technique and results in the attempts to prepare naturally occurring minerals of the dolomite type and complex silicate-carbonates. The following double compounds have been prepared : Na₂CO₃, CaCO₃, K₂CO₃, CaCO₃, Na₂CO₃, MgCO₃, K₂CO₃, MgCO₃, etc. The last compound can be obtained in a vitreous state. Subsequent heating of the glass to 200—400° causes the appearance of crystals of the trigonal or hexagonal form common to the other double carbonates. Attempts to make dolomite were unsuccessful, magnesium carbonate acting on the sodium calcium carbonate so as to form the sodium magnesium double compound with calcium carbonate set free.

R. A. MORTON.

Oxidation of alkali sulphites to dithionates. R. HAC (Coll. Czech. Chem. Comm., 1929, 1, 259— 262).—The normal sulphites of sodium and potassium in aqueous solution are oxidised to dithionates when warmed with lead dioxide, which is reduced to red lead; manganese dioxide does not react.

R. CUTHILL.

Preparation of potassium nitrate. A. L. MEHRING, W. H. Ross, and A. R. MERZ.—See B., 1929, 430.

Copper oxide in the borax bead. W. D. BANCROFT and R. L. NUGENT (J. Physical Chem., 1929, 33, 729—744).—When copper oxide is used to colour a boric acid glass, some reduction to cuprous oxide occurs. The percentage of cupric oxide in the mass increases with increasing alkalinity and decreases with a rise in temperature. Cupric oxide colours a glass blue, whilst the green colour is due to cuprous oxide. The cuprous copper in borax glasses can be determined by treatment with ferric sulphate solution and by titrating the ferrous iron produced. The coloration of glazes, glass, and certain minerals is discussed. L. S. THEOBALD.

Berthollet's explosive silver and the formation of silver mirrors. F. BAUM (Chem.-Ztg., 1929, 53, 354-374).—A discussion of the various theories which have been advanced to explain the formation of an explosive compound of silver by the interaction of silver oxide and ammonia and of silver nitrate and ammonia in the presence of an alkali hydroxide.

A. R. POWELL.

Basic phosphate of calcium and of strontium and the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. J. R. LORAH, H. V. TARTAR, and (MISS) L. WOOD (J. Amer. Chem. Soc., 1929, 51, 1097—1106).—The final product of the hydrolysis of calcium phosphate is $3Ca_3(PO_4)_2$, $Ca(OH)_2$. Strontium phosphate hydrolyses similarly. Hydrolysis proceeds more rapidly in alkaline solution. Basic barium phosphate appears not to exist. Isotherms (25°) are given for the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. The curves are of the type given by Freundlich's adsorption isotherm equation. In the case of the basic phosphate either the calcium hydroxide penetrates the phosphate very slowly or else solid solutions are formed. S. K. TWEEDY.

Co-ordination number 5 in hydrates. F. SIERRA (Anal. Fis. Quím., 1929, 27. 220—227).— Zinc sulphate hexahydrate is obtained by evaporating a saturated solution of the heptahydrate at $45-50^{\circ}$. In a current of dry air at 50° it yields the monohydrate, from which no further water is lost below 150°. The hexahydrate has d_4^{25} 2.0537, molecular volume 131·1. Hence, the molecular volume of the water is 15 for the first five molecules, and 9.7 for the last. This is in agreement with the constitution $Zn(H_2O)_5(SO_4,H_2O)$ for the hexahydrate (Moles, A., 1926, 336). The hexahydrate cannot be prepared by desiccating the heptahydrate at 40—50°, since the former already loses water at that temperature. R. K. CALLOW.

Strontium thiosulphate. R. PORTILIO (Anal. Fís. Quím., 1929, 27, 243—250).—Strontium thiosulphate is prepared by mixing cold concentrated solutions of strontium chloride and sodium thiosulphate. It separates from aqueous solution when alcohol is added as the pentahydrate, d_{12}^{32} 2·202; molecular heat of solution in 800 mols. of water —7·34 g.-cals. at 17°. Water is lost slowly on keeping, and rapidly at 50°, to yield the monohydrate, d_{13}^{32} 2·916, molecular heat of solution in 800 mols. of water +2·38 g.-cals. at 17°. This can be dehydrated only at 180° with decomposition. R. K. CALLOW.

Tetrathionates. I. Barium tetrathionate. R. PORTILIO (Anal. Fís. Quím., 1929, 27, 236— 242).—Barium tetrathionate is prepared by triturating a paste of barium thiosulphate and water with iodine and extracting the iodide with alcohol, and is purified by separation from the aqueous solution by addition of alcohol. It forms needles $(+H_2O)$, d_1^{23} 2.777, molecular heat of solution in 800 mols. of water -7.0 g.-cals. at 17°. The water of crystallisation is removed only at 60° with decomposition. The aqueous solution decomposes when kept or warmed. The aqueous-alcoholic solution is stable.

R. K. CALLOW. [Preparation of] pure carbon monoxide. J. G. THOMPSON.—See B., 1929, 431.

The "Ditte reaction." L. RODRIGUEZ PIRE (Anal. Fís. Quím., 1929, 27, 192—219).—A quantitative study, using pure materials, has been made of the oxidation of carbon monoxide by iodine pentoxide (Ditte, Ann. Chim. Phys., 1870, 13, 318). Carbon monoxide, prepared from pure formic acid and sulphuric acid, is absorbed practically completely by ammoniacal cuprous chloride provided that proper precautions are taken in the preparation of the reagent

and in the manipulation. Iodic acid prepared from sulphuric acid and barium iodate cannot be obtained free from traces of sulphate (cf. Guichard, A., 1909, ii, 477). Pure iodic acid is best prepared by the action of purified fuming nitric acid on purified iodine. It separates in different crystalline forms from concentrated and from dilute nitric acid. Dehydration takes place in two stages: first, rapidly, at 110°, and then slowly to completion at 200° (cf. Baxter and Tilley, A., 1909, ii, 225). The loss of weight of the product in a stream of pure, dry air at 25-60° is of the order of 0.00005% per hr. The completeness of the oxidation of carbon monoxide by iodine pentoxide depends primarily on the rate at which the gas is passed. The amount unchanged was 0 000007% at 100°, 0.000087% at 25°, and 3% at 0°. The reaction being exothermic, the incompleteness of the reaction at 0° is attributed to the formation of a layer of iodine on the pentoxide. The decomposition of pure iodine pentoxide does not take place below 270°. In presence of a little sulphuric acid, unstable, complex products are formed. Preliminary determinations of the at. wt. of iodine from the ratio $I_2: O_5$ from the Ditte reaction gave figures of the same order as the accepted value. R. K. CALLOW.

Reactions of the halogens with carbon sulphidoselenide. H. V. A. BRISCOE, J. B. PEEL, and P. L. ROBINSON (J.C.S., 1929, 1048-1050).--Carbon sulphidoselenide reacts with chlorino and bromine at ordinary temperatures, giving respectively thiocarbonyl tetrachloride and selenium tetrachloride, and thiocarbonyl tetrabromide and selenium tetrabromide, or, under certain conditions, the compound $C_2S_2SeBr_6$. C. W. GIBBY.

Rapid concentration of germanium and gallium contained in zinc oxide carrying them. C. JAMES and H. C. FOGG (J. Amer. Chem. Soc., 1929, 51, 1459—1460).—A solution of the zinc oxide in hydrochloric acid is filtered and the hot filtrate rendered basic by the slow addition of some of the original zinc oxide. The mixture is filtered and the residue dissolved in acid, the solution being distilled and treated in the usual manner to obtain the two elements. S. K. TWEEDY.

Zirconium. IV. Precipitation of zirconium by phosphates. R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1929, 51, 1311—1315; cf. A., 1928, 858).—A five-fold excess of ammonium phosphate, phosphoric acid, or microcosmic salt in presence of 0.344M-sulphuric acid efficiently removes zirconium from solution as phosphate, but sodium phosphate is inefficient except when used in forty-fold excess. Acid must be present; sulphuric acid is preferable to hydrochloric or nitric acid. Zirconium sulphate yields a precipitate with sodium cobaltinitrite.

S. K. TWEEDY.

Preparation and properties of the ammonium phosphates. W. H. Ross, A. R. MERZ, and K. D. JACOB.—See B., 1929, 431.

Synthesis of arsenic phosphates. S. M. HORSCH and G. BETSIS (Prakt. Acad. Athenes, 1928, 3, 216—219; Chem. Zentr., 1928, ii, 2632).—Arsenic orthophosphate, AsPO₄, is obtained by the interaction of arsenious oxide and pyrophosphoric acid at 230— 245° and then at 280°; the *compound* $4AsPO_4, 3H_4P_2O_7$ is similarly obtained. A. A. ELDRIDGE,

Antimony phosphate. S. M. HORSCH (Prakt. Acad. Athenes, 1927, 2, 517; Chem. Zentr., 1928, ii, 2632-2633).—When orthophosphoric acid is heated at 330° with powdered antimony, vigorous reaction with liberation of antimony hydride takes place. After heating at 370° and extraction with water, crystals of antimony phosphate, 5SbPO₄,2H₂O, are obtained. The compound may also be produced by interaction of antimony chloride with pyrophosphoric acid or ammonium hydrogen phosphate (affording SbPO₄,2H₂O). A. A. ELDRIDGE.

Salts of bismuth and sodium phosphate. O. CALCAGNO (An. Of. Quim. Prov. Buenos Aires, 1928, 2, 1-22).-The mechanism of the formation of normal bismuth phosphate when a solution of di- or tri-sodium phosphate is added to a bismuth nitrate solution containing up to three molecules of free nitric acid is discussed. The action of sodium acetate in bringing about the precipitation of bismuth "subnitrate" from a nitric acid solution of bismuth nitrate is described : a considerable excess of concentrated sodium acetate solution causes the precipitate to redissolve owing to the formation of the compound $(AcO)_2(BiOH)$, which, however, breaks up immediately into acetic acid and basic bismuth acetate. The reactions between solutions of di- and tri-sodium phosphates and bismuth nitrate in presence of nitric and acetic acids and sodium acetate, and the conditions governing the precipitation of normal and basic bismuth phosphates from glycerol solutions of sodium bismuthite are described. H. F. GILLBE.

Reaction between sulphur dioxide and nitrogen peroxide. W. MANCHOT and H. SCHMID (Ber., 1929, 62, [B], 1261-1263; cf. A., 1927, 32).-Re-examination of the interaction between sulphur dioxide and nitrogen dioxide or trioxide at a high temperature or between sulphur trioxide and nitric oxide confirms the conclusion of Briner (this vol., 40) that the compound S₂N₂O₉ is formed; the constitution 2SO₃,NO ascribed previously to it is incorrect. A compound with nitrogen content exceeding the ratio S: N=1:1 does not appear to be formed by the action of liquid sulphur dioxide on an excess of liquid nitrogen peroxide. The action of nitrosyl chloride on silver sulphate gives products with the ratio S: N=1: 1.94, 124, 1.22, and 1.73, but it is difficult to ascertain whether the excess of nitrogen is due to unremoved nitrosyl chloride. H. WREN.

Preparation of selenic acid and its salts. E. R. HUT and C. R. McCROSKY (J. Amer. Chem. Soc., 1999, 51, 1457—1458).—Selenious acid, or a salt, is refuxed with 30% hydrogen peroxide for about 3hrs. (cf. Meyer and Heider, A., 1915, ii, 630). About 90% oxidation is obtained. S. K. TWEEDY.

Molybdates. V. G. ARANDA (Anal. Fís. Quím., 1929, 27, 165—168).—Preparation of normal barium, strontium, and lead molybdates by fusion of the chloride of the metal with normal sodium molybdate yields on prolonged heating or on employment of a

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sufficiently high temperature crystalline molybdates, d 4.9747, 4.6624, and 6.9208, respectively.

H. F. GILLBE. Molybdates. V. G. ARANDA (Anal. Fís. Quím., 1929, 27, 251; see preceding abstract).—Grey lead molybdate has d_{45}^{25} 6.6933. R. K. CALLOW.

Silicododecatungstic acid. I. Preparation of silicotungstic acid. A. G. SCROGGIE (J. Amer. Chem. Soc., 1929, 51, 1057-1062).-In the isolation of silicotungstic acid (Drechsel, A., 1887, 703) the ether may be replaced by many esters, ketones, and aldehydes. This fact supports Rosenheim's suggestion that the acid is of the oxonium salt type (A., 1918, ii, 77). Further, the hydrochloric acid may be replaced by nitric acid, 20% sodium chloride, and solutions of some lithium salts. The silicotungstic acid is efficiently isolated by means of common salt and ethyl acetate alone. In the analysis of the acid, the sample is preferably ignited at 400-500°, and titrations are best carried out with very dilute alkali solutions, using chlorophenol-red as indicator. The acid prepared by North's directions is impure (J. Amer. Pharm. Assoc., 1924, 13, 1001). Dehydration of the acid is best effected by dehydrating agents under reduced pressure; 4 mols. of water are held tenaciously. The acid reacts with alkali as follows : $4H_2O_3O_2, 12WO_3, 4H_2O + 24NaOH = H_2SiO_3 +$ 12Na₂WO₄+19H₂O. An improved method of pre-

paring the acid is given. S. K. TWEEDY.

Preparation of oxygen fluoride. P. LEBEAU and A. DAMIENS (Compt. rend., 1929, **188**, 1253— 1255).—A gas containing 70% of the compound F_2O (A., 1927, 1044) is obtained by the passage of fluorine in finc bubbles at the rate of 1 litre/hr. through a 2% solution of sodium hydroxide 1 cm. deep by means of a platinum tube 2 mm. in diameter. The gas (b. p. -167°) formed according to the equation $2F_2+2NaOH=2NaF+F_2O+H_2O$ is collected over water, liquefied in liquid air, and fractionated. There is evidence of the formation of an unstable intermediate compound with marked oxidising properties.

J. GRANT.

Oxidations with fluorine. XIII. Action of fluorine on alkaline acetate solutions. F. FICH-TER and E. BRUNNER (Helv. Chim. Acta, 1929, 12, 573—576; cf. A., 1926, 925).—When fluorine is passed into a solution of potassium acetate made alkaline with excess of potassium carbonate small quantities of methyl alcohol and traces of formaldehyde are formed. The gaseous products contain ethylene and ethane. With an alkaline solution of potassium propionate ethyl alcohol is obtained. The formation of alcohols from alkaline solutions of fatty acid salts, which is known to take place electrolytically, also occurs by the action of fluorine. O. J. WALKER.

Fluorides of manganese and of cadmium. P. NUKA (Z. anorg. Chem., 1929, 180, 235–240).— Contrary to the statements found in the literature, manganous fluoride is not insoluble in water. This salt can be prepared as a white powder by heating in a stream of carbon dioxide at 290–300° the double *fluoride* of manganese and ammonium, NH_4MnF_3 , which can be obtained by precipitating a solution of manganous chloride with a large excess of ammonium 780

fluoride. The solubilities of manganous fluoride at 40, 60, and 100° are 0.66, 0.44, and 0.48 g. per 100 g. of solution. By allowing a solution of manganous fluoride to crystallise at the ordinary temperature a hydrate, $MnF_2, 4H_2O$, was obtained. The solubility of this substance at 20° is 1.05 g. of the anhydrous salt in 100 g. of solution. A hydrate of the double fluoride of manganese and ammonium could not be obtained. The corresponding double *fluorides* of potassium and sodium are obtained as white precipitates by adding excess of a saturated solution of the alkali fluoride to a solution of manganous chloride. The solubility of ammonium manganofluoride at 20° is 1.2 g. per 100 g. of solution; the solubilities of the alkali double fluorides are somewhat smaller.

By adding ammonium fluoride to a very concentrated solution of cadmium nitrate at the ordinary temperature a white, glistening precipitate of the hydrate $CdF_{2,}2H_{2}O$ was obtained. This substance loses water on long keeping, or on heating at 50°. The solubility of the dihydrate could not be determined, and it appears probable that it can exist in several modifications. As in the case of manganese fluoride, solutions of cadmium fluoride become turbid on heating due to precipitation of the anhydrous salt. O. J. WALKER.

Oxidation of halogen acids by sulphuric acid. K. PROSKOURIAKOFF (J. Physical Chem., 1929, 33, 717-719).-The temperatures and acid concentrations at which iodine or bromine is liberated from potassium iodide or bromide, respectively, and sulphuric acid have been determined. At 100°, 60°, 50°, 45°, and 36° iodine can be detected with concentrations of sulphuric acid which are 25%, 30%, 35%, 40%, and 50%, respectively. With potassium (?) bromide the temperatures are 169°, 100°, 46°, and 36° for the detection of bromine with 60%, 70%, 80%, and 90% sulphuric acid, respectively. At 100°, 70% sulphuric acid is necessary to oxidise hydrobromic acid. Mercuric sulphate does not catalyse the liberation of iodine by sulphuric acid between 36° and 100°. L. S. THEOBALD.

Polyhalides. I. Chloroiodic acid, $HICl_4, 4H_2O$. V. CAGLIOTI (Atti R. Accad. Lincei, 1929, [vi], 9, 563—568).—The analogy between iodine and the noble metals is extended by the preparation of a chloroiodic acid, $HICl_4, 4H_2O$, by passing chlorine through a suspension of iodine in concentrated hydrochloric acid. The reddish-orange solution so obtained crystallises almost completely at 0° into tabular orange-yellow crystals of the free acid, which has a high vapour pressure and an irritating odour. The derivation of such salts as KCl, ICl₃, RbCl, ICl₃, CsCl, ICl₃, and MgCl₂, 2ICl₃, 8H₂O from this acid is confirmed by the possession by such compounds of a common absorption band. F. G. TRYHORN.

Mechanism of oxidative processes. XVI. Rusting of iron. H. WIELAND and W. FRANKE.— See B., 1929, 476.

Reactions between ferrous compounds and nitric oxide. I. L. CAMBI and A. CLERICI (Atti R. Accad. Lincei, 1929, [vi], 9, 519—523).—Addition of an alkali hydroxide solution to a solution of nitric oxide in aqueous ferrous sulphate (NO : FeSO₄=0.8:1) precipitates a black compound which rapidly becomes red, and causes foaming through evolution of nitrogen and nitrous oxide. Even at 0° the precipitate decomposes with the evolution of nitrous oxide, and after 48 hrs. is completely converted into ferric hydroxide, although kept in an atmosphere of nitric oxide. It is suggested that compounds of ferrous salts with nitric oxide may decompose according to the equations $2[>Fe-NO] \rightarrow 2Fe^{III} + N_2O$, 2[>Fe- $NO] \rightarrow 2Fe^{III} + \frac{1}{2}N_2 + NO$, and $2[>Fe-NO] \rightarrow Fe^{II} + 2NO$. Decomposition occurs by the first process in alkaline solution and by the second alone in acid media. The third process also occurs to some extent in acid solution. F. G. TRYHORN.

Action of oxalic acid and malonic acid on tetramminocobaltic complexes and analogous compounds. W. SCHRAMM (Z. anorg. Chem., 1929, 180, 161—183; cf. A., 1927, 33, 542).—A comparison is made of the action of oxalic and malonic acids on cobaltic compounds having a complex cation which contains the group CoA_4 , where A represents an equivalent of ammonia, ethylenediamine, or phenylenediamine. Oxalic acid displaces the groups H_2O , OH, Cl, Br, NO₃, CO₃, and C₃H₂O₄ more or less readily from the complex forming the corresponding oxalato-compounds, $[CoA_4C_2O_4]X$, which are stable towards the free mineral acid formed at the same time. The malonato-group in the compound

 $[Co(NH_3)_4C_3H_2O_4]Br$ is not attacked by oxalic acid, whilst the nitrito-groups in the substance

 $[Co(NH_3)_4(NO_2)_2]NO_3$ are displaced only with difficulty. The primary action of malonic acid on the complex salts is in general to displace mineral acid from the anion of the complex salt. This acid is then taken up by the complex cation. With dimitritotetramminocobaltic nitrate and with oxalato-complex compounds of the type [CoA4C2O4]X malonic acid does not react as a rule. Malonato-complex compounds, $[CoA_4C_3H_2O_4]X$, are obtained only when the displaced mineral acid is removed from the solution hydrolytically, as in the case of the carbonic acid in the carbonato-complex salts, [CoA4CO3]X. The iodide [Co(NH₃)₄CO₃]I, however, is exceptional and does not react with malonic acid. The malonate, [Co(NH₃)₄CO₃]₂C₃H₂O₄, forms with malonic acid the diaquo-salt, $[Co(NH_3)_4(H_2O)_2]_2(C_3H_2O_4)_3.$ The corresponding oxalate shows a similar change with oxalic acid. Although the sulphito-group of the compounds of the type [CoA4SO3]X can be removed from the solution by hydrolysis, such compounds do not form malonato- and oxalato-complex salts by the action of malonic and oxalic acids, respectively, because the free sulphurous acid reduces the tervalent cobalt. The preparation of the following compounds is also described : malonatotetramminocobaltic chloride and nitrate and the compounds [Co en₂ C₂O₄]Cl,H₂O, [Co pn₂ Cl₂]Cl,HCl,2H₂O, and [Co pn₂ C₂O₄]Cl,3H₂O (en=ethylenediamine, pn=propylenediamine).

O. J. WALKER.

Spinels of the type $M_2^{11}M^{1V}O_4$. G. NATTA and L. PASSERINI (Atti R. Accad. Lincei, 1929, [vi], 9, 557-563).—Cobaltous orthostannate, d 6.108, greenish-blue, has been prepared by calcining at 900° the

precipitate produced by the addition of sodium hydroxide solution to a solution of stannic chloride and cobalt chloride. Magnesium orthostannate, white, d 4.378, was prepared analogously. X-Ray examination of these products shows that cobaltous orthostannate crystallises in the cubic system and possesses a unit cell containing 8 mols., of edge 8.605+ 0.005 Å, and of volume $637 \cdot 16 \times 10^{-24}$ c.c., d_{calc} 6.307. Magnesium orthostannate is isomorphous with the cobalt salt and has a unit cell with edge 8.580 ± 0.007 Å. and with volume 631.63×10^{-24} c.c., $d_{calc.}$ 4.864. Calculation of the structure factor shows that these compounds belong to the type of the spinels, viz., 8f, 16c, 32b (space-group Oi-7). The preparation of these compounds confirms the generalisation that the ionic diameters of the anions and cations determine the possibility of the formation of compounds of the F. G. TRYHORN. spinel type.

Nitrites. I. Nitrites of nickel and cobalt; "pyridinates." L. LE BOUCHER (Anal. Fís. Quím., 1929, 27, 145—156).—Compounds of heavy metal nitrites with pyridine have been prepared by addition of a concentrated solution of sodium nitrite to an aqueous solution of a salt of the metal in presence of pyridine; the precipitate which is formed contains, after washing with a mixture of water and pyridine, variable proportions of the two solvents. In a dry atmosphere containing pyridine vapour anhydrous compounds are produced. The following compounds are described : Ni(NO₂)₂,6C₅H₅N, deep blue, m. p. 57°; Ni(NO₂)₂,4C₅H₅N, light blue, m. p. 74°; Co(NO₂)₂,6C₅H₅N, red, m. p. 57°; Co(NO₂)₂,3C₅H₅N, violet-red, m. p. about 90°; Co(NO₂)₂,2C₅H₅N, deep red, m. p. about 100° with partial decomposition. The densities are 1.325, 1.400, 1.256, 1.446, and 1.594, respectively. H. F. GILLBE.

Dissociation of hydrated nitrates. J. G. VIANA and E. MOLES (Anal. Fis. Quím., 1929, 27, 157— 164).—Systematic dehydration of the hexahydrates of cobalt and nickel indicates that loss of nitric acid sets in only after 4 mols. of water have been lost, *i.e.*, when the composition of the salt corresponds with that of a salt of orthonitric acid. H. F. GILLBE.

Chloropyridino-derivatives of rhodium. Rhodium tripyridinotrichlorides and dipyridinotetrachlorides etc. M. DELÉPINE (Bull. Soc. chim., 1929, [iv], 45, 235-249).-Rhodium gives two series of dipyridinotetrachlorides which are similar in properties to the corresponding cis- and trans-iridium compounds (A., 1923, i, 89, 135, 243, 480, 944; 1927, 433), differing mainly in stability and in reaction velocities. The cis-rhodium salts are orange and the transderivatives red, the trans-pyridine salt being sparingly and the cis-salt moderately soluble. The silver salts are insoluble, the alkali salts soluble. Sodium rhodium hexachloride when warmed with pyridine is converted into tripyridinorhodium trichloride, (+2CHCl₂), soluble in chloroform; a second isomeride was not obtained. When heated with pyridine at 130° for 8 hrs. the trichloride is converted into tetrapyridinorhodium dichloride (+6H2O) (cf. Jorgensen, A., 1883, 1058). Cold pyridine in presence of pyridine hydrochloride converts sodium rhodium hexachloride into a mixture of cis- and trans-dipyridinorhodium

tetrachlorides, in which the cis-salt preponderates. The isomerides are separated by washing and decantation with cold water, the mother-liquors being concentrated at 40°, and treated with pyridine hydrochloride, or by dissolution in ammonia. The following cis-dipyridino-derivatives, $Rh(C_5H_5N)_2Cl_4\cdot M$, are described : potassium (+H₂O), pyridinium, ammonium, and silver. The pyridine salt on crystallisation from water affords cis-dipyridinoaquorhodium trichloride (+H₂O, lost at 120—125°), which with silver nitrate gives silver dipyridinonitratorhodium tri-chloride, $[Rh(C_5H_5N)_2:Cl_3:NO_3]Ag,2H_2O$; the corresponding potassium salt undergoes immediate decomposition into dipyridinoaquorhodium trichloride. The following trans-dipyridino-derivatives are described : pyridinium, potassium (+H₂O), ammonium (+H₂O), and silver. Boiling water converts the dipyridine salt into trans-dipyridinoaquorhodium trichloride [+H₂O lost at 110°; at 130° 1.5H₂O is lost, giving the insoluble complex Rh₂(H₂O)(C₅H₅N)₄Cl₆], yielding silver trans-dipyridinonitratorhodium trichloride, with silver nitrate, converted by hydrochloric acid or chlorides into the dipyridinoaquotrichloride. The transderivative is less stable than the cis-isomerides. Cold pyridine (6 mols.) alone converts sodium rhodium hexachloride into a mixture of cis- and trans-dipyridino-derivatives and a complex rose compound, probably the *trans*-dipyridino-tetrachloride of a tripyridinoaquorhodium trichloride,

 $[\mathrm{Rh}(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{2}\mathrm{Cl}_{4}][\mathrm{Rh}(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{3}(\mathrm{H}_{2}\mathrm{O})\mathrm{Cl}_{2}].$ Ammonia converts the *cis*- or *trans*-dipyridinotetrachlorides or the dipyridinoaquotrichlorides into pentammoniochlororhodium dichloride, pyridine similarly affording the tetrapyridinorhodium dichlorides, the *trans*isomeride yielding the insoluble intermediate complex *compound*, [Rh(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{2}\mathrm{Cl}_{4}][Rh(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{4}\mathrm{Cl}_{2}]. Attempts to obtain the quadrivalent rhodium complex, Rh(\mathrm{C}_{5}\mathrm{H}_{5}\mathrm{N})_{2}\mathrm{Cl}_{4}, by syn-crystallisation of *cis*-ammonium dipyridinorhodium tetrachloride and *cis*-dipyridinoplatinous dichloride failed. R. BRIGHTMAN.

Some complex ammonio-pyridines of iridium. M. DELÉPINE and J. PINEAU (Bull. Soc. chim., 1929, [iv], 45, 228–235).—Potassium pyridinoiridium pentachloride with ammonia (d 0.923) in 15 hrs. at 100° gives traces of the chloropentammine, [IrCl(NH₃)₅]Cl₂, and a non-crystalline product, converted through the mercurichloride, Cl₂[IrCl(NH₃)₄C₅H₅N],2HgCl₂, into chlorotetramminopyridinoiridium chloride,

 $Cl_2[IrCl(NH_3)_4, C_5H_5N], 2H_2O$ (*picrate, dichromate, and sulphate*). Potassium mercuri-iodide also affords a precipitate. *trans*-Dipyridinoiridium tetrachloride similarly affords the double *salt*,

 $[Ir(C_5H_5N)_2Cl_4]_2[IrCl(NH_3)_4C_5H_5N]$, and pyridinoiridium pentachloride the double *salt*,

 $[Ir(C_5H_5N)Cl_5][IrCl(NH_3)_4,C_5H_5N]$. trans-Sodium dipyridinoiridium tetrachloride and ammonia in 30 hrs. afford the complex double salt (A),

 $[Ir(C_5H_5N)_2Cl_4]_3[Ir(NH_3)_3,H_2O,(C_5H_5N)_2],6H_2O,$ decomposed by pyridine hydrochloride in boiling solution into pyridine dipyridinoiridium tetrachloride and *dipyridinoaquotriamminoiridium trichloride* (+3H_2O), which gives precipitates with potassium ferricyanide, sodium pyrophosphate, mercuric salts, picric acid, tannin, potassium bromide and iodide, and is converted at 115° in 3 hrs. into dipyridinotrianminochloroiridium dichloride. When heated with 12 times its weight of ammonia $(d \ 0.92)$ at 100° for 36 hrs. the complex double salt (A) affords 80% of chlorodipyridinotriamminoiridium dichloride $(+2H_2O)$, which with sodium bromide and iodide affords the corresponding halides, X₂[IrCl(NH₃)₃(C₅H₅N)₂], H₂O. The sulphate, SO₄[IrCl(NH₃)₃(C₅H₅N)₂], 3H₂O, is obtained by double decomposition. R. BRIGHTMAN.

Dissolution of metals and alloys. M. CENT-NERSZWER (Z. physikal. Chem., 1929, A. 141, 297– 320).—A summary of the general results of work carried out in the author's laboratory during the past 10 years. F. L. USHER.

Quantitative emission spectrum analysis. W. GERLACH and E. SCHWEITZER (Z. anal. Chem., 1929, 77, 213—217).—Polemical against Thurnwald (this vol., 530). The presence of potassium, nickel, or iron in the solution interferes with the accurate comparison of the zinc and silver lines, and absorption of the solution in carbon electrodes leads to variations in the concentration of the dissolved salts.

A. R. POWELL. Use of 0.1 N-hydrochloric acid for standardising electrometric p_{π} measurements. N. F. MAC-LAGAN (Biochem. J., 1929, 23, 309-318).-The advantages of using hydrochloric acid are pointed out. Some of the factors influencing the P.D. at the liquid junction 0.1N-HCl|sat.KCl have been investigated and a simple method of forming the junction is described which is reproducible to ± 0.05 millivolts or $\pm 0.001 p_{\rm H}$. A new type of flowing junction for these solutions is also described. The degree of reproducibility of junctions formed with agar bridges and with ground glass surfaces is considered. Observations on the time change at the junction 0.1N-HCl|sat.KCl,xN-HCl are presented. Impurities of a certain sample of potassium hydrogen phthalate which could not be removed by recrystallisation affected the $p_{\rm H}$ of the 0.05N-solution.

S. S. ZILVA. Use of cresol-red in acid solutions. F. R. MCCRUMB and W. R. KENNY (J. Amer. Chem. Soc., 1929, 51, 1458—1459).—Attention is directed to the use of cresol-red as an indicator in acid solutions. Some applications and advantages are given.

S. K. TWEEDY.

Accuracy of titrations, critical concentration of the burette liquid, and sensitivity of indicators. H. Ruoss (Z. anal. Chem., 1929, 77, 175–185).— Mathematical expressions are deduced to show the magnitude of the errors involved in acidimetric titrations by varying the concentration of the acid and to express the sensitivity of various indicators under different conditions. A. R. POWELL.

Change in colour of indicators at boundary surfaces. A. THIEL (Z. Elektrochem., 1929, 35, 266—267).—The variations in the colour of indicators at phase boundaries, observed by Deutsch (A., 1928, 1183), such that lower $p_{\rm H}$ values are indicated, are discussed particularly in regard to those indicators that owe their colour-changes to basic functions, e.g., tropæolin-OO, thymol-blue. H. T. S. BRITTON.

Determination and control of acidity in the crystallisation of annuonium sulphate. J. A. CRANSTON and (MISS) J. STOCKDALE.—See B., 1929, 430.

Determination of chloride in bromides. R. K. MCALPINE (J. Amer. Chem. Soc., 1929, 51, 1065– 1073).—A method previously described (Berg. A., 1926, 1017) is modified so that potassium permanganate may be used in place of bromate. The bromide is converted into bromoacetone and the chloride is then determined gravimetrically as silver chloride. S. K. TWEEDY.

Iodo-oxidimetric determinations. A. SCHWICK-ER (Z. anal. Chem., 1929, 77, 161–169).—Acid iodate solutions may be titrated directly with potassium hydrogen sulphite solutions stabilised with 5-10% of alcohol. This reaction may be utilised for several indirect titrations, e.g., the determination of hydrazine, ferrocyanide, thiocyanate, arsenic trioxide, and antimony trioxide. In every case an excess of iodate solution is added to the acidified solution, containing tartaric acid in the case of antimony, and, after 5—10 min., the liberated iodine and excess of iodate are titrated with hydrogen sulphite. A. R. POWELL.

Determination of small amounts of dissolved oxygen [in water]. F. R. MCCRUMB and W. R. KENNY.—See B., 1929, 456.

Determination of small quantities of hydrogen sulphide in gases. H. BACH.—See B., 1929, 422

Volumetric determination of sulphate ion. D. Köszegi (Z. anal. Chem., 1929, 77, 203-209).-The sulphate solution is treated at $80-100^\circ$ with 0.1N-barium chloride solution in slight excess 5 gof sodium acetate are added followed by sufficient standard potassium dichromate to precipitate the excess of barium used, and finally the excess of dichromate is determined iodometrically in the filtered solution. If iron or alumina is present the solution is made ammoniacal before addition of barium chloride. A. R. POWELL.

Electrolytic analysis of nitrates. M. A. RABINO-VITSCH and A. S. FOKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 315—318).—Nitrates are reduced in an alkaline solution by hydrogen to ammonia. The hydrogen is prepared by the decomposition of sodium amalgam by an alkali solution in the presence of tungsten, vanadium sulphate, or chloroplatinic acid as catalysts. The amalgam is prepared continuously in the course of the analysis. A. FREIMAN.

Colorimetric determination of phosphoric acid. C. BORDEIANU (Ann. sci. Univ. Jassy, 1929, 15, 372—379).—The method previously described (B., 1927, 422) can be applied to urine, glycerophosphates, and glucose syrup, and to hypophosphites after oxidation with nitric acid. Free phosphoric acid in the presence of glycerophosphates can be determined, since the observation of Bally and Gaumé that nitric acid does not decompose glycerophosphates is confirmed. The total phosphate in glycerophosphates is determined after warming for 1 hr. with a mixture of nitric and sulphuric acids. Glucose syrup is purified and decolorised by filtration through charcoal, which may, if very active, lower the phosphate content somewhat. The errors introduced when the difference in concentration between the standard and the solution to be analysed is appreciable may be marked but do not reach the values found by Defay with cystine (A., 1926, 1115). Results obtained by the new method are compared with those obtained by established methods.

L. S. THEOBALD.

Quantitative analysis of phosphoric acid. IV. Gravimetric and volumetric determination as ammonium phosphomolybdate. M. ISHIBASHI (Mem. Coll. Sci. Kyoto, 1929, 12, 135-153) .- To determine the conditions under which phosphoric acid can be accurately determined gravimetrically as ammonium phosphomolybdate the influence of temperature, concentration of nitric acid, amount of ammonium nitrate and molybdate, and quantity of phosphate taken was examined. Results accurate to $\pm 0.05\%$ are obtained by precipitating ammonium phosphomolybdate from dilute nitric acid solution, containing a concentration of ammonium nitrate between 0-6 and 2.5N, at 40-65°. The precipitate is washed with 2% nitric acid, heated gently for 10 min., then at 250-300° for 0.5 hr., and cooled over freshly-fused calcium chloride. The P2O5 is determined from the weight of phosphomolybdate by using the theoretical factor 0-0378. The molar ratio of ammonium molybdate to ammonium phosphate should be between 1.5 and 3.0, and 0.01-0.13 g. of ammonium phosphate should be taken for analysis. The influence of a number of substances on the precipitation was studied. Hydrochloric, sulphuric, tartaric, oxalic, and citric acids should be excluded. Pemberton's method for the volumetric determination of phosphoric acid precipitated as ammonium phosphomolybdate was found to give accurate results when the factor 0-0003030 was substituted for the theoretical value 0.0003089. C. J. SMITHELLS.

Analytical application of complex-chemical and induced reactions. F. FEIGL and P. KRUM-EOLZ (Ber., 1929, 62, [B], 1138-1142; cf. A., 1928, 1107).-Silicic acid is detected by mixing 1 c.c. of the solution in dilute nitric or hydrochloric acid (the acidity must not exceed 0.2-0.5N) heating to incipient ebullition with 2 drops of a solution of ammonium molybdate in nitric acid, cooling, treating with 1-2drops of a 0.25% solution of benzidine or benzidine hydrochloride in 10% acetic acid, and then with an equal volume of saturated sodium acetate. A blue recipitate or coloration is produced which, with minute amounts, is best observed after extraction "th amyl alcohol. The extreme sensitiveness of the reaction (1 in 8×10^6) requires the use of Jena glass resels and blank tests. In the presence of phosphoric and, the preliminary removal of the insoluble phosphomolybdate is necessary. The reaction is adapted for the detection of fluorine by warming the substance under investigation with quartz sand and concentrated suphuric acid in a porcelain crucible covered with a watch glass on which hangs a drop of water; the drop is tested for silica as described above. The smallest amount of fluorine so detected is 0.005 mg.

The reduction of lead salts to metallic lead by alkali

stannite solution is enormously accelerated by the presence of traces of bismuth, the precipitated bismuth obviously acting as nucleus for the lead, otherwise slowly separated. A method which permits the detection of 0.02 μ g. of bismuth is given. Reduction of antimony salts to metallic antimony is also accelerated by the presence of bismuth, as, to a smaller extent, is that of copper hydroxide. Detection of bismuth in the presence of copper is effected by treating the acid solution with 25% sodium hydroxide until copper hydroxide is precipitated, dissolution of the precipitate with 5% potassium cyanide, and addition of 1 drop of 3% lead acetate and 3 c.c. of stannite solution; 2 parts of bismuth in the presence of 50,000 parts of copper are detected in 3 min.

H. WREN.

Uranyl zinc acetate as reagent for the detection and determination of sodium. I. M. KOLTHOFF (Chem. Weekblad, 1929, 26, 294—298; cf. Barber and Kolthoff, A., 1928, 859).—The reagent is specific, and very delicate; 0.03 mg. of sodium in 1 c.c. of solution gives a perceptible precipitate. Potassium salts do not interfere unless present in great excess, but lithium must first be removed as the fluoride by addition of ammoniacal ammonium fluoride solution and alcohol. The use of the reagent for the detection and determination of traces of sodium is briefly reviewed. S. I. LEVY.

Analysis of fluorspar. G. E. F. LUNDELL and J. T. HOFFMAN.—See B., 1929, 471.

Sensitive test for magnesium. W. L. RUIGH (J. Amer. Chem. Soc., 1929, 51, 1456—1457).—One drop of a 0.5% solution of *op*-dihydroxyazo-*p*-nitrobenzene in 1% sodium hydroxide solution is added to the magnesium solution rendered slightly acid with hydrochloric acid and excess of dilute sodium hydroxide is then added. A sky-blue magnesium lake is formed. Nickel and cobalt behave similarly; excess of ammonium salts must be absent (cf. Suitsu and Okuma, J. Soc. Chem. Ind. Japan, 1926, 29, 132). S. K. TWEEDY.

Ceric sulphate in volumetric analysis. VI. Oxidation of hydrogen peroxide by ceric sulphate. Indirect determination of lead. N. H. FURMAN and J. H. WALLACE, jun. (J. Amer. Chem. Soc., 1929, 51, 1449-1453; cf. this vol., 669).-The titration of ceric sulphate with hydrogen peroxide, and vice versa, is accurate in solutions containing moderate amounts (e.g., 2-5N) of sulphuric or nitric acid. The forward reaction is also accurate in solutions containing hydrochloric acid up to 5N. Lead dioxide may thus be indirectly determined by utilising the fact that hydrogen peroxide reacts with the dioxide in presence of nitric acid (Schlossberg, A., 1903, ii, 184). S. K. TWEEDY.

Determination of thallous salts using potassium permanganate in a hydrochloric acid medium. A. JILEK and J. LUKAS (Chem. Listy, 1929, 23, 155—162).—Titration at 75° following the above procedure does not give accurate results unless 2 g. of potassium chloride are added per 150 c.c. of reaction mixture containing 0.2 g. of thallium; the acidity of such mixtures may be doubled without affecting the result. The function of potassium chloride is to maintain sparingly soluble thallium chloride in solution; the chlorides of lithium, rubidium, and cæsium, but not of sodium and ammonium, act equally well in this respect.

R. TRUSZKOWSKI. Iodometry. III. Copper as a standard in iodometry. S. POPOV, (MISS) M. JONES, C. TUCKER, and W. W. BECKER (J. Amer. Chem. Soc., 1929, 51, 1299-1306; cf. A., 1925, ii, 1093).-The reaction between copper sulphate and potassium iodide solutions was investigated. In neutral solutions, variation of the iodide concentration between 4 and 12% has no appreciable influence on the amount of copper sulphate decomposed, although cuprous iodide may absorb iodine to a slight extent (Bray and MacKay, A., 1910, ii, 996). When 4% potassium iodide solution is used, the order of mixing the reactants, keeping for 10 min., and the presence of cuprous iodide are without influence. The amount of iodine liberated is always raised with increased hydrogen-ion concentration; the effect is possibly due to atmospheric oxidation of the cuprous ions. An improved electrolytic method of determining copper is described; solvent action on the platinum anode may be avoided by having 0.3 c.c. of sulphuric acid or 0.15 c.c. of this acid and 0.15 c.c. of nitric acid in 200 c.c. of electrolyte (0.1N-copper sulphate). Specific directions are given for carrying out the hæmotoxylin test for copper (cf. Mendel and Bradley, A., 1905, ii, 737). The results indicate that, provided the salt and acid concentrations are kept very small, pure copper or copper sulphate solution may be used as a standard in iodometry. S. K. TWEEDY.

Iodometry. IV. Potassium permanganate as a standard in iodometry. S. Popov and A. H. KUNZ (J. Amer. Chem. Soc., 1929, 51, 1307-1311; cf. preceding abstract) .-- In the thiosulphate-iodine titration there is no appreciable oxidation of the iodide ion by air in a solution containing 6% of potassium iodide and 0.1 M-sulphuric acid, even after 10 min., providing the titrations are performed in the dark; the presence of manganous and potassium sulphates, and the rate and mode of addition of the permanganate also are without influence. The potassium iodide used must be free from alkali. The slight difference in the permanganate-thiosulphate ratio produced by using potassium iodide at different concentrations (2% and 6%) is attributable to "loss of oxygen" by the permanganate during the reduction process. For standardisation purposes, 6% potassium iodide must be used; the acid concentration may be 0.1M-sulphuric acid.

S. K. TWEEDY.

Quantitative spectral analysis of solutions. F. GROMANN (Z. anorg. Chem., 1929, 180, 257-274). —The amount of mercury present in small quantities of mercuric sulphide is determined by dissolving the sulphide in aqua regia, placing the solution in the lower of two electrodes across which a spark is formed, and examining the intensity of photographic blackening by certain persistent lines of the mercury spectrum. The following general precautions must be observed in quantitative spectral analysis : The electrodes must not get worn; the upper electrode must be kept dry; spirting of the solution in the lower electrode must be avoided and only a small portion of it allowed to evaporate; the surface of the solution must be kept at the same level in com. parative measurements. For the lower electrode containing the aqua regia solution an alloy of 60% Pb and 40% Cd was used, the upper electrode being made of nickel. A special form of spark gap and exciter is described. The sensitivity of the method is increased by the addition of cupric sulphide to the mercuric sulphide. By comparison of the intensity of blackening by the mercury resonance line 2536.52 and the copper line 2618.4 it is possible to estimate approximately the concentration of a solution containing mercury without using comparison solutions. The smallest concentration that can be determined is 0.0004% mercury. The concentrations of the solutions examined were 0.01, 0.02, 0.04, 0.1, 0.2, 0.4% mercury and under the best conditions the accuracy is within $\pm 10\%$. O. J. WALKER.

Determination of very small quantities of mercury. A. STOCK and W. ZIMMERMAN (Z. angew. Chem., 1929, 42, 429—430; cf. A., 1928, 726; Thilenius and Winzer, this vol., 531).—The effect of carbamide in the colorimetric determination by means of diphenylcarbazone is apparent if the acidity of the test solution is kept low. S. I. LEVY.

Mercury poisoning and its chemical detection. FRIEDERICH and BUHR (Süddeut. Apoth.-Ztg., 1928, 68, 702-703; Chem. Zentr., 1928, ii, 2739).-Chlorine is passed through urine (1000 c.c.) which is simultaneously evaporated (to 150 c.c.). The excess of chlorine is removed with carbon dioxide, the cold liquid is filtered, treated with a few drops of copper sulphate solution, slightly acidified with hydrochloric acid, and treated with hydrogen sulphide. The centrifuged precipitate, suspended in water, is redissolved with the aid of chlorine, carbon dioxide is passed, and the sulphide is reprecipitated. After redissolution and removal of chlorine, ammonium oxalate is added until the copper oxalate redissolves, the mercury is deposited on a copper wire, and identified as iodide. It is determined electrolytically in a solution containing ammonium oxalate and oxalic acid. A. A. ELDRIDGE.

Molybdomanganimetry of iron salts. Its mechanism and limitations. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 9, 479-488; cf. Fontes and Thivolle, A., 1926, 1282; 1923, ii, 583).-The reaction of ferrous salts with the phosphomolybdate reagent is reversible, the blue colour being reduced by ferric salts. The equilibrium is only slowly established, and for the determination of small amounts of ferrous salts in presence of ferric salts the method is unsatisfactory. In the determination of ferrous salts large errors are produced by the presence of hydrochloric acids, but these can be corrected by the previous addition of manganese sulphate. The presence of either sulphuric acid or sodium sulphate considerably weakens the intensity of the blue colour. The reduction of ferric salts by copper in presence of either small quantities of hydrochloric acid or organic material containing phosphorus such as blood-serum or glycerophosphates, gives rise to large errors in the titration. Addition of manganese sulphate does not correct the errors if the hydrochloric acid is present before the reduction. These difficulties are not apparent if zinc be substituted for copper.

E. Ĥ. SHARPLES. Titration of potassium ferrocyanide, using diphenylamine as internal indicator. I. M. KOLTHOFF (Chem. Weekblad, 1929, 26, 298—301; cf. Moll, this vol., 165; Cone and Cady, A., 1927, 1046).—Potassium ferrocyanide may be very accurately titrated by means of zinc sulphate solution, which has been standardised against a known ferrocyanide solution. It is added to the ferrocyanide solution to be titrated, in presence of sulphuric acid, potassium ferricyanide, and the indicator. Sulphides, thiosulphates, and thiocyanates present in the ferrocyanide interfere, and are first oxidised by addition of sodium hydroxide and hypobromite; excess of the latter is reduced by addition of arsenious acid.

S. I. LEVY.

Qualitative analysis of a mixture of ferrocyanide, ferricyanide, and thiocyanate. P. C. BANERJEE (J. Indian Chem. Soc., 1929, 6, 259—262). —The cold neutral solution of the three acids is treated with a solution of cerous nitrate which precipitates ferrocyanide, the filtrate is treated with nickel nitrate to remove ferricyanide, and finally thiocyanate is detected by addition of ferric chloride. The cerous nitrate precipitate is treated with sodium hydroxide and ferrocyanide confirmed by adding ferric chloride. Ferricyanide is confirmed by treating the nickel precipitate similarly and adding ferrous chloride. A. R. POWELL.

Rapid method of detecting elements of groups II—IV by means of organic reagents. P. Agostini (Annali Chim. Appl., 1929, **19**, 164—173).— The method described serves for the detection of all metals giving chlorides soluble in hydrochloric acid with the exception of the alkali and alkaline-earth metals and magnesium. T. H. POPE.

Analysis of chrome ores. T. R. CUNNINGHAM and T. R. MCNEILL.—See B., 1929, 478.

Rapid method for dissolving high-chromium steels for determination of sulphur. B. S. EVANS.—See B., 1929, 476.

Gravimetric determination of tungsten in presence of vanadium. A. JÍLEK and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 263-274).-To determine tungstate in presence of vanadate, 1 c.c. of concentrated hydrochloric acid is added to 100 c.c. of the neutral solution, and the vanadium reduced to the quadrivalent state with hydroxylamine hydrochloride at the b. p., and then after addition of a 2% solution of arsenic acid the tungsten is precipitated at the b. p. as quinine arsenotungstate by means of a 2% solution of quinine hydrochloride. The precipitate is then ignited to give tungsten trioxide, and weighed. The organic matter in the filtrate is destroyed by treatment with sulphuric acid and cupric oxide, and after reduction of the arsenic acid with sulphur dioxide copper and arsenic are separated as sulphides. By treatment of the alkaline solution with hydrogen peroxide, the vanadium is re-oxidised

to vanadate, then precipitated with mercurous nitrate and weighed as vanadic oxide after ignition. R. CUTHILL.

Colorimetric micro-determination of uranium salts. M. TISSIER and H. BÉNARD (Compt. rend. Soc. Biol., 1928, 99, 1144—1146; Chem. Zentr., 1928, ii, 2582).—The reaction with potassium ferrocyanide is employed. A. A. ELDRIDGE.

Volumetric determination of vanadium by means of potassium iodate. E. H. SwIFT and R. W. HOEPPEL (J. Amer. Chem. Soc., 1929, 51, 1366—1371).—To 25 c.c. of vanadate solution in an atmosphere of carbon dioxide hydrochloric acid is added so that, after the subsequent addition of a slight excess of standard potassium iodide solution, the mixture contains 6 to 8M-hydrochloric acid: $2H_3VO_4+2HI+4HCl=2VOCl_2+I_2+6H_2O$. Five c.c. of carbon tetrachloride are then added and the whole is titrated with standard potassium iodate solution: $2I_2 + HIO_3 + 5HCl = 5ICl + 3H_2O$; $2HI + HIO_3 +$ $3HCl=3ICl+3H_2O$. Hydrochloric acid must be added during the titration so that the solution is always 6M in acid, for at this concentration quadrivalent vanadium is not oxidised by the iodine monochloride formed in the titration. Phosphate, arsenate, or ferric iron may be present. Tungstic acid may also be present if it is kept in solution by phosphoric acid. S. K. TWEEDY.

Simple viscosimeter. R. A. VAN LINGE (Chem. Weekblad, 1929, 26, 301).—A pipette having a capillary tube in place of the lower limb is provided at the upper end with a three-way tap, which permits of easy filling to a constant level; a half turn allows the measured quantity to flow through the capillary. S. I. LEVY.

Preparation of a stabilised electrode and its use in the determination of halogens. N. JOASSART and E. LECLERC (Bull. Soc. chim. Belg., 1929, 38, 121-131).—A method for the determination of halogens in acid solution using an electrode in a medium containing gelatin is described.

F. J. WILKINS.

Apparatus for extraction with filtration. A. KULMAN (Oil Fat Ind. Russia, 1928, No. 8, 7—11; Chem. Zentr., 1929, i, 110).—An apparatus for the determination of loss of weight on extraction is described. A. A. ELDRIDGE.

Bending glass tubing. R. N. ALLEN (Phillipine J. Sci., 1929, 38, 299).—Asbestos fibre is tamped tightly into the bore of the tube where the desired bend is to be made; the glass may be then heated and bent without any collapse occurring. The fibre may be removed when cool with a piece of wire, as it does not fuse into the glass. B. W. ANDERSON.

Modern chemical balances. L. RAMBERG (Svensk Kem. Tidskr., 1929, 41, 106—119).—A discussion of the relative advantages and disadvantages of the various types of balances employed in chemical work. With regard to the usual form of microbalance, it is pointed out that a serious error, which may amount to 0.005 or even 0.01 mgm., may easily arise through the practical impossibility of ensuring that the rider always takes up exactly the same position in any notch on the graduated rider arm (cf. A., 1925, ii, 319). H. F. HARWOOD.

Gas analysis [apparatus]. J. T. DONNELLY, C. H. FOOTT, and J. REILLY.-See B., 1929, 421.

Modified Hempel gas burette. G. H. W. LUCAS. -See B., 1929, 457.

Crucible tongs for analytical work. L. RAM-BERG (Svensk Kem. Tidskr., 1929, 41, 78-79) .- An improved form of crucible tongs is described. The lower ends are formed from nickel wire, 2 mm. thick, shaped so as to permit of crucibles of different sizes being encircled and lifted. Owing to the special construction of the nickel ends, even the thinnest and smallest platinum crucibles can be handled without risk of deformation, whilst the tongs can also be employed for lifting dishes up to 6 cm. diameter. H. F. HARWOOD.

Ebullioscopic and tonometric determinations.

W. SWIENTOSLAWSKI (Rocz. Chem., 1929, 9, 266-308).—A description of various ebullioscopic apparatus designed by the author, and of the technique of their application to a number of problems.

R. TRUSZKOWSKI.

Barium sulphate as an indicator of the degree of hydration of sulphuric acid in drying appar-clear until diluted to about 93% concentration; between 93% and 84%, needle crystals of the com-pound $BaSO_4, 2H_2SO_4, H_2O$ separate freely; on further dilution, the needle crystals change to the fine crystals of barium sulphate. This change is easily detected, and may be used as an indication that the acid is too dilute for further effective drying. S. I. LEVY.

Two laboratory rotating furnaces. F. HEIN-RICH (Chem. Fabr., 1929, 173-174).-The simpler model is intended for rotation in a gas-fired muffle furnace, the larger for direct heating by gas. S. I. LEVY.

Micro-determination of vapour density. J. B. NIEDERL (Z. anal. Chem., 1929, 77, 169-174).-An apparatus for the determination of the vapour density of liquids of low b. p. comprises a cylindrical container (50 c.c.) filled with mercury and provided with a capillary tube reaching to the bottom inside and bent outside in the form of an inverted U leading into a collecting cylinder in which the displaced mercury is collected. After heating the apparatus to 10° above the b. p. of the liquid the vapour density of which is required, the weight of mercury displaced by expansion and collected in the cylinder is determined. The apparatus is cooled and again filled with mercury, about 5 mg. of liquid are introduced in a fine capillary tube into the middle of the mercury in the container, and the heating is repeated. The additional weight of mercury collected is a measure of the volume of the A. R. POWELL. vapour of the liquid tested.

Electrically heated thermostat. P. VAN CAMPEN (Z. Elektrochem., 1929, 35, 265-266).-Difficulty often arises in the ordinary electrical controlling device of the heating of a thermostat through the formation of sparks between the mercury surface and the platinum wire in the regulator. A method is described in which very small currents, 10-4 to 10-5 amps., are allowed to pass through the regulator and then on to the grid of an amplifying thermionic valve. The amplified current activates an electrical relay. The temperature can be regulated to $\pm 0.002^{\circ}$.

H. T. S. BRITTON,

Pulfrich step-photometer as a turbidity S. GARTNER (Kolloid-Z., 1929, 48, measurer. 10-15).-A modification of the Pulfrich step. photometer, which enables the instrument to be used as a nephclometer, is described. Some experimental results, obtained with the modified instrument, E. S. HEDGES. are given.

Apparatus for continuous automatic measurement of the alveolar carbon dioxide. REGELS. BERGER (Z. ges. exp. Mcd., 1928, 61, 747-756; Chem. Zentr., 1928, ii, 2671).

Determination of available oxygen by the Bunsen method. T. W. PARKER and P. L. ROBIN-SON (J.C.S., 1929, 1106-1108).—The tendency of potassium iodide solution to be sucked back, in the usual procedure of Bunsen's method, and the necessity of transferring the solution to another vessel for titration, can be obviated. A detachable absorption flask contains a wide tube, ground in and filled with glass beads, serving as a reservoir for potassium iodide solution if the pressure rises, and as an inlet for air if it falls. C. W. GIBBY.

Improved calcium chloride tube. D. V. N. HARDY (J.C.S., 1929, 1108) .- A U-tube is fitted with two stopcocks, by rotating which access of air can be prevented. The interior of one of them is shaped so as to act as a water trap. C. W. GIBBY.

Solid and liquid states of helium. W. H. KEESOM (Natuurwetensch. Tijds., 1929, 11, 65-79).-An account is given of the work of Kamerlingh Onnes on the liquefaction of helium, and of the apparatus employed to attain the lowest recorded temperature of 0.8-0.9° Abs. By increasing the pressure over liquid helium at very low temperatures, solid helium has been obtained, and the pressuretemperature curve for solid helium mapped, from $4\cdot2^{\circ}$ Abs. at 126 atm. to $1\cdot2^{\circ}$ Abs. at 25 atm. The curve bends sharply at the lower end, becoming nearly parallel with the *T*-axis, so that it does not cut the vapour-pressure curve for liquid helium; it is therefore impossible to solidify helium by cooling alone, and solid helium below the critical temperature must always melt before vaporising. The experiments were carried out first in metal containers, later in glass vessels, but although the presence of solid helium was conclusively proved by the arrest of a magnetically controlled stirrer, no difference in appearance or refractive index and no line of demarcation between solid and liquid could be observed. The existence of two liquid modifications of helium. with a transition point at 2.3° Abs. and 38 mm., has been proved from the dielectric constant, specific gravity, and surface-tension curves, all of which show change of direction at 2.3° Abs., and by recording the rate of change of vapour pressure with rising and falling temperature. The modification stable at the lower temperatures has the lower density and surface tension, and the higher latent heat of vaporisation; the heat of transformation is calculated as 0.13 g.-cal. per g. The transition temperature is that at which the triple point was to have been expected for solidliquid-gas phases; the existence of the second liquid modification with this transition temperature indicates a triple point of a character hitherto unknown for elementary substances, and the possibility that the new liquid modification may be crystalline. It is probable also that there is a second triple point corresponding with the co-existence of the solid and both liquid modifications. S. I. LEVY.

Geochemistry.

Helium in New Zealand. C. C. FARE and M. N. ROGERS (New Zealand J. Sci. Tech., 1929, 10, 300-308).—Analyses are given of natural gas from a large number of sources in New Zealand. Helium is an almost universal constituent. C. W. GIBEY.

Larnite (calcium orthosilicate, a new mineral) and associated minerals from a limestone contact-zone in Co. Antrim. C. E. TILLEY (Min. Mag., 1929, 22, 77-86).-At the contact of dolerite with chalk on Scawt Hill, near Larne, the finely granular rock shows an unusual assemblage of minerals, including spurrite (2Ca2SiO4,CaCO3), larnite (Ca2SiO4), merwinite (3CaO,MgO,2SiO2), gehlenite, spinel, and calcite. Optical data are given for each of these. The larnite is readily decomposed with gelatinisation by weak acids, and it is slowly attacked by water with the production of calcium hydroxide. It is monoclinic with optical characters agreeing with the artificial α -Ca₂SiO₄. When the larnite-rock is heated to dull redness and allowed to cool it falls to powder, due to the inversion to γ -Ca₂SiO₄. These contact-metamorphic minerals were probably formed at a high temperature, followed by rapid cooling. L. J. SPENCER.

Renardite. A. SCHOEP (Bull. Soc. Franç. Min., 1928, **51**, 247—252; Chem. Zentr., 1929, i, 374).— Renardite, a new uranium mineral from Chinkolobwe, has *d* greater than 4, n_a 1.715, n_β 1.736, n_γ 1.739 (± 0.003), and contains : insol. (quartz) 2.11, PbO 12.26, P_2O_5 8.15, $Fe_2O_3 + Al_2O_3 + CoO$ 3.68, MoO₃ 0.74, UO₃ 64.82, H₂O 8.74%, corresponding with the formula PbO,4UO₃, P_2O_5 , 9H₂O. A. A. ELDRIDGE.

Friedelite, schallerite, and related minerals. L. H. BAUER and H. BERMAN (Amer. Min., 1928, 13, 341–348).—Chemical analyses and physical properties are recorded. CHEMICAL ABSTRACTS.

Dipyrite and associated contact minerals from the Franklin mountains of Texas. J. T. LONS-DALE (Amer. Min., 1929, 14, 26-32).

Larsenite, calcium-larsenite, and associated minerals at Franklin, N.J. C. PALACHE, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, 13, 334– 340).—Larsenite, H 3, has a:b:c=0.4339:1:0.5234. Chemical analyses are recorded.

CHEMICAL ABSTRACTS.

Zircon from North Burgess, Ont. C. PALACHE and H. V. ELLSWORTH (Amer. Min., 1928, 13, 384— 391).—Zircon has a: c=1:0.6429. Heating increases the density and reduces the refractive index. A chemical analysis is recorded.

CHEMICAL ABSTRACTS.

Nature and origin of the amphibole asbestos of S. Africa. M. A. PEACOCK (Amer. Min., 1928, 13, 241—286).—Analyses of blue crocidolite correspond with the formula

 $3H_2O_2Na_2O_3(Fe,Mg)O_2Fe_2O_3,17SiO_2$; amosite, grey, is an orthorhombic amphibole with ferrous oxide as the dominant base. Optical data and chemical analyses are recorded. CHEMICAL ABSTRACTS.

Uranium/thorium ratio in Monazites. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 229-236).-The fact that the thorium/ uranium ratio in some uranium-rich minerals increases with the geological age of the specimen has led to the conclusion that the parent of the thorium disintegration series is an isotope of uranium (thorouranium, at. no. 92). An attempt has been made to find whether an analogous relation exists in monazite pebbles, crystals, and sands from known localities. i.e., in uranium-poor minerals. Although the results do not conflict with the theory of Riss (Sitzungsber. Akad. Wiss. Wien, 1924, 133, 91), they are not considered sufficient to support it in view of experimental difficulties and the lack of data. No noteworthy connexion has been found between the uranium/thorium ratio and the amounts of thorium and uranium present. This ratio, although of the same order of magnitude for all the specimens analysed, was not constant. Determinations of uranium gravimetrically and by the radium emanation method have given results which agree within the limits of experimental error, showing that in the samples used no detectable amount of any uranium isotope outside the uranium-radium series was present. F. L. USHER.

Dyscrasite and the silver-antimony constitution diagram. G. M. SCHWARTZ (Amer. Min., 1928, 13, 495-503).—Dyscrasite is considered to have the formula Ag₃Sb, a known compound in the system silver-antimony. The origin of an intergrowth, as found in ores at Cobalt, Ont., is discussed. CHEMICAL ABSTRACTS.

X-Ray study of lateritic rocks and of sporogelite. W. F. DE JONG (Z. Krist., 1928, 66, 303— 308; Chem. Zentr., 1928, ii, 2545).—A scheme for the weathering of magmatic rocks is based on X-ray studies of bauxite, kaolinite, diaspore, felspar, and hydrargillite, and of desiccated aluminium hydroxide. A. A. ELDRIDGE.

Heating curves of manganite. N. KURNAKOV and V. ČERNYCH (Zentr. Min. Geol., 1928, A, 359– 361; Chem. Zentr., 1929, ii, 2342).—Loss of water, without loss of oxygen, occurs when manganite, Mn_2O_3, H_2O , is heated at 365–400°.

A. A. ELDRIDGE.

Hydrotalcite and pyroaurite. N. KURNAKOV and V. ČERNYCH (Zentr. Min. Geol., 1928, A, 353-

359; Chem. Zentr., 1928, ii, 2341-2342).-Hydrotalcite, $9Mg(OH)_2$, $4Al(OH)_3$, $8H_2O$, has $d \ge 0.027 - 2.0210$, H 2; in pyroaurite, d 2.049-2.083, the alumina is replaced by iron. Water is eliminated from limonite at 180°, hydrargillite at 240°, brucite at 410°, diaspore (hydrotalcites) at 540°; magnesium carbonate is decomposed at 700°. A. A. ELDRIDGE.

Formation of cupriferous "black earths," Niari, French Congo. R. BURKHARDT (Arch. Sci. phys. nat., 1929, [v], 11, 59—82).—Analyses are given of sandstones, limestones, "black earths," and "red earths" occurring in the French Congo. The

two latter contain small quantitics of copper. C. W. GIBBY. Constitution of the augite of Monti Rossi (Etna). G. G. CRISTALDI and G. COLUMBA (Annali Chim. Appl., 1929, 19, 173—182).—Crystals of this augite contain (1) nitrides and yield, on the average, 0.1493% of ammonia on hydrolysis, and (2) a magnetic ilmenite, d 4.32, with the ratio FeTiO₃: Fe₂O₃ nearly 1. The residual portion of the average mass has a constraint of the average for the second sec augitic mass has a composition differing appreciably from those published and may be regarded as containing diopside-hedenbergite 89.93, spinels 5.42, and pseudo-giadeite 4.65%. T. H. POPE. pseudo-giadeite 4.65%.

[Gudmudite, plumboferrite, hæmatophanite, and jacobsite.] K. JOHANSSON (Z. Krist., 1928, 68, 87-118; Chem. Zentr., 1928, ii, 2449).-Gudmudite, FeSbS, from Gudmunstorp, near Sala, silver-white to steel-grey, H 6, contained Fe 26.83, Sb 57.76, S 15.41%; a:b:c=0.6729:1:1.1868, rhombic. Plumboferrite, d 6.07, from Jakobsberg contained PbO 33.03, FeO 0.71, MnO 1.41, CaO 0.40, MgO 0.34, K_2O 0.13, Na_2O 0.17, Fc_2O_3 63.01, Sb_2O_3 0.25, FeTiO₃ 0.15, insol. 0.15%, corresponding with the formula (Pb, etc.)O,2Fe₂O₃; hexagonal, a:c=1:3.9719. The unit cell, a=11.82, c=47.14 Å., contains 42 mols. Hæmatophanite, d 7.70, occurring with plumboferrite, contained PbO 73·26, FeO 0·22, MnO 0·29, CaO 0·26, MgO 0·06, K₂O 0·17, Na₂O 0·38, Fe₂O₃ 22·01, FeTiO₃ 0·20, Cl 2·17, H₂O 0·73, insol. 0·42%, corresponding with the formula Pb(Cl,OH)₂,4PbO,2Fe₂O₃; tetragonal-holohedral, $c:a=1\cdot95:1$; the unit cell, $a=7\cdot801$, $c=15\cdot23$ Å., contains 3 mols. Jacobsite, H = 1.001, c=15.23 A., contains 3 mols. Jacobsite, H = 6, d = 4.76, from Jakobsberg, Wermland, contained MgO 9.26, MnO 13.94, FeO 2.49, 2.57, FeTiO₃0.17, Fe₂O₃ 73.96%, corre-sponding with the formula MgFe₂O₄, (Mn, Fe)Fe₂O₄; cubic g=8.42 Å the unit cell containing A mole cubic, a=8.42 Å., the unit cell containing 4 mols.;

space-group O_4 . Analyses of a disintegration product of jacobsite, and of a yellowish-green garnet are given. A. A. ELDRIDGE.

Occurrence of germanium in topaz. J. PAPISH (Science, 1928, 68, 350-351).-Germanium was detected in all the specimens of cassiterite and topaz examined. CHEMICAL ABSTRACTS.

Norbergite from Franklin, N.J. E. S. LARSEN, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, 13, 349-353) .-- Norbergite is orthorhombic; optical properties, and an analysis of a specimen, $d^{-3.20}$, H 5.5, are recorded. CHEMICAL ABSTRACTS.

Humite group. E. S. LARSEN (Amer. Min., 1928, 13, 354-359).-Chemical and optical data are recorded. CHEMICAL ABSTRACTS.

Formula of glauconite. A. F. HALLIMOND (Amer. Min., 1928, 13, 589-590).-A discussion. CHEMICAL ABSTRACTS.

Chemistry, optics, and genesis of the hastingsite group of amphiboles. M. BILLINGS (Amer. Min., 1928, 13, 287-296).

"Bauxite" from Kashmir. T. V. M. RAO (Min. Mag., 1929, 22, 87-91).—Six analyses of material from the "bauxite" deposits of Jammu in Kashmir show the extreme values : Al_2O_3 61.70– 80.74, H_2O 12.15–14.99, SiO_2 0.84–14.07, TiO_2 2.48–4.36, Fe_2O_3 0.75–3.56, with small amounts of alkalis, lime, magnesia, and carbon. The material is hard enough to scratch glass and has an average density of 3.2. Under the microscope it is very dense and opaque, and although some diaspore was detected optically, the bulk of the material is thought to be the monohydrate (Al₂O₃,H₂O) called bohmite L. J. SPENCER. (A., 1927, 748).

Petrology of the Whin sill. S. I. TOMKELEV (Min. Mag., 1929, 22, 100-120).—The Whin sill of the north of England (A., 1928, 1211), although very uniform in texture and in chemical and mineralogical composition over a wide area, shows at times some variations. Descriptions with analyses are given of a coarse gabbroid type occurring as bands and streaks in the normal dolerite, of a coarse rock with red granophyric spots, of red felsitic veins, and of spheroidal aplitic inclusions. The coarsely crystallised varieties evidently contained more volatile consti-tuents, and it is suggested that they represent a "wet" differentiation portion of the magma before injection took place in the sill. L. J. SPENCER.

Asymmetric synthesis. R. BOUSSET (Compt. rend., 1929, 188, 1407-1410).-A theoretical discussion of the conditions under which asymmetric synthesis may be effected. J. W. BAKER.

Electrosynthesis of hydrocarbons. L. BER-MEJO and L. BLAS.—See this vol., 775.

Preparation of free methyl. F. PANETH and W. HOFEDITZ (Ber., 1929, 62, [B], 1335-1347).-When a rapid stream of hydrogen or nitrogen charged

Organic Chemistry. with lead tetramethyl is passed at a very low pressure through a heated quartz tube a mirror of lead 15 obtained. When the gaseous products of the decomposition of lead tetramethyl are passed over such a lead mirror at a suitable distance from the point of decomposition, the mirror disappears, but another mirror is produced if the tube is heated at a further point. The product formed by the action of the vapours on the lead mirror can be condensed in a tube cooled in liquid air and, after volatilisation, can be decomposed by heat. The ability of the vapours to combine with lead vanishes very rapidly, but it is possible by suitably heating a tube containing a lead mirror to cause the appearance and disappearance of the mirrors to occur at a distance of 30 cm. Attempts to condense the vapour by liquid air are accompanied by complete loss of activity. The "solvent" action of the vapours on their own lead mirror is apparent, since the edge of the latter on the side opposite to the flame is sharply defined. It appears therefore that the thermal decomposition of lead tetramethyl results in the very transitory production of a gaseous material capable of converting lead into a substance closely similar to, if not identical with, lead tetramethyl. Insight into the nature of the agent is derived from the observation that it transforms an antimony mirror into two substances, m. p. below -20° and $+13.5^{\circ}$, respectively, and a zinc mirror into zinc dimethyl. Since the possible decomposition products of lead tetramethyl, methane, ethane, ethylene, and acetylene are inactive towards metallic mirrors, whether cold or heated, the phenomena can be accounted for only by regarding the aggressive agent as the free methyl radical which has a short, but measurable, life period. Attempts to measure the latter constant are based on the passage of lead tetramethyl vapour under constant conditions through a tube heated at one point and observation of the relationship between the distance between standard antimony mirrors and this point and the time required for the complete disappearance of the antimony mirrors. In a hydrogen atmosphere at 2 mm. pressure, the concentration of free methyl sinks to its half value in approximately 0.006 sec. and free methyl consequently disappears practically completely in 0.1 sec.

The formation of metallic hydrides by the action of the silent discharge in mixtures of hydrogen and methane is probably accompanied to a greater or less extent by that of metallic methyls, and the latter substances are probably necessary intermediates in the production of the hydrides in those cases in which the action is not observed without the presence of methane. H. WREN.

Action of sulphur on *n*-heptane and *n*-butane. R. B. BAKER and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 1566—1567).—*n*-Heptane and sulphur at 150—250° or at 300—350° give a very small yield of a *hiophen*, (?) $C_7H_{10}S$, b. p. 160—161°, d_4^{25} 0.9221, but no mercaptans or sulphides. *n*-Butane and sulphur at 335° give a trace of thiophen (cf. Friedmann, A., 1916, i, 735). H. E. F. NOTTON.

Isomeric heptanes. I. Preparation [with R. E. MIRKER]. II. Properties. G. EDGAR and G. CAINGAERT (J. Amer. Chem. Soc., 1929, 51, 1483— 1491, 1540—1550).—The preparation for the first time of considerable quantities of the pure isomeric heptanes is described. *n*-Heptane (1), b. p. 98:4° (all b. p./760 mm.), m. p. -90.5° , is obtained from Jeffery pine oil (Kremers, A., 1921, i, 705). 5-Methylhexane (2), b. p. 90:0°, m. p. -119.1° ; dl- γ -methylhexane (2), b. p. 91:8°; γ -ethylpentane (4), b. p. 93:3°; β 8-dimethylpentane (7), b. p. 80:8°, m. p. $-123:4^{\circ}$; dl- $\beta\gamma$ -dimethylpentane (6), b. p. 89:7°; and $\beta\beta\gamma$ -trimethylbutane (9), b. p. 80:9°, m. p. -25.0° , are prepared by the method of Chavanne (A., 1919, i, 380; 1922, i, 417; 1924, i, 1025). The unsaturated hydrocarbons obtained by dehydrating $\beta\beta$ -dimethylpentan- γ -ol and $\gamma\gamma$ -dimethylpentan- β -ol both yield mixtures of heptanes when hydrogenated. $\beta\beta$ -Dimethylpentane (5), b. p. 78.9°, m. p. -125.6°, is obtained conveniently, but in small yield, from magnesium *n*-propyl bromide and *tert*.-butyl chloride in presence of mercuric chloride, and $\gamma\gamma$ -dimethylpentane (8), b. p. 86.0°, m. p. -135.0°, from magnesium ethyl bromide, *tert*.-amyl chloride, and mercuric chloride. The properties of the products are compared with published data.

The values of 27 fundamental and derived constants (some taken from previous papers; cf. Smyth and Stoops, A., 1928, 935; Stewart, A., 1928, 1079; Freyer and others, this vol., 637), all determined on the same material, are given for each of the above isomerides. The density, refractive index, dielectric constant, coefficient of expansion, and dispersion and derived constants are affected by changes in constitution in the following way. The values for isomerides containing β -methyl groups are smaller, and for those containing γ - or $\beta\gamma$ -substituents greater, than those for *n*-heptane. With two or more substituents the effect is additive. The order of increasing magnitude of these constants is, therefore : 5, 7, 2, 1, 3, 9, 8, 6, 4. On the other hand, constants related to the internal pressure, e.g., surface tension, b. p., a (van der Waals), and critical solution temperature in aniline, also, less regularly, critical temperature, velocity of sound, adiabatic and isothermal compressibilities, give the order: 5, 7, 9, 2, 8, 3, 6, 1, 4. The two orders differ only in the positions of *n*-heptane and $\beta\beta\gamma$ -trimethylbutane. The critical pressures and viscosities show no relation to other properties. The X-ray diffraction results are discussed. Available data for the hexanes, octanes, nonanes, and decanes are tabulated. In general, these show the same relationships between structure and physical properties as do the heptanes. The results should be of value in the identification of new paraffin hydrocarbons.

H. E. F. NOTTON.

Determination of unsaturation with potassium bromide-bromate mixture. F. CORTESE (Rec. trav. chim., 1929, 48, 564-567).—Francis' method (B., 1926, 811) for the determination of unsaturation by titration with a potassium bromide-bromate mixture is found to be trustworthy for aliphatic olefines and diolefines whether these contain conjugated linkings or not, but is not trustworthy for certain ring structures and for substances of unknown constitution. Thus the values so obtained for furan and a phenylbutadiene polymeride were only half the true values. J. W. BAKER.

Unsaponifiable matter from oils of elasmobranch fish. V. Constitution of squalene as deduced from its degradation products. I. M. HEILBRON, W. M. OWENS, and I. A. SIMPSON (J.C.S., 1929, 873-883).—The conclusions of André and Canal (B., 1927, 416) that squalene is not a single substance or a dihydrotriterpene are contested. Under all methods of attack squalene gives decomposition products typical of those expected from a triterpene hydrocarbon. No definite evidence of the existence of any single monoterpene in the fraction obtained by distillation of squalene at 300—350 mm. in a current of nitrogen can be obtained, only constantboiling mixtures of mono- and di-hydromonoterpenes being produced. Repetition of the hot-wire decomposition (Chapman, J.C.S., 1923, **123**, 769) has failed to confirm the existence of heparene, $C_{10}H_{18}$, although a squalene fraction, b. p. 60—100°/20 mm., when heated with 99% formic acid, gives a liquid, b. p. 125—130°/3 mm., d_{20}^{30} 0.9098, n_{20}^{30} 1.4998, probably a diterpene (dimyrcene ?).

Majima and Kubota's ozonolysis experiments (A., 1923, i, 1, 174) are mainly confirmed; their two unidentified substances, m. p. 195° and 136°, are lævulaldehyde peroxide and methylheptenone peroxide, respectively.

Oxidation of squalene in acetone solution at the ordinary temperature by solid potassium permanganate has led to the isolation of succinic acid, methylheptenone, and dihydro- ψ -ionone; this proves the presence in squalene of the carbon skeleton :

 \hat{C} ·C(C):C·C·C· \hat{C} (C):C·C·C(C):. Treatment of squalene with chromyl chloride leads chiefly to the production of resins, but some formaldehyde, acetaldehyde, and succinic acid can be isolated.

Squalenes obtained from Centrophorus granulosus or from Scymnorhinus lichia in ethereal solution, by bromination at -25° , give a crude squalene dodecabromide resolvable into two dodecabromides, m. p. 198° and 178°, insoluble and soluble, respectively, in ethyl acetate; the first and more stable dodecabromide definitely has the formula $C_{30}H_{50}Br_{12}$. It is concluded that squalene exists as an isomeric mixture of dihydrotriterpenes to which the formulæ

 CMe_2 ·CH·CH₂·[CH₂·CMe:CH·CH₂]₄·CH₂·CMe:CHMe and

CMe₂·CH·CH₂·[CH₂·C(:CH₂)·CH₂·CH₂]₄·CH₂·CMe: CHMe are given. R. J. W. LE Fèvre.

Unsaponifiable matter from oils of elasmobranch fish. VI. Constitution of squalene as deduced from a study of the decahydrosqualenes. I. M. HEILBRON and A. THOMPSON (J.C.S., 1929, 883-892) .--- Squalene is treated with hydrogen in the presence of nickel catalyst until 5 mols. are absorbed. The hydrogenation is selective, isomeric decahydrosqualenes being formed accompanied by about 25% of dodecahydrosqualene (squalane) : evidently products hydrogenated to a lower degree than decahydrosqualene are also formed. The mixed hydrosqualenes, b. p. 227-230°/3 mm., were ozonised in chloroform solution; the ozonide had d < 1. Decomposition of the ozonide by boiling water in an atmosphere of nitrogen leads to the following products : (1) neutral, methyl isohexyl ketone (semicarbazone, m. p. 149-150°), hexahydro- ψ -ionone, a ketone, C₁₉H₃₈O, probably ynd-trimethylhexadecan-o-one, b. p. 136-139°/ 1.5 mm., n_D²⁰ 1.4461 (semicarbazone, m. p. 71.5-73.5°), and a ketone, $C_{24}H_{48}O$, probably $\gamma\eta\lambda o$ -tetramethyl-eicosan- τ -one, b. p. 195–205°/3 mm., mixed with squalene; (2) acid, γ -methyl-*n*-valeric acid, $\delta \theta$ -dimethylnonoic acid, b. p. 105-108°/3 mm. (amide, m. p. 80-81°) (also obtained from synthetic hexahydro- ψ -ionone by the action of chromic acid in acetic acid

solution) and an acid, $C_{17}H_{54}O_{2}$, probably $\gamma\eta\lambda$ -trimethyltetradecoic acid, b. p. $182-192^{\circ}/5$ mm. In some experiments 80-dimethylnonaldehyde (?) (semicarbazone, m. p. $115-116^{\circ}$) can be isolated.

In connexion with the identity of the kotone $C_{19}H_{38}O$ (above) farnesol was hydrogenated at 100° by hydrogen in the presence of nickel on charcoal; the hexahydrofarnesol, b. p. 125–128°/3 mm., d_4^{18} 0.8361, n_1^{18} 1.4469, obtained is converted successively into hexahydrofarnesyl bromide, b. p. 122°/4 mm., d_4^{18} 1.001, n_1^{18} 1.4605, ethyl hexahydrofarnesylacctoacetate, b. p. 175–178°/3 mm., d_4^{18} 0.9014, n_1^{18} 1.4484, and $\beta\zeta_{5}$ -trimethyl- ξ -pentadecanone, b. p. 142–143°/3 mm., d_4^{18} 0.8403, n_1^{18} 1.4435 (semicarbazone, m. p. 70–70.5°).

It is concluded that in addition to the structures I and II given (preceding abstract), squalene exists in a third isomeric form,

CMe₂:CH·CH₂·CH=CMe·[CH₂]₂·CH:CMe·[CH₂]₂·CH; CMe⁻[CH₂]₂·CH:CMe·[CH₂]₂·CMe:CHMe. The addition of hydrogen to the squalene molecule probably proceeds from the terminal grouping CMe:CHMe common to the three forms. R. J. W. LE FRVE.

Hepta-a di-inene and nona-a0-di-inene. LRS-PIEAU and JOURNAUD (Compt. rend., 1929, 188, 1410-1411).-The action of the magnesium compound of βδ-dibromo-Δª-butene on epidibromohydrin yields β '-dibromo- $\Delta^{\alpha'}$ -heptadi-inene mixed with its higher homologue. Separation is difficult, so that on conversion into the diacetylene a mixture of C, and Cs hydrocarbons is obtained. Heptadi-inene, CH: $[CH_2]_n$ C:CH (n=3), b. p. 111.5-112.5°, d^n $0.8164, n_D^{17} 1.451$, and nonadi-inene (n=5), b. p. 55-55.5°/13 mm., m. p. -21°, d²¹ 0.8159, n²¹ 1.452, are readily obtained by the action of monosodioacertlene on, respectively, tri- and penta-methylene bromide. the reaction proceeding smoothly under ordinary pressure (cf. Lebeau and Picon, A., 1913, i, 438). With alcoholic silver nitrate these diacetylenes yield disilver derivatives (each combined with 2AgNO2) which react with iodine to yield the hexaiolides (CI2:CI)2(CH2)n, m. p. 75.5-76.5° and 107-108°, respectively. J. W. BAKER.

Characteristic reaction of primary aci-nitrocompounds. H. WIELAND and Z. KITASATO (Ber., 1929, 62, [B], 1250-1253).—Methazonic acid in anhydrous pyridine is converted by benzoyl chloride at -15° to -5° into dibenzoylchloroglyozime,

OBz·N:CH·CCI:N·OBz, m. p. 165°, the constitution of which is established by its formation from anlichloroglyoxime, whereas amphi - chloroglyoxime affords a chlorinated dibenzoyl derivative, m. p. 165°, which depresses the m. p. of the compound from methazonic acid. Under similar conditions, accphenylnitromethane gives the chloride of benzoylbenzhydroxamic acid, m. p. 109°, prepared also from benzhydroxamyl chloride. Secondary aci-nitro-derivatives do not appear to undergo this change but to be normally benzoylated. H. WREN.

Methyl alcohol from hydrogen and carbon monoxide. II. Dimethyl ether. R. L. BROWN and A. E. GALLOWAY.—See B., 1929, 426.

Rapid dehydration of alcohol using barium oxide and metallic calcium. G. F. SMITH.—See B., 1929, 449. Configuration of pentaerythritol. III. J. BORSEKEN and B. B. C. FELIX (Ber., 1929, 62, [B], 1310-1316; cf. A., 1928, 616, 1213).—In reply to Kenner (this vol., 171) and Semenzov (*ibid.*, 538), who have pointed out that a pyramidal arrangement of the groups in pentaerythritol is not incompatible with an asymmetric configuration, it is maintained that such molecules would only with difficulty retain their unsymmetrical nature in solution and would pass by oscillation through symmetrical phases which would render impossible fission into optical antipodes. Until evidence of *cis-trans*-isomerism of the acetals is forthcoming the optical resolution is regarded as establishing the tetrahedral configuration.

Aminoacetaldehyde diethylacetal is condensed with pentaerythritol by hydrogen chloride in absolute alcohol to the compounds $[NH_2 \cdot CH_2 \cdot CH_2 \circ CH_2 \circ CH_2]_2 C$, m. p. 62—64°, and $(OH \cdot CH_2)_2 C \cdot C_2 H_4 \circ O_2 \cdot CH \cdot CH_2 \cdot NH_2$, m. p. 124°. The former compound is resolved by malic acid into the l-base, m. p. 60—70°, $[\alpha]_D^m - 0.43°$ in water, and the d-base, m. p. 72—74°, $[\alpha]_D^m + 0.95°$ in water.

Camphor does not react in the usual manner with pentaerythritol, whereas its diethylacetal gives the dicamphoracetal, m. p. 156° , $[\alpha]_D^m - 29\cdot3^{\circ}$ in chloroform, and monocamphoracetal, m. p. 135° , $[\alpha]_D^m - 18\cdot6^{\circ}$ in chloroform. Indications of the existence of isomerides are not obtained.

p-Cresol is hydrogenated under pressure in presence of nickel to 4-methylcyclohexanol, which is transformed by phosphorus tribromide into the corresponding bromide, b. p. 55°/15 mm. Successive treatment with magnesium and ethyl orthoformate transforms the bromide into hexahydro-p-tolualdehydediethylacetal, b. p. 110°/15 mm., d¹⁶ 0.8801, n¹³ 1.4572, which is hydrolysed, converted into the aldehyde sodium hydrogen sulphite compound, and condensed with formaldehyde in the presence of potassium hydrorde to 4:4-dihydroxymethyl-1-methylcyclohexane, b. p. 105°/0 mm.; m. p. 45°. The last-mentioned compound condenses with pyruvic acid to the spiran, C₆H₉Me:C₂H₄O₂:CMe·CO₂Et, b. p. 82-89°/0 mm., # 1044 (1.049), no 1.4635 (1.4638); the corresponding acid, m. p. 111°, is partly resolved into its optical antipodes by means of quinine. H. WREN.

Trifluoro-alcohols. II. Trifluoroisopropyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1929, 38, 99-109; cf. A., 1927, 1055).-Trifluoroisopropyl alcohol, b. p. 77.7° (corr.)/754 mm., m. p. -52°, * 1.2799, $n_{\rm D}^{15}$ 1.3172, is prepared by an improved method of catalytic hydrogenation of trifluoroacetone under pressure. The alcohol has acidic properties. The dissociation constant in water is 2×10^{-7} at 25°. It reacts with potassium carbonate to yield the Phanum derivative. No ethylenic compound can be ottained from the alcohol by treatment with zinc choride, oxalic acid, or concentrated sulphuric acid. the last reagent yields trifluoroisopropylsulphuric acid, solated as the barium salt (+2H2O), which decomposes when kept or heated to give the alcohol, barium suphate, and sulphuric acid. Hydrogen bromide does not attack the alcohol. The action of phosphorus tribromide yields trifluoroisopropylphosphorous momide, C3H4F3OPBr2, m. p. 48°, b. p. 156-157°, 4ª 1-988. When this compound is treated with

bromine (1 mol.) and the product distilled, decomposition takes place partly with the formation of *trifluoroisopropyl bromide*, b. p. 49°, d^{13} 1.633. The distillation residue, containing the phosphorous bromide compound, yields when treated with water *trifluoroisopropyl phosphorous acid*, isolated as the *barium* salt. *Trifluoroisopropyl acetate* has b. p. $85\cdot6^{\circ}/75$ mm., d^{13} 1.1823, $n_{\rm D}^{\rm m}$ 1.3314. The allophanate has m. p. 159.7° (decomp.). The physical properties of trifluoro-alcohols are compared and discussed.

R. K. CALLOW.

Acetylene oxides and α -lactones. W. MADE-LUNG and M. E. OBERWEGNER (Naturwiss., 1929, 17, 430).—The isolation of phenylacetylene oxides, and hydroxy- and alkyloxy-derivatives of these, which in the enol form have α -lactone structures, is mentioned. S. I. LEVX.

 $\alpha \alpha' \beta \beta'$ -Tetrabromoethyl ether and so-called "tetrabromobutaldehyde." H. HIBBERT, S. Z. PEREN, and K. A. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 1551—1555).—Vinyl ether, conveniently prepared by the continued action of $\beta\beta'$ -dichloroethyl ether on strongly heated powdered potassium hydroxide, gives with bromine in chloroform $\alpha \alpha' \beta \beta'$ -tetrabromoethyl ether, m. p. 63—65°. This is, as suggested by Stepanov (A., 1927, 42; cf. A., 1923, i, 439), identical with the compound described by Freundler (A., 1907, i, 285) as tetrabromobutaldehyde. With ethylene glycol at 100° it gives β -bromoethylidene ethylene ether (57% of the theoretical). H. E. F. NOTTON.

Mechanism of organic reactions. I. Wandering of acyl groups in glyceryl esters. H. HIBBERT and N. M. CARTER (J. Amer. Chem. Soc., 1929, 51, 1601—1613).—Reactions of glyceryl esters which are accompanied by acyl wandering are reviewed (cf. Fairbourne and Cowdrey, this vol., 292). Hydrolysis of $\alpha\gamma$ -benzylideneglyceryl benzoate (A., 1928, 1213) with aqueous alcohol containing a little hydrochloric acid and p-nitrobenzoylation of the oily product yields a mixture of glyceryl α -benzoate β -p-nitrobenzoate and glyceryl α -benzoate $\beta\gamma$ -di-*p*-nitrobenzoate (Bergmann, A., 1921, i, 444). Similarly, $\alpha\gamma$ -benzylideneglyceryl p-nitrobenzoate, m. p. 156°, $\alpha\beta$ -benzylideneglyceryl p-nitrobenzoate, m. p. 90—91°, and $\alpha\beta$ -isopropylideneglyceryl p-nitrobenzoate are all hydrolysed by dilute hydrochloric acid to glyceryl a-p-nitrobenzoate; whilst $\alpha\gamma$ -benzylideneglyceryl p-bromobenzoate, m. p. 146°, $\alpha\beta$ -benzylideneglyceryl p-bromobenzoate, m. p. 72°, and $\alpha\beta$ -isopropylideneglyceryl p-bromobenzoate, m. p. 39–40°, are all hydrolysed to glyceryl α -p-bromobenzoate, m. p. 70°. These results illustrate the tendency of β -acyl groups to migrate to the α -position in reactions involving the use of acids. The mechanism of the change is discussed. Conclusions as to the constitution of polyhydroxy-derivatives, based on the progressive hydrolysis of their acyl derivatives must, accordingly, be regarded as untrustworthy. The structure of glyceryl ay-ditrityl ether (cf. Helferich, A., 1928, 44) has been confirmed by the hydrolysis of its methyl ether, m. p. 158.5°, by hydrogen bromide in glacial acetic acid at 0° to β -methyl glyceryl ether.

H. E. F. NOTTON.

Reactions in liquid hydrogen sulphide. VI. Reactions with organic compounds. R. W.

BORGESON and J. A. WILKINSON (J. Amer. Chem. Soc., 1929, 51, 1453-1456; cf. A., 1928, 961).-Saturated aromatic hydrocarbons and vaseline, ethyl ether, phenols, saturated monobasic acids, alkyl and aryl halides, amides (picramide reacts slowly) and alkylamines are all soluble and non-reactive. Amylene and trimethylethylene are miscible with and non-reactive towards liquid hydrogen sulphide unless the temperature is raised to about 18°, when an unstable white solid separates on re-cooling to -77° . The odour of a mercaptan is produced on dissolution of unsaturated compounds. Aldehydes react as follows: R.CHO+ $H_{2}S \rightarrow R \cdot CH(OH) \cdot SH \rightarrow R \cdot CHS + H_{2}O$, the water forming white crystals of H₂S,xH₂O. Sugars are insoluble. Grignard reagents react vigorously, liberating the corresponding hydrocarbon. Alkylamines react to form unstable viscid liquids or crystalline solids. Phenylhydrazine yields yellow crystals of NHPh·NH₂, H₂S. Acyl halides react as follows: (i) $R \cdot COCl + H_2S \longrightarrow R \cdot CO \cdot SH + HCl$; (ii) $R \cdot CO \cdot SH + H_2 S \longrightarrow R \cdot CS \cdot SH + H_2 O$. Dithioacetic acid thioanhydride, (CSMe)2S, m. p. 225°, is obtained by dissolving acetyl chloride or bromide in liquid hydrogen sulphide. S. K. TWEEDY.

Formylmethanedisulphonic and bromoformylmethanedisulphonic acids. H. J. BACKER (Rec. trav. chim., 1929, 48, 571-576).-Formylmethanedisulphonic acid (I) [silver +H20 (cf. Schroeter, A., 1898, i, 614) and thallous $+H_2O$, salts] is best prepared by Rathke's method (A., 1872, 388), when it is obtained as its potassium hydrogen sulphite derivative (solubility, in absence of air at 25°, 2.12 g./100 g. of water). The solubilities of the potassium $+H_2O$, and barium $+4H_2O$ (lit. $+2H_2O$) and anhydrous, salts at 25° are respectively 1.02, 0.3935, and 0.3245 g./100 g. of water. Bromoformylmethanedisulphonic acid [potassium $+H_{2}O$ (solubility, 8.92 g./100 g. of water at 25°) and barium $+2H_2O$ salts] is obtained by bromination of I, its potassium hydrogen sulphite derivative, or its barium salt at 100°, but interaction of potassium bromoformylmethanedisulphonate and potassium hydrogen sulphite yields only the hydrogen sulphite derivative of I in accordance with the equation $C(CH:O)Br(SO_3K)_2 + 2KHSO_3 + H_2O = KHSO_3$. $OHC \cdot CH(SO_3K)_2 + KHSO_4 + HBr.$ J. W. BAKER.

Electrolysis of animonium acetate and ammonium hexoate. F. FICHTER and W. LINDEN-MAIER.—See this vol., 775.

Thiocyanogen value of fats. H. P. KAUFMANN [with A. BROCKE].—See B., 1929, 441.

Preparation of unsaturated acids and esters. E. PHILIPPI (Monatsh., 1929, 51, 277–279).—Elaidic acid and its ethyl ester are best obtained (45% yield) by von Farnsteiner's method (A., 1899, ii, 705). Ethyl $\beta\beta$ -dimethylacrylate, b. p. 61·5°/30 mm., is obtained in 75% yield by Weinig's method (A., 1895, i, 17) from ethyl α -bromoisovalerate, b. p. 106–108°/ 30 mm. (Schleicher, A., 1892, 427). Ethyl $\Delta\gamma$ -pentenoate is obtained from allyl alcohol (Coffey and Ward, J.C.S., 1921, **119**, 1303) through allyl bromide, and ethyl allylacetoacetate, b. p. 118–121°/26–33 mm. (Brühl, A., 1894, ii, 433), hydrolysis of the latter being best accomplished by the (slightly modified) method of Zeidler (A., 1877, iii, 437). Vinylacetic acid is obtained in slightly less than the stated yield by Bruylant's method (A., 1924, i, 1053) using allyl chloride in place of the bromide or iodide. Sorbic acid is obtained in 63% yield by Doebner's method (A., 1900, i, 536) if the starting material is carefully purified, and Δ^{β} -hexenoic acid is best obtained by Fittig's method (A., 1872, 486). J. W. BAKER.

Action of ammonia and amines on the esters of unsaturated acids. E. PHILIPPI and E. GALTER [and, in part, M. ZORZI and E. BERTEL] (Monatsh. 1929, 51, 253-266; cf. Philippi and Spenner, A., 1915, i, 222).-Interaction of unsaturated esters with ammonia, methylamine, and piperidine at a lower temperature favours amide formation, whilst addition occurs mainly with the use of a solvent (alcohol or water) at a higher temperature. With $\alpha\beta$ -unsaturated acids addition is the main reaction, with By-acids amide formation preponderates, whilst yd-acids in general show very little tendency to react. Examples of the following types of possible action are given: (1) simple addition, (2) amide formation, (3) (1) and (2) combined, (4) abnormal reactions such as ring formation or rearrangement of the position of the double linking, (5) no action. Thus ethyl crotonate and anhydrous ammonia at the ordinary temperature give a 55% yield of ethyl β-aminobutyrate, whilst with piperidine a 60% yield of ethyl β-piperidinobutyrate, b. p. 125°/15 mm. (decomp. into its components by distillation under atmospheric pressure), is obtained. Ethyl acrylate and piperidine give ethyl β-piperidinopropionate, b. p. 104-106°/ 12-13 mm. (yield 87%). Amide formation alone occurs with methyl Δ^{β} -hexenoate and ammonia, yielding Δ^{β} -hexenoamide, m. p. 75°, and with ethyl phenylisocrotonate, whilst methyl sorbate yields only 10% of the amide together with unidentified products. With anhydrous methylamine ethyl crotonate yields ethyl \$-methylaminobutyrate together with \$-methylaminobutyrmethylamide, b. p. 146°/56 mm., whilst ethyl $\Delta \gamma$ -pentenoate (allylacetate) yields only a trace of the acid amide, most of the ester being recovered unchanged. Rearrangement occurs when ethyl \$\$-dimethylacrylate reacts with ammonia or methylamine, the products being, respectively, ethyl β-amino- and β-methylamino-isovalerate, b. p. 71.5-72°/11 mm., accompanied in the latter case by β -methylamino. isovalermethylamide, b. p. 138-140°/15 mm. No action occurs between ammonia (or methylamine) and ethyl oleate, elaidate, and a-ethylacrylate, or between piperidine and ethyl ßß-dimethylacrylate.

J. W. BAKER.

Esters of butenoic acids. P. BRUYLANTS (Bull. Soc. chim. Belg., 1929, **38**, 133-143; cf. A., 1928, 401, and Auwers, A., 1923, i, 746).—Ethyl vinylacetate, b. p. $124\cdot0-124\cdot2^{\circ}/755$ mm., $d_4^{\circ\circ}$ 0.91224, $n_{11}^{\circ\circ}$ 1.41054, is best prepared by esterification of the acid, using sulphuric acid. Esterification of the nitrile by alcohol and sulphuric acid yields a product containing ethyl crotonate and unchanged nitrile. The product obtained from $\beta\gamma$ -dibromobutyronitrile by esterification and treatment with zinc contains unchanged nitrile. Ethyl vinylacetate is isomerised completely to ethyl crotonate by boiling with sodium phenoxide. Ethyl crotonate, b. p. $136\cdot6-136\cdot8^{\circ}/749$ mm., $d_{4^{\circ}}^{2\circ}$ 0·91752, $n_{1^{\circ}}^{2\circ}$ 1·42524, is best obtained by esterification of the acid. Dehydration of ethyl β -hydroxybutyrate in chloroform solution by phosphoric oxide yields ethyl crotonate accompanied by ethyl vinylacetate. Ethyl isocrotonate, b. p. $125\cdot5-126^{\circ}/749$ mm., $d_{4^{\circ}}^{2\circ}$ 0·91820, $n_{1^{\circ}}^{2\circ}$ 1·42423, is prepared by treatment of pure sodium isocrotonate in alcohol with ethyl iodide. Ethyl methylacrylate, b. p. $118\cdot4-118\cdot6^{\circ}/753$ mm., $d_{4^{\circ}}^{2\circ}$ 0·91063, $n_{1^{\circ}}^{2\circ}$ 1·41472, may be obtained either from ethyl β -chloroisobutyrate by interaction with pyridine in presence of a little sodium iodide, followed by dry distillation, or from ethyl α -bromoisobutyrate by interaction with diethylaniline. cycloPropanecarboxylic acid has $d_{4^{\circ}}^{2\circ}$ 1·42293. The ethyl ester has b. p. $132\cdot4-132\cdot6^{\circ}/750$ mm., $d_{4^{\circ}}^{2\circ}$ 0·96078, $n_{1^{\circ}}^{2\circ}$ 1·41902.

R. K. CALLOW. Highly unsaturated acids of sardine oil. I. New acid, $C_{16}H_{26}O_2$, and the highly unsaturated C_{18} -acids. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1929, 4, 83—91).—The highly unsaturated acids from Japanese sardine oil were separated by the method already described (A., 1925, i, 1129; B., 1927, S3) and converted into the methyl esters; by distillation of the product in a vacuum, a lower fraction, b. p. 215°/15 mm., was obtained together with a higher fraction [saponification value, 198·8; iodine value (Rosenmund and Kuhnhenn) 179·6°, n_{10}^{∞} 1·4628] containing considerable quantities of admixed esters of a low degree of unsaturation. Bromination of the lower-boiling ester fraction affords an ether-insoluble bromide, m. p. 220° (decomp.), separated by benzene into a soluble fraction (A) (Br=66·52%, sinters 165°, m. p. 198°) and an insoluble fraction (B) [Br=69·25%, darkens above 200°, m. p. 240° (decomp.)].

By treatment with zinc and glacial acetic acid for 5 hrs. at 100° in an atmosphere of carbon dioxide, A gives a 74% yield of esters, from which two fractions (E and F) are obtained by distillation; E consists essentially of methyl hiragonate, $C_{17}H_{28}O_2$, b. p. 180— 190°/15 mm., d_1^{45} 0.9160, n_{15}^{15} 1.4792, giving an etherinsoluble bromide, $C_{17}H_{28}O_2Br_6$, m. p. 180° (yield 57%), and affording by hydrolysis hiragonic acid, $C_{16}H_{26}O_2$, d_1^{40} 0.9324, n_{15}^{45} 1.4876, which by bromination gives a 57% yield of a bromide, $C_{18}H_{26}O_2Br_6$, m. p. 190°. By hydrogenation hiragonic acid yields palmitic acid accompanied by small quantities of acids with more than 16 C-atoms. Fraction F contains a methyl ester, $C_{19}H_{32}O_2$, b. p. 205—215°/15 mm., d_{15}^{16} 0.9168, a_{15}^{15} 1.4856, giving a 49% yield of a bromide, $C_{19}H_{32}O_2Br_6$ or $C_{19}H_{32}O_2Br_8$, m. p. 215° (decomp.), and affording by hydrolysis a product consisting mainly of an acid, $C_{19}H_{30}O_2$, d_{15}^{4} 0.9329, n_{15}^{15} 1.4935, giving a 49% yield of a bromide, $C_{18}H_{30}O_2Br_6$, m. p. 215° (decomp.). Hydrogenation affords mainly stearic acid, accompanied by small quantities of C_{16}^{-} and C_{20} -acids.

By debromination with zinc and glacial acetic acid, B gives a 76% yield of a product from which, after removal of unsaponifiable matter, distillation furnishes two fractions (G), b.p. $205-215^{\circ}/15 \text{ mm.}$, and (H), b.p. $215-230^{\circ}/15 \text{ mm.}$; G appears to consist of a mixture of methyl esters, $C_{19}H_{30}O_2$ and $C_{19}H_{32}O_2$, in which the former predominates, d_1^{15} 0.9172, n_D^{15} 1.4862, giving a bromide, $C_{19}H_{30}O_2Br_8$, m. p. 215° (decomp.), and affording by hydrolysis a mixture of acids, $C_{18}H_{28}O_2$ and $C_{18}H_{30}O_2$, d_1^{15} 0.9332, n_D^{15} 1.4942. The acid $C_{18}H_{28}O_2$ predominates, and bromination affords a bromide, $C_{18}H_{28}O_2Br_8$, m. p. 220° (decomp.); hydrogenation yields stearic acid with small quantities of C_{16} -acids. Fraction H was not examined further. C. W. SHOPPEE.

Iwashi (sardine) acid. M. TSUJIMOTO (Bull. Inst. Tokyo Ind. Res. Lab., 1928, 23, No. 3, 1–23). For the acid, $C_{22}H_{34}O_2$, d_4^{15} 0.9410, n_5^{15} 1.5057, iodine value (bromopyridine method) 388.8, the following alternative formulæ are deduced from ozonisation experiments

(i) CHEt[:CH·[CH₂]₂·CH]₃:CH·CH₂·CH:CH·[CH₂]₂·CO₂H, (ii) CHEt[:CH·[CH₂]₂·CH]₂·CH·CH₂·CH:CH· CO₂H, (ii) CHEt[:CH·[CH₂]₂·CH]₂·CH·CH₂·CH·CH· CH·[CH₂]₂·CH:CH·[CH₂]₂·CO₂H.

CHEMICAL ABSTRACTS.

Lactic acid tests. H. V. ARNY and M. C. DIMLER (J. Amer. Pharm. Assoc., 1929, 18, 459—462).— From an examination of published tests for the determination of lactic acid in presence of other organic acids the most satisfactory was found to be a combination of extraction with ethyl acetate (Ohlsson, A., 1916, ii, 542) and the resorcinol test of Brauer (A., 1920, ii, 517). E. H. SHARPLES.

Active molecule of oxalic acid. F. OBER-HAUSER and J. SCHORMÜLLER (Annalen, 1929, 470, 111-128; cf. Oberhauser and Hensinger, A., 1928, 505; Tschitschibabin, this vol., 48).-A qualitative test for manganese, sensitive for 0.1 mg. of manganese per litre consists of treating a manganese salt with hydrogen peroxide, mercuric chloride, and oxalic acid, when precipitation of mercurous chloride occurs. Activation of oxalic acid may be carried out by treating the anhydrous acid with potassium permanganate in acetone, showing that the nature of the solvent is of little importance. Prolonged exposure of a mixture of a ferrous salt, oxalic acid, and mercuric chloride to air causes a separation of mercurous chloride. Oxygen facilitates the change, whilst an inert gas prohibits it. A convenient method for the preparation of activated oxalic acid consists in treating the acid with hydrogen peroxide in presence of a small amount of a ferrous salt (ferric salts have no effect). The reduction of mercuric chloride by such a mixture has been studied in detail, and it is found that 1 g.-atom of ferrous iron causes precipitation of 100-500 mols. of mercurous chloride. No stoicheiometrical relationship exists between the ferrous iron and (or) hydrogen peroxide, and the activated oxalic acid. The order of addition of the reagents is important : no precipitation of mercurous chloride occurs when the ferrous salt is added to the mixture. No formic acid is formed during the activation (cf. Krauss and Bruchhaus, this vol., 541), and the activated oxalic acid is the stronger reducing agent. The active acid is also produced during the anodic oxidation of oxalic acid, by the action of nitrites, and by ammonium or potassium persulphates. In this last case activation is presumably due to Caro's acid, since hydrogen peroxide and sulphates have no action. When a mixture of oxalic acid and ammonium oxalate is heated no activation occurs, but exposure of

such a solution to a mercury-quartz arc lamp gives an active product. The activated acid loses its activity when heated for a short time, and addition of mercuric chloride to an activated solution shows that the activity is less than that of a solution previously treated with the chloride. Attempts to isolate the active acid were negative, and the absorption spectra of ordinary and active oxalic acids are identical. The reduction of mercuric chloride is considered to be a chain reaction. The constitution of the active acid is discussed briefly. H. BURTON.

Mechanism of the cleavage of ethyl $\alpha\delta$ -dibromoadipate by secondary amines. New synthesis of cyclobutane derivatives. R. C. FUSON and T. Y. KAO (J. Amer. Chem. Soc., 1929, **51**, 1536— 1539).—Evidence in favour of the mechanism proposed for this reaction (A., 1928, 738; this vol., 425) is afforded by the formation of ethyl 1-cyanocyclobutane-1: 2-dicarboxylate, b. p. 152—154°/9 mm., d²⁰ 1·1103, n_D^{20} 1·4519, from ethyl ms- $\alpha\delta$ -dibromoadipate and sodium cyanide in boiling absolute alcohol. This yields, after hydrolysis, decarboxylation, and treatment with hydrochloric acid at 190°, trans-cyclobutane-1: 2-dicarboxylic acid (Perkin, J.C.S., 1894, **65**, 580). H. E. F. NOTTON.

Stereochemistry of the glutaconic acids. I. R. MALACHOWSKI (Ber., 1929, 62, [B], 1323-1326). -trans-Glutaconic acid is converted by boiling acetic anhydride into the hydroxyanhydride, which is gradually added to water at 10-12°; as soon as the solution ceases to give a green colour with ferric chloride, it is evaporated as rapidly as possible under greatly diminished pressure at the ordinary temperature, thus yielding cis-glutaconic acid, m. p. 136-136.5° (corr.) [when mixed with the ordinary glutaconic acid, m. p. 111-114°]. When solid or dissolved in ether the new acid can be preserved for weeks, whereas in aqueous solution or when melted it passes into the ordinary acid. The two acids are closely similar in m. p. and solubility, but differ completely from one another in crystalline form. The dissociation constant of the cis-acid is $k^0 = 1.43 \times 10^{-4}$, of the trans-acid $k^0 = 1.74 \times 10^{-4}$. At 15-20° about 40% of the cis-acid is transformed into the trans-acid in aqueous solution within 16 hrs. Acetic anhydride at 40° effects almost quantitative conversion of the cisacid into the anhydride, whereas the trans-acid is only slightly anhydrised under these conditions.

H. WREN.

 $\gamma\gamma$ -Dimethylpimelic acid. G. KOMPPA (Ber., 1929, 62, [B], 1371—1372).—4: 4-Dimethylpiperidine hydrochloride is converted by benzoyl chloride and excess of alkali into 1-benzoyl-4: 4-dimethylpiperidine, b. p. 174—177°/10 mm., d_1^{4es} 1.0511, n_D^{4es} 1.54534, converted by phosphorus pentachloride into benzonitrile and $\alpha\varepsilon$ -dichloro- $\gamma\gamma$ -dimethylpentane, b. p. 58— 59°/8 mm., d_4^{4s} 1.0917, n_D^{5s} 1.48990. $\gamma\gamma$ -Dimethylpimelonitrile, m. p. 123°, from the dichloride and potassium cyanide, is hydrolysed by concentrated hydrochloric acid at 120° to $\gamma\gamma$ -dimethylpimelic acid, m. p. 83° (dianilide, m. p. 165°; diamide, m. p. 176°). H. WREN.

Composition of sodium bismuth tartrate. J. H. YOE and J. H. MOTE (J. Amer. Pharm. Assoc., 1929, **18**, 450–459).—Sodium bismuth tartrate prepared by the action of bismuth hydroxide on tartaric acid in presence of excess of cold alkali is a sodium tetrabismuth tartrate.

E. H. SHARPLES.

Action of cyanogen chloride, bromide, and iodide on ethyl sodiomalonate. Synthesis of ethane- and ethylene-tetracarboxylic esters. G. MIGNONAC and O. W. RAMBECK (Compt. rend., 1929, 188, 1298-1301).-The action of a very slow current of cyanogen chloride on an alcoholic solution of ethyl sodiomalonate gives, instead of ethyl cyanomalonate (cf. Haller, A., 1882, 1189), ethyl ethylmalonate. presumably owing to alcoholysis of the sodium derivative. In an ethereal suspension, pure ethyl cyanomalonate, b. p. $138-140^{\circ}/14$ mm., d_4^{20} 1.1128, n_p^{20} 1.4295 (cf. Haller, loc. cit.), is obtained. Little of the substance is formed if cyanogen bromide is used in alcohol or ether; hydrogen cyanide is lost, giving ethyl ethylenetetracarboxylate, with some ethyl ethanetetracarboxylate. With cyanogen iodide, hydrogen cyanide is not evolved, and ethyl ethanetetracarboxylate is almost exclusively formed. E. W. WIGNALL.

Constitution of gum arabic. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, 51, 1519—1525).—The λ -arabinosic acid (O'Sullivan, J.C.S., 1884, 45, 41) obtained by hydrolysing arabic acid with 2% sulphuric acid shows all the reactions of an aldobionic acid. It yields on hydrolysis galactose, and on oxidation (Heidelberger and Goebel, A., 1927, 1114) saccharic acid, and is, therefore, a *d*-galactosido*d*-glycuronic acid, [α] $_{55}^{55}$ +2.5°, changing to +1.71° with lactonisation (calcium salt). It is oxidised by barium hypoiodite to a *glycuronogalactonic acid* (*calcium* salt). A preliminary examination of arabic acid indicates that it contains *d*-galactose (2 mols.), aldobionic acid (1 mol.), *l*-arabinose (3 mols.), and rhamnose (1 mol.) residues, approximately in the proportions stated.

H. E. F. NOTTON. Claisen ester condensation with ethyl thioacetate. R. B. BAKER and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 1567-1570).-Ethyl thio-acetate, Ac SEt (Michler, A., 1875, 761), b. p. 116-117°, d_4^{25} 0.9755, n_D^{25} 1.4503, and sodium at 50° give ethyl acetothioacetate (15% of the theoretical yield), CH₂Ac·CO·SEt, b. p. 60°/2 mm., d²⁵₄ 1.0684, n²⁵₁ 14885, which contains 31% of the enolic modification (bromine titration). Its copper salt is stable, but those of other metals decompose, giving metallic sulphides. It undergoes acid and ketonic hydrolysis in the same way as ethyl acetoacetate and readily decomposes when heated into dehydracetic acid. A mixture of ethyl acetate and ethyl thioacetate (equal mols.) gives with sodium a product containing 98% of ethyl acetothioacetate and 2% of ethyl acetoacetate. Ethyl thioacetate does not condense with acetone in presence of sodium, but with acetonitrile it gives cyanoacetone H. E. F. NOTTON. (7% of the theoretical yield).

Constitution of substances of high mol. wt. R. O. HERZOG (Naturwiss., 1929, 17, 271).—The small elementary cell recorded in X-ray studies of substances of high mol. wt. is equally consistent with long chains or small molecules. Constitutional formulæ may exceed and extend outside the elementary cell and the classical conception of a molecule is of little service in the study of substances of high mol. wt. Staudinger (*ibid.*, 141) misunderstands the position.

R. A. MORTON.

Tests for acetone and acetaldehyde. H. LEFF-MANN (Amer. J. Pharm., 1929, 101, 337-340).—The newer reagents suggested in recent literature have been examined, and found to have no great advantages. S. I. LEVY.

Hydrogenation of acetaldehydeacetals. M. CABANAC (Compt. rend., 1929, 188, 1257—1259).— When the vapour of acetaldehydediethylacetal, mixed with hydrogen, is passed over finely-divided nickel, reaction begins at about 200°. At 210° ethyl alcohol and ether are formed. Acetaldehydedipropylacetal yields similarly ethyl propyl ether and propyl alcohol, and the dibutylacetal yields ethyl butyl ether and butyl alcohol. R. K. CALLOW.

Action of potassium cyanide on chloroaldehydes. F. D. CHATTAWAY and H. IRVING (J.C.S. 1929, 1038—1048).—The following compounds were prepared in the yields stated by the rapid interaction of a solution of anhydrous chloral in the requisite alcohol on a suspension of potassium cyanide in the same alcohol : methyl dichloroacetate (84%), ethyl dichloroacetate (88%), n-propyl dichloroacetate, b. p. 176° (70%), and allyl dichloroacetates are greatly reduced when the reaction conditions are modified to favour the formation of chloral cyanohydrin (e.g., slow addition of the cyanide to chloral alcoholate in alcoholic solution) or when potassium cyanide acts on an alcoholic solution of chloralcyanohydrin itself.

Addition of dichloroacetaldehyde ethyl alcoholate to potassium cyanide-ethyl alcohol suspension led to a 38% yield of ethyl chloroacetate. Similar treatment of monochloroacetaldehyde with either aqueous or alcoholic potassium cyanide gave not more than 10% yields of ethyl acetate.

By the action of potassium cyanide on a solution of buyl chloral hydrate in ethyl alcohol ethyl α -chlorocrotonate, ethyl $\alpha\beta$ -dichlorobutyrate (which rapidly lost hydrogen chloride at the ordinary temperature, generating the previous ester), and butylchloralcyanohydrin, m. p. 101—102°, were obtained. By using exactly 1 mol. of potassium cyanide the following α -chlorocrotonates were prepared in the yields indicated: ethyl (90%), methyl (85%), n-propyl (67%), n-butyl (70%). Butylchloralcyanohydrin itself reacted with potassium cyanide in alcoholic solution, gving ethyl α -chlorocrotonate.

Potassium cyanide and butyl chloral hydrate, in ameus solution, gave butylchloralcyanohydrin accompanied by α -chlorocrotonic acid; potassium ranide and chloral-ammonia suspended in aqueous ammonia reacted with formation of dichloroacetanide. Similar treatment of butyl chloral hydrate led to α -chlorocrotonamide. Chloral diacetate and potassium cyanide reacted violently, in presence of thyl alcohol, affording ethyl acetate and dichloroacetate. Addition of potassium cyanide to a solution of butyl chloral hydrate in benzene gave, after 10 days, 6.keto-2:4:7-tri-($\alpha\alpha\beta$ -trichloropropyl)cyclo-2:4:6:7tetramethylene-1:3:5-dioxaimine, I, (?) m. p. 99.5-100.5°,

$$0 < \stackrel{\text{CH}(\text{CCl}_2 \cdot \text{CHMeCl}) \cdot \text{CO} \cdot \text{NH}}{\text{CH}(\text{CCl}_2 \cdot \text{CHMeCl})} O > \text{CH} \cdot \text{CCl}_2 \cdot \text{CHMeCl}. (I.)$$

Previous mechanisms for these reactions are destructively criticised and the theory is advanced that the potassium cyanide first causes the elimination of hydrogen chloride from the aldehyde-hydrate, -alcoholate, or -ammonia, probably by the intermediate replacement of a chlorine atom by a cyanogen group [e.g., removal of 1 mol. of hydrogen chloride bypotassium cyanide from 6-nitro-2:4-bis(trichloromethyl)-1:3-benzdioxin, giving 6-nitro-2(or 4)-di-

$$NO_2 \cdot C_6 H_4 < \underbrace{O_{CH(CCl_3)} > O_{CH(CCl_3)} (II.)}_{CH(CCl_3) > O}$$

chloromethylene-4(or 2)-trichloromethyl-1: 3-benzdioxin, II, m. p. 136·5°], followed by elimination of the very slightly ionisable hydrogen cyanide, leaving an unsaturated compound which by intramolecular rearrangement gives an acid, an ester, or an acid amide: :CCl·CH(OH)·OH(OR)(NH₂)^{KON}

:C:C(OH)·OH(OR)(NH₂) \longrightarrow :CH·CO·ÓH(OR)(NH₂). R. J. W. LE FÈVRE.

a-Bromoaldehydes and their derivatives. A. KIRRMANN (Ann. Chim., 1929, [x], 9, 223-286).-A detailed account of work some of which has been published previously (A., 1927, 340, 442). The following data seem to be new or revised. The dimethylacetals of propaldehyde, b. p. 89°, d²¹ 0.849, n²¹ 1.3799 (Newbury and Barnum, A., 1891, 284); butaldehyde, b. p. 114°, d^{21} 0.847, n^{21} 1.3900; *n*-hex-aldehyde, b. p. 52—53°/12 mm., 158°/760 mm., d^{21} 0.846, n^{21} $1.40\hat{6}$, are obtained from the aldehyde in the usual manner, whilst the diethylacetal of n-valeraldehyde, b. p. 59°/12 mm., d²² 0.829, n²² 1.4029, is obtained directly by the action of triethoxymethane on magnesium butyl bromide. From these are obtained a-bromopropaldehyde, d²⁰ 1.595, n⁵⁰ 1.4804 (yield very small), together with its dimethylacetal, b. p. 49-50°/12 mm., 151° (corr.)/760 mm., d²⁰ 1.360, n^{20} 1.4482, and some dibrominated products; α -bromon-butaldehyde, d²⁰ 1.469, n²⁰ 1.4683, together with its dimethylacetal, b. p. $64^{\circ}/12 \text{ mm.}, d^{21} 1.303, n^{21} 1.4509,$ para-a-bromo-n-butaldehyde, m. p. 98°, and aa'-di-bromo-n-butaldehyde, b. p. $53^{\circ}/17 \text{ mm.}, d^{21} 1.862, n^{21}$ 1.5098 ; a-bromo-n-hexaldehyde, b. p. 63-64°/12 mm., d^{21} 1·292, n^{21} 1·463; α -bromo-*n*-heptaldehyde, d^{19} 1·239, n^{19} 1.4623 (65–75% yield) (divertiane, m. p. 112°), together with $\alpha\alpha'$ -dibromo-n-heptaldehyde, b. p. 96°/11 mm., d^{22} 1.565, n^{22} 1.496 (not pure); and α -bromo-*n*-valeraldehyde, d^{29} 1.368, n^{20} 1.4640 (which polymerises to the corresponding aldol, b. p. 195°/5 mm., da 1.479, nº 1.497, depolymerisation occurring during distillation under ordinary pressure), together with the unstable $\alpha \alpha$ -dibromo-n-valeraldehyde, b. p. 65°/11 mm., $d^{\alpha 1}$ 1.735, $n^{\alpha 1}$ 1.5035. They exhibit the usual aldehydic properties, but, contrary to Franke (A., 1900, i, 427), are stable to boiling water and are only partly attacked by sodium methoxide in boiling methyl alcohol or toluene, or by sodium acetate and acetic acid. They react normally with amines in ethereal solution. Thus α -bromo-*n*-heptaldehyde and trimethylamine yield the quaternary ammonium salt,

m. p. 126°, decomp. 150°, with elimination of trimethylamine hydrobromide; diethylamine yields α -diethylamino-n-heptaldehyde, b. p. 107°/12 mm., 225°/760 mm., d^{22} 0.853, n^{22} 1.4352 (hydrochloride, m. p. 73°), which is oxidised by silver nitrate to α -hydroxy*n*-heptoic acid (barium salt $+0.5H_{2}O$) and heptoic acid; whilst ethylamine and ammonia react similarly, although in these cases it is not possible to isolate the a-aminoaldehyde. In the following reactions the a-bromoaldehydes behave abnormally. Magnesium alkyl bromides react to yield ketones of the type CH_aR·CO·R', which further react to yield the tertiary alcohols, CH.R. CR', (OH), the latter being partly dehydrated to the olefines, CHR.CR',. Thus a-bromo*n*-heptaldehvde yields methyl hexvl ketone (20%), b. p. 64°/12 mm., d16 0.823, n18 1.4195 (semicarbazone, m. p. 123°), dimethylhexylcarbinol, b. p. S1°/13 mm., d¹⁹ 0.823, n¹⁹ 1.4299, β-methyl-Δβ-octene (5%), b. p. 42°/14 mm., 146° (corr.)/760 mm., d¹⁶ 0.738, n¹⁶ 1.4243, and the bromohydrin, b. p. 106-107°/ 12 mm., d^{16} 1.207, n^{16} 1.4751, the last being obtained by a normal reaction. Similar results are obtained with zinc methyl. From α -bromo-*n*-valeraldehyde is obtained (?) y-ethyl- $\Delta \gamma$ -n-heptene, b. p. 144° (corr.), d^{a_1} 0.742, n^{a_1} 1.4259. By the action of lead or silver hydroxides α -bromo-*n*-heptaldehyde is converted into n-heptoic acid, thus reacting as if it possessed the structure of a-heptoyl bromide, b. p. 80°/12 mm., d¹⁸ 1.211, n^{18} 1.4605, with which, however, it is not identical. An electronic explanation of these reactions is discussed and it is assumed that in the abnormal reactions ketens intervene as unisolated intermediates. By the action of sodium on the vinyl bromides CHR:CHBr and CRBr:CH2 (loc. cit.) are obtained mixtures of the ethylene CHR.CH, and the acetylene CR:CH, whilst magnesium yields the ethylene and a magnesium vinyl bromide, the presence of the latter being shown by its action with water and iodine. J. W. BAKER.

Action of metallic sodium on brominated cyclic acetals. H. S. HILL and G. J. C. POTTER (J. Amer. Chem. Soc., 1929, 51, 1509-1514).--Acraldehyde and ethylene glycol in presence of excess of dry hydrogen bromide give ethylene y-bromopropylidene ether (65% of the theoretical yield), b. p. 72-73°/10 mm. (slight decomp.). This is converted by sodium in boiling ether into (a) β -hydroxyethyl Δ^{a} -n-propenyl ether, b. p. 60-61°/16 mm.; (b) adipylidene diethylene ether, crystals, b. p. 139-140°/10 mm., identified as described by Read and Hibbert (A., 1924, i, 709), and (c) ethylene propylidene ether, probably formed as a secondary product from (a). Ethylene γ -bromobutylidene ether (56% yield), b. p. 76-78°/ 10 mm., prepared from crotonaldehyde, yields with sodium (a) β -hydroxyethyl Δ^{α} -n-butenyl ether, b. p. $60-65^{\circ}/10 \text{ mm.}, (b) \beta \epsilon$ -dimethyladipylidene diethylene ether (?), b. p. $150-170^{\circ}/15$ mm., and (c) ethylene butylidene ether. Thus, unlike the β -brominated cyclic acetals (A., 1928, 1213), the γ -bromo-derivatives undergo in part a Wurtz condensation in presence of sodium. The new unsaturated ethers (a) are readily, but not explosively, isomerised by 50% sulphuric acid to ethylene propylidene and butylidene ethers. H. E. F. Norron.

Chlorides of a-ethylenic alcohols. C. COURTOT and J. PIERRON (Compt. rend., 1929, 188, 1501-1504; cf. this vol., S02) .- Oxidation of ethyl- and propyl-vinylcarbinols with a mixture of chromic and sulphuric acids at $34-35^{\circ}$ gives, respectively, 40 and 45% yields of ethyl vinyl ketone, b. p. $68-70^{\circ}/$ 200 mm., d1 0.8524, np 1.4233 (picrate of diethylamine additive compound, m. p. 78°), and propyl vinyl ketone, b. p. 88—90°/150 mm., d_4^{14} 0.8518, n_p^{11} 1.4275 (picrate of diethylamine additive compound, m. p. S1°). α-Chloro-α-phenylpropane is similarly oxidised at 68° directly to phenyl ethyl ketone (yield 77%), at which temperature the chloro-compound suffers 97% hydrolysis in 75 min., whilst only 24.5% hydrolysis occurs in 48 hrs. at the ordinary temperature.

J. W. BAKER.

Action of organomagnesium compounds on ethyl ethylcyanoacetate. A. MAVRODIN (Compt. rend., 1929, 188, 1504-1506) .- Ethyl othylcyanoacetate reacts in its enolic form with the Grignard reagent in boiling other, the hydrocarbon being eliminated and the unchanged cyano ester being recovered after hydrolysis. In boiling toluene, however, the cyano-group also reacts, the ultimate product being a β -diketone formed thus :

CHEt(CN)·CO, Et MgRX CEt(CN):C(OMgX)·OEt+RH $\overset{2RMgX}{\sim}CR(:NMgX)\cdot CEt(MgX)\cdot CR(OEt)(OH) \longrightarrow$

R·CO·CHEt·CO·R. Thus with magnesium ethyl iodide is obtained $\gamma \epsilon$ -diketo- δ -ethyl-n-heptane, b. p. 91—92°/10 mm. (25—30% yield), converted by semicarbazide acetate into 3:4:5-triethylpyrazole-1-carboxyamide, m. p. 95°; and with magnesium phenyl bromide a 60% yield of $\alpha\gamma$ -diketo- $\alpha\gamma$ -diphenyl-β-ethylpropane (Béhal and Auger, A., 1890, i. 388) is obtained. This is converted by semicarbase acetate into 3: 5-diphenyl-4-ethylpyrazole, m. p. 167° (picrate, m. p. 161°), and by hydroxylamine into 2 : 4-diphenyl-3-ethylisooxazole, m. p. 93–94°. J. W. Baker.

Complex compounds of diacetyldioxime. J.V. DUBSKY and F. BRYCHTA (Pub. Fac. Sci. Univ. Masaryk, 1928, No. 103, 28 pp.).—See this vol., 543.

Sulphite-cellulose process. I. Action of hydrogen sulphite solutions on sugars. T. MARUSAWA, D. NAITO, and J. UCHIDA (Mem. Ryojun Coll. Eng., 1929, 1, 351–393; cf. Marusawa, B., 1917, 868; 1918, 52; Hägglund, this vol., 297, 428). -An investigation has been made of the products formed in solutions containing about 0.08 mol. per litre of dextrose, mannose, xylose, or lævulose and 0.3 mol. per litre of sodium hydrogen sulphite, with varying additions of sodium sulphite or sulphurous acid. At the ordinary temperature dextrose, mannose, and xylose form loose compounds, largely dissociated, with sodium hydrogen sulphite, and the sulphur dioxide they contain may be directly deter-The dismined after treatment with acid or alkali. sociation constants of the hydrogen sulphite compounds under the specified conditions are, respectively, 0.38, 0.12, and 0.15. Lævulose forms no compound under these conditions. When the solutions are heated at 130°, the amounts of sugar and hydrogen sulphite rapidly diminish, and thiosulphate is formed. If the hydrogen-ion concentration is lowered by the

addition of sodium sulphite, very little thiosulphate is formed, and the rate of decomposition of the hydrogen sulphite ions is diminished. Addition of sulphurous acid causes an increase in the rate of decomposition of the hydrogen sulphite ions with formation of thiosulphate, accompanied by sulphate and polythionates, and there is less loss of sugar. The formation of thiosulphate is greatest with dextrose and least with lævulose. It is suggested that on heating the hydrogen sulphite combines with the sugar in equimolecular proportions to form stable compounds, different from those formed at low temperatures. These compounds are of two types, one of which (A) is decomposed by heating with dilute hydrochloric acid, with the formation of thiosulphate, whilst the other (B) is stable to hydro-chloric acid and is only slowly decomposed by heating with alkaline hypobromite solution. The acidic A-compound is formed first, and decomposes to a greater or smaller extent, according to the conditions. as shown in the equation $2R \cdot C(OH) \cdot SO_3H' = 2R \cdot CO_2H + S_2O_3'' + H_2O$, hydrogen ions favouring this decomposition. In presence of sodium sulphite the neutral B-compound, which is probably cyclic, is formed, probably from the A-compound by intra-molecular change. The B-compound may be decomposed by sodium hydroxide and sodium peroxide and its sulphur content then determined. The decomposition of hydrogen sulphite ions is catalysed by the thiosulphate formed by decomposition of the A-compound, and the former decomposition is decreased by addition of sodium sulphite, in the first place, because of the decreased formation of thiosulphate from the A-compound, and, secondly, because of the decreased activity of the thiosulphate in absence of hydrogen ions. The reaction between sugars and hydrogen sulphites is, therefore, best studied at low hydrogen-ion concentrations. The "loosely combined" sulphur dioxide, determined, in solutions which have been heated, by titration with iodine, includes thiosulphate and polythionates. At the point at which free sulphur begins to separate, the "loosely combined " sulphur dioxide, then principally thiosulphate and polythionates, reaches a maximum. R. K. Callow.

Compounds of alkaline-earth hydroxides with sugars. J. E. MACKENZIE and J. P. QUIN (J.C.S., 1929, 951-964).—Notwithstanding the discordant literature of the subject the following definite compounds can be prepared : monolime-monosucrose (penta- or hexa-hydrate, dihydrate, and anhydrous), dime-monosucrose (hexahydrate and anhydrous), tilme-monosucrose (hexahydrate and anhydrous), monostrontia-monosucrose (hexahydrate), distrontiamonosucrose (anhydrous), monobaryta-monosucrose (ahydrous), monolime-monoglucose (monohydrate), monolime-monofructose (hexahydrate, dihydrate), monolime-monomaltose (monohydrate), monolimemonolactose (anhydrous). For these are given : analytical data, solubilities, rotations, and results of diffusion experiments. Attempts to obtain compounds containing larger proportions of the earths than those mentioned were unsuccessful. The methylglucosides, -fructosides, -maltosides, and -lactosides were unaffected by calcium hydroxide. The constitution attributed to lime-glucose is $OH \cdot CH_2 \cdot (CH \cdot OH)_4 \cdot CH < O > Ca$ and that to the corresponding compounds of other reducing sugars either $R \cdot CH < O > Ca$ or $R \cdot C < O > Ca > CH_2OH$ (R=residue

of sugar molecule). The alkaline earth-sucrose compounds are probably of similar nature to those formed by combination of sucrose with sodium or potassium chlorides. R. J. W. LE FÈVRE.

Determination of reducing sugars in presence of hydrocyanic acid. H. HÉRISSEY and A. CHAL-META (Ann. Falsif., 1929, 28, 214—223).—See A., 1928, 1358.

Determination of reducing sugars by the ferricyanide method. A. IONESCU-MATIU (Ann. Sci. Univ., Jassy, 1929, 15, 363-371).—See A., 1928, 398.

Unsaturated reduction products of sugars. XI. 2-Deoxycellobiose (cellodesose) and derivatives of 2:3-bisdeoxycellobiose. XII. Reduction products of sugars. M. BERGMANN and W. BREUERS (Annalen, 1929, 470, 38-51, 51-61).-XI. When cellobial (A., 1921, i, 648; 1924, i, 265) is shaken with 2N-sulphuric acid at 0° and then freed from acid by barium hydroxide and carbonate, there is obtained 2-deoxycellobiose [cellodesose (cf. A., 1922, i, 227)] (I), decomp. 200° (corr.) after sintering at 184°, $[\alpha]_D^m + 23\cdot2°$ in water, $[\alpha]_D^m + 9\cdot82°$ in pyridine after 5 min. $\rightarrow +37\cdot8°$ after 24 hrs. The reducing power (Fchling's solution) of this sugar is only one third of that of cellobiose. When I is treated with methyl alcohol containing 1% of hydrogen chloride two 2-deoxymethylcellobioses [methylcellodesosides], A, m. p. $169-171^{\circ}$ (corr.), $[\alpha]_{D}^{22} + 40^{\circ}$ in water, and *B*, m. p. about 220° (decomp.), $[\alpha]_{D}^{20} - 19.9^{\circ}$ in water, are produced. Fission of an equimolecular mixture of A and B with 0.01N-hydrochloric acid at 100° is almost complete after 30 min. Treatment of penta-acetyl- ψ -cellobial (A., 1921, i, 648) with methyl alcohol containing 0.25% of hydrogen chloride and subsequent acetylation of the residue with acetic anhydride and pyridine give penta-acetyl- ψ -cellobial-a-methyl-lactolide, m. p. 131.5-132.5° (corr.), $[\alpha]_{\rm P}^{\rm ap}$ $+65.4^{\circ}$ in s-tetrachlorocthane: in the absence of acetylation a tetra-acetate, m. p. 203-205° (corr.), results. Hydrolysis of the penta-acetate with barium hydroxide and aqueous-acetone yields ψ -cellobial- α -methyl-lactolide (II), m. p. 112—113° (corr.), $[\alpha]_D^{21}$ +97.3° in water. This is very sensitive towards acids and the dry substance readily absorbs water. Reduction of II with hydrogen and a palladium catalyst in presence of methyl alcohol affords 2: 3-bis-





chloric acid proceeds rather more readily than a mixture of the deoxymethylcellobioses under the same conditions.

XII. Reduction of triacetyl-4-glucal (A., 1924, i, 266) with hydrogen in presence of acetic acid and palladium-black (cf. Wieland, A., 1912, i, 247; Tausz and Putnoky, A., 1920, ii, 61) affords az-anhydro-nhexane-adsz-tetrol diacetate (III), b. p. 102-103°/0.7 mm., n¹⁸_D 1.4511, together with dihydro-4-glucal triacetate, b. p. $150-157^{\circ}/1\cdot 2-1\cdot 5$ mm., n_{11}^{17} 1.4545. Diacetyl-4-glucal is reduced in presence of platinumblack (Willstätter, A., 1921, ii, 185) to III and dihydro-\u03c6-glucal diacetate. Hydrolysis of III with barium hydroxide in aqueous acetone gives ac-anhydro-n-hexane-adez-tetrol (IV), b. p. 122°/1.5 mm., n_{11}^{20} 1.4832, which when treated with thionyl chloride and pyridine yields an ester, $C_6H_{10}O_4S$, m. p. 99°, $[\alpha]_{10}^{\infty}$ +8.62° in s-tetrachloroethane. With benzaldehyde and zinc chloride at 100°, IV yields a benzylidene derivative, $C_{13}H_{16}O_3$, m. p. 137—137.5° (corr.). $\alpha \epsilon$ -Anhydro- $\delta \zeta$ -dichlorohexane- $\alpha \epsilon$ -diol has b. p. 55°/0.8 mm. Reduction of hexa-acetyl- ψ -cellobial (A., 1921, i, 648) in presence of acetic acid and palladium-black (Tausz-Putnoky) gives ac-anhydroδ-glucosidyl-n-hexane-αδεζ-tetrol penta-acetate (V), m. p. 133—134° (corr.), $[\alpha]_D^m + 18\cdot1°$ in s-tetrachloroethane, also formed together with bisdeoxycellobiose penta-acetate, m. p. 153-155° (corr.), [a]19 +32.1° in s-tetrachloroethane, by similar reduction of pentaacetyl-4-cellobial. If this last substance is reduced by Willstätter and Waldschmidt-Leitz's method (A., 1921, ii, 185), $\alpha \epsilon$ -anhydro- δ -glucosidyl- Δ^{β} -hexene- $\alpha \delta \epsilon \zeta$ tetrol penta-acetate, m. p. 109–110° (corr.), $[\alpha]_{\rm p}^{20} + 20^{\circ}$ in s-tetrachloroethane, results; with an active catalyst, however, V is produced. When diacetylarabinal (Gehrko and Aichner, A., 1927, 544) is boiled with water and the dry residue is acetylated with acetic anhydride and pyridine in the cold, diacetyl- ψ -arabinal, b. p. 120—124°/0.6 mm., n_{11}^{24} 1.4625, is obtained. H. BURTON.

Microcolorimetric determination of lactose. F. GONZÁLEZ and A. GIMENO (Anal. Fís. Quím., 1929, 27, 39-47).—The micro-method of Folin and Wu for the determination of dextrose may be satisfactorily employed for lactose. H. F. GILLEE.

Derivatives of volemitol. V. ETTEL (Coll. Czechoslov. Chem. Comm., 1929, 1, 288-293).-Volemitol, m. p. 153-154°, extracted from Lactarius volemus by an improved method, is best purified by crystallisation from a mixture of pyridine and alcohol. The trimethylene derivative, m. p. 212-213°, $[\alpha]^p$ -13.84° in chloroform, is obtained by heating with formaldehyde and hydrochloric acid. The triethylidene derivative, m. p. 161-162°, [a]²⁰ -72.35° in chloroform, -117.6° in pyridine, -225.2° in quinoline, obtained by treating the solution in 50% sulphuric acid with paracetaldehyde, is not identical with the compound prepared by Bougault and Allard (A., 1903, i, 62). The tribenzylidene derivative, m. p. 214-215°, [a]²⁹ -1.7° in chloroform, -48.4° in pyridine, -138.4° in quinoline (cf. La Forge and Hudson, A., 1920, i, 595; 1928, 1213), is best obtained by the action of benzaldehyde in alcoholic hydrochloric acid. The hepta-acetate has m. p. 120—121°, $[\alpha]_{D}^{\infty}$ +20.7° in chloroform, pyridine, or acetic acid (cf. Bourquelot, A., 1896, i, 273; Bougault and Allard, *loc. cit.*). The *heptaphenylurethane*, m. p. 266° (decomp.), is obtained by the action of phenylcarbimide in pyridine. The action of acetone or chloral yields no crystalline products.

R. K. CALLOW.

Digitalis glucosides. III. Gitoxigenin and isogitoxigenin. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1929, 82, 403-409).—An improved yield of isogitoxigenin is obtained by treatment of gitoxigenin with stronger alkali than that previously employed (A., 1928, 1376); the "isogitoxigenonic acid methyl ester " formerly obtained (loc. cit.), by oxidation of isogitoxigeninic acid methyl ester with chromic acid, has now been found to contain a relatively resistant lactone group, and is re-named methyl isogitoxigonate. When oxidised with hypobromito, isogitoxigeninic acid yields a lactone acid, isogitoxigenic acid, $C_{23}H_{34}O_6$ (not $C_{21}H_{30}O_6$ as previously stated), m. p. 260°, $[\alpha]_{13}^{23} - 50°$ in 95% alcohol, which, with concentrated hydrochloric acid, gives anhydroisogitoxigenic acid, C₂₃H₃₂O₅. m. p. 215°. Methyl isogitoxigeninate gives, with hydroxylamine, an oxime, m. p. 287°; isogitoxigenin, when oxidised with chromic acid, yields isogitoxigenone, m. p. 278-279°. The apparent structural dissimilarities between gitoxigenin and the other cardiac aglucones, suggested by the previous work (loc. cit.), therefore disappear. C. R. HARINGTON.

Starch. XXII. Amylose and amylopectin. H. PRINGSHEIM and A. STEINGROEVER (Ber., 1929, 62, [B], 1352-1359).—If amylose acetate is heated with naphthalene at 260-270°, an acotate with the initial specific rotation remains. Hydrolysis of this product with alcoholic potassium hydroxide followed by very cautious desiccation of the resulting material with alcohol and ether affords an amylosan with the unchanged specific rotation of amylose which has no reducing action, is hydrolysed by amylase, and yields a blue colour with iodine. The preparation dissolves easily at the atmospheric temperature in water to a clear solution which appears stable. Cryoscopic determinations indicate an increase in mol. wt. with each measurement of the f. p., so that the minimum value, about 600, must be regarded only as an upper limit of the actual mol. wt. Freezing favours aggregation until the substance ultimately separates in an insoluble form. The same product is prepared by boiling a solution of amylose acetate in chloroform with benzenesulphonic acid, followed by precipitation with alcohol and hydrolysis. The ash content of the preparations is invariably less than 0.5% and cannot therefore account for the depression of f. p.; they cannot be regarded as causative of disaggregation, since this effect is not produced by sodium thiocyanate in M/1000 solution. The b. p. of water is not raised by either preparation, but depressed by several hundredths of a degree. Determinations of mol. wt. by the Barger-Rast method indicate the formula $(C_6H_{10}O_5)_2$, whereas the cryoscopic method indicates $(C_6H_{10}O_5)_4$.

Amylopectin is converted by acetic anhydride and pyridine into a product which, after successive treatment with ice and dehydration with alcohol, yields

to boiling ethyl acetate a material identical in solubility with amylose triacetate. The portion insoluble in ethyl acetate, after purification by means of chloroform, gives amylopectin triacetate, which slowly yields homogeneous solutions in cold chloroform or glacial acetic acid; these are too viscous and cloudy to allow polarimetric measurement. Degradation of amylopectin triacetate with benzenesulphonic acid in chloroform could not be effected satisfactorily; the acetate which slowly separates from the solution is hydrolysed to a non-reducing product, $[\alpha]_p + 165^\circ$, which gives a red colour with iodine and has a mol. wt. corresponding with $(C_6H_{10}O_5)_2$ to $(C_6H_{10}O_5)_3$ in freezing water. When large amounts of acetic anhydride are added to the chloroform and benzencsulphonic acid the solution remains homogeneous. Addition of alcohol to the solution precipitates a product, $[\alpha]_{D} + 172.5^{\circ}$ in chloroform, with all the properties of amylose triacetate. This is hydrolysed to a material only partly soluble in water and giving a blue colour with iodine. H. WREN.

Constitution of starch. K. H. MEYER, H. HOPFF, and H. MARK (Ber., 1929, 62, [B], 1103-1112).—The formation of maltose derivatives from starch by enzymatic degradation and also by the action of acetyl bromide leads to the conclusion that maltose is present in some form as a component of starch. a-Linkings must therefore be present in starch, possibly alternating with β-linkings. Application of Hudson's rules to β-maltose and β-glucose establishes that all the increments of β -glucose are present in β-maltose and the latter substance contains a dextrose residue corresponding exactly with a residue present in a chain with a-1: 4-linking. Examination of various carefully dried starches in formamide shows that pure wheat starch has $[\alpha]_{D} + 220^{\circ}$, whilst other varieties have somewhat lower values which approximate to those of wheat starch as their purity increases. For exclusive α -1:4-glucosyl residues the value $[\alpha]_{D}$ +226° is calculated, so that it appears that in starch the dextrose residues are united to one another solely by α -bridges; this is true also for glycogen. Extension of the comparison to aqueous solution necessitates the use of the highest observed values for $[\alpha]_{D}$, since the activity first increases and then falls on boiling the solution, as a consequence of slow dispersion and incipient hydrolysis. The maximal value is $[\alpha]_D$ +212°, which is probably below the theoretical, whereas the calculated datum is about $+230^{\circ}$.

The assumption of the presence in starch of a small, uniform unit which builds the different varieties of starch by differing types of association is regarded as improbable. The great variability of starches and the non-homogeneity of starch preparations indicates in general that much greater variations occur in the length of the main valency chains than in those of cellulose. Examination of the kinetics of the hydrolysis of starch by acids shows that the action has the same order of magnitude in the initial stages and subsequently and proceeds at about the same rate as a glucosidic hydrolysis. The temperature coefficient of the change indicates that it is a normal chemical reaction and not a diffusion phenomenon,

as might be expected from the complicated structure of the amylose used. The occurrence of maltose as the final product of the degradation of starch by enzymes and acetyl bromide appears incompatible with the presence exclusively of dextrose residues, but the enzymatic action is certainly very complex and does not permit conclusions with regard to the constitution of starch, whilst the change with acetyl bromide is effected with undissolved starch, so that steric influences may play a part. The structure of starch is therefore considered to resemble in principle that of cellulose in an arrangement of dextrose residues as a diagonal screw. The cellobiose chain thus appears stretched, whereas the maltose chain has a zig-zag formation. The remarkable difference in behaviour of cellulose and starch towards water is thus explained. The observation that starch micelles can be oriented only with difficulty if at all suggests that the main valency chains are shorter than in cellulose and not arranged in longitudinal bundles, but according to some unrecognised principle of structure. H. WREN.

"Salt hydrolysis" of starch. N. IVANOVSKY (Zhur. exp. Biol. Med., 1928, 10, 292—294).—"Salt hydrolysis" of starch to erythrodextrin was not observed. Starch is not affected by hæmin, hæmoglobin, or hæmolysed red blood cells.

CHEMICAL ABSTRACTS.

Allylcelluloses. I. SAKURADA (Z. angew. Chem., 1929, 42, 549-550).—See this vol., 430.

Celluloseglycollic acid. I. SAKURADA (Z. angew. Chem., 1929, 42, 640—643).—Sce this vol., 430.

Cellulosexanthoacetic acid. T. NAKASHIMA (Z. angew. Chem., 1929, 42, 546—549).—See this vol., 430.

Cellulosexanthamides. T. NAKASHIMA (Z. angew. Chem., 1929, 42, 643-645).—See this vol., 430.

Constitution of cellulose xanthate. II. T. LIESER (Annalen, 1929, 470, 104-110).-Treatment of cellulose xanthate (B., 1928, 742) with nitrosomethylurethane in methyl alcohol affords a monomethylcellulose, (C6H10O5)(C6H9O4.OMe), insoluble in organic solvents, which swells in sodium hydroxide solution. Similar treatment of cellulose gives products containing 0.75 and 0.87% OMe. Hydrolysis of the methylated cellulose first with 75% sulphuric acid at the ordinary temperature and then with hot 8% sulphuric acid (by dilution) gives dextrose and 2-methylglucose [phenylhydrazone, m. p. 176° (uncorr.)]. This last compound is also obtained by hydrolysis of 3:4:6-triacetyl-2-methylmethylglucoside, m. p. 121° (uncorr.) [obtained by methylation of 1-chloro-3:4:6-triacetylglucose (Brigl, A., 1922, i, 225) with methyl iodide and silver oxide], with 10% hydrochloric acid. H. BURTON. hydrochloric acid.

Lignin. I. Chemical and physical behaviour of phenol-lignins. E. WEDEKIND and J. R. KATZ (Ber., 1929, 62, [B], 1172—1177; cf. Hillmer, B., 1926, 46).—Acetylation of the simple phenol-lignins leads smoothly and under varied experimental conditions to compounds of constant analytical composition, and the simple acetylphenol-lignin, like acetyl-

resorcinol-lignin and methylphenol-lignin, has relatively great solubility in a variety of organic media. Determinations of mol. wt. in glacial acetic acid give values of 250-270 for less than 0.5% solutions which increase rapidly with increasing concentrations. In phenol and naphthalene the minimal mol. wt. 1800 is observed. In bromoform and chloroform, the compound gives colloidal solutions. Unexpectedly this is found to be the case also in glacial acetic acid, acetone, and alcohol, so that osmotic measurements are here valueless. Analytical results indicate $C_{19}H_{20}O_6$ as the simplest possible formula for acetyl-phenol-lignin, whence $C_9H_{10}O_3$ for lignin. Since, however, this expression is not compatible with any constitution assigned to lignin and it has not previously been assumed that less than two methoxyl groups are present in the simplest lignin, the formula for acetylphenol-lignin is doubled $(C_{38}H_{40}O_{12})$, and thus after subtraction of two methoxyls, four acetyls, and two phenols, the expression $C_{16}H_{16}O_6$ is derived for the simplest lignin skeleton. For acetylresorcinol-lignin the constitution

 $C_{16}H_{14}O_4Ac_2(OMe)_2[C_6H_3(OAc)_2]_2$ is similarly obtained. The addition of phenol to lignin is considered to occur at the double linking, thus leading to the constitution I for phenol-lignin, based on the lignin formula of Jonas.



Judged by its Röntgen spectrum, phenol-lignin appears amorphous. Acetylphenol- and acetylresorcinol-lignin have rings of which the identity periods are approximately 4 A., thus indicating a naphthalene or conjugated benzene system. Willstätter lignin exhibits two rings, the inner, smaller, one being indistinct and not present in the phenol-lignin. Will-stätter lignin derived from radial and tangential sections of wood shows no marked effect of direction, but a slight asymmetry. Röntgenographic examin-ation of various species of wood gives essentially only the diagram of cellulose. The solubility of derivatives of phenol- and resorcinol-lignin in chloroform, benzene, etc. permits their examination in unimolecular films on water. The molecules appear to be large discs either lying flat on the water surface or overlapping like tiles. It is very probable that macro-molecules in Staudinger's sense exist and have a disc form, thus being differentiated sharply from the linear form of the cellulose molecule. H. WREN.

Preparation of salts of methylguanidine stable in air. W. TRAUBE and K. GORNIAK (Z. angew. Chem., 1929, 42, 379—381).—Molecular proportions of dicyanodiamide and methylamine hydrochloride are fused together, the cooled mass is dissolved in absolute alcohol and treated with sodium ethoxide, the solution separated from sodium chloride, and neutralised with sulphuric acid. The crude sulphate is separated from hygroscopic impurities by dissolving in a little water and reprecipitating with alcohol, and finally crystallised from water; the pure salt, m. p. 238°, is no longer hygroscopic, and easily yields the stable picrate, m. p. 198-199°, and nitrate, m. p. 148-149°. By employing formic in place of sulphuric acid, the somewhat hygroscopic formate, m. p. 122°, is obtained. The nitrite forms stable prisms, m. p. 150°. Acetylmethylguanidine, m. p. 171-172°, is obtained in needles and elongated plates by warming the free base in alcoholic solution with ethyl acetate; its hydrochloride has m. p. 172. Benzoylmethylguanidine, obtained in the same way from ethyl benzoate, crystallises from hot water in hexagonal prisms, m. p. 156°; the hydrochloride forms needles, m. p. 220-221°. Oxalylmethylguanidine, m. p. 205-209° (decomp)., and iminomalonylmethylguanidine, obtained from the free base by the action of ethyl oxalate and ethyl cyanoacetate, respectively, are both soluble in water; the latter separates with 1 mol. water of crystallisation, m. p. 162° (decomp)., and forms a red isonitroso-compound. S. I. LEVY.

β-Chloro-substituted organic compounds of arsenic. V. V. NEKRASSOV and A. S. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 71–78).—See A., 1928, 1230.

Hydrogenation and decomposition of organic compounds of silicon at high temperatures and pressures. V. IPATIEV and B. DOGLOV (Ber., 1929, 62, [B], 1220-1226).-Tetraethylsilane suffers 50% decomposition after 3 days at 350° according to the scheme 2SiEt₄=C₂H₆+Et₃Si SiEt₃. The gaseous products contain also methane and silicon tetrahydride, whilst the formation of a difficultly volatile, viscous oil indicates more profound condensation, Triethylsilane appears to be formed. Phenyltriethylsilane suffers only 15% decomposition after 24 hrs. at 450°, 60% after 3 days at 350°. The product contains benzene, unchanged phenyltriethylsilane, triethylsilicol (due to presence of atmospheric oxygen in the bomb), tetracthylsilane, and diphenyldiethylsilane. A dimeride of phenyltriethylsilane is also formed. Tetraphenylsilane is extremely stable over the range $300-450^\circ$, being unaffected except for the production of 2-3% of oil after 8 days at 450° . At 490°, the molecule becomes completely degraded, probably suffering profound condensation. The crystalline substance so obtained cannot be melted, sublimed, distilled, or dissolved in any medium.

H. WREN.

Yields of Grignard reagents. I. Alternating properties of *n*-alkyl bromides. II. Effect of rapid addition of halide on yield. H. GILMAN, E. A. ZOELLNER, and J. B. DICKEY (J. Amer. Chem. Soc., 1929, **51**, 1576—1583, 1583—1587).—The yields of Grignard reagents obtained from 14 alkyl bromides and from nine other halides by an improved optimum procedure have been accurately determined by an acid titration method (cf. Gilman and others, A., 1923, ii., 272; 1928, 1212; this vol., 546). The *n*-alkyl halides containing an even number of carbon atoms appear to give higher yields than the preceding homologues. A slight decrease in yield is noted with increasing mol. wt. For a given alkyl group the order of decreasing yield is n-, sec-, tert.-alkyl, and bromides give higher yields than the corresponding iodides. The method gives good yields of magnesium α - and β -naphthyl bromides.

The decrease in the yield of Grignard reagent caused by adding all the alkyl halide to the magnesium at once, instead of in the course of 30-35 min., has been determined for the above 23 halides. With alkyl halides the decrease is about 10-18% of the theoretical yield, with the aryl halides 3-7%, and with benzyl chloride only 0.3%. The alkyl iodides show a greater decrease than the bromides, and the branched alkyl a greater than the *n*-alkyl halides.

H. E. F. NOTTON.

Active magnesium-copper alloys for the preparation of Grignard reagents. H. GILMAN and L. L. HECK (Bull. Soc. chim., 1929, [iv], 45, 250-254).—Further comparative experiments on the use of active magnesium-copper alloys for the preparation of Grignard reagents from β-bromostyrene, n-butyl chloride, and pinene hydrochloride show that alloys containing 13.3, 14.5, and 19.6% of copper are more efficient than activated magnesium, the alloy containing 14.5% of copper being superior to that containing 12.75% of copper (A., 1928, 253). The results indicate maximum efficiency for an alloy containing 15% of copper. The colour reaction previously described (A., 1928, 160) was used in determining the rate of formation of the Grignard compound. Treatment of activated magnesium or magnesium-copper alloys with dry hydrogen at 360° (cf. Ray and Dutt, A., 1928, 630) reduced their catalytic activity. R. BRIGHTMAN.

Formation of di-p-tolyl in preparation of magnesium benzyl chloride. Preliminary formation of free radicals in preparation of Grignard reagents. H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1929, 51, 1571-1576).-The hydro-carbon, m. p. 119-120°, obtained in small yield in many reactions involving the use of magnesium benzyl chloride (cf. A., 1925, i, 802) is now shown to be di-p-tolyl. It is also obtained when this reagent reacts with cupric chloride, azobenzene, or formaldehyde, and must, therefore, be present in the reagent itself. It is probably formed from the free benzyl radicals, which are the initial products of the reaction (cf. this vol., 179). This is confirmed by the presence of di-p-tolyl (0.2% yield ; also traces of o-tolyl derivatives, oxidised to phthalic acid) in the product from magnesium benzyl chloride and hydrochloric acid at 0°. The possibility that the di-p-tolyl might have arisen from traces of *p*-chlorotoluene in the benzyl chloride was excluded by a special test. Difficulty vas experienced in obtaining a negative Beilstein test for chlorine on samples of benzoic acid.

H. E. F. NOTTON.

Forced reaction between some hydrocarbons and organomagnesium halides. H. GILMAN and J. A. LEERMAKERS (Rec. trav. chim., 1929, 48, 577— 579).—No action can be detected between magnesium benzyl chloride or magnesium ethyl bromide and di- or tri-phenylmethane when they are refluxed in beuzene, toluene, or xylene under varying conditions, almost the whole of the hydrocarbon being recovered in the pure state. J. W. BAKER.

Thermal decomposition of organo-magnesium alkoxides. D. IVANOV (Compt. rend., 1929, 188, 1259-1260).-A study of the thermal decomposition of magnesium ethoxy-, n- and iso-propoxy-, iso- and tert.-butoxy-, cyclohexyloxy-, and phenoxy-bromides, and of the n-amyloxy- and benzyloxy-chlorides shows that the decomposition temperature is 330— 350° for derivatives of primary alcohols, 190-220° for those of secondary, 140-160° for those of tertiary alcohols, 380-400° for the benzyloxy-, and 500° for the phenoxy-derivative. It is suggested that the initial reaction is a double decomposition between two molecules of the alkoxide with the formation of magnesium oxide and halide, the corresponding ethylenic hydrocarbon, and the alcohol. These are actually the principal products, accompanied by polymerisation products of the hydrocarbon and traces of other compounds. The magnesium halide catalyses the dehydration of the alcohol. R. K. CALLOW.

Reactions of organic mercury compounds with organic halides. II. F. C. WHITMORE and E. N. THURMAN (J. Amer. Chem. Soc., 1929, 51, 1491-1503).—Organic halides have been refluxed with mercury diphenyl, or di-p-tolyl in toluene, carbon tetrachloride, or chloroform for 300 hrs., or until reaction has taken place. The following do not react : ethylidene, benzylidene, and benzoyl chlorides, dodecyl, ethylene and cyclohexyl bromides, tetrachloroand hexachloro-ethane, sec.-butyl, allyl, benzyl, and 2:4:6-trinitrophenyl iodides, benzotrichloride, phenyl β-bromoethyl ether, phenyl γ-bromopropyl ether, ethyl dichloroacetate, methyl a-bromoisobutyrate and a-bromocamphor. The following give with mercury diaryls arylmercuric halides (I) and tarry products : bromonitromethane, acetyl iodide, dibenzoylmethyl bromide, ω - bromoacetophenone, phenylacetylenyl iodide, and iodoacetonitrile. Ethyl bromomalonate reacts partly, giving I, ethyl malonate, p-bromotoluene, and (?) ethyl ethylenetetracarboxylate. On the other hand five halides undergo definite reactions of four types. (a) Diphenylmethyl bromide gives with mercury di-p-tolyl, diphenyl, and di-n-butyl, respectively, diphenyl-ptolylmethane (80%), triphenylmethane (90%), and aa-diphenylpentane (35% of theory). (b) tert.-Butyl bromide gives almost quantitatively isobutylene, I, and toluene. tert.-Amyl iodide and ethyl a-bromoethane-aab-tricarboxylate yield similarly trimethylethylene and ethyl ethylenetricarboxylate, respectively. (c) 9-Bromofluorene with mercury diaryls gives 9:9'-difluorenylidene and I. (d) Stilbene dibromide gives stilbene, I, and p-tolyl bromide. Thus, in general, mercury diaryls react with organic halides similarly to, but much less readily than other types of bases. Contrary to the statement of Kharasch (A., 1922, i, 189), 2:4:6-trinitrophenylmercuric chloride and mercury bis-2:4:6-trinitrophenyl react normally with iodine, giving iodo-2:4:6-trinitrobenzene, but no hexanitrodiphenyl.

H. E. F. NOTTON.

1:2-Dimethylcyclopropanes. J. BAUDRENG-HEIN (Bull. Acad. Roy. Belg., 1929, 15, 53-80).--

1:2-Dimethylcyclopropanes have been prepared from 88-dibromopentane, obtained by either of the following processes: (1) Condensation of magnesium methyl bromide and crotonaldehyde and decomposition of the product with water gives a 75% yield of Δ^{γ} -penten- β -ol, (I), b. p. 122—122·1°/760 mm., d^{20} 0·8962, $n_{\rm D}^{20}$ 1·4163, but if sulphuric acid is used in the decomposition of the product a relatively large proportion of the ether (CHMc:CH·CHMe⁻)₂O, b. p. 158—158·5°, d^{20} 0·8047, n_D^{20} 1·4306 (also prepared by the action of 10% sulphuric acid on the alcohol), is obtained. Anhydrous hydrogen chloride converts I into β-chloro-Δr-pentene, b. p. 100.5°/771.6 mm., d²⁰ 0.9004, n²⁰_D 1.4322, which, since it is readily hydrolysed, is best obtained by direct distillation of the alcoholic solution without washing. Hydrogen bromide slowly converts this into the bromopentene (also obtained by direct action of hydrogen bromide on I), which is very readily hydrolysed and is converted by further treatment with hydrogen bromide (after distillation to remove an anticatalyst) into a mixture of β_{γ} - and βδ-dibromopentanes. A similar mixture is obtained by the action of hydrogen bromide on the acetate of I obtained by the action of potassium acetate on the bromopentene, but with the acetate, b. p. 138.5- $139^{\circ}/753$ mm., d^{20} 0.8962, n_{10}^{20} 1.4163, prepared by the action of acetic anhydride on I, the main product is the bromopentinene, further absorption of hydrogen bromide being extremely slow. By the action of phosphorus tribromide on I only 69% of monobrominated products are obtained, isomerisation occurring, since conversion into the acetates yields a mixture which was not further investigated. By the action of zinc and boiling 80% alcohol on the mixed dibromopentanes a mixture of Δ^{β} -pentene (44% from the dibromopentanes obtained from the chloropentene, 16% from the mixture obtained from the acetate) and stereoisomeric 1:2-dimethylcyclopropanes, which is separated by conversion of the former into By-dibromopentane by the action of bromine in potassium bromide solution, and distillation of the cyclic hydrocarbons, b. p. 30-36°. (2) By the action of hydrogen chloride on aldol only resins are obtained, and only a 50% yield of β -chloro-*n*-butaldehyde results with crotonaldehyde. (3) Pentane- $\beta\delta$ -diol is obtained by reduction of methyl β-hydroxypropyl ketone (Claisen, A., 1899, i, 667) with platinum-black and hydrogen, and hence is converted into β8-dibromopentane and the dimethylcyclopropanes. (4) Pentane- $\beta\delta$ -diol, obtained by the action of magnesium methyl bromide on aldol (Franke and others, A., 1907, i, 171), is difficult to separate from magnesium salts by extraction with ether, but the product is readily converted directly by the action of 48% hydrobromic acid into a mixture of the bromohydrin and dibromopentane, which yields a mixture of dibromopentanes by the action of hydrogen bromide at 100°, since by the action of zinc it yields a mixture of the ethylenic and cyclic hydrocarbons. (5) Catalytic reduction of acetylacetone with platinum-black yields a mixture of pentan-β-ol and pentane- $\beta\delta$ -diol (30%), and with active platinum containing a trace of iron a mixture of the diol and methyl β-hydroxypropyl ketone is obtained. Reduction with sodium and alcohol, however, gives a 70% yield of the diol. The dibromopentanes ob-

tained from this, on treatment with zinc, yield only 1% of the ethylenic derivative, the main product being 1:2-dimethylcyclopropane. By repeated fractional distillation of the 1:2-dimethylcyclopropanes, b. p. $30-36^{\circ}$, the two stereoisomeric forms, b. p. $28\cdot8-29^{\circ}$, d^{20} 0.6769, n_{20}^{20} 1.37129, and b. p. $37\cdot2-37\cdot4^{\circ}$, d^{20} 0.6928, n_{20}^{20} 1.38223, respectively, are obtained. The latter form is more resistant to the action of bromine. Exaltation of the molecular refractivities for various wave-lengths are tabulated and discussed.

J. W. BAKER.

Oxidation of organic halogen compounds. C. COURTOT and J. PIERRON (Bull. Soc. chim., 1929, [iv], 45, 286-293).-The oxidation of α-olefinic secondary chlorides to ketones is related to the mobility of the halogen in presence of water. Thus, 1-chloro-∆²-cyclohexene, b. p. 65-66°/40 mm., obtained in 93% yield by the action of dry hydrogen chloride on $\Delta^{1:3}$ -dihydrobenzene at -5° to -8° , is hydrolysed by water at 15° in 48 hrs. and at 60-65° in 75 min. Oxidation with sulphuric acid and sodium dichromate at 60-65° gives 60% of Δ^2 -cyclohexen-1-one, b. p. $63^{\circ}/14$ mm. Chlorocyclohexane is only partly (8.7%) hydrolysed at 90-95°, and on oxidation at 40-45° affords adipic acid. Chlorocyclopentane is neither hydrolysed nor oxidised at 50-55°; at 90-95° 71% is hydrolysed and oxidation gives glutaric acid. Similarly 9-chlorofluorenone is neither oxidised nor hydrolysed at 15°, but at 95-97° is rapidly hydrolysed, and oxidation affords fluorenone. δ-Chloro- Δ^{β} -hexene, b. p. 65—67°/110 mm., obtained in 81% yield by saturating Δ^{β} -hexen- δ -ol with hydrogen chloride at 0°, does not combine with halogen hydride. Hydrolysis is complete in 90 min. at 40° and 81% is hydrolysed in 48 hrs. at 15°. Oxidation at 60—65° gives 55% of Δ^{β} -hexen- δ -one, b. p. 137—140° (2:4-dinitrophenylhydrazone, m. p. 100-101°), converted by hydrogenation in presence of platinum-black into ethyl propyl ketone, b. p. 121–124° (semicarbazone, m. p. 112°). γ -Chloro-δ-methyl- Δ [§]-heptene, b. p. 75–78°/53 mm., obtained by the action of hydrogen chloride on 8-methyl-16hepten-y-ol at 0°, is readily hydrolysed, 93% at 15° in 48 hrs., 90% at 45-50° in 75 min., and at 45-50° is oxidised to S-methyl-∆8-hepten-y-one, b. p. 96-98°/ 70 mm., 170-172°/735 mm. (semicarbazone, m. p. 167°, 2:4'-dinitrophenylhydrazone, m. p. 147°), some δ -methyl- $\Delta^{\gamma\epsilon}$ -heptadiene being also formed. Δ^{β} -Hexenδ-one and δ-methyl-Δδ-hepten-γ-one do not react with magnesium methyl iodide at the ordinary temperature, and accordingly do not exist in the enolic form. Oxidation of the Δ^{a} -sec.-chloride accordingly offers an alternative route for proparing the Δ^{α} -ketone.

R. BRIGHTMAN.

p-Bromoethylenic derivatives of benzene and their magnesium organo-compounds. II. R. QUELET (Bull. Soc. chim., 1929, [iv], 45, 255—274). p-Bromostyrene does not react with magnesium activated by bromine in ether. With p-bromopropenylbenzene reaction is incomplete, about 10% of the bromide being recovered unchanged, and the normal magnesium derivative undergoes partial condensation. p-Bromo- Δ^{α} -butenylbenzene, p-bromoallylbenzene, and p-bromo- Δ^{γ} -butenylbenzene behave similarly and the yield of magnesium derivative at the
ordinary temperature as determined by Gilman's method (A., 1923, ii, 272) is considerably higher than that found by Job and Reich's method. The formation of the complex magnesium derivative is accelerated by heat. On decomposition with water, magnesium *p*-propenylbenzene bromide affords 43% of propenylbenzene, b. p. 68%/12 mm., d_4^r 0.918, n_5^r 1.558 (dibromo-derivative, m. p. 66.5%), and some pp'-dipropenylbenzene, m. p. 186\%, together with a non-crystalline semi-fluid substance, probably the decomposition product of the complex magnesium derivativo. Δ^{α} -Butenylbenzene, b. p. 80°/12 mm., d_4^{μ} 0.907, $n_{\rm P}^{\mu}$ 1.550, allylbenzene, b. p. 154°/730 mm., and $\Delta \gamma$ -butenylbenzene, b. p. 65°/12 mm., are similarly obtained accompanied by similar uncrystallisable non-volatile products. About 20% of the p-bromoallyl benzene is recovered unchanged.

The following have been prepared from the above magnesium derivatives by the usual methods : p-allylphenol, b. p. 120°/12 mm., 235°/732 mm., p-allylbenzoic acid (yield 25%), m. p. 104—105° (silver salt, dibromo-derivative, m. p. 154°), p-diallylbenzene, b. p. 94°/12 mm., d¹¹ 0.915, n¹¹₁ 1.526 (tetrabromo-derivative, m. p. 109°), p-allylbenzaldehyde (with ethyl orthoformate, yield 12%), b. p. 113°/12 mm., n¹⁵₁ 1.555 [semicarbazone, m. p. 197°, bromo-derivative, b. p. 193—195°/15 mm (decomp.)] n-propenylphenol 193—195°/15 mm. (decomp.)], *p*-propenylphenol, m. p. 93°, b. p. 136—137°/12 mm., p-*propenylbenzoic* acid (yield 30%), m. p. 215°, sublimes above 190° (silver salt), p-propenylallylbenzene (from magnesium p-propenylbenzene bromide and allyl bromide), b. p. 107—108°/11 mm., d_4^{11} 0.918, n_B^{11} 1.559 (tetrabromo-derivative, m. p. 73°), p-propenylbenzaldehyde (yield 15%), b. p. 132°/17 mm., d_4^{11} 1.044, n_B^{11} 1.607 (semicarbazone, m. p. 230°), and p-propenylphenylethyl-carbinol, m. p. 57°, b. p. 143—145°/11 mm. (phenyl-urethane, m. p. 235—236°), which on dehydration with phosphoric anhydride in benzene affords p-dipropenylbenzene, m. p. 63-64°, b. p. 123-125°/12 mm. (tetrabromo-derivative, m. p. 168-169°). Comparison of the p-diallyl-, p-dipropenyl-, and p-allylpropenylbenzene shows that under 12 mm. migration of the double linking from the β - to the α -position raises the b. p. by 15°. The low m. p. of the totrabromoderivative of *p*-allylpropenylbenzene is attributed to disymmetry of the molecule and is not really an exception to the rule that the bromides of Δ^{α} -derivatives have higher m. p. than the bromides of the Δ^{β} derivatives. R. BRIGHTMAN.

2-Methylnaphthalenes. III. K. DZIEWOŃSKI and A. WULFFSOHN (Bull. Acad. Polonaise, 1929, A, 143-148).—Sulphonation of 2-methylnaphthalene with an equimolecular quantity of chlorosulphonic acid in nitrobenzene at 30-40° gave 2-methylnaph-Malene-8-sulphonic acid (sodium salt; chloride, m. p. 94-96°; amide, m. p. 172-174°; anilide, m. p. 162-164°). Its constitution was established by conversion into 7-methyl-α-naphthol, m. p. 109-111° [acetate, m. p. 39-41°; azo-derivative with p-nitroaniline, m. p. 250° (decomp.)], by fusion of the sodium salt with potassium hydroxide. A. I. VOGEL.

2:3- and 1:4-Dinitronaphthalene. L. K. CHUDOZILOV (Coll. Czech. Chem. Comm., 1929, 1, 302-305).-See A., 1927, 49.

Pyrogenic decomposition of the perhydrides of fluorene and acenaphthene under pressure of hydrogen. M. A. ORLOV and M. A. BELOPOLSKY (Ber., 1929, 62, [B], 1226-1234).-Hydrogenation of fluorene at 210-230° with initial pressure 60-70 atm., twice in presence of nickel oxide, and then in that of a mixture of nickel oxide and hopcalite (mixture of oxides of silver, manganese, copper, and cobalt), affords a complex mixture of products. Treatment of the mixture at 380°/70-75 atm. initial pressure leads to the gasification of about 32% of it and the production of monocyclic and, probably, dicyclic naphthenes. The presence of perhydroindenes in the fractions of higher b. p. is established by their conversion when passed through a tube heated at 750° into indene, cyclopentadiene, naphthalene, and chrysene; under similar conditions, these products are obtained also from perhydroindene. When distilled with aluminium chloride, fluorene affords coke and diphenvl.

Perhydroacenaphthene is remarkably stable towards heat, but, at about 450° yields gases and petroleum hydrocarbons containing benzenoid compounds. When passed through a tinned iron tube at 650° it gives ethylene and propylene, cyclopentadiene, toluene, indene, and methylindene. The presence of indenes in coke-oven tar and primary tar is probably due to the decomposition of fluorene hydrides. the presence of which has been established in coal. H. WREN.

meso-Derivatives of anthracene and dianthryl. V. I. MINAEV and B. P. FEDOROV (J. Russ. Phys. Chem. Soc., 1929, 61, 143-150).-Sodium sulphite and 9-nitroanthracene react to form sodium anthracene-9-sulphonate, which on treatment with alkali hydroxide yields anthranol, and 9-anthramine on heating with ammonia in a sealed tube. Sodium dianthryl 9-sulphate is also obtained as a by-product, which can be easily reduced to the parent hydrocarbon, dianthryl, hydrolysed to give 9-hydroxydianthryl, and, on heating with ammonia in a sealed tube, made to yield 9-dianthrylamine, m. p. 305° (decomp.). M. ZVEGINTZOV.

(Pyrogenic decomposition of chrysene under pressure of hydrogen.] N. ORLOV and N. LICHAT-SCHEV (Ber., 1929, 62, [B], 1378; cf. this vol., 549).-H. WREN. A correction.

Pervlene and its derivatives. XXII. A. ZINKE and N. SCHNIDERSCHITSCH (Monatsh., 1929, 51, 280-284).-Catalytic reduction of perylene with hydrogen and palladised charcoal in acetic acid at 990-1000 mm. yields octahydroperylene (I), m. p. 159-161°, whilst

CH,

by extraction of the residual catalyst with acetic acid hexahydroperylene CH₂ (Zinke and Unterkreuter, A., 1920, CH₂ i, 541) is obtained. Similar reduction (I.) of perylene-3: 10-quinone yields the corresponding hexahydroperylene-3: 10-CH2 diol, m. p. 298-300° (diacetate, m. p. JCH₂ 342-343°), whilst from the 1:12quinone is obtained hexahydroperylene-

 CH_2 1:12-diol, m. p. 260° (decomp.) (diacetate, m. p. 192-194°), together with a small quantity of a substance, m. p. 146-150° (possibly the octahydrodiol). Similar reduction of perylene-3:9-quinone yields an unidentified substance, m. p. 251-253°. J. W. BAKER.

Nitration of bromoanilines in sulphuric acid. R. LUKEŠ and J. FRAGNER (Coll. Czech. Chem. Comm., 1929, 1, 294-301).-Nitration of o-bromoaniline in concentrated sulphuric acid yields 6-bromo-m-nitroaniline. m-Bromoaniline, under the same conditions, yields 3-bromo-p-nitroaniline, m. p. 175-176°, accompanied by 5-bromo-o-nitroaniline, m. p. 151-152°, in small quantity. The constitution of 3-bromo-pnitroaniline is confirmed by bromination to 2:3:6tribromo-p-nitroaniline, m. p. 159°, by conversion into 2:4-dibromonitrobenzene, m. p. 61°, and by conversion into o-bromonitrobenzene, m. p. 44-45° (lit. 41°), by the action of nitrous fumes. 3-Bromop-nitroaniline has also been prepared by the nitration of *m*-bromoacetanilide and converted into 2:3:6tribromo-p-nitroaniline as described by Claus and Wallbaum (A., 1898, i, 18), who give m. p. 172° and 131°, respectively. R. K. CALLOW.

Transformation of phenylnitroamines into nitroanilines. I. A. E. BRADFIELD and K. J. P. ORTON (J.C.S., 1929, 915-921).-The isomeric change of aromatic nitroamines into nitroanilines under the influence of mineral acids in aqueous or aqueous acetic acid media (cf. Orton and Pearson, J.C.S., 1908, 93, 725; Orton, Reed, and Thomas, Brit. Assoc. Reps., 1912, 117; Chem. News, 1912, 106, 236) has been reexamined. Quantitative measurements (using a colorimetric method) of the velocity of transformation of the nitroamines derived from 2:4-dichloro- and 2:4-dibromo-aniline, and 3-bromo-p-toluidine, in 50% and 98% acetic acid media, show that although the appropriate nitroaniline is the main product, by-products arise, one of which is a substance capable of diazo-coupling with a phenol. The formation of the nitroaniline and by-products proceeds as a reaction of the first order and no stoicheiometrical relation exists between the proportions of the products; the ratio varies with the experimental conditions, but in general has the same value for equivalent concentrations of different catalysing acids. By contrast with the chloroamine transformation (A., 1928, 628), the anion of the acid catalyst is not fundamentally concerned in the reaction, and the chlorination of an anilide by the chloroamine of another finds no complete and simple parallel, although it is sometimes possible for the nitro-group to migrate from a nitroamine to a carbon atom of another aniline or anilide. The catalytic behaviour of nitric acid for the transformation is anomalous, but this is not due to nitration effects. The results confirm the preliminary work (loc. cit.), and are in harmony with the view that an intramolecular process is the essential part of the transformation. 3-Bromo-p-tolylnitroamine, m. p. 65°, was prepared from 3-bromo-p-toluidine by nitration with nitric acid $(d \ 1.50)$ in acetic acid and acetic anhydride at 0°, and separated from the accompanying 3-bromo-5-nitro-p-tolylnitroamine by addition of three-quarters of the calculated quantity of N-hydrochloric acid; 2:4-dichlorophenylnitroamine and 2:4-dibromophenylnitroamine, m. p. 77°, were obtained by the method of Orton (J.C.S., 1902, 81, 806;

A., 1907, i, 205). These nitroamines are highly sensitive to light. C. W. SHOPPEE.

Pyridine as catalyst in production of dimethyl- α -naphthylamine. F. G. GERMUTH (J. Amer. Chem. Soc., 1929, 51, 1555—1557).—Addition of 4 c.e. of pyridine to each g.-mol. of α -naphthylamine increases the yield of dimethyl- α -naphthylamine obtainable by treatment with methyl sulphate (2 mols.) and 40% sodium hydroxide from 51.3% to 65.8%. Larger amounts produce no further increase.

H. E. F. NOTTON. Constitution of Bandrowski's base. J. J. RITTER and G. H. SCHMITZ (J. Amer. Chem. Soc., 1929, 51, 1587—1589).—The constitution assigned by Bandrowski (A., 1889, 973; cf. Erdmann, A., 1904, i, 778, 935) to the base, m. p. 238°, obtained by oxidising p-phenylenediamine with potassium ferricyanide is confirmed by the observation that 1 mol. of the base, when oxidised with lead peroxide and 25% sulphuric acid, yields 1 mol. of p-benzoquinone. A compound analogous to that formed from p-toluidine (Green, J.C.S., 1893, 63, 1395) should give 2 mols. of quinone. H. E. F. NOTTON.

Reduction of esters of benzeneazohydroxybenzoic acids. E. PUXEDDU (Gazzetta, 1929, 59, 212—218).—Reduction of an alkyl benzeneazophenolcarboxylate involves, in addition to the loss of the benzeneazo-group, the removal of the alkyl group. Thus methyl 5-benzeneazosalicylate (Limpricht, A., 1891, 1036) (methyl ether, m. p. 66°) is reduced by phenylhydrazine or by tin and hydrochloric acid to 5-aminosalicylic acid, which is also obtained from ethyl 5-benzeneazosalicylate, m. p. 100° (methyl ether, m. p. 64°), or from the phenyl ester, m. p. 149°.

E. W. WIGNALL.

Stereochemistry of aromatic compounds. VIII. Optically active heterocyclic compounds and azo-dyes of the dinaphthyl series. R. KUHN and P. GOLDFINGER (Annalen, 1929, 470, 183-200; cf. Mascarelli, this vol., 181).-Azo-2: 2-naphthalene is reduced by stannous chloride and alcoholic hydrogen chloride (cf. Jacobsen, A., 1922, i, 589) to 2:2'-diamino-1: 1'-dinaphthyl (I), m. p. 193° (corr.). When I is treated with *d*-camphorsulphonic acid in alcoholic chlorobenzene, d-2: 2'-diamino-1: 1'-dinaphthyl dcamphorsulphonate, m. p. 243° (corr.), $[\alpha]_{D}^{20} + 491.8^{\circ}$ in pyridine, separates. d-2: 2'-Diamino-1: 1'-dinaph*thyl* (II), m. p. $242.5-243^{\circ}$ (corr.), $[\alpha]_{D}^{20} + 149.5^{\circ}$ in pyridine, exhibits *lavo*-rotation ($[\alpha]_{10}^{20} - 30^{\circ}$) in N. hydrochloric acid. The l-isomeride (III) has m. p. 243°, $[\alpha]_{\rm D}^{18}$ +46.8° in 2N-hydrochloric acid. Resolution of I is not readily effected with α -bromo- π -camphorsulphonic acid. Condensation of 6:6'-diaminodi-o-tolyl (Meisenheimer and Höring, A., 1927, 766) with benzil at 180-200° affords a condensation product, m. p. 213° (corr.): the corresponding substances from I, II, and III have m. p. 277.5° (corr.), yielding a turbid liquid which becomes clear at 291.5°, m. p. 295°, $[\alpha]_{10}^{24}$ -1910° in pyridine, and m. p. 281°, $[\alpha]_{10}^{24}$ +823.4° in pyridine, respectively. The dibenzylidene derivative of II has m. p. 146° (corr.), $[\alpha]_D^{20} + 129^\circ$ in pyridine, -130° in sulphuric acid, whilst the condensation product with dinitrobenzil has m. p. 335°, $[\alpha]_{D}^{21}$ - 1611° in pyridine. Accetylation of an optically

impure specimen of III with acetic anhydride and pyridine gives a diacetyl derivative, m. p. 237°, [a]2 +151.6° in acetic acid, which when reduced with hydrogen in presence of platinum oxide and acetic acid, yields an inactive product. Similar results are obtained with the diacetyl derivative, $[\alpha]_{0}^{21} - 92^{\circ}$ in acetic acid, and the benzil condensation product, of II. Racemisation of II is not effected by heating with N-hydrochloric acid at 100°, but at 135° some optically inactive naphthocarbazole, m. p. 157° (Meisenheimer and Witte, A., 1904, i, 193) (picrate, m. p. 221°), is formed. When II is diazotised and coupled with resorcinol, a deep-red azo-dye, $C_{32}H_{22}O_4N_4$, darkens and decomp. about 300°, $[\alpha]_{3533}^{20}$ -1730° in pyridine, is obtained. The rotation-dispersions of most of the above optically active compounds, for different wave-lengths, are given. H. BURTON.

Volatility and structures of azides and aliphatic diazo-compounds. N. V. SIDGWICK (J.C.S., 1929, 1108-1110).-Comparison of the b. p. of azides and aliphatic diazo-compounds with the corresponding halides and nitro-compounds, shows that the b. p. of the former lie near those of the bromides, or between these and the iodides (cf. Forster and Newman, ibid., 1910, 97, 2572), whilst the b. p. of the latter lie very near those of the chlorides. The open-chain formulæ R.N.NIN, R2C:NIN, contain semi-polar double linkings, the presence of which always causes a rise in the b. p.; the b. p. would therefore be expected to lie near those of the nitro-compounds rather than the chlorides or bromides. The results appear to indicate that the ring formulæ should be retained for both azides and diazo-compounds. C. W. SHOPPEE.

Constitution of normal diazotates and diazohydrates. A. HANTZSCH (Ber., 1929, 62, [B], 1235-1241).-The observation of Cambi and Szegö (A., 1928, 1369) that the absorption curves of normal and iso-diazotates are differentiated by the presence or absence of a characteristic band has been anticipated by Hantzsch and Lifschitz (A., 1912, ii, 1116), who have been led to the conclusion that the light absorption of the azo-group in azo-compounds R.N.N.R and particularly in the isomeric diazo-compounds, Ar·N2·SO3H, Ar·N2·CN, and Ar·N2·OMe, is so unusually variable that no certain interpretation with regard to constitution can be based on the absorption curves. Cambi and Szegö's assertion that "normal and iso-diazotates cannot possibly be stereoisomerides" is without foundation and their method of determining constitution by optical means leads to untenable conclusions when applied to other azo-compounds such as tolueneazodimethylamine and potassium hyponitrite. Reply is made to Angeli (A., 1928, 1129). H. WREN.

Introduction of the triphenylmethyl group into phenols. II. D. V. N. HARDY (J.C.S., 1929, 1000—1011).—Phenols and phenolic ethers fall into three groups according to their behaviour towards an acetic-sulphuric acid solution of triphenylmethylcarbinol (the Baeyer-Villiger reaction). Those which condense (Group I) include phenol, anisole, phenetole, o-cresol, o-tolyl methyl ether, o-tolyl ethyl ether, m-cresol, pyrocatechol, guaiacol, veratrole, resorcinol

and its dimethyl ether, quinol, pyrogallol and its trimethyl ether, thymol, α - and β -naphthol; those which reduce the carbinol to triphenylmethane (group II) include p-cresol, p-tolyl methyl and ethyl ethers, m- and p-chlorophenol, quinol dimethyl ether. To group III, those which do not react, belong o- and p-nitrophenol, pieric acid, o- and p-nitroanisole, salicylic acid, methyl salicylate, trichlorophenol, trichloroanisole, tribromophenol. o-Chloro- and obromo-phenol exhibit anomalous behaviour, condensing and yielding triphenylmethane simultane-ously. Mechanisms for the Baeyer-Villiger reaction suggested by the author (with Boyd, A., 1928, 516) and by van Alphen (ibid., 57) are discussed. It is considered that the primary reaction is between the triphenylmethyl cation and the undissociated phenol, since phenolic ethers react similarly to phenols. It is suggested that the formation of triphenylmethane by members of group II is preceded by elimination of triphenylmethyl as the anion from an intermediate complex, and the nature of the subsequent oxidation products, in particular those derived from p-cresol, is discussed. A number of reactions which appear to involve the triphenylmethyl anion are instanced. In general, the triphenylmethyl group enters the nucleus para to hydroxyl or methoxyl, but occasionally o-substitution occurs. Contrary to the statement of Schorigin (A., 1928, 59), di-triphenylmethylation has been observed for α -naphthol and 1 : 3-dimethoxybenzene. The preparation of the following tetraphenylmethanes is described : 4-ethoxy-, m. p. 191°, converted by boiling acetic-hydriodic acid into 4-hydroxy-; 3:4-dihydroxy-, m. p. 262° (cf. lit.); 3:4-dimethoxy-, m. p. 170° (lit.), converted by acetic-hydriodic acid into the foregoing hydroxy-compound; 2:4-dihydroxy-, m. p. 268° (decomp.) (lit.); 1:3-dimethoxy-, m. p. 180° (lit.), together with 1:3-dimethoxy-4:6-bistriphenylmethylbenzene, m. p. 271°; 3:4:5-trihydroxy-, m. p. 255° (decomp.) after darkening at 230° (compound $+2COMe_2$); 3:4:5-trimethoxy-, m. p. 178°; 4-hydroxy-2-methyl-5isopropyl., which is dimorphous, α -form, m. p. 106– 107°, β -form, m. p. 157°; 3-chloro-4-hydroxy-, m. p. 193·5°, together with triphenylmethane (I), m. p. 93°; 3-bromo-4-hydroxy-, m. p. 186–187°, together with I. Guaiacol yields a mixture of 4-hydroxy-3methoxy- and 3-hydroxy-4-methoxy-tetraphenylmethanes hydrolysed by acetic and hydriodic acids to 3:4-dihydroxytetraphenylmethane, m. p. 262°. a-Naphthol affords 4-triphenylmethyl-a-naphthol, m. p. 204-204.5° (compound +1EtOH), together with 2:4bistriphenylmethyl-1-naphthol, m. p. 235–236°; β -naphthol gives 1-triphenylmethyl- β -naphthol, m. p. 228°. m-Chloro- and p-chloro-phenol, quinol di-methyl ether, p-tolyl ethyl ether, and p-tolyl methyl ether all give I as the sole identifiable product: the yield is 98.4% in the last case. *p*-Cresol yields I together with an acidic substance, isolated as a brown, amorphous powder, shrinking about 85°, and melting at 100-110° (decomp.). o-Tolyl ethyl ether affords 4-ethoxy-3-methyltetraphenylmethane, m. p. 144° (cf. van Alphen, A., 1927, 867), also obtained synthetically as follows: triphenylcarbinol and o-toluidine were condensed with acetic and hydrochloric acids, and the product was hydrolysed to 4-amino-3-methyltetraphenylmethane; the diazonium sulphate of the latter, when treated with boiling ethyl alcohol, gave the above ethoxy-compound, m. p. 143°. By the Sandmeyer reaction, the foregoing diazonium sulphate affords 4-chloro-3-methyltetraphenylmethane, m. p. 160°. o-Diphenylenephenylcarbinol condenses with phenol to yield o-diphenylene-4-hydroxydiphenylmethane (lit.), converted by acetic-hydriodic acid into o-diphenylenephenylmethane, m. p. 145°. Diphenylyldiphenylcarbinol similarly affords diphenylyl-4-hydroxytriphenylmethane, m. p. 183°, also prepared from diphenylyldiphenylmethyl chloride and phenol; it is stable toward acetic and hydriodic acids.

The stability of tetrarylmethane derivatives (cf. Boyd and Hardy, *loc. cit.*) has been further investigated, and a tabular summary is given. The decompositions mentioned are analogous to those of 2-hydroxytriphenylmethane (Schmidt, Diss., Heidelberg, 1898) and of the hexamethyl ether of phloroglucinolphthalein (A., 1928, 884), and afford additional evidence of the reversibility of the Bacyer-Villiger reaction. C. W. SHOPPEE.

Germicidal action of hydroxydiaryl sulphides. G. E. HILBERT and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, **51**, 1526—1536).—*p*-Methoxydiphenyl sulphide, b. p. 194—195°/13 mm., prepared by modifications of (a) Hinsberg's (A., 1903, i, 251; 1908, i, S75; 1909, i, 6) and (b) Ziegler's (A., 1890, 1292) methods, is converted by a mixture of 48% hydromethods. bromic acid and acetic anhydride at 80-90° into p-hydroxydiphenyl sulphide (115), m. p. 50—51°, b. p. 164—165°/3 mm. (p-nitrobenzoate, m. p. 74—75°), and by 21% hydrobromic acid in glacial acetic acid at 60° , or by boiling 48% aqueous hydrobromic acid into diphenyl disulphide and *p*-bromophenol. The new phenol may also be obtained directly from benzenesulphinic acid and phenol [cf. (a)], or from magnesium p-anisyl bromide and chlorothiolbenzene, but not from p-hydroxybenzenediazonium chloride and sodium phenyl sulphide. o-Methoxy-, b. p. 150-152°/3 mm.; m-methoxy-, b. p. 156°/4 mm., diphenyl sulphides, and p-methoxyphenyl p-tolyl sulphide, m. p. 45-46°, b. p. 181-182°/4 mm., prepared by method (b), are demethylated to o-hydroxydiphenyl sulphide (33), b. p. 140°/3 mm. (p-nitrobenzoate, m. p. 72-73°); m-hydr-oxydiphenyl sulphide (68), b. p. 159-161°/3 mm. (p-nitrobenzoate, m. p. 103°), and p-hydroxyphenyl p-tolyl sulphide (50), m. p. 67-68°, b. p. 178-180°/ 3 mm. A new method, probably of general applica-ation for preparing diphenyl sulphide is by decomation, for preparing diphenyl sulphide is by decomposing the yellow intermediate product from benzenediazonium chloride and sodium phenyl sulphide at 5° with copper powder. p-Methoxydiphenylsulphone is demethylated to p-hydroxydiphenylsulphone (<10), m. p. 136-137°. The high phenol coefficients (given in parentheses) and low toxicities of the hydroxydiphenyl sulphides are noteworthy. H.E.F. Norron.

Esters of hydrogenated aromatic alcohols [cyclohexyl stearate]. R. H. VAN SCHAACK, jun.— See B., 1929, 427.

Manufacture of condensation product from m-cresol and acetone [2:2'-dihydroxy-4:4'-dimethyl-ββ-diphenylpropane]. Schering-Kahl-BAUM A.-G. and H. JORDAN.—See B., 1929, 467.

Reactivity of the nitro-group in 4:5-dinitroveratrole towards sodium methoxide at 35° and 45°. A. H. PARIJS (Rec. trav. chim., 1929, 48, 560-563) .- The velocity of the bimolecular reaction between 4:5-dinitroveratrole and sodium methoxide has been determined at 35° and 45° by titrating the unchanged sodium methoxide with acetic acid. The bimolecular velocity coefficients at 35° and 45° are, respectively, 0.0029 and 0.0088 min.-1 The corresponding values for o-dinitrobenzene (cf. Steger, A., 1899, i, 745, whose values need to be halved) are 0.0242 and 0.0695, respectively, hence the introduction of two methoxy-groups into o-dinitrobenzene retards the reaction with sodium methoxide to a greater extent than does the introduction of a single methoxy- or ethoxy-group in the 5-position in 1-chloro-2: 4-dinitrobenzene. The solubility of 4:5. dinitroveratrole in absolute methyl alcohol at 15°. 25°, 35°, and 45° is, respectively, 7.66, 10.54, 18.21, and 24.95 g. per litre. J. W. BAKER.

Hydroxy- β -orcinol [2:3:5-trihydroxy-p-xylene]. Y. ASAHINA and E. ISHIBASHI (Ber., 1929, 62, [B], 1207—1208; cf. this vol., 818).—p-Xyloquinone is converted by acetic anhydride and concentrated sulphuric acid into hydroxy- β -orcinol triacetate, m. p. 108°, from which hydroxy- β -orcinol, m. p. 158°, is derived; the corresponding tribenzoate has m. p. 156°. H. WREN.

Hoesch synthesis of phenolic ketones. II. Condensation of arylglyoxylonitriles with phloroglucinol. W. BORSCHE, C. WALTER, and J. NIEMANN (Ber., 1929, 62, [B], 1360—1366).—Contrary to the observations of Marsh and Stephen (A., 1925, i, 1158), the condensation of arylglyoxylonitriles with phloroglucinol leads to the formation of imino lactones, $(OH)_{3}C_{6}H_{2}$ $C(:NH) \cdot O_{C_{6}}H_{2}(OH)_{2}$ [I].

Treatment of a solution of benzoyl cyanide (1 mol.) and phloroglucinol (2 mols.) in ether with hydrogen chloride affords 2:4:6:2':4':6'-hexahydroxylri-phenylacetiminolactone (I; Ar=Ph), m. p. 286-287° [monohydrate; hydrochloride, m. p. 215-220° (decomp.); penta-acetate (also dihydrate), m. p 181°]. Similarly, 4-methoxybenzoyl cyanide yields 2:4:6:2':4':6'-hexahydroxy-4''-methoxytriphenylacetiminolactone (I; Ar=OMe C₆H₄), m. p. 259-260° after blackening (also monohydrate). 4-Chlorophenylacetonitrile and *p*-nitrosodimethylaniline in boiling methyl alcohol in presence of sodium hydroxide afford the 4-dimethylaminoanil of 4-chlorobenzoyl cyanide, m. p. 146-174°, converted by 5N-hydrochloric acid into 4-chlorobenzoyl cyanide, b. p. $117-118^{\circ}/16$ mm., m. p. $40-41^{\circ}$, which with phloroglucinol yields 4''-chloro-2:4:6:2':4':6'-hexahydroxytriphenylacetiminolactone (I, Ar=Cl·C₆H₄), decomp. 270-280° after blackening (hydrochloride, decomp. 235-240° when rapidly heated ; penta-acetate, m. p. 265-267° after softening at 255° and then darkening). Resorcinol and 4-chlorobenzoyl cyanide afford 4"-chloro-2:4:2':4'-tetrahydroxytriphenylacetolactone, decomp. 276° after becoming red.

4-Chloro-oximinoacetophenone, m. p. 158-160°, from 4-chloroacetophenone and isoamyl nitrite, is converted by acetic anhydride into 4-chlorobenzoic acid. Similarly, 4-bromo-oximinoacetophenone, m. p. 161°, vields 4-bromobenzoic acid. H. WREN.

Configuration of inactive inositol. S. POSTER-NAK and T. POSTERNAK (Compt. rend., 1929, 188, 1296-1298).-The synthesis of i-inositol by Wieland and Wishart (A., 1914, i, 953) did not decide its stereochemical structure; the preparation of a lævorotatory tetraphosphoric acid of the substance (A., 1928, 271) showed, however, that it could not have the structure 123456, and the optical inactivity of the monophosphoric acid (Anderson, A., 1914, i, 1191) excluded the structure 1234. The action of fuming nitric acid on a mixture of inositol-mono- and -di-phosphoric acids gives a product of the composition of a tartaric acid phosphate, which is hydrolysed to r-tartaric and mesotartaric acids; since the structure $\frac{135}{246}$ contains only *trans*-hydroxyl groups, it is now excluded. Further, the oxidation of inositol by alkaline potassium permanganate at 0° gives, in addition to trihydroxyglutaric and tetrahydroxyadipic acids, allomucic acid [new m. p. 176° (decomp.), identical with a specimen prepared from mucic acid and freed from the latter by treatment of the aqueous solution of the ammonium salt with alcohol]; the only remaining structure for inositol

OH HO H HO HO HO (I.)

consistent with this is 12345, i.e. (I). Anderson's monophosphoric acid is accord-H HO H OH H OH H OH I-diphosphoric acid is accord-ingly $\frac{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5}{3 \cdot 4 \cdot 5}$ -inositol-3(or 6)-phosphoric acid, and the OH I-diphosphoric acid contains its accordits second phosphoric acid group on a 1, 2, 4, or 5 carbon atom. To form allo-

mucic acid, the ring opens at the 5,6 or 6,1 linking; other products are probably formed by ring-fission elsewhere. It is suggested that natural inositol should be considered as a reserve carbohydrate which by its special configuration can break down to various substances, according to the point of ring-fission as determined by the positions at which phosphoric acid is attacked. E. W. WIGNALL.

Synthesis of isomeric ephedrines and their homologues. W. N. NAGAI and S. KANAO (An-nalen, 1929, 470, 157-182).—Benzaldehyde condenses with nitroethane in presence of 25% aqueous potassium hydrogen carbonate, yielding \$-nitro-aphenylpropyl alcohol, b. p. 123—124°/4 mm., reduced by zinc dust and 25% acetic acid to β-hydroxylaminoa phenyl propyl alcohol, m. p. 78-79°. Treatment of this with aqueous formaldehyde affords the methylenenitrone, OH·CHPh·CHMe·N CH^{CH}², m. p. 100°, reduced by zinc dust and acetic acid to a mixture of dl-ephedrine (I), m. p. 75° [hydrochloride, m. p. 187-188°; chloroplatinate, m. p. 199°; chloroaurate, m. p. 112-113°; N-p-nitrobenzoyl derivative, m. p. 162°; quaternary ammonium iodide, C12H20ONI, m. p. 228-229°, from I (1 mol.) and methyl iodide (4.5 mols.)], and *dl-iso*ephedrine (II), m. p. 118° [*hydrochloride*, m. p. 164°; *oxalate*, m. p. 218° (de-comp.); *chloroaurates*, m. p. 117° and 194°; *copper oxide* compound, $2C_{10}H_{15}ON,CuO,2H_2O$, m. p. 129° (decomp.) N a site here of derived in m. p. 165-(decomp.), N-p-nitrobenzoyl derivative, m. p. 165-

166°; quaternary ammonium iodide, C₁₂H₂₀ONI, m. p. 183°, by the action of methyl iodide]. When I is treated with *d*-tartaric acid in warm methyl alcohol, l-ephedrine d-hydrogen tartrate (+MeOH), m. p. 69°, separates on cooling : evaporation of the residue and further cooling affords d-ephedrine d-hydrogen tartrate, m. p. 145—146°. *l*-Ephedrine, m. p. 40—40.5°, $[\alpha]_{P}^{29}$ —34.69° in water (hydro-chloride, m. p. 216—217°; N-p-nitrobenzoyl derivative, m. p. 187-188°, [a]³⁰ -51.77° in chloroform, which on heating with concentrated hydrochloric acid gives d-isoephedrine O-p-nitrobenzoate), is identical with the natural product from Ma Huang. d-Ephedrine (hydrochloride, m. p. 216—217°; N-p-nitrobenzoyl derivative, m. p. 187—188°, $[\alpha]_D^{20} + 51 \cdot 12^{\circ}$ in chloroform) has m. p. $40-40.5^{\circ}$, $[\alpha]_{D}^{\infty} + 34.42^{\circ}$ in water. Treatment of II with aqueous tartaric acid yields 1-isoephedrine d-hydrogen tartrate, m. p. 178° (decomp.), furnishing l-isoephedrine, m. p. 118-118.5°, $[\alpha]_{D}^{*}$ -51.93° in alcohol (hydrochloride, m. p. 182-182.5°, $[\alpha]_{D}^{*}$ -61.88° in water; N-p-nitrobenzoyl derivative, m. p. 177°, $[\alpha]_{D}^{*}$ -140.47° in chloroform), and purification of the residual base with *l*-tartaric acid gives *d*-isoephedrine, m. p. 117— 118°, $[\alpha]_D^{20}$ +51.87° in alcohol [hydrochloride, m. p. 182–182.5°, $[\alpha]_{D}^{20}$ +61.61° in water; oxalate, m. p. 219° (decomp.); N-p-nitrobenzoyl derivative, m. p. 177°, $[\alpha]_{D}^{20}$ +140.85° in chloroform], identical with the natural product.

Reduction of β-nitro-α-phenylpropyl alcohol with iron and aqueous-alcoholic sulphuric acid below 45°, or with tin and hydrochloric acid yields a mixture of dl-norephedrine [3-amino-a-phenylpropyl alcohol], m. p. 104—105° [hydrochloride, m. p. 194°; sulphate, m. p. 285—286°; oxalate, m. p. 245° (decomp.); dioxalate, m. p. 182—183° (decomp.); chloroplatinate, decomp. 221.5°; chloroaurate; copper oxide compound, decomp. 169° after darkening at 120°; N-acetyl derivative, m. p. 135°, converted by heating with concentrated hydrochloric acid into dl-norisoephedrine; N-p-nitrobenzoyl derivative, m. p. 189°], and drine; N-p-nitrobenzoyl derivative, m. p. 189°], and dl-norisoephedrine, m. p. 71° [hydrochloride, m. p. 169°; sulphate, m. p. 290—291° (decomp.); oxalate, m. p. 235°; dioxalale, m. p. 171° (decomp.); okloro-platinate, m. p. 199·5° (decomp.); chloroaurate, m. p. 132—133°; copper oxide compound, m. p. 154° (decomp.); N-acetyl derivative, m. p. 85—86°; N-p-nitrobenzoyl derivative, m. p. 170°]. Resolution of these amines is accomplished by d- and l-tartaric oxide. d Norechadrine. m. p. 52° [σ]²⁷ ±14:76° in of these amines is accomplished by d- and l-tartaric acids. d-Norephedrine, m. p. 52°, $[\alpha]_D^{sp} + 14.76°$ in alcohol [d-hydrogen tartrate (+EtOH), m. p. about 160°, $[\alpha]_D^{sp}$ (alcohol free) +34.69°; hydrochloride, m. p. 171—172°, $[\alpha]_D^{sp} + 33.4°$ in alcohol; sulphate (+2H₂O), m. p. (anhydrous) 285—286° (decomp.), $[\alpha]_D^{sp} + 31.51°$; oxalate, m. p. 245°; chloroplatinate, m. p. 221.5° (decomp.); chloroaurate, m. p. 188°; N-p-nitrobenzoyl derivative, m. p. 175—176°, $[\alpha]_D^{sp}$ $+49.95^{\circ}$ in chloroform, when heated with concentrated hydrochloric acid gives *l*-norisoephedrine p-nitrobenzoate], 1-norephedrine, m. p. about 50°, $[\alpha]_{D}^{20} - 14.56^{\circ}$ in alcohol [1-hydrogen tartrate (+EtOH),m. p. 160° after sintering at about 130°, $[\alpha]_D^\infty$ (alcohol free) $-34\cdot46^\circ$; hydrochloride, m. p. 171–172°, $[\alpha]_D^\infty$ (alcohol 285–286° (decomp.), $[\alpha]_D^\infty$ –31.99°; oxalate, m. p.

245° (decomp.); chloroplatinate, m. p. 221° (decomp.); chloroaurate, m. p. 188°; N-p-nitrobenzoyl derivative, m. p. 175–176°, $[\alpha]_{\rm D}^{33}$ –49.58° in chloroform, converted by treatment with concentrated hydrochloric acid into d-norisoephedrine p-nitrobenzoate; trimethylammonium iodide, m. p. 211-212°, [a] -22.23° , obtained also from *l*-ephedrine and methyl iodide], l-norisoephedrine, m. p. 77.5—78°, [α]²⁰ -32.64° in alcohol [d-hydrogen tartrate, m. p. 202° (decomp.); [a]²⁰ -13.39°; hydrochloride, m. p. 180-181°, [a]²⁰ -42.68°; sulphate, m. p. 290-291° (decomp.), $[\alpha]_{\rm D}^{-39.99°}$; oxalate, m. p. 235°; chloro-platinate, m. p. 199°; chloroaurate, m. p. 137–138°; N-p-nitrobenzoyl derivative, m. p. 199°, [a]²⁰ -105.13° in chloroform], and d-norisoephedrine, m. p. 77.5-78°, $[\alpha]_{\rm B}^{\circ} + 33.14^{\circ}$ in alcohol [1-hydrogen tartrate, m. p. 202°, [a]²⁰ +13.36°; hydrochloride, m. p. 180-181°, $[\alpha]_{10}^{30} + 42.53^{\circ};$ sulphate, m. p. 290–291° (decomp.), $[\alpha]_{10}^{30} + 40.12^{\circ};$ oxalate, m. p. 235° (decomp.); chloroplatinate, m. p. 198°; chloroaurate, m. p. 137-138°; N-p-nitrobenzoyl derivative, m. p. 199.5°, $[\alpha]_{1D}^{20}$ +104.96° in chloroform; trimethylammonium iodide, m. p. 216—216.5°, $[\alpha]_{D}^{20}$ +36.65°], are described. When dl-N-benzoylnorephedrine, m. p. 143°, is treated with concentrated sulphuric acid, 2:5-diphenyl-4methyloxazoline (III) [picrate (IV), m. p. 140-141°], results. This is converted by boiling with dilute hydrochloric or sulphuric acid into dl-norisoephedrine O-benzoate [hydrochloride (V), m. p. 220°; sulphate, m. p. 182° (decomp.); picrate, m. p. 186° (decomp.), also obtained by crystallising IV from hot alcoholl. Treatment of V with concentrated sulphuric acid gives III; with ammonia, dl-N-benzonorisoephedrine, m. p. 128°, is obtained.

Reduction of β -nitro- α -phenylpropyl alcohol with zinc dust and 50% acetic acid in presence of 2 mols. of formaldehyde affords a mixture of dl-methulephedrine [β -dimethylamino- α -phenylpropyl alcohol], m. p. 63.5-64.5° (hydrochloride, m. p. 207-208°; oxalate, m. p. 170-171°; picrate, m. p. 124-125°; chloroaurate, m. p. 137°), and dl-methylisoephedrine, b. p. 135.5° (corr.)/16 mm., d_4^{20} 0.9917, n_D^{20} 1.5143 (picrate, m. p. 148-148.5°; oxalate), separated by means of the difference in solubility of the hydrochlorides in acetone. 1-Methylephedrine, m. p. 87- 87.5° , $[\alpha]_0^\circ - 29.2^\circ$ in methyl alcohol [d-hydrogen tarirate, m. p. 87–88°, $[\alpha]_{D}^{20}$ –6.77°; hydrochloride, m. p. 192° after sintering at 189°, [0]p -29.95° oxalate, m. p. 187° (decomp.); picrate, m. p. 142°; chloroaurate, m. p. 128-129°; copper oxide compound, m. p. 86-87°], d-methylephedrine, m. p. 87- 87.5° , $[\alpha]_{10}^{20} + 29.17^{\circ}$ in methyl alcohol [1-hudrogen tartrate, m. p. 87–88°, $[\alpha]_{D}^{\circ}$ +6.6°; hydrochloride, m. p. 192°, [a] +30.07°; oxalate, m. p. 187°; chloroaurate, m. p. 127-128°; methiodide, m. p. 211°, [a]20 $+22\cdot1^{\circ}$], d-methylisoephedrine, b. p. 145-145.5° (corr.)/24 mm., m. p. 28-28.5°, d_{4}^{24} 0.98566, n_{12}^{24} 1.5109, $[\alpha]_{12}^{23}$ +48° in methyl alcohol [d-hydrogen tartrate, m. p. $(+2H_2O)$ 83.5–84°, (anhydrous) about 150°; chloroaurate, m. p. 127°], and 1-methyliso-ephedrine, b. p. 145° (corr.)/24 mm., m. p. 28–28.5°, d_4^{24} 0.9854, n_D^{24} 1.5108, $[\alpha]_D^{29}$ -48.34° in methyl alcohol [1-hydrogen tartrate, m. p. (+2H₂O) 83.5-84°, (anhydrous) about 150°; chloroaurate, m. p. 128°; hydrochloride; oxalate; methiodide, m. p. 216-216.5°, $[\alpha]_{li}^{\infty}$ -36·1°], are described. *d*- and *l*-Methylephedrines are also obtained from *d*- and *l*-ephedrines and methyl iodide. H. BURTON.

A homologue of ephedrine. J. SAEM and B. SANCHEZ (Bull. Soc. chim., 1929, [iv], 45, 284– 286).—p-Tolyl ethyl ketone, b. p. 234—235° (yield 60% from propionyl chloride and toluene in presence of aluminium chloride and carbon disulphide; cf. Klages, A., 1902, i, 611), is converted by bromination in benzene in a current of carbon dioxide into α -bromoethyl p-tolyl ketone, m. p. 80° (yield 75%), which with an 8% solution of methylamine in benzene affords (yield 45%) p-tolyl α -methylaminoethyl ketone hydrochloride, m. p. 232° (methiodide, m. p. 199– 200°; picrate, m. p. 170°). By hydrogenation in presence of platinum-black the latter is converted into p-tolyl- α -methylaminoethylcarbinol, b. p. 114° (hydrochloride, m. p. 222°; methiodide, m. p. 175°; picrate, 179°), which is rather more toxic for rabbits than natural ephedrine, but exerts a smaller hypertension (cf. Hyde, Browning, and Adams, A., 1928, 1143). R. BRIGHTMAN.

Formation of bases from carbonyl compounds. III. Synthesis of *dl*-ephedrine and other aminoalcohols. A. SKITA and F. KEIL [in part, with L. BOENTE] (Ber., 1929, 62, [B], 1142-1151; cf. A., 1928, 1228; Manske and Johnson, this vol., 441) .-Catalytic hydrogenation of acetonylacetone in presence of cyclohexylamine and colloidal platinum affords 2:5-dimethyl-N-cyclohexylpyrrolidine, b. p. $100^{\circ}/16 \text{ mm.}, d_4^{29} 0.8927, n_D^{20} 1.47339$ (picrate, m. p. 111-114°), and ε-cyclohexylaminohexan-β-ol, b. p. 153°/21 mm., m. p. 76—77° (picrate, m. p. 76—77°). γ -Methylacetylacetone and cyclohexylamine similarly afford S-cyclohexylamino-y-methylpentan-B-ol, b. p. 104-106°/1 mm. (picrate, m. p. 157-159°). Benzoylacetone and methylamine analogously yield the diastereoisomeric γ -methylamino- α -phenylbutan- α -ols (1), b. p. 155—156°/16 mm., $d_4^{2^{\circ}5}$ 1·0107, $n_1^{\circ}5$ 1·52032 (pale yellow picrate, m. p. 193—194°), and (11) b. p. 155— 156°/16 mm., $d_4^{2^{\circ}5}$ 1·0079, $n_2^{2^{\circ}5}$ 1·52298 (dark yellow picrate, m. p. 118—119°). Benzil and methylamine give β -methylamino- $\alpha\beta$ -diphenylpentan- α -ol, b. p. 195— 200°/20 mm., m. p. 134° (hydrochloride, m. p. 250°; acetate, m. p. 144-145°, whilst β-cyclohexylaminoαβ-diphenylethan-α-ol, m. p. 162—163° (hydrochloride, m. p. 264-265°), is derived from benzil and cyclohexylamine. Methyl propyl diketone and methylamine afford β-methylaminohexan-y-ol, b. p. 81°/18 mm., m. p. 78° (hydrochloride, m. p. 146-147°), and 4-hydroxy-1:4-dimethyl-5-propyl-2-α-hydroxybulyl-pyrrolidine, b. p. 154-156°/15 mm. (diacetyl deriv-ative, m. p. 165-168°/16 mm.). Phenyl methyl diketone and methylamine give β -methylamino- α -phenylpropan- α -ol (*dl*-ephedrine), m. p. 75°, in 50% yield. Hydrogenation of *dl*-ephedrine in presence of formaldehyde and colloidal platinum gives almost quantitatively B-dimethylamino-a-phenylpropan-a-ol (N-methylephedrine), m. p. 63-64.5° (hydrochloride, m. p. 205°). Acetylacetone and dimethylamine in presence of ammonium chloride and colloidal platinum are hydrogenated to δ -dimethylaminopentan- β -ol, b. p. H. WREN. 61-62°/11 mm.

Action of chlorine compounds on cholesterol. VII. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 302-304).-Iodine trichloride and cholesterol in ether yield an amorphous substance, m. p. 72-73°, containing no hydroxyl group, apparently a mixture of an iodo- and a chloro-compound. By the action of sulphur monochloride at 100°, followed by treatment with water, a reddish-brown product, m. p. 72-85°, containing 26.37% S, 3.61% Cl, is obtained. The sulphur is probably present as ·CH·SH·, being eliminated by aqueous potassium hydroxide or con-centrated nitric acid. In chloroform solution, antimony trichloride after 2 hrs. gives a violet coloration (cf. Steinle and Kahlenberg, A., 1926, 633). Calcium chloride gives an additive compound. Stannic chloride in excess in benzene at the ordinary temperature affords a brown product, m. p. 65-70°, containing chlorine, which gives Liebermann's reaction, yields a non-crystalline bromide, and contains no hydroxyl group. Stannic chloride alone gives the same product. R. BRIGHTMAN.

Sterol group. III. Acetylation and catalytic hydrogenation of ergosterol. I. M. HEILBRON and W. A. SEXTON. IV. Existence of isomeric ergosterols. I. M. HEILBRON, W. A. SEXTON, and F. S. SPRING (J.C.S., 1929, 921—926, 926—931).— Catalytic hydrogenation of ergosterol using palladiumblack in ether at 15° or in alcohol at 70° yields α -ergostenol, m. p. 130—131°; the process is selective and by arrest after the addition of 2 atoms of hydrogen a good yield is obtained of dihydroergosterol, m. p. 173°, $[\alpha]_{EHI}^{\infty}$ —21·7° (acetate, m. p. 180°) (cf. Windaus and Brünken, A., 1928, 424). Use of glacial acetic acid as solvent at 70° affords allo- α -ergostanyl acetate, m. p. 144—145° (cf. Reindel and Walter, A., 1928, 295), hydrolysed by 10% alcoholic potassium hydroxide to allo- α -ergostanol monohydrate, m. p. 144— 145° (cf. Reindel and Walter, *loc. cit.*).

When a solution of ergosterol in glacial acetic acid is treated with anhydrous potassium acetate at 100° for 5—6 hrs. in an atmosphere of carbon dioxide ergosteryl α -acetate, m. p. 132—133°, is obtained; it regenerates ergosterol by hydrolysis with 5% alcoholic potassium hydroxide. The α -acetate passes into ergosterol β -acetate by treatment with boiling acetic anhydride, or when heated above its m. p., and by catalytic hydrogenation with palladium-black in ether furnishes α -ergostenyl acetate, m. p. 109—110°. The authors suggest that the third double linking, which is hydrogenated only in hot glacial acetic acid, joins two quaternary carbon atoms, since this behaviour is reminiscent of that of abietic acid (cf. A., 1922, i, 547; 1925, i, 1419.)

IV. Homogeneous samples of ergosterol obtained from two different sources, although possessing identical m. p. and closely similar optical properties, behave differently towards catalytic hydrogenation. Thus with palladium-black in ether at 15°, Böhringer's product (I), m. p. 161—162°, $[\alpha]_{3+41}^{21:5}$ —159·3°, absorbs 4 atoms of hydrogen to yield α -ergostenol, m. p. 130—131°, $[\alpha]_{3+41}^{21:5}$ —171·0°, slowly absorbs slightly less than 2 atoms of hydrogen. Hydrogenation of II is completed by addition of fresh catalyst,

yielding a tetrahydro-derivative, separable into β-ergostenol, m. p. 114-116° (acetate, m. p. 94-96°), and a-ergostenol, m. p. 130-131°. Failure to obtain complete hydrogenation with the first portion of the catalyst is not due to poisoning, since the same specimen of catalyst rapidly converted I into a-ergostenol. Acetylation of either I or II with acetic anhydride affords products possessing identical m. p. and specific rotations, provided that the duration of treatment is the same : with increasing time the m. p. falls and the specific rotation rises. The difficulty of hydrogenating I persists after acetylation, but both I and II furnish α-ergostenyl acetate, m. p. 109-110°, $[\alpha]_{5401}^{21}$ +6.3° by treatment with palladium-black. Hydrolysis of the ergosteryl β -acetate from II, m. p. 172—174°, with 5% alcoholic potassium hydroxide affords an ergosterol, m. p. 161—162°, $[\alpha]_{3461}^{s1}$ —160.0°, hydrogenated rapidly and completely in the presence of palladium-black to a-ergostenol, m. p. 130-131°, $[\alpha]_{5481}^{\infty}$ +19°; the form of the hydrogen-absorptiontime curve is precisely similar to that given by I. Another specimen of ergosterol, $[\alpha]_{3401}^{22}$ -161.2°, obtained from Boot's when treated with twice the amount of catalyst used to hydrogenate I, absorbed 4 atoms of hydrogen without any marked break at the dihydro-stage, to yield a-ergostenol, m. p. 129-131°. C. W. SHOPPEE.

Zymosterol, a dextrorotatory sterol of yeast. H. PENAU and G. TANRET (Compt. rend., 1929, 188, 1317—1319; cf. following abstract).—Zymosterol has the formula $C_{27}H_{42}O_{2},H_2O$, *i.e.*, that of a hydroxyergosterol (cf. Maclean, A, 1928, 329); after losing water above 80°, it has m. p. 100—101°, rising after several resolidifications to 106—108°. In alcoholic chloroform at 16° the values $[\alpha]_{4360} + 60 \cdot 5^{\circ}, [\alpha]_{5461} + 39 \cdot 9^{\circ},$ $[\alpha]_{5780} + 34 \cdot 8^{\circ}$ are found (cf. Maclean); the dispersion ratio $[\alpha]_{4360} : [\alpha]_{5780}$ is thus 1.73 (cf. the value 2.85 for ergosterol). The iodine value (190—201) confirms the presence of three ethylenic double linkings; the *acetyl* derivative, $C_{27}H_{40}(OAc)_2$, has m. p. 115°, $[\alpha]_D$ $+20^{\circ}$; the digitonin complex contains 28.6% of zymosterol. Zymosterol in acetic anhydride and sulphuric acid gives the green Liebermann reaction, with a characteristic blue intermediate stage; the Salkowsky reaction is negative; with antimony pentachloride a faint rose coloration is given, and similarly there is a faint Rosenheim reaction, but these may be due to traces of ergosterol. Fresh yeast which contains 0.1—0.15% of ergosterol contains 0.1% of zymosterol. E. W. WIGNALL.

Physical and biological study of the dextrorotatory sterol from yeast [zymosterol]. R. FABRE and H. SIMONNET (Compt. rend., 1929, 188, 1312—1315; cf. preceding abstract).—The ultra-violet absorption curves of zymosterol show no maximum from 4500 to 2500 Å., and the general absorption is very much weaker than that of ergosterol; no change in the absorption is produced by irradiation in an inert atmosphere. The antirachitic potency of the irradiated product is only about 1/100 that of irradiated ergosterol (this vol., 359) and may be due to contamination with the latter substance. E. W. WIGNALL.

Superheating of uniform organic compounds. V. Aryl naphthenates and the mechanism of their transformations. S. SKRAUP and O. BINDER (Ber., 1929, 62, [B], 1127-1138; cf. A., 1927, 659).-Thermal decomposition of the phenyl esters of cyclopentane-, cyclobutane-, and probably cyclopropane-carboxylic acids resembles that of cyclohexanecarboxylic esters in yielding the corresponding o-hydroxyphenyl ketones; the sensitiveness of the compounds to heat increases with diminishing size of the ring. Introduction of a methyl group in position 1 increases the thermostability and causes ultimate rupture into phenyl formate and unsaturated hydrocarbon. The primary fission of phenyl naphthenates into phenol and a cyclic keten which subsequently unite to an o-hydroxyphenyl ketone is possible for the unsubstituted compounds, but not for their 1-methyl derivatives. When gently warmed, diphenylketen and phenolafford phenyl diphenylacetate; athigher temperatures, however, nuclear substitution predominates. The intermediate formation of ketens is established by use of azobenzene which gives heterocyclic compounds decomposing at a higher temperature into benzophenoneanil and phenylcarbimide. The hypothesis that phenyl esters of fatty acids decompose primarily into phenyl formate and Δ^{α} -alkylenes which then yield acetylene and paraffins does not appear tenable, since hexadecene affords a dimeride and products of higher b. p., but not acetylenc. Treatment of a phenyl ester of a naphthenic acid, $C_{10}H_{18}O_2$, from Galician petroleum causes loss of carbon dioxide and union of the residues with production of an alicyclically substituted benzene. the behaviour being neither that of a fatty ester nor that of a nuclear carboxylated naphthene.

The following observations appear new: cyclopentanecarboxylic acid, b. p. 112-113°/14 mm. (by hydrogenation of cyclopentenecarboxylic acid) and its phenyl ester, b. p. 137°/13 mm.; o-hydroxyphenyl cyclopentyl ketone, b. p. 125-135°/13 mm.; phenyl cyclobutanecarboxylate, b. p. 127°/13 mm.; o-hydroxyphenyl cyclobutyl ketone, b. p. 139-140°/15 mm.; methyl cyclobutanecarboxylate, b. p. 40°/13 mm.; phenyl cyclopropanecarboxylate, b. p. 117-118°/ 13 mm.; 1-methylcyclohexanecarboxylic acid, b. p. 127-130°/13 mm. (amide, m. p. 67°), conveniently prepared by oxidation of methylcyclohexylphenol by potassium permanganate in alkaline solution; phenyl 1-methylcyclohexanecarboxylate, b. p. 149-150°/ 13 mm.; phenyl 1-methylcyclopentanecarboxylate, b. p. 137°/14 mm.; phenyl naphthenate, C16H22O2, b. p. 161-171°/13 mm.; p-anisyl naphthenate, C₁₇H₂₄O₃, b. p. 198-200°/13 mm.; benzyl o-hydroxyphenyl ketone, b. p. about 165°/23 mm.; m. p. 55°

H. WREN.

Synthesis of chaulmoogric acid from hydnocarpic acid. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1929, 51, 1515—1518).—The following have been prepared by standard methods from natural hydnocarpic acid: ethyl hydnocarpate, b. p. 143—144°/2 mm., n_{15}^{∞} 1.4582, d_{45}^{∞} 0.9087, $[\alpha]_{\rm D}$ +70.5°; hydnocarpyl alcohol (λ - Δ^2 -cyclopentenylundecan- α -ol), m. p. 23°, b. p. 144—145°/2 mm., d_{45}^{ω} 0.8022, n_{15}^{ω} 1.4709, $[\alpha]_{\rm D}$ +75.2° in chloroform; hydnocarpyl bromide, b. p. 156—157°/2 mm., d_{45}^{ω} 1.0763, n_{10}^{ω} 1.4857, $[\alpha]_{\rm D}$ +27.4° in chloroform (cf. Sacks and Adams, A., 1926, 1137); ethyl hydnocarpylmalonate, b. p. 182—183°/2 mm., d_{45}^{ω} 0.9519. $n_{\rm D}^{23}$ 1.4601, $[\alpha]_{\rm D}$ +25.6° in chloroform, and hydnocarpylacetic acid (μ - Δ^2 -cyclopentenyltridecoic acid), which, after purification, is identical with natural chaulmoogric acid. H. E. F. NOTTON.

Phenols from chaulmoogric acid and re-sorcinol. W. S. HINEGARDNER and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1503-1509).-Dihydrochaulmoogric acid, resorcinol, and zinc chloride at 120° give dihydrochaulmoogrylresorcinol (4-12-cyclopentyltridecoylresorcinol, (I) (50% of theory), m. p. 89.5° (oxime, m. p. 169—170°). Chaulmoogryl chloride (cf. Power and Gornall, J.C.S., 1904, 85, 855), resorcinol dimethyl ether, and aluminium chloride in carbon disulphide give 3-hydroxy-4-chaulmoogryl-anisole (II), m. p. 65°, $[\alpha]_{15}^{25}$ +6.98°, and 1-chaul-moogryl-2:4-dimethoxybenzene (III), m. p. 46°, $[\alpha]_{1}^{25}$ +18.8°. Demethylation does not occur at 30-35°, or when ferric chloride is used in place of aluminium chloride. Chaulmoogryl chloride with potassium resorcinoxide in ether gives resorcinol dichaulmoograte, m. p. 51°, b. p. 270-281°/2-3 mm., [a]³⁵ +45.93°, and with resorcinol in nitrobenzene in presence of aluminium chloride, 4-chaulmoogrylresorcinol (IV), m. p. 83°, $[\alpha]_{\rm D}^{\infty} + 1.38°$ (oxime, m. p. 161°), which is also formed in small yield from resorcinol, chaulmoogric acid, and zinc chloride. By amalgamated zinc and boiling dilute hydrochloric acid I is reduced to 4-v-cyclopentyltridecylresorcinol, m. p. 73-74°; II to 3-hydroxy-4-ν-Δ2-cyclopentenyltridecylanisole, m. p. 47.5° , $[\alpha]_{15}^{25} + 6.15^{\circ}$; III to 2 : 4-dimethoxy- ν - Δ^2 -cyclopentenyltridecylbenzene, b. p. 250–252°/2 mm, n³⁵ 1.5414, d_{25}^{25} 0.955, $[\alpha]_{15}^{25} + 9.53$, and IV to 4- ν - Δ^2 -cyclopentenyltridecylbenzene, b. p. 250–252°/2 mm, n³⁵ pentenyltridecylresorcinol, m. p. 68°, b. p. 245-247°/ 2-3 mm., optically inactive. The new phenols are only slightly toxic to animals and to B. typhosum.

H. E. F. NOTTON. Chaulmoogryl-substituted phenols and ethylm-chaulmoogryloxybenzoate. I. DE SANTOS and A. P. WEST (Philippine J. Sci., 1929, 38, 293–298).— Treatment of 2:4-dichlorophenol, 2:4-dibromophenol, quinol, and ethyl m-hydroxybenzoate, respectively, with chaulmoogryl chloride (prepared from chaulmoogra oil) after subsequent heating and extraction yielded the following compounds: 2:4-dichlorophenyl chaulmoograte, m. p. 53–55°, 2:4-dibromophenyl chaulmoograte, m. p. 57–60°, quinol ester of chaulmoogric acid, m. p. 54–57°, and ethyl m-chaulmoogryloxybenzoate, m. p. 56–59°.

B. W. ANDERSON.

Hydrolysis of nitriles with orthophosphoric acid. S. C. J. OLIVIER (Rec. trav. chim., 1929, 48, 568—570; cf. Berger and Olivier, A., 1928, 44). Although 2:4-dibromobenzonitrile (Montagne, A., 1913, i, 55) is not hydrolysed by boiling 92.5%(crystalline) phosphoric acid, a 90% yield of 2:4-dibromobenzoic acid is obtained by heating the nitrile for 2 hrs. at 160—170° with phosphoric acid to which has been added sufficient phosphoric oxide to combine with the water present. J. W. BAKER.

Electrolytic reduction of benzoic acid. F. SOMLÓ.—See this vol., 776.

Action of sunlight on the cinnamic acids, and the salts of *trans*-cinnamic acid. Trimorphism of *cis*-cinnamic acid. A. W. K. DE JONG (Chem.

Weekblad, 1929, 26, 270-275).-An historical survey is used as the basis of a tentative explanation of the mechanism of formation of truxillic and truxinic acids from the cinnamic acids and the salts. The trimorphism of the cis-acid is discussed. S. I. LEVY.

Preparation of active sandaraco-pimaric acid and its derivatives. F. BALAS and J. BRZAK (Coll. Czech. Chem. Comm., 1929, 1, 306-314).-By extraction of sandarac resin with warm 1% sodium hydroxide solution and subsequent fractionation, l-sandaraco-pimaric acid, $C_{20}H_{30}O_2$, m. p. 173°, is obtained in 0.7% yield. The substance resembles the inactive acid, m. p. 173°, isolated by Henry (J.C.S., 1901, 79, 1144) and Wolff (A., 1907, i, 145). It has $[\alpha]_D - 18.8^\circ$ in alcohol, -13.0° in chloroform. Crystallographic data [F. ULRICH] are recorded. The sodium, potassium, ammonium, silver, di-d-amylamine, piperidine, and cinchonidine salts are described. From the silver salt is obtained the methyl ester, m. p. 69°, $[\alpha]_{\rm D} = -27.91^{\circ}$ in methyl alcohol, d_4^{20} 1.0318, $n_{\rm D}^{20}$ 1.5207, [R] 93.29. Crystallographic data [R. NOVAČEK] are recorded. The ethyl ester, b. p. 177°/0.5 mm., has $[\alpha]_{\rm p} = -24.37^{\circ}$ in alcohol, d_4^{20} 1.0167, $n_{\rm p}^{20}$ 1.5150, $[R]_{\rm p}$ 97.97. R. K. CALLOW.

Oxidation by air of abietic acid. G. DUPONT and J. DUBOURG (Bull. Inst. Pin, 1928, 205-207; Chem. Zentr., 1928, ii, 2355-2356).-Atmospheric oxidation of abietic acid appears to afford a monoacid glycol with an acetylated hydroxyl group, the phenanthrene group being no longer present, i.e., C14H21(OH)(OAc)·CO,H. Distillation of the oxidised abietic acid with sulphur gave small quantities of retene (from the residual abietic acid) and oily substances containing neither phenanthrene nor methylphenanthrene. Formulæ are proposed.

A. A. ELDRIDGE. Resin acids. G. ROUIN (Bull. Inst. Pin, 1928, 221-231; Chem. Zentr., 1928, ii, 2722).-When heated in a vacuum (20 mm.) at 190-200°, abietic acid forms dextrorotatory oily products containing d-pyroabietic acid, which appears to be an isomeride of abietic acid, and a hydrocarbon, C19H30, but no abietic anhydride. Abietic acid, m. p. 171-173°, is a hydrate, $4C_{20}H_{30}O_2, H_2O$; pyrogenation in a vacuum affords the anhydrous acid.

A. A. ELDRIDGE.

Resin acids. G. ROUIN (Bull. Inst. Pin, 1928, 197-204; Chem. Zentr., 1928, ii, 2555).-Tetrahydroxyabietic acid, m. p. 243-245°, obtained by ordation of abietic acid $(\alpha_i - 100^\circ)$ with permangan-ate, has [M. MANVILLE] $\alpha_i - 43.7^\circ$, $\alpha_v - 51.3^\circ$, $\alpha_i - 81^\circ$. Formic, butyric, and valeric acids and acetone, but not propionic acid, were produced in the oxidation. A. A. ELDRIDGE.

Mixed glycerides of salicylic acid. I, II. . HUMNICKI (Bull. Soc. chim., 1929, [iv], 45, 275-279, 279-283).-I. Salicyloyl chloride, from thionyl chloride and sodium salicylate, with aa'-dichlorolydrin affords β-salicyldichlorohydrin, m. p. 46-48° identical with the product obtained by Fritsch and Göttig (A., 1891, 707), the constitution of which is thereby confirmed. Attempts to convert the dichlorohydrin into the di-iodohydrin with aqueous or

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alcoholic potassium iodide at 100-150° or. with sodium iodide in 15% acetone solution (cf. Finkel-stein, A., 1910, i, 453) failed. With lead iodide at 140° β-salicyldichlorohydrin yields an oil containing 33.83% of iodine. Esterification of aa'-di-iodohydrin with salicylic acid in presence of hydrogen chloride gives an oily product containing excess of iodine. Salicylic acid and glycerol in a current of dry hydrogen iodide at 130°, or salicyloyl chloride and $\alpha \alpha'$ -di-iodohydrin, afford β -salicyldi-iodohydrin, d¹⁵ 2.61.

II. The following β -acyldichlorohydrins have been prepared by the action of fatty acids on glycerol in presence of hydrogen chloride (cf. Whitby, A., 1926, presence of hydrogen chloride (cf. whitely, A., 1926, 819) : β-isovaleryl-, b. p. 127—140°/36 mm., d^{29} 1·444, n_D^{30} 1·450; β-lauryl-, b. p. 204—206°/15 mm., d^{29} 1·032, n_D^{39} 1·4584; β-hexoyl-, b. p. 140—145°/15 mm., d^{29} 1·074, n_D^{39} 1·4403; β-myristicyl-, m. p. 27—29°; β-stearyl-, m. p. 36—37°, and oleyl-, b. p. 260—275°/ 15 mm., d¹⁰ 994, n²⁰₁ 1.4754, -dichlorohydrins. Acetylsalicylic acid and glycerol in the same way afford salicylic acid and aa'-dichlorohydrin. B-Lauryl- and oleyl-dichlorohydrin were also obtained by the action of the acid chloride on aa'-dichlorohydrin. B-Acetyldichlorohydrin, similarly prepared, has b. p. 193-R. BRIGHTMAN. $195^{\circ}, d^{20}$ 1.281, $n_{\rm D}^{20}$ 1.4542.

Electrolytic reduction of salicylic acid. B. RUTOVSKI and A. KOROLEV (Trans. Sci. Chem.pharm. Inst. Moscow, 1928, 177-180; Chem. Zentr., 1928, ii, 2353).-By Weil's method, electrolytic reduction of salicylic acid afforded salicylaldehyde in a yield of 33% of the theoretical. If magnesium butyrate is added in order to avoid sparking and explosion of the benzene, the chief product (45%) of the theoretical) is saligenin. Tesh and Lowy's method gave unsatisfactory results.

A. A. ELDRIDGE.

Condensation of aromatic aldehydes with glycine and acetylglycine. H. D. DAKIN (J. Biol. Chem., 1929, 82, 439-446).-The reaction between glycine and an aromatic aldehyde in presence of acetic anhydride is complicated by the tendency to the formation of the N-arylidene derivative of glycine (for which an alternative ring structure is proposed). It is accordingly found that improved yields of the azlactones of a-acetamidocinnamic acid and homologues are obtained using acetylglycine. Benzylideneglycine, from glycine with a large excess of benzaldehyde in presence of acetic anhydride, has m. p. 207° after darkening at 180°. Glycine is conveniently acetylated by warming in suspension in acetic acid with the theoretical amount of acetic anhydride. Acetylglycine was condensed with benzaldehyde to give the azlactone of α -acetamidocinnamic acid; with salicylaldehyde to give the azlactone of o-acetoxy-a-acetamidocinnamic acid, m. p. 203-205°, yielding on treatment with alkali and acidification a-acetamidocoumarin, m. p. 203-204°; with p-hydroxybenzaldehyde, yielding the azlactone and acid obtained by Bergmann and Stern (A., 1926, 743); with piperonal to give the azlactone of α -acetamido-piperonylic acid, m. p. 183–184° (acid, m. p. 220– 221°); with p-nitrobenzaldehyde to give the azlactone of a-acetamido-p-nitrocinnamic acid, m. p. 185-186° (acid, m. p. 234-235°). C. R. HARINGTON.

Isomerism among 9-substituted fluorenes? A. KLIEGL [with E. THOMAE] (Ber., 1929, 62, [B], 1327—1335).—Fluorenone is reduced by zinc dust and boiling acetic acid to a mixture of fluorenyl alcohol, m. p. 156°, and fluorenopinacol, m. p. 190— 192° (cf. Gomberg and Bachmann, A., 1927, 245), with small amounts of 9-acetoxyfluorene, difluorenyl ether, and diphenylenephenanthrone; indications of the formation of an isomeric form of fluorenyl alcohol are not obtained. 9-Methoxyfluorene, m. p. 43.5°, is prepared by the action of boiling methyl alcohol and powdered silver nitrate on 9-chlorofluorene.

Attempts to repeat the preparation of β -fluorene-9-carboxylic acid, m. p. 232°, according to the directions of Schlenk and Bergmann (A., 1928, 1034) resulted in the formation of an acid, m. p. 221-223° (slight decomp.), identical in m. p. with the ordinary α -acid but differing therefrom by crystallising in needles. The technical acid also separates in needles from benzene; this was the sole form in which the acid could be isolated from sodiofluorene prepared by a variety of methods. Similarly, endeavours to isolate Schlenk's \$-9-methoxyfluorene-9-carboxylic acid, m. p. 172-173°, gave only the known acid, decomp. 184°, according to the rate of heating. Schlenk's "isomeric " benzhydrylfluorene, m. p. 187°, is recognised as a mixture of benzhydrylfluorene, m. p. 217°, with s-tetraphenylethane and little difluorenyl, m. p. 240°. The action of 9:9-dichlorofluorene on disodiobenzophenone yields, according to Schlenk and Bergmann, diphenyldiphenylene-ethylene oxide and two isomeric diphenyldiphenylene-ethylenes, m. p. 225° and 213°, respectively; the "isomeride " of m. p. 213° is considered to be an isomorphous mixture of the compound, m. p. 225°, and diphenyldiphenylene-ethylene oxide for the following reasons. The m. p. is depressed slightly by addition of an approximately equal quantity of the "ethylene," m. p. 225°, and raised by similar addition of the oxide. Fractional crystallisation from benzene permits the isolation of the "ethylene," m. p. 225°, or the oxide, according to the relative amount present in the original mixture. If approximately equal quantities of "ethylene," m. p. 225°, and oxide are mixed in hot light petroleum, b. p. 120-180°, and the solution is cooled, the product separates in a form indistinguishable from the "isomeride" except in being colourless. Treatment of the "isomeride" with acetyl chloride places beyond doubt the presence in it of the oxide which when homogeneous is converted by the reagent exclusively into benzoylphenylfluorene; from the "isomeride" a mixture of the last-named compound and the "ethylene," m. p. 225°, is produced. There appears, therefore, no present reason for abandoning the tried hypothesis of the uniplanar arrangement of the rings in fluorene.

H. WREN. Hexahydrophthalic acids. G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1929, [iv], 45, 293— 299).—Hydrogenation of phthalic acid or of methyl phthalate in acetic acid in presence of platinumblack affords the *cis*-hexahydro-derivative, hydrogenation of the free acid being very slow. The l-quinine salt of *cis*-methyl hexahydrophthalate, m. p. 141.5—142°, $[\alpha]_{\rm p}$ —136.5°, with alcoholic sodium

hydroxide yields 1-cis-methyl hydrogen hexahydrophthalate, m. p. $48-49^\circ$, $[\alpha]_p - 6.67^\circ$, which on cold hydrolysis loses its activity and yields inactive cis. acid, m. p. 190° (decomp.). Similarly, the cis-hexahydrophthalamide, obtained in 85% yield from the hydrophonatalinic, obtained in 65_{6} yield nom the anhydride, on resolution with quinine affords the 1-cis-hexahydrophthalamide, m. p. 165° (decomp.), $[\alpha]_{D} = -15 \cdot 4^{\circ}$ [quinine salt, m. p. 149—150° (decomp.), $[\alpha]_{D} = -128^{\circ}$], which, like the racemic amide, when heated at 190—200° for 1 hr., gives the inactive imide, m. p. 134.5—135°. These results support the Baver formula and not that of Sachse (A., 1890, 1386) if the formulæ are regarded as rigid. Since, however, the trans-acid affords an anhydride, m. p. 140°, differing from the cis-anhydride, m. p. 32°, and existing at least partly in the simple form $C_6H_{10} < CO > O$ (mol. wt. in camphor 218), a result more readily interpreted by the Sachse formula, the authors regard cyclohexane as possessing a mobile non-planar structure, pure substances consisting of mixtures of molecules with different configurations, the mobility of which can be diminished or suppressed by the two substituent radicals (cf. Mohr, A., 1919, ii, 229; Böeseken, A., 1921, i, 843). R. BRIGHTMAN.

cis-trans-Isomerism and steric hindrance. VIII. Methyl hydrogen hexahydrophthalates. G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1929, [iv], 45, 299—302).—At 39° cis-hexahydrophthalic acid is esterified with methyl alcohol in presence of hydrogen chloride about 1.4 times more slowly than the trans-isomeride, m. p. 213—218° (decomp.) (anhydride, m. p. 142°). Similarly, the trans-methyl hydrogen hexahydrophthalate, m. p. 95—96°, is hydrolysed by sodium or potassium hydroxide in 75% alcohol at 39°, five times, and by aqueous sodium hydroxide at 39° and at 0° six times and ten times, as rapidly as the cis-isomeride.

R. BRIGHTMAN. Additive Conjugated compounds. VII. formation of cyclohexenes. E. H. FARMER and F. L. WARREN (J.C.S., 1929, 897-909).-The possibility of modifying the cyclohexene ring-forming tendencies of butadienoid hydrocarbons has been studied using maleic anhydride as an addendum. The formula, CH-CH₂-CH-CO>O, given by Diels and Alder (A., 1928, 1018) to the condensation product from butadiene and maleic anhydride is correct, since \$\$'-dicarboxyadipic acid is obtained from it by the action of dilute aqueous potassium permanganate. Maleic anhydride and By-dimethylbutadiene yield directly 4:5-dimethyl-cis- Δ^4 -tetrahydrophthalic anhydride, m. p. 78°, which, by heating with water, gives 4:5-dimethyl-cis- Δ^4 -tetrahydro-phthalic acid, m. p. 180—192°. Ozonolysis of a chloroform solution of the anhydride leads to the ketonic acid [COMe CH2 CH(CO2H)]2 (or its cyclised equivalent, 3-acetyl-4-methylcyclopentan-4-ol-1:2-dicarboxylic acid), m. p. 186°.

 $\alpha\zeta$ -Dibromo- $\Delta^{\beta\delta}$ -hexadiene, when heated with maleic anhydride in benzene solution, forms 3: 6-dibromomethyl-cis- Δ^4 -tetrahydrophthalic anhydride, m. p. 98°. This compound, by boiling with aqueous sodium carbonate, is converted into the *dilactone*, m. p. 159-163° after previous softening at 147°, of 3:6-dihydroxymethyl-*cis*- Δ^4 -tetrahydrophthalic acid. The dilactone, by catalytic reduction, gives the *lactone*, m. p. 119-120°, of 3:6-dihydroxymethylhexahydrophthalic acid. Attempts to oxidise the last-named acid to hexahydroprehnitic acid failed, only oxalic acid being definitely isolated.

It is concluded that *cyclo*hexene formation from open-chain butadienes is complete and remains unaffected (except as regards velocity) by variation of positions of alkyl substituents.

Maleic anhydride and ethyl trans-trans-muconate combine when heated to give 3: 6-dicarbethoxy- Δ^3 tetrahydrophthalic anhydride, m. p. 185-188°, converted by alcoholic hydrogen chloride into the corresponding tetraethyl ester, m. p. 75°; the last-named compound, by alternate addition of bromine and removal of hydrogen bromide with diethylamine or pyridine, gives, after two such series of operations, an acid, $C_{10}H_8O_8$ (dihydroprehnitic acid ?), m. p. 241° (decomp.). The above dicarbethoxy- Δ^3 -tetrahydrophthalic anhydride gives oxalic acid extensively on treatment with permanganate or ozone. The corresponding acid is reduced by hydrogen and colloidal palladium to 3:6-dicarboxyhexahydrophthalic acid (hexahydroprehnitic acid) (monohydrate, m. p. 168°, tetraethyl ester, b. p. 238°/15 mm., dianhydride, m. p. 223-225°). Ethyl cis-cis-muconate does not react with maleic anhydride.

Sorbic acid and maleic anhydride in benzene solution at 100° yield 6-carboxy-3-methyl-cis- Δ^5 -tetrahydrophthalic anhydride, m. p. 174°; boiling with water gives the corresponding acid, m. p. 194°, with anhydride formation, catalytic hydrogenation (palladium) of which gives 6-carboxy-3-methyl-cis-hexahydrophthalic acid (monohydrate, m. p. 194—196°).

Permanganate oxidation of cyclopentadiene- and cyclohexadiene-maleic anhydride condensation products gives in the first case a tetrabasic acid (either cyclopentane-1:2:3:4-tetracarboxylic acid or cyclobutane-1:2:3-tricarboxy-4-acetic acid), m. p. 181-182° (with anhydride formation) (tetraethyl ester, b. p. 226°/14 mm.), and in the second case, 3:6-dicarboxyhexahydrophthalic acid, m. p. 168° (above).

Addition of maleic anhydride to trans-hexatriene occurs in benzene solution at the ordinary temperature, giving 3-ethylidene-cis- Δ^4 -tetrahydrophthalic anhydride, m. p. 51.5°, b. p. 148°/6 mm. (anilic acid, m. p. 174°); the corresponding acid, obtained by boiling with water, has m. p. 164—166° (with anhydride formation). Ozonolysis of the above anhydride yields acetaldehyde and a strongly enolic aldehyde; oxidation of the above acid by permanganate yields finally only oxalic acid.

cis-Hexatriene and maleic acid combine to give an impure liquid anhydride, b. p. 120-150°, which yields an anilic acid and an ethylidene-cis-tetrahydrophthalic acid identical with those of the *trans*-series. After many distillations the same ethylidene-cistetrahydrophthalic anhydride was isolated in a crystalline condition. R. J. W. LE FÈVRE.

Synthesis of an isomeride of thyroxine, and of related compounds. C. R. HARINGTON and

W. MCCARTNEY (J.C.S., 1929, 892-897).-Di-(4-methoxyphenyl)methyl chloride (A., 1922, i, 148) condenses with ethyl potassiophthalimidomalonate in xylene at 145° to give a 75% yield of ethyl di-(4methoxyphenyl)methylphthalimidomalonate, m. p. 106° which by hydrolysis with potassium hydroxide and decarboxylation at 180-200°/13 mm. affords the anhydride of α -o-carboxybenzamido- $\beta\beta$ -di-(4-methoxyphenyl)propionic acid, m. p. 209-210°, hydrolysed by hydriodic acid (d 1.7) and acetic anhydride to α -amino- $\beta\beta$ -di-(4-hydroxyphenyl)propionic acid (I), m. p. 241° (decomp.) after softening at 190–200°; by treatment with iodine and ammonia I is converted into \$\$-di-(3:5-di-iodo-4-hydroxyphenyl)-α-aminopropionic acid, m. p. 218°. Decarboxylation of I at 290-315°/2 mm. in portions of 0.5 g. furnishes $\beta\beta$ -di-(4-hydroxyphenyl)ethylamine, m. p. 207-208° (hydrochloride, m. p. 275° tribenzoyl derivative, m. p. 200°), which by treatment with iodine and ammonia affords $\beta\beta$ -di-(3: 5-di-iodo-4-hydroxyphenyl)ethylamine (II), m. p. 232-233° (decomp. with liberation of iodine). Similarly, diphenylmethyl bromide (cf. A., 1925, i, 656) with ethyl potassiophthalimidomalonate gives ethyl diphenylmethylphthalimidomalonate, m. p. 117° (yield 57%), hydrolysed, decarboxylated, and dehydrated to the anhydride of α -o-carboxybenzamido- $\beta\beta$ -diphenylpropionic acid, m. p. 214-215°; the latter by hydrolysis with hydriodic acid $(d \ 1.7)$ and acetic anhydride affords α-amino-ββ-diphenylpropionic acid, m. p. 236° (decomp.). Bromination of 3:5-di-iodothyronine in glacial acetic acid gives a 45% yield of 3':5'-dibromo-3:5-di-iodothyronine, m. p. 244.5°.

Although I is isomeric with and retains the characteristic o-di-iodophenolic group of thyroxine, it exhibits no trace of any type of physiological activity; II is similarly inactive. An improved preparation of $\beta\beta$ -diphenylethylamine, m. p. 39-40°, b. p. 180°/ 15 mm. (hydrochloride, m. p. 259°; picrate, m. p. 216-217°), is described. C. W. SHOPPEE.

Alkyl- and aralkyl-resorcinolcarboxylic acids. H. STENZL.—See B., 1929, 427.

Substances related to cochinillic and carminic acids. II. Synthesis of α -coccinic acid (m-oxyuvitic acid). A. N. MELDRUM and R. L. ALIM-OHANDANI (J. Indian Chem. Soc., 1929, 6, 253-258).-Condensation of 3-methoxy-p-toluic acid with chloral hydrate in presence of sulphuric acid affords, in addition to 3-methoxy-6-888-trichloro-a-hydroxyethylp-toluic acid (I) (A., 1925, i, 1272), small amounts of 3-methoxy-6-aßß-tetrachloroethyl-p-toluic acid (II), m. p. 200-201°, and the 2-sulpho-derivative (barium salt) of I. When I is heated with sulphuric acid for a short time or treated with hydrogen chloride in presence of sulphuric acid at the ordinary temperature, II results. Reduction of II with zinc dust and acetic acid gives 3-methoxy-6-\$\$-dichloroethyl-ptoluic acid, converted by treatment with sulphuric acid at 70-80° into 2-methoxy-4-methyl-5-carboxymethylbenzoic acid, m. p. 164-165° (barium salt +1.5H₂O). Treatment of II with hot 20% potassium hydroxide solution affords aww-trichloro-4-methoxy-6-methylstyrene-3-carboxylic acid, m. p. 185-187° Hydrolysis of I with barium hydroxide solution yields 4-methoxy-5-carboxy-2-methylmandelic acid, +H2O,

m. p. 105—110° with effervescence after sintering at 95—100°, m. p. (anhydrous) 162—163° (barium salt $+4H_2O$), oxidised by potassium permanganate to 4-methoxy-5-carboxy-o-toluoylformic acid, m. p. 211—212° (barium salt $+2H_2O$), and converted by treatment with sulphuric acid at 80—100° into 3-methoxy-6-aldehydo-p-toluic acid, m. p. 176—177°. Oxidation of this with potassium permanganate affords 4-methoxy-6-methylisophthalic acid, m. p. 250—252°, obtained also by similar oxidation of I. Demethylation of this methoxy-derivative with 10% hydriodic acid yields 4-hydroxy-6-methylisophthalic acid [α -coccinic acid], m. p. 320—322° [(decomp.); (lit. 298° and 310°); barium salt $+2H_2O$, loses 0.5H₂O at 110—125°; calcium salt $+4H_2O$, loses 2.5H₂O at 110—115°]. The α -coccinic acid (m-oxyuvitic acid) of Oppenheim and Pfaff (A., 1874, 1161) is impure. H. BURTON.

[Attempted] syntheses of ψ -opianic acid. I. S. N. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 207-229).-Various unsuccessful synthetic schemes are described. Reduction of 6-nitro-2: 3-dimethoxybenzaldehyde (I), m. p. 110°, obtained together with the 5-nitro-isomeride by nitration of o-veratraldehyde (cf. Perkin, Robinson, and Stoyle, A., 1925, i, 39), with ferrous sulphate and ammonia gives 6-amino-2: 3-dimethoxybenzaldehyde (hydrochloride; benzoyl derivative, m. p. 150°; phenylhydrazone, m. p. 133°), which readily eliminates water from 2 mols., forming an azomethine, m. p. 235°. Attempts to introduce a cyano-group in place of the amino-group failed. Attempts to oxidise \u03c4-meconine with various oxidising agents were either negative or resulted in complete degradation (cf. Salomon, A., 1887, 585; Edwards, Perkin, and Stoyle, A., 1925, i, 404). Bromination of ψ -meconine at 150° in bright sunlight yields a small amount of a substance, m. p. above 280°, together with an acid (probably 6-bromo-2-aldehydo-3:4-dimethoxybenzoic acid), m. p. about 200°, and a compound, m. p. about 90°. Methyl 4-meconinate, m. p. 72-73° (from the silver salt and methyl iodide), is converted by treatment with thionyl chloride in pyridine, phosphorus pentachloride in chloroform, hydrogen chloride in presence of ether and anhydrous sodium sulphate, or hydrobromic and acetic acids, into ψ -meconine. The last-named substance is unaffected by phosphorus pentachloride at 160°, or hydrobromic and acetic acids. 2-Aminoveratric acid is converted by the usual method into 2-cyanoveratric acid, (II), m. p. 208-209°, which is readily hydrolysed by dilute hydrochloric acid to hemipinic acid. Attempted conversion of II into 2-aldehydoveratric acid by Stephen's method (A., 1925, i, 1131) resulted in the formation of hemipinimide.

When 2:3-dimethoxycinnamic acid (improved method of preparation given) is treated with an excess of nitric acid ($d \cdot 5$) below 0°, a dinitro-2:3-dimethoxycinnamic acid, m. p. 198°, is formed. With nitric acid ($d \cdot 42$) at 10—20°, about 10% of 6-nitro-2:3-dimethoxycinnamic acid (III), m. p. 220° (methyl ester, m. p. 150°; ethyl ester, m. p. 90°), is obtained together with the 5-nitro-isomeride, m. p. 231° (methyl ester, m. p. 154—155°), separable through the solubility of the methyl esters in alcohol. Condensation of I with malonic acid in presence of pyridine and piperidine affords III, oxidised by potassium permanganate in presence of aqueous sodium carbonate and benzene to I. Reduction of III with ferrous sulphate and ammonia gives 6-amino-2:3-dimethoxycinnamic acid, m. p. 179°, converted by the usual method into 6-cyano-2:3-dimethoxycinnamic acid, (IV), m. p. 238°. Hydrolysis of this with 10% sodium hydroxide solution yields 6-carboxy-2:3-dimethoxycinnamic acid (V), m. p. 194°. Oxidation of IV with potassium permanganate affords indefinite products, whilst V furnishes a substance, m. p. 202°. H. BURTON.

Tautomerism of o-nitro-compounds. F. ARNDT (Ber., 1929, 62, [B], 1167-1171; cf. A., 1928, 752, 759).—A reply to Tanasescu (A., 1928, 177, 178). H. WREN. "Oxidising "action of alkalis. II. Aromatic hydroxyaldehydes. G. LOCK (Ber., 1929, 62, [B], 1177-1188; cf. this vol., 67).-Hydroxyaldehydes which contain a free hydroxyl group in the ortho- or para-position to the aldehydo-group are not affected by solutions of potassium hydroxide, but react with the powdered alkali at about 110° with formation of molecular quantities of hydroxy-acid and hydrogen. This is true also of dihydroxybenzaldehydes which contain a hydroxyl group in the meta- as well as in the para-position; for example, protocatechualdehyde and its 3-methyl ether. Hydroxyaldehydes containing a hydroxyl group in the meta-position undergo the Cannizzaro reaction with cold potassium hydroxide solutions, whereas at a higher temperature the alkali reacts with the hydroxybenzyl alcohol thus produced, giving hydrogen and hydroxy-acid, so that the final products of the two types of change are ultimately identical quantitatively. The reaction may be expressed by the scheme $C_6H_4(OK)\cdot CHO+KOH=$ $C_6H_4(OK)\cdot CO_2K+H_2$, but the possibility of the intermediate formation of potassium hydride is not excluded. The following new data are recorded: 6-bromo-3-hydroxybenzyl alcohol, m. p. 142°; 6-nitro-3-hydroxybenzyl alcohol, m. p. 120.5° after softening (potassium and lead salts); 4-nitro-3-hydroxybenzyl alcohol, m. p. 97°; isovanillyl alcohol, m. p. 132°. H. WREN.

Action of diazomethane on piperonal. II. E. MOSETTIG (Ber., 1929, 62, [B], 1271-1278; cf. A., 1928, 887).—Safrole oxide, b. p. 140—145°/9 mm., is little affected by distillation under ordinary pressure or by prolonged agitation with concentrated sodium hydrogen sulphite solution, but is isomerised when boiled with pumice fragments soaked in 50% sulphuric to 3:4-methylenedioxyphenylpropaldehyde acid (semicarbazone, m. p. 192-193.5° when slowly heated). It is converted by cautious treatment with hydrogen chloride in light petroleum into the corresponding *chlorohydrin*, $C_{10}H_{11}O_3Cl$, m. p. 47–485 after softening at 46°. The oxide is transformed by aqueous piperidine into $\beta(\text{or } \alpha)$ -piperidino- γ -3':4'methylenedioxyphenylpropan- α (or β)-ol, m. p. 42-44° (hydrochloride, m. p. 165-167° after softening at 163-165°; chloroplatinate). Similarly, with aqueous dimethylamine the oxide affords β -(or α)-dimethylamino- γ -3': 4'-methylenedioxyphenylpropan- α (or β)-ol (picrate, m. p. 164-165° after softening at 163°; very hygroscopic hydrochloride).

Finely-divided piperonal is added to an ethereal methyl-alcoholic solution of diazomethane at -15° . The products formed are piperonylacetone, acetopiperone, and safrole oxide (identified as the corresponding chlorohydrin and as the additive products with piperidine and dimethylamine). The same compounds result when an ethereal methyl-alcoholic solution of diazomethane is poured into an ethereal solution of piperonal. Acetopiperone when subjected to the same conditions as piperonal does not appear to react with diazomethane. Piperonylacetone reacts slowly, very probably with production of an oxide. H. WREN.

Synthesis of safrovanillin from isosafroeugenol. K. KAFUKU and N. ISHIKAWA (Bull. Ind. Dep. Centr. Res. Lab. Formosa, 1928, 24, 24— 27).—Oxidation of isosafroeugenol with ozonised oxygen affords (60—80% yield) 3-hydroxy-4-ethoxybenzaldehyde, m. p. 125° (oxime, m. p. 181—183°; semicarbazone, m. p. 202—203°).

CHEMICAL ABSTRACTS.

Intermolecular condensation of styryl ketones. III. Further examples of the ready formation of bis-(styryl ketones). I. M. HEILBRON and F. IRVING (J.C.S., 1929, 931-936).—The interaction of benzaldehyde and methyl n-alkyl ketones gives both the simple styryl ketone and its dimeride. The solvent appears to be one of the main factors determining the formation of the mono- or bis-form; in aqueous alcohol the styryl ketone is formed, probably owing to its ready separation and consequent removal from the action of the alkali; in absolute alcohol the dimeride is produced even at the same alkali concentration. The dimerides are more readily produced from the higher members of the series, and less easily with substituted benzaldehydes. Dimerides are formed from branchedchain ketones only when at least one methylene group separates the radical from the carbonyl group. The styryl ketones differ widely from their bis-forms in m. p. and crystallise well; the bis-forms usually separate in masses of felted needles. By condensing the appropriate reactants with alkali under given conditions are obtained : bis(styryl n-propyl ketone), m. p. 194-195° (cf. Vorländer, A., 1898, i, 27); bis(styryl n-butyl ketone), m. p. 175-176°; bis(styryl isobutyl ketone), m. p. 202°, also prepared from styryl isobutyl ketone (cf. Gheorghiu and Arventiev, A., 1928, 522); bis(4-isopropylstyryl isobutyl ketone), m. p. 192-194°; bis(styryl n-hexyl ketone), m. p. 152° bis(4-methoxystyryl n-hexyl ketone), m. p. 145-146° bis(styryl isohexyl ketone), m. p. 177°; bis(styryl-n-heptyl ketone), m. p. 144°; and bis(styryl n-octyl kdone), m. p. 131-135°. Alkali condensation has also been employed to obtain the following styryl ketones : styryl n-hexyl ketone, m. p. 32-33° (cf. A., 1905, i, 214); 4-methoxystyryl n-hexyl ketone, m. p. ^{55°}; styryl *n*-heptyl ketone, m. p. 52° (cf. A., 1905, i, 214); and styryl n-octyl ketone. It is probable that the styryl y-methylamyl ketones (active and inactive) described by Rupe and Wild (A., 1917, i, 538) are dimerides. C. W. SHOPPEE.

Natural system for polymorphic forms of p-methylchalkone [p-tolyl styryl ketone]. Isomeric relationships in the chalkone series.

VII. C. WEYGAND and H. BAUMGARTEL (Annalen, 1929, 469, 225-256; cf. A., 1926, 1041; this vol., 564).—Instead of three modifications α , β , and γ , as previously recorded, p-tolyl styryl ketone has been prepared in 13 crystalline forms, 7 of which are termed principal as distinct from subsidiary forms. All three of the earlier modifications belong to the principal group. The following classification is made, the figures after the m. p. indicating the velocity of crystallisation from a fused mass at 18-20° in 0.001 mm. per sec.: I, m. p. 74.5°; 89; II, m. p. 56.5°; 39; III, m. p. 55.5°; 30; (1 subsidiary form); IV, m. p. 54.5°; 114; V, m. p. 45.5°; 19; VI, m. p. 48°; 4; (1 subsidiary form); VII, m. p. 44.5°; 20; (4 subsidiary forms). Details of preparation are given, together with the results of a study of the mechanism of transformation. R. A. MORTON.

Relative stability of isomerides according to absorption spectra. V. Dehydration of glycols; isomeric change of ethylene oxides. (MME.) P. RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1929, 188, 1301-1303; cf. A., 1928, 760, 881, 1000; this vol., 441).-By dehydration of aa-di-pinacols (I, II) or ethylene oxides (III, IV), only methyl aa-diphenylethyl ketone (V) or phenyl phenylisopropyl ketone (VI) can be formed; from the glycols CRPh(OH) CH2 OH (VII) (where R= Me or CH₂Ph), only the aldehydes CHRPh·CHO (VIII) and the ketones CH2Ph·CO·R (IX) and CH₂R·COPh (X). The absorption spectra of the above compounds have been examined; that of VI is nearer the visible than that of V, and those of IX and X are nearer the visible than those of the aldehydes VIII. Accordingly, from the rules given (loc. cit.) the compounds I-IV would be expected to give at low temperatures V and at high temperatures VI, and the compounds VII to give at low temperatures VIII and at high temperatures IX and X, and it is found that, by distillation over infusorial earth at 200-300° under reduced pressure, V and VIII are actually obtained. At 400-500° the pinacols yield the hydrocarbon which is derived from V or VI by heating, and of which the absorption curve is very much nearer the visible; the glycols VII give ketones or hydrocarbons.

The following new rules are proposed : if isomerides are heated and yield several transposition products, the latter are formed in such a sequence that the ultra-violet absorption is displaced towards the visible, provided that no carbon radical is lost, and the formation of the various products depends less on the structure of the isomeride than on the temperature. Thus I, III, and the two stereoisomerides of each of II and IV give the same product; $\alpha\alpha$ - or $\alpha\beta$ -diphenylethylene glycol both give, at 200—300°, diphenylacetaldehyde, whilst at 500° these all give deoxybenzoin. These rules do not apply to transpositions brought about by reagents, in which case the latter may have a specific effect; thus, I and III are converted by acetic anhydride and a trace of sulphuric acid into VI, but by concentrated sulphuric acid into V, which is, however, the product when either reagent acts on II or IV. E. W. WIGNALL.

Spectrochemistry of α -diketones and ethylene oxides. K. VON AUWERS (Ber., 1929, 62, [B], 1317—1319; cf. Moureu, A., 1927, 246, 1173; 1928, 180, 419, 1334).—The data d_4^{15*8} 1·0919, n_a^{15*8} 1·52767, n_{11e}^{15*3} 1·53404, and d_4^{15*4} 1·0756, n_a^{16*4} 1·58698, n_{11e}^{15*3} 1·59953, are recorded for the diketonic and ketoenolic varieties of benzylmethylglyoxal, respectively, whereas acetylphenylethylene oxide has d_4^{96*0} 1·0733, n_4^{96*1} 1·51529, n_{11e}^{16*} 1·52016. The diketone and keto-enol can be sharply differentiated spectroscopically, whereas discrimination between diketone and oxide appears impossible by this method. Comparison of Schlotterbeck's "trichloroacetone" (A., 1907, i, 185, 478; 1909, i, 553), d_4^{19*0} 1·4962, n_4^{10*1} 1·47310, n_{11e}^{10*1} 1·47729, with chloral, d_4^{21*4} 1·5059, n_a^{21*4} 1·44988, n_{11*}^{21*4} 1·45412, confirms the conclusion of Arndt and Eistert (A., 1928, 739) that the compound is $\alpha\alpha\alpha$ -trichloropropylene $\beta\gamma$ -oxide. H. WREN.

Oximes of unsaturated ketones. K. VON AUWERS (Ber., 1929, 62, [B], 1320—1323).—Phenyl p-ethoxystyryl ketone, m. p. 74—75°, is converted by hydroxylamine in alkaline solution into 5-phenyl-3:4'-ethoxyphenylisooxazoline, m. p. 107—108°, whereas in acidic solution it affords the corresponding oxime, m. p. 134—140°, converted by phosphorus pentachloride in ether into cinnam-p-phenetidide, m. p. 143—144°. Phenyl α -bromostyryl ketone and hydroxylamine in alkaline solution yield 3:5-diphenylisooxazole, m. p. 140°, whereas in acid solution the oxime, m. p. 151°, is obtained; it is transformed in boiling alcoholic alkali hydroxide into 3:5-diphenylisooxazole. H. WREN.

Condensation of aldehydes with nitrodiacetoresorcinol. J. ALGAR and (MISS) N. M. MAC-DONNELL (Proc. Roy. Irish Acad., 1929, 38, B, 171-174).—Nitration of 4:6-diacetoresorcinol with a mixture of nitric (d 1.5) and sulphuric acids in the cold affords 2-nitro-4:6-diacetoresorcinol (I), m. p. 235.5°, converted by an excess of fuming nitric acid into 2:4:6-trinitroresorcinol. Reduction of I with ferrous sulphate and sodium hydroxide yields a small amount of 2-amino-4:6-diacetoresorcinol, m. p. 185°, whilst condensation of I with benzaldehyde and furfuraldehyde in presence of aqueous methylalcoholic potassium hydroxide gives the corresponding dibenzylidene, m. p. 220°, and difurfurylidene derivatives, m. p. 262-265° (decomp.), respectively. With piperonal, a diflavanone (II), m. p. 262°, is



obtained : this does not give a coloration with ferric chloride solution, and dissolves in sulphuric acid to a violet-red solution. H. BURTON.

Dichalkones derived from diacetoresorcinol. J. ALGAR and P. J. HANLON (Proc. Roy. Irish Acad., 1929, 38, B, 175—178).—Condensation of 4:6-diacetoresorcinol with p-dimethylaminobenzaldehyde in presence of alcohol and a small amount of piperidine yields the corresponding di-p-dimethylaminobenzylidene derivative (designated α -), scarlet, m. p. 240–241°, whilst in presence of 80% alcohol an isomeride (I)

$$\begin{array}{c} \text{HO} \\ \text{NMe}_2 \cdot \text{C}_6 \text{H}_4 \cdot \text{CH:CH:CH:CO} \\ \text{CH}_2 \\ \text{CO} \\ \text{CH}_2 \end{array}$$

(termed β -), orange-red, m. p. 262—263°, results. The lighter colour and smaller fusibility of the β -form indicates the flavanone structure. *Difurfurylidene*-4: 6-*diacetoresorcinol*, m. p. 226—227°, is obtained using aqueous-alcoholic sodium hydroxide as the condensing agent. H. BURTON.

Oxidation-reduction. XIII. Indophenols used as oxidation-reduction indicators. H. D. GIBBS, W. L. HALL, and W. M. CLARK (U.S. Public Health Rep., Suppl. 69, 1928, 35 pp.) .-- Indophenols are best prepared by treating benzoquinonechloroimides with phenols and a slight excess of 3N-sodium hydroxide solution at about 0°, with subsequent purification of the sodium salts, which, however, is not easy, as their aqueous solutions are generally unstable. Reduction of the indophenols to the leuco-compounds (substituted diphenylamines) is carried out by treating a saturated aqueous solution of the salt with 20% potassium sulphide. The m. p. of the free indophenols vary considerably with the rate of heating, and have little significance. Various methods of analysis are quoted. The nomenclature is discussed and the name benzenoneindophenol (I) adopted for the parent substance (indophenol). The

$$0 = \underbrace{1_{\frac{2}{6}}^{\frac{2}{3}}}_{\frac{6}{5}} = N - \underbrace{1_{\frac{6}{5}}^{\frac{2}{3}}}_{\frac{6}{5}} OH (I.)$$

following substituted benzenoneindophenols are described, many of which are new: 2-methyl-, m. p. 162°; 3-methyl-, m. p. 110—111° (decomp.); 2:6-dimethyl-; 3-methyl-6-isopropyl-, m. p. 134°, decomp. 151°; 2-methyl-5-isopropyl-, m. p. 121—125°; 2-methoxy-, m. p. 171°; 3-methoxy-; 2-chloro-; 2- and 3-bromo-; 2:6-dichloro-; 2:6-dichloro-3'methyl-; 2:6-dichloro-2'-methyl-; 2:6:3'- and 2:6:2'-trichloro-; 2:6-dibromo-; 2:6-dibromo-3'methyl-; 2:6-dibromo-2'-methyl-; 2:6-dibromo-3'methyl-; 2:6-dibromo-2'-methyl-; 2:6-dibromo-2'methyl-5'-isopropyl-; 2:6-dibromo-3'-methoxy-; 2:6:3'- and 2:6:2'-tribromo-; 3'-chloro-2:6-dibromo-, and 3'-methyl-. Sodium 2:6-dibromobenzenoneindophenol-2'- and -3'-sulphonates, benzenoneindoo-phenol (I, OH in 2'-position; 3-methyl- and 2-bromoderivatives), and 1-naphthanoneindophenol-2-sulphonic acid (3'-methyl-, 3':5'-dichloro-, and 3':5'dibromo-derivatives), are also described.

H. BURTON. Ready conversion of certain derivatives of hydroxyquinol trimethyl ether into quinone compounds. T. Szźki (Ber., 1929, 62, [B], 1373– 1378).—Opianic acid and hydroxyquinol trimethyl ether are converted by 73% sulphuric acid into 3-2': 4': 5'-trimethoxyphenylmeconine,

 $(OMe)_2C_6H_2 < OC_{CH} \cdot C_6H_2(OMe)_3$, m. p. 115—119⁴. Under similar conditions, methyl opianate and 2 mols. of hydroxyquinol trimethyl ether give methyl 4:5:2':4':5':2'':4'':5'' - octomethoxytriphenyl-

methane-6-carboxylate, m. p. 143°, whereas nitroopianic acid affords 4-nitro-3-2': 4': 5'-trimethoxyphenylmeconine, m. p. 184°. Trimethoxyphenylmeconine is readily oxidised by nitric acid (d 1.48) in glacial acetic acid to 2-methoxy-5-meconyl-p-benzoquinone, m. p. about 220° after softening at 202-204°. 2-Methoxy-5-4'-nitromeconyl-p-benzoquinone, m. p. 199-200° (decomp.), is prepared by nitration of the last-named substance or by oxidation of 4-nitro - 3-2': 4': 5' - trimethoxyphenylmeconine. 2. Methoxy-5-phthalidyl-p-benzoquinone has m. p. 152-154°. The following quinones are prepared by use of nitric acid in acetic acid : 2-methoxy-5-benzoyldiphenylmethyl-p-benzoquinone, m. p. 181°, from benzoyl-2:4:5-trimethoxytriphenylmethane; 2-methoxy-5aa-diphenylethyl-p-benzoquinone, m. p. 198°, from 2:4:5-trimethoxy-aaa-triphenylethane; 2-methoxy-5-ab-diphenylisopropyl-p-benzoquinone, m. p. 183-184°. Reduction of the requisite quinones by sulphur dioxide yields 2-methoxy-5-meconylquinol, m. p. 210° (diacetyl compound, m. p. 158°), and 2-methoxy-5-phthalidylquinol, m. p. 204° (diacetate, m. p. 178°). H. WREN.

o-Quinamines of the naphthalene series and their rearrangement into homologues of β-naphthylacetic acid. K. FRIES and A. KÜSTER (Annalen, 1929, 470, 20-37).-When 1-bromo-2keto-1-methyl-1: 2-dihydronaphthalene (Fries and Engel, A., 1924, i, 1187) is treated with alcoholic aniline, 1-anilino-2-keto-1-methyl-1: 2-dihydronaphthalene, m. p. 141°, results. This is reduced by zinc dust and acetic acid, yielding 1-methyl-β-naphthol, and is brominated in alcoholic solution to the corresponding 1-2': 4'-dibromoanilino-derivative, m. p. 174°. The following substituted -2-keto-1-methyl-1:2-dihydronaphthalenes are prepared by similar methods: 1-p-bromoanilino-, m. p. 148°; 6-bromol-anilino-, m. p. 149°; 6-bromo-1-p-bromoanilino-, m. p. 168°; 6-bromo-1-2': 4'-dibromoanilino-, m. p. 185°, converted by treatment with zinc dust and acetic acid into 2:4-dibromoaniline and 6-bromo-1-methyl-β-naphthol, m. p. 152°; 4:6-dibromo-1andino- (I), m. p. 200°, converted by treatment with cold concentrated sulphuric acid into p-aminophenyl β-4:6-dibromo-1-methylnaphthyl ether, m. p. 137°. Bromination of I in alcoholic solution, or treatment of 1:4:6-tribromo-2-keto-1-methyl-1:2-dihydronaphthalene with an equimolecular quantity of alcoholic aniline, affords the N-bromo-derivative, m. p. 187°, of I, which when treated with hydrochloric, hydrobromic, or sulphurous acids passes into 4:6-dibromo-1-p-bromoanilino-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 201°. 1-Acetanilido-2-keto-1-methyl-1: 2-dihydronaphthalene, m. p. 174°, when treated with sodium ethoxide undergoes an aldol-like

(II.) condensation, yielding a mixture of 2-keto-1-phenyl-8-methyl-6:7benzo-2:8-dihydroindole (II), m. p. 178°, and 9-hydroxy-2-keto-1-phenyl-8-methyl-6:7-benzo-2:3:8:9tetrahydroindole (III), m. p. 174°

(methyl ether, m. p. 184°). Treatment of III with sulphuric acid or alcoholic-hydrochloric acid gives II, whilst reduction with hydrogen in presence of palladinised barium sulphate and acetic acid yields the

Me

corresponding 2:3:4:5:8:9-hexahydro-derivative, m. p. 159° (acetyl derivative, m. p. 152°). Similar reduction of II affords the corresponding 2:3:4:5:8:9hexahydro-derivative, m. p. 145°, but with stannous chloride and acetic acid the corresponding 2:3:5:8tetrahydro-derivative, m. p. 189°, results. 3:4:5:9-Tetrabromo - 2 - keto - 1 - phenyl - 8 - methyl - 6:7-benzo-2:3:4:5:8:9-hexahydroindole, m. p. 200° (de-comp.), is obtained by bromination of II in chloro-form solution. When II is reduced by Clemmensen's method aniline is eliminated and β -1-methylnaphthylacetic acid (IV), m. p. 166°, results : this is formed presumably through the intermediate β -1-anilino-1-methyl-1: 2-dihydronaphthylacetic acid. Distillation of the sodium salt of IV with copper powder and soda-lime affords 1:2-dimethylnaphthalene. 1-Propionanilido-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 142°, when treated with sodium ethoxide yields 2-keto-1-phenyl-3: 8-dimethyl-6: 7-benzo-2: 8dihydroindole, m. p. 165°, reduced by Clemmensen's method to a-(B-1-methylnaphthyl) propionic acid, m. p. 128°. Similarly, 6-bromo - 1 - acetanilido - 2 - keto - 1methyl-1: 2-dihydronaphthalene, m. p. 226°, affords a mixture of 9-hydroxy-2-keto-1-phenyl-8-methyl-6:7-4'-bromobenzo-2:3:8:9-tetrahydroindole, m. p. 201°, and 2-keto-1-phenyl-8-methyl-6:7-4'-bromobenzo-2:8dihydroindole, m. p. 174°. The last-named compound is reduced by Clemmensen's method to 3-6-bromo-1methylnaphthylacetic acid, m. p. 210°.

H. BURTON.

Anthraquinol-a-carboxylolactones. R. SCHOLL and F. RENNER [with O. BÖTTGER, S. HASS, and H. K. MEYER] (Ber., 1929, 62, [B], 1278-1295; cf. this vol., 567).-Anthraquinone- and 2-methylanthraquinone-1-carboxylic acids are converted into the corresponding anthraquinol-a-carboxylolactones by the following methods. (1) Short treatment with zinc dust and glacial acetic acid in the presence of acetic anhydride; protracted heating or absence of acetic acid leads to quantitative formation of the acetylated lactones. (2) By treatment of the esters with alkaline or acid reducing agents : the aryl esters react readily with sodium hyposulphite, zinc dust and ammonia, or zinc dust and acetic acid. The alkyl esters of the 2-methyl acid but not those of the parent acid react to a slight extent in the same sense. (3) From the acid chloride or amide and sodium hyposulphite and sodium hydroxide. The anthraquinone-1-carboxylic acids, their esters, chlorides, and amides, are considered

to belong to the normal type, $C_6H_4 < \stackrel{CO}{CO} > C_6H_3 \cdot CO_2H$,

and not to the pseudo-series I (X=0), since the amide

 $C_6H_4 < CX_{CR}$

is converted into a vat by sodium hyposulphite and sodium hydroxide from which it is precipitated by air, and the normal structure is established for the esters (following

abstract). The constitution does not appear deducible from the colour. The most striking property of the lactones is the change from red to blue when they are brought into alkaline solution. In pyridine, anthraquinol - 1 - carboxylolactone dissolves at the ordinary temperature to a red solution from which the red *pyridine* compound, $C_{15}H_8O_3, C_5H_5N$, separates. If the pyridine solution is treated with water it becomes pure blue but red again when heated or treated with much pyridine. It is considered that the red, homopolar phenolic lactone (I: N=H; X=H+OH)with pyridine alone yields a homopolar pyridine compound $(I; R=H; X=H+OH, C_5H_5N)$ which passes into the blue, heteropolar pyridinium salt $(I; R=H; X=H+O[(H_2O)_n, HC_5H_5N])$ of the hypothetical heteropolar acid.

The following substances are described : anthraquinol-1-carboxylolactone and its 10-acetyl derivative. m. p. 196°; phenyl anthraquinone-1-carboxylate, m. p. 213°; methyl, ethyl, phenyl, and p-bromophenyl 2-methylanthraquinone-1-carboxylates, m. p. 178-179°, 144°, 218-219°, and 226°, respectively; 2-methylpyridazoneanthrone, m. p. 332°, from the phenyl ester and hydrazine hydrate in boiling benzene; 2-methylanthraquinol-1-carboxylic acid; 2-methylanthraquinol-1-carboxylolactone, m. p. about 265° (decomp.) after becoming lighter in colour at about 235°; 2-methylanthraquinone-1-carboxylamide, gradual decomp. about 260° after softening at about 255°; acetyl-2-methylanthraquinol-1-carboxylolactone, m. p. 238°. 2-Methylanthraquinol-1-carboxylolactone can be sharply titrated with potassium permanganate in acetone and acetic acid or with bromine in pyridine. The anthraquinol-1-carboxylolactones are highly sensitive to atmospheric oxidation in neutral, acid and alkaline solution and are readily oxidised by lead peroxide, ferric chloride, bromine, permanganate, etc. For preparative purposes the most suitable reagent is hot nitrobenzene, which transforms the 2-methyl derivative into 9:9'-dihydroxy-2:2'-dimethyl-9:9'-dianthronyl-1: 1'-dicarboxylodilactone (II), m. p. about



290° (decomp.) after darkening at about 270° when rapidly heated. The compound is also prepared by the action of finely-divided silver or dimethylaniline on the acid chloride in benzene. Con-

centrated sulphuric acid causes fission with oxidation to 2-methylanthraquinone-1-carboxylic acid. It is reduced by zinc dust and glacial acetic acid, very slowly by sodium hyposulphite and ammonia to the monomeric lactone. With aqueous or, preferably, alcoholic alkali the dilactone yields an olive-green solution apparently containing a quinhydrone-like compound of the salts of the anthraquinone- and anthraquinol-carboxylic acids. Sodium ethoxide appears to cause a radical dissociation into an anthroxyl with univalent oxygen; the same change is induced by exposing the dilactone in acetic acid to ultra-violet light and by heating its solution in certain organic media. H. WREN.

Nature of anthraquinone- α -carboxylic esters. R. SOHOLL and J. DONAT [with H. SEMP and L. WANKA] (Ber., 1929, 62, [B], 1295—1301; cf. preceding abstract).—Esters of anthraquinone- and 2-methyl-anthraquinone-1-carboxylic acid are obtained (1) from the acid and alcohol in presence of hydrogen chloride or sulphuric acid, (2) from the acid chloride and alcohol or phenol, (3) from the silver salt and alkyl iodide, and (4) by oxidation of 2-methylanthracene-1-carboxylic esters. Method 1 is inapplicable to the 2-methyl

derivative on account of steric hindrance. The esters of anthraquinone-1-carboxylic acid prepared according to 1, 2, and 3 are identical with one another, as are those of 2-methylanthraquinone-1-carboxylic acid obtained according to 2, 3, and 4. The normal structure, $C_6H_4 < CO > C_6H_2R \cdot CO_2R'$, is therefore assigned to them. Indications of the existence of isomeric acid chlorides are not obtained. The following compounds are described : calcium anthracene-1-carboxylate; anthracene-1-carboxyl chloride, which does not appear suitable for the Friedel-Crafts synthesis; anthracene-1-carboxylic anhydride, m. p. 206°; ethyl anthraquinone-1-carboxylate, m. p. 169°; 2-methylanthracene-1-carboxylic acid, m. p. 212.5°, and the corresponding acid chloride, ethyl ester, m. p. 87-90°, and phenyl ester, m. p. 137-140°; phenyl 2-methylanthraquinone-1-carboxylate, m. p. 218-219°. H. WREN.

Congo copal oil. L. WESTENBERG (Rec. trav. chim., 1929, 48, 580—582).—Catalytic dehydrogenation of Congo copal oil with sulphur yields a hydrocarbon, $C_{13}H_{14}$, m. p. 26°, b. p. 295° (corr.) (picrale, m. p. 139°), which is possibly identical with that obtained from Manila copal by by Ruzicka and others (A., 1927, 60). Oxidation with chromic and acetic acids converts it into a monobasic acid, $C_{12}H_{12}O_4$, m. p. 204°, and a substance $(C_4H_4O)_n$, m. p. 69°.

J. W. BAKER.

Lichen substances. V. Constitution of thamnolic acid. Y. ASAHINA and S. IHARA (Ber., 1929, 62, [B], 1196-1207).-Thamnolic acid, isolated by Hesse from Thamnolia vermicularis, has been considered to have the composition $C_{20}H_{18}O_{11}$ and to be converted by barium hydroxide into thamnolinic acid, methyl alcohol, and carbon dioxide: $C_{20}H_{18}O_{11}+3H_2O=C_{16}H_{20}O_9+CH_3\cdotOH+3CO_2$. The acid has been isolated from Cladonia flabelliformis, Flk., var. polydaciyla, and is shown by direct comparison to be identical with that from Thamnolia vermicularis. Analyses and titration with 0.1N-sodium hydroxide in the presence of hæmatoxylin indicate the molecular formula C19H16O11 on the assumption that one methoxyl group is present. The aniline salt, m. p. 206-208°, phenylhydrazone, m. p. 173-174°, and p-nitrophenylhydrazone, m. p. 238-239°, are described. Warm potassium hydrogen carbonate solution or potassium or barium hydroxide converts thamnolic acid into orcinol monomethyl ether and evernic acid in addition to much dark-coloured resin. The formation of Hesse's thamnolinic acid could not be observed and his compound is probably evernic acid, for which the m. p. 172° is now found after crystallisation from light petroleum; specimens crystallised from water or alcohol have lower m. p., due to partial decomposition by heat and retention of products of decomposition by the crystals. Thamnolic acid is converted by aniline at 200° into the evernanilide, m. p. 175°, prepared also from its components, whilst methyl alcohol at 150° transforms it into methyl evernate, m. p. 67-68°. Thamnolic acid is little affected by boiling glacial acetic acid, which, at 150°, converts it into orcinol monomethyl ether, the monomethyl ether of p-orsellinic acid, and thamnol, C8H8O4, m. p. 185° (more conveniently prepared by heating thamnolic acid with

pelargonic acid in open vessels). The acidic and aldehydic nature of thamnol is established by its solubility in sodium hydrogen carbonate and sulphite and by the isolation of its anil, m. p. 128-129°, phenylhydrazone, m. p. 194° (decomp.), and p-nitrophenylhydrazone, m. p. about 320° (decomp.). The triacetate, m. p. 133° (? corresponding anil, m. p. 129°), is described. Reduction of thamnol by Clemmensen's method yields hydroxy-β-orcinol [2:3:5-trihydroxy-p-xylene], m. p. 156° (triacetate, m. p. 107-108°), identified by comparison with the synthetic product (cf. Asahina and Ishibashi, this vol., 806). Thamnolic acid, when heated in potassium hydrogen carbonate solution with gradual addition of sodium sulphite, is converted into the monomethyl ether of orcinoldi-carboxylic acid, m. p. 205-206° (decomp.), which is regarded as the parent of the monomethyl ethers of orcinolcarboxylic acid according as one or other of the carboxyl groups is eliminated as carbon dioxide. Thamnolic acid has therefore the constitution

 $0 \underline{\mathrm{Me}} \cdot C \underbrace{CH}_{C(CO_2H):C(OH)} C \cdot CO \cdot O \cdot C \underbrace{C(OH)}_{C(COH):C(OH)} C \cdot CO_2H,$

in which the position of the depside linking is arbitrary. H. WREN.

New dihydroterpene. S. BLANCO (J. Amer. Pharm. Assoc., 1929, 18, 474—477).—Steam-distillation of the alcoholic extract of the fruits of *Pittosporum resiniferum* gave an oil having d^{20} 0.7692, n_D^{20} 1.435, α_D^{20} +20.02° (100 mm. tube), 40.03° (200 mm. tube), saponif. value 0.67 (after acetylation 8.56). On fractionation it gave 26% of a fraction, b. p. 150—154° (mainly 152—153°), d^{25} 0.947, n^{27} 1.464, α_D^{25} +39.34°, most of which was collected at 152—153°, which gave a *nitrolbenzylamide*, m. p. 148—149° (cf. Bacon, A., 1909, i, 659). E. H. SHARPLES.

Derivatives of perillaldehyde. B. RUTOVSKI and A. KOROLEV (Trans. Sci. Chem.-pharm. Inst. Moscow, 1928, 153—156; Chem. Zentr., 1928, ii, 2355). -Methyl, ethyl, and isoamyl perillacrylates were prepared. By condensation of perillaldehyde with acetone or acetaldehyde in presence of sodium hydroxide, perillylideneacetone, diperillylideneacetone, and perillylideneacraldehyde were obtained Perillaldehyde, benzoylglycine, sodium acetate, and acetic anhydride afforded 2-phenyl-4-perillylideneoxazoline,

 $\begin{array}{c} \text{CH}_2: \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \Rightarrow \text{C} \cdot \text{CH} : \text{C} < \overset{\text{CO} \cdot \text{O}}{\text{N} = \text{CPh}}, \quad \text{yellow}, \\ \text{m. p. } 137 - 138^\circ, \text{ in } 65 - 70\% \text{ of the theoretical yield.} \end{array}$

A. A. ELDRIDGE. Menthol. II. Menthyl esters of 2-nitro-4carboxyphenylarsinic and -arsenious acids. K. L. MCCLUSKEY (J. Amer. Chem. Soc., 1929, 51, 1462—1465).—2-Nitro-4-carboxyphenylarsinic acid (Maschmann, A., 1924, i, 1357) is reduced by sulphur dioxide and concentrated hydrochloric acid to dichloro-2-nitro-4-carboxyphenylarsine, m. p. 173—174°. This is hydrolysed by water to 2-nitro-4-carboxyphenylarsenious acid (unchanged at 290°) and converted by thionyl chloride into the corresponding chloride, which with menthol yields 2-nitro-4-carbomenthyloxyphenylarsenious acid, decomp. above 100°. This is oxidised by 3% hydrogen peroxide in acetone to menthyl 3-nitro-4-arsinobenzoate, decomp. 210-211° [sodium salt (also $+4H_2O$]. H. E. F. NOTTON. Determination of configuration in the terpene series. III. J. VON BRAUN, H. KRÖPER, and W. REINHARDT (Ber., 1929, 62, [B], 1301—1307).—The replacement of the amino- by the hydroxyl group by means of nitrous acid is frequently accompanied by intramolecular transformation, whereas the structural relationship appears to be generally preserved if the amine is converted into its benzoyl derivative, which is decomposed by phosphorus pentachloride or pentabromide into benzonitrile, and the chloride or bromide which is readily transformed into the alcohol (cf. von Braun and Jostes, A., 1926, 825).

Menthonylamine hydrochloride is slowly but completely hydrogenated in aqueous solution in presence of palladised charcoal to dihydromenthonylamine, b. p. $85^{\circ}/13 \text{ mm.}, \alpha_{p} + 2 \cdot 5^{\circ} (l=1)$ [hydrochloride, m. p. 123– 124°, $[\alpha]_{p}^{15} + 5 \cdot 74^{\circ}$ in water (c=19.83); benzoyl derivative, b. p. 201-202°/0.3 mm.]. The benzoyl compound is treated with phosphorus pentachloride and the product is distilled under atmospheric pressure, whereby dihydromenthonyl chloride, b. p. 85-87°, 10 mm., d^{12} 0.8752, $[\alpha]_D^{12}$ -2.56°, is obtained. Di-hydromenthonyl iodide, b. p. 108-112°/10 mm., d_1^{14} 1.1533, $[\alpha]_{0}^{14} - 9.69^{\circ}$, from the chloride and sodium iodide in acetone, is converted by trimethylamine in benzene into the corresponding quaternary iodide, m. p. 235–236°, $[\alpha]_D^{18} + 4.13^{\circ}$ in alcohol, identical with the product obtained by exhaustive methylation of dihydromenthonylamine with methyl iodide and sodium hydroxide.

Dihydro- α -campholenonitrile is reduced by sodium and alcohol or by hydrogen in presence of nickel and decahydronaphthalene at 250° to dihydrocamphylamine, b. p. 88°/13 mm., d_{*}^{20} 0.8640, $[\alpha]_{\rm D}^{20} + 34.72°$ [hydrochloride, m. p. 255° (decomp.); picrate, m. p. 197°; corresponding phenylthiocarbamate, m. p. 116°]. The benzoyl compound, b. p. 190°/0·2 mm., $[\alpha]_{\rm D}^{22}$ +26·37° in alcohol, is transformed into dihydrocamphyl chloride, b. p. 88°/13 mm., d_{*}^{23} 0.9983, $[\alpha]_{\rm D}^{25}$ +46·65°. Dihydrocamphyl iodide, b. p. 115—120°/ 13 mm., d_{*}^{20} 1.0051, $[\alpha]_{\rm D}^{20}$ +44·72°, is transformed into dihydrocamphyltrimethylammonium iodide, m. p. 277— 278°, $[\alpha]_{\rm D}^{20}$ +23·74° in water, also obtained by exhaustive methylation of dihydrocamphylamine.

H. WREN.

Oxidation of $d-\Delta^4$ -carene with Beckmann's chromic acid mixture. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1929, 909—910).—Oxidation of $d-\Delta^4$ -carene from Andropogon Jwarancusa with Beckmann's chromic acid mixture gave *l-trans*-caronic acid, m. p. 202—203°, $[\alpha]_{5461}$ in alcohol —11.85°, together with small quantities of terebic acid, m. p. 173—174°, dimethylmalonic acid, m. p. 185—186°, and a neutral oil yielding a semicarbazone, m. p. 205—207°, which was not further investigated. A. I. VOGEL.

Syntheses in the hydroaromatic series. III. Syntheses of terpenes, camphors, hydroaromatic and heterocyclic systems. O. DIELS and K. ALDER [with W. LÜBBERT, E. NAUJOKS, F. QUERBERITZ, K. RÖHL, and H. SEGEBERG] (Annalen, 1929, 470, 62—103).—When 2:5-endomethylenehexahydrobenzaldehyde (I) (semicarbazone, m. p. 160.5°; cf. A., 1928, 1018) is heated with acetic anhydride and sodium acetate, the enol acetate (II), b. p. 109—111°/

16 mm., of norcamphenilanealdehyde, results. Fission of this with ozone in presence of benzene and water and subsequent treatment with semicarbazide affords the semicarbazone, m. p. 196-197°, of norcamphor, m. p. 91-92° (cf. Hintikka and Komppa, A., 1918, i, 543). Reduction of I in presence of acetic acid by Skita's method gives 2:5-endomethylenehexa-hydrobenzyl acetate, b. p. 103-104°/13 mm., also formed from II by Paal's method. Treatment of 2:5-endomethylenehexahydrobenzyl alcohol (III), b. p. 101—102°/10 mm. (phenylcarbimide derivative, m. p. 118—119°), with hydriodic acid (d 1.96) at 110— 120°, yields the corresponding *iodide*, b. p. 107-109°/14 mm., which when treated with trimethylamine in benzene at 120° affords 2 : 5-endomethylenehexahydrobenzyltrimethylammonium iodide, m. p. 266-267°. Thermal decomposition of the corresponding hydroxide gives 2:5-endomethylenehexahydrobenzyldimethylamine, b. p. 182° (picrate, m. p. 172°). Treat-ment of the sodium derivative of III with carbon disulphide and methyl iodide in toluene affords the corresponding xanthate, C₇H₁₁·CH₂·O·CS₂Me, b. p. 182°/15 mm., which when distilled under ordinary pressure decomposes into carbonyl sulphide, methylmercaptan, and norcamphene, b. p. 123°/755 mm., d¹³ 0.8789 (nitrosochloride, m. p. 125°). Magnesium phenyl bromide converts I into phenyl-2:5-endo-methylenecyclohexylcarbinol, b. p. 162-165°/20 mm., dehydrated by potassium hydrogen sulphate at 190° to 2-benzylidene-1: 4-endomethylenecyclohexane, b. p. 145-147°/15 mm. When I is kept in the ice-chest for some days a trimeride, m. p. 178-179° after slight previous sintering, is formed.

When myrcene is warmed with maleic anhydride, cis-4-isohexenyl- Δ^4 -tetrahydrophthalic anhydride (IV), b. p. 202—206°/12 mm., m. p. 34—35°, results. Treatment of the corresponding acid, m. p. 122-123°, with 35% hydrobromic acid at 100° in a sealed tube gives 1:1-dimethyloctahydronaphthalene-6:7-di-carboxylic acid, m. p. 206–207° (anhydride, m. p. 215–217°). Reduction of IV with hydrogen in presence of colloidal palladium and alcohol yields cis-4-isohexyl- Δ^4 -tetrahydrophthalic anhydride, b. p. 207°/11 mm., m. p. 42°; the corresponding acid is converted into trans-4-isohexyl- Δ^4 -tetrahydrophthalic acid, m. p. 169—170°, by heating with 30% hydrobromic acid at 100° in a sealed tube. Treatment of a chloroform solution of IV with ozone and subsequent decomposition of the ozonide with water and hydrogen peroxide affords $4-\beta$ -carboxyethyl- Δ^4 -tetrahydrophthalic acid (lead salt). Crotonaldehyde combines with butadiene at 150° to give 6-methyl- Δ^3 -tetrahydro-benzaldehyde, b. p. 75°/22 mm. (semicarbazone, m. p. 168°), reduced catalytically by Paal's method to hexahydro-o-tolualdehyde, b. p. 61-62°/11 mm. (semi-carbazone, m. p. 155°). This is oxidised by atmo-spheric oxygen to trans-hexahydro-o-toluic acid (amide, m. p. 175-176°). From crotonaldehyde and isoprene, $\alpha\gamma$ - and $\beta\gamma$ -dimethylbutadienes, there are obtained 3: 6-dimethyl- Δ^3 -tetrahydrobenzaldehyde, b. p. 92–93°/25 mm. (semicarbazone, m. p. 179–180°), 2:4:6-trimethyl- Δ^4 -, b. p. 81–82°/12 mm. (semi-carbazone, m. p. 183°), and 3:4:6-trimethyl- Δ^3 -tetrahydrobenzaldehyde, b. p. 89°/12 mm. (semicarbazone, m. p. 181°), respectively : aay-trimethylbutadiene

affords a compound, $C_{11}H_{18}O$, b. p. 93—95°/18 mm. Acraldehyde combines with isoprene, $\beta\gamma$ - and $\alpha\gamma$ -dimethylbutadienes, at 100°, yielding 3(4?)-methyl- Δ^3 . b. p. 63—64°/10 mm. (semicarbazone, m. p. 146°), 3:4-dimethyl- Δ^3 -, b. p. 79°/10 mm. (semicarbazone, m. p. 172°), and 2:4(3:5?)-dimethyl- $\Delta^{3(4)}$ -tetrahydrobenzaldehydes, b. p. 71—73°/10 mm. (semicarbazone, m. p. 174°), respectively. Crotonaldehyde and myrcene combine at 150°, forming 6-methyl-3-isohexenyl- Δ^3 -tetrahydrobenzaldehyde, b. p. 143—144°/12 mm.; with acraldehyde at 100° the aldehyde, $C_{13}H_{20}O$, b. p. 134—136°/17 mm., results. α -Phellandrene reacts similarly with acraldehyde and eroton-

Pr^{\$}·CH CH CH·CHO CH₂ CM_c CH·R

aldehyde, giving aldehydes, b. p. 128-130°/ 12 mm. and 143-144°/ 18 mm., respectively, with the annexed structure (where R=H and Me,

respectively). Cinnamaldehyde and $\alpha\gamma$ -dimethylbutadiene combine at 200° to give an aldehyde, $C_{15}H_{18}O$, b. p. 156—158°/16 mm. Crotonic acid and butadiene react at 150—170°, yielding an acid, $C_8H_{12}O_2$, m. p. 68°, reduced catalytically by Paal's method to trans-hexahydro-o-toluic acid; with $\alpha\alpha\gamma$ -trimethyl- and $\alpha\gamma$ -dimethyl-butadienes, the acids, $C_{11}H_{18}O_2$ and $C_{10}H_{16}O_2$, m. p. 88·5—89° and 98°, respectively, result. Sorbic acid and maleic anhydride afford an acid, $C_{10}H_{12}O_6$, decomp. 198°, whilst ethyl sorbate furnishes a substance, m. p. 117—118°.

cycloPentadiene and crotonaldehyde combine at 100° to give a mixture of cis- and trans-6-methyl-2: 5endomethylene- Δ^3 -tetrahydrobenzaldehyde, which yields semicarbazones, m. p. 158° and 181°, respectively; the aldehyde regenerated from the semicarbazone, m. p. 181°, has b. p. 80°/45 mm. During this reaction the cis-aldehyde is first produced and on further heating rearranges into the trans-isomeride. Reduction of the more fusible semicarbazone with hydrogen in presence of colloidal palladium and alcohol yields the semicarbazone, m. p. 166.5°, of cis-6-methyl-2: 5-endomethylenehexahydrobenzaldehyde, b. p. 85°/23 mm. Similarly, the less fusible semicarbazone affords the semicarbazone, m. p. 174°, of trans - 6-methyl - 2: 5 - endomethylenehexahydrobenzaldehyde, b. p. $90^{\circ}/12$ mm. Atmospheric oxidation of these aldehydes gives cis- and trans-2:5-endomethylenehexahydro-o-toluic acids, b. p. 136-137°/ 13 mm., and m. p. 66°, respectively.

Condensation of 3(4?)-methyl- Δ^4 -tetrahydrobenzaldehyde with acetone in presence of aqueous barium hydroxide affords the corresponding benzylideneacetone, b. p. 121—122°/12 mm. 2:4:6-Trimethyl- Δ^4 -tetrahydrobenzaldehyde and acetone condense in presence of sodium ethoxide, yielding 2:4:6-trimethyl- Δ^4 -tetrahydrobenzylideneacetone [ψ -irone], b. p. 138—139°/20 mm. (p-bromophenylhydrazone, m. p. 175°; thiosemicarbazone, m. p. 191—192° after sintering at 187°). 2:4:6:6-Tetramethyl- Δ^4 -tetrahydrobenzylideneacetone[methylirone] (p-bromophenylhydrazone, m. p. 155—156°) is obtained similarly.

Dehydration of β -methylpentane- $\beta\delta$ -diol affords $\alpha\gamma$ -dimethylbutadiene, oxidised by potassium permanganate to formic and acetic acids, and reduced catalytically to β -methyl- Δ^{β} -pentenc. The dibromide, b. p. 94-95°/62 mm., of this substance affords av-dimethylbutadiene when heated with quinoline at 155°. This butadiene combines with maleic anhydride in benzene, forming 3:5-dimethyl- Δ^4 -tetrahydrophthalic anhydride (V), m. p. 56-57°. The three hydrocarbons, C_6H_{10} , described by Harries (A., 1901, i, 194), Saytzev (A., 1877, ii, 298), and Kyriakides (A., 1914, i, 506), are all ay-dimethylbutadiene, since they react with maleic anhydride, yielding V. Isoprene, a-methyl-, By-dimethyl-, and ad-dimethylbutadienes combine with maleic anhydride to give 5-methyl-, m. p. 63—64°, 6-methyl-, m. p. 62°, 4:5-di-methyl-, m. p. 78—79°, and 3:6-dimethyl- Δ^4 -tetrahydrophthalic anhydrides, m. p. 95-96°, respectively; aay-trimethylbutadiene affords a compound, m. p. 49°.

CH-CH-CH-CH-CO/

Maleic anhydride and N-CH-CH-CH-CO NMe O methylpyrrole react slowly at the ordinary temperature, yielding the anhydride, m. p.

98-99°, possessing the annexed formula.

H. BURTON. Fenchene series. I. Ozonisation and con-titution of fenchenes. G. KOMPPA and R. H. stitution of fenchenes. G. KOMPPA and R. H. Roschier (Annalen, 1929, 470, 129-156).—Decomposition of an acetic acid solution of the ozonide from \hat{l}_{α} -fenchene (A., 1917, i, 398), by warming on the water bath, affords about 50% of d- α -fenchocamphorone, together with $1-\alpha$ -fenchenylanic acid (I), m. p. $71\cdot5-72^{\circ}$ (anilide, m. p. $149\cdot5-150^{\circ}$; various salts are described briefly), and the corresponding impure aldehyde. Dehydration of r-fenchyl alcohol

with potassium or sodium hydrogen sulphate at 180° gives a mixture of hydrocarbons, b. p. 145-160°, separated into the following fractions: (A) b. p. 151–153°, d_4^{17} 0.8598, n_D^{17} 1.46620 (nearly pure dl-β-fenchene), (B) b. p. 145–147°, d_4^{17} 0.8547, n_D^{17} 1.46072 [impure γ-fenchene (II; R=H, R'=Me)], and (C) b. p. 141–143°, d_4^{17} 0.8476, n_D^{17} 1.45424 [a mixture of δ - or 130-fenchene (II; R=Me, R'=H) and cyclofenchene]. Decomposition of the ozonide from A, in the above manner, yields dl-\$-fenchocamphorone (semicarbazone, m. p. 193-195°), oxidised by alkaline potassium permanganate to dl-apofenchocamphoric acid, m. p. 144-145° (various salts described). A small amount of cis-apocamphoric acid is obtained during the oxidation of an impure specimen of the ketone, showing that A contains some α -fenchene. β -Fenchocamphorone is identical with β -isocamphenilone (Nametkin and Chuchrikova, A., 1915, i, 701). fraction B contains some β -fenchene, since decomposition of the ozonide gives \$-fenchocamphorone in addition to 3-acetyl-5: 5-dimethylcyclopentanealdehyde, b. p. 118—120°/10 mm., d_4^{20} 1.0215, n_D^{20} 1.4700 [disemicarbazone, m. p. 219° (decomp.)], and 3-acetyl-5:5dimethylcyclopentanecarboxylic acid (III), d10 1.0924, ⁿ₅ 1.4774 (semicarbazone, m. p. 220—221°; various salts described). Oxidation of III with sodium hypobromite yields trans-apofenchocamphoric acid, m. p. 147-148° (cf. Nametkin, A., 1924, i, 1084). Ozonisation of fraction C affords small amounts of III and a ketone, C9H14O (semicarbazone, m. p. 209°), oxidised by alkaline potassium permanganate to a dicarboxylic acid, C₉H₁₄O₄, m. p. 117-118°, together with dl-cis-fenchocamphoric acid, m. p. 173-174°. This acid is obtained also by oxidation of C with potassium permanganate.

During the ozonisation of the hydrocarbon fractions, b. p. below 147°, cyclofenchene, b. p. 142-143°/752 mm., d_4^{165} 0.8624, n_D^{165} 1.45364 (hydrochloride, m. p. 26—28°; hydrobromide, b. p. 92—93°/12 mm., m. p. 4°), remains unchanged. Treatment of this with acetic and sulphuric acids gives the acetate, b. p. $89-90^{\circ}/10 \text{ mm.}, d_{4}^{20} 0.9648, n_{D}^{20} 1.45810, \text{ of isofenchyl}$ alcohol, b. p. 84.5-85°/10 mm., d4 0.9543, np 1.47664 (phenylcarbimide derivative, m. p. 94-96°), oxidised by potassium permanganate at 60° to *dl-iso*fenchone (Wallach, A., 1908, i, 809), and dl-cis-fenchocamphoric acid. cycloFenchene appears to be identical with β-pinolene (Aschan, A., 1912, i, 198). Physical constants for the five fenchenes are given.

H. BURTON.

Tricyclene series. G. KOMPPA (Ber., 1929, 62, [B], 1366-1370; cf. this vol., 192).-The following additional data are recorded : phenylurethane of tricyclenol, m. p. 86°; tricyclenyl chloride, b. p. 75–76°/6 mm., d_1^{xy} 1.0348, n_D^{xy} 1.49336; $\beta\omega$ -dichlorocamphane, m. p. 53-55°. H. WREN.

Synthesis of coumarin derivatives. II. R. WEISS and A. KRATZ (Monatsh., 1929, 51, 386-396).—The synthesis of coumarin derivatives by the interaction of *m*-dihydroxybenzene derivatives with ethyl ethoxymethyleneacetoacetate (I) in the presence of sodium ethoxide (this vol., 73) is extended, and it is found that ethyl ethoxymethylenemalonate (II) may be used in a similar manner. Thus with resorcinol II yields ethyl 7-hydroxycoumarin-3-carboxylate, m. p. 165-170°, but with 2-nitroresorcinol is obtained 7-hydroxy-8-nitrocoumarin, +0.5H2O, m. p. 228° [not identical with the 7-hydroxynitrocoumarin obtained by direct nitration (Clayton, J.C.S., 1910, 97, 1396)], together with a *tetrahydro*-(3:5:3':5' or 2:4:2':4')dinitro-(4:4' or 3:3')-diphenyl, darkening at 270°. With I, however, 7-hydroxy-3-acetyl-S-nitrocoumarin, m. p. 230-231° (decomp.), is obtained. Similarly with I, 4-chlororesorcinol yields 6-chloro-7-hydroxy-3-acetylcoumarin, m. p. 241-242° (p-toluenesulphonyl derivative, m. p. 160-161°). Condensation of 4-ethylresorcinol with acetic acid in the presence of anhydrous zinc chloride at 140° yields 5-ethylresacetophenone (III), m. p. 115°, which is reduced with amalgamated zinc and hydrochloric acid to 4:6-diethylresorcinol (IV), m. p. 65-71°, identical with the product obtained by similar reduction of 2:4-dihydroxy-1: 5-diacetylbenzene (Eijkman and others, A., 1905, i, 359). By condensation with I, IV yields 5-hydroxy-3-acetyl-6:8-diethylcoumarin, m. p. 192° (p-toluenesulphonyl derivative, m. p. 99°), which reacts with hydrazine hydrate to yield the azine, m. p. 214°, of the unknown 2:6-dihydroxy-3:5-diethylbenzaldehyde. Similar condensation of IV with II yields ethyl 5-hydroxy-6: 8-diethylcoumarin-3carboxylate, m. p. 156°, together with the corre-sponding free acid, m. p. 212°. Condensation of III with II yields ethyl 5-hydroxy-6(?8)-acetyl-8(?6)-ethylcoumarin-3-carboxylate, m. p. $180-185^{\circ}$, which is hydrolysed with alcoholic potassium hydroxide to the corresponding 5 - hydroxy - 6(8) - acetyl-8(6) - ethyl $coumarin, m. p. <math>180^{\circ}$. 4:6-Dichlororesorcinol, m. p. $108-109^{\circ}$, is obtained pure by rechlorination with sulphuryl chloride of the product obtained by the method described in the literature, which yields an indefinite mixture of mono- and di-chloro-compounds. It condenses with I to yield 6:8-dichloro-5-hydroxy-3-acetylcoumarin, m. p. $235-236^{\circ}$ (decomp.) (p-toluenesulphonyl derivative, m. p. $150-151^{\circ}$).

J. W. BAKER.

Styrylpyrylium salts. XI. Determination of the reactive group in ketones of the type $CH_3 \cdot CO \cdot CH_2 R$ by the benzo- β -naphthaspiropyran colour change. I. M. HEILBRON and F. IRVING (J.C.S., 1929, 936-946).-The reaction whereby benzo- β -naphthaspiropyrans substituted in the 3-position ionise on being heated in inert solvents giving coloured solutions, a reaction which is not observed with the isomeric 3'-substituted compounds, has been utilised in determining the mode of condensation of salicylaldehyde with ketones, CH₃·CO·CH₂R (cf. Dickinson and Heilbron, A., 1927, 884). The compound I obtained by Dickinson (A., 1926, 1144) by condensing salicylaldehyde with benzyl methyl ketone and a little piperidine condenses with 2-naphthol-1-aldehyde in the presence of absolute alcohol and dry hydrogen chloride to give 3-phenylbenzo-\beta-naphthaspiropyran, m. p. 208-209°, which is identical with the spiropyran obtaned from the condensation product of salicylaldehyde and benzyl methyl ketone in the presence of dry hydrogen chloride, and β-naphthol-1-aldehyde. This spiropyran gives a purple colour when heated in solvents of high b. p. and hence the condensation has taken place on the methylene group. The compound II, m. p. 145°, obtained by Dickinson (loc. cit.) from o-methoxybenzaldehyde, benzyl methyl ketone, and hydrogen chloride, and also a new isomeric compound, m. p. 180°, isolated in the same condensation, are bimolecular and are probably stereoisomeric cyclic compounds (cf. Japp and Maitland, J.C.S., 1904, 85, 1473). The structure of Gheorghiu and Arventiev's styryl isobutyl ketone III (A., 1928, 522) has been confirmed by synthesis from ethyl isopropylacetoacetate; the latter condenses with benzaldehyde and 8% aqueous sodium hydroxide to γ -benzylidene- α -isopropylacetoacetic acid, m. p. 134° (decomp.), decomposed by heating with copper powder to the ketone III, which was isolated as the semicarbazone, m. p. 167°. Methyl isobutyl ketone, salicylaldehyde, and 20% sodium hydroxide yielded 2-hydroxystyryl isobutyl ketone, m. p. 104°, which, with β -naphthol-1-aldehyde, gave 3'-isopropylbenzo- β -naphthaspiro-pyran, m. p. 118°; the last did not acquire colour when heated in solvents of high b. p. The same spiropyran is obtained by condensation of methyl isobutyl ketone and salicylaldehyde and hydrogen chloride, followed by reaction of the pyrylium salt with β-naphthol-1-aldehyde and hydrolysis. 3'-Octylbenzo-\beta-naphthaspiropyran, m. p. 101-102°, and 3-octyldi-β-naphthaspiropyran, m. p. 157°, were prepared from 2-hydroxystyryl nonyl ketone and methyl nonyl ketone, respectively. A. I. VOGEL.

Styrylpyrylium salts. XII. spiroPyrans from 9-methyl and 9-ethylxanthylium salts. F. IRVING (J.C.S., 1929, 1093-1095).-Condensation of 9-methylxanthenol and β-naphthol-1-aldehyde in the presence of hydrogen chloride afforded xanthoβ-naphthaspiropyran, m. p. 201°, which gave a red colour on heating in diphenyl ether (cf. preceding abstract). Benzoxanthaspiropyran, m. p. 154°, prepared from 9-methylxanthenol, salicylaldehyde, and hydrogen chloride, and 3'-methylxantho- β -naphtha-spiropyran, m. p. 271°, prepared from 9-ethylxanthenol, β-naphthol-l-aldehyde, and dry hydrogen chloride, do not give colours when heated in solvents of high b. p. The three spiropyrans give xanthylium salt colorations with trichloroacetic but not with acetic acid. A. I. VOGEL.

Hydroxyquinolsulphonephthalein (2:7-dihydroxysulphonefluorescein); 2:4:5-trihydroxybenzoylbenzene-o-sulphonic acid and derivatives. W. R. ORNDORFF and M. L. WILLARD (J. Amer. Chem. Soc., 1929, 51, 1466-1474).-Hydroxyquinol and o-sulphobenzoic anhydride (equal mols.) at 100° yield mainly 2:4:5-trihydroxybenzoylbenzeneo-sulphonic acid, m. p. 210° (optical properties; am-monium, barium, and zinc salts; also the tetrasodium salt and tetra-acetate of the tautomeric lactonic modification). When this is heated at 140°, with or with-out hydroxyquinol (1 mol.), it yields 2:7-dihydroxysulphonefluorescein (optical properties). This is best prepared from hydroxyquinol triacetate and o-sulphobenzoic anhydride at 140°; it is also formed from hydroxyquinol itself and the acid chloride or anhydride. The free fluorescein and the following intensely coloured derivatives (red or violet in solution): ammonium, barium, zinc, potassium, and aniline, m. p. above 300°, salts ; trimethyl ether (sodium salt), and dimethyl ether, are assigned quinonoid formulæ. The colourless tetra-acetate and tetrabenzoale are derived from the corresponding lactone. The fluorescein is brominated in ethyl alcohol to a dibromoderivative (triammonium salt, tetra-acetate) and condensed by sulphuric acid at 120° to violet "sulphoneviolein," $C_{19}\dot{H}_{10}O_7S$. Pale yellow 2:7-dihydroxy-sulphonefluorescin, obtained by reduction with zinc dust and formic acid, is readily oxidised and gives a tetra-acetate (silver salt). H. E. F. NOTTON.

Brazilin and hæmatoxylin. IX. Compounds of the phenoxyacetone series. P. PFEIFFER and J. WILLEMS (Ber., 1929, 62, [B], 1242-1250).-The action of zinc on a mixture of ethyl phenoxyacetate and ethyl bromoacetate gives ethyl y-phenoxyaceloacetate in 2-3% yield; the copper compound, m. p. 155.5-156° (decomp.), and p-nitrophenylhydrazone, m. p. 136-137°, are described. Addition of hydrogen cyanide to the ester affords the corresponding hydroxynitrile. Phenoxyacetyl chloride is converted by a suspension of methyl sodiomalonate in benzene into methyl phenoxyacetylmalonate, m. p. 51.5-52.5 (sodium salt; copper compound, m. p. 154.5°). Ethyl bromoacetate, ethyl m-methoxyphenoxyacetate, and zinc yield ethyl y-m-methoxyphenoxyacetoacetate, b. p. 176°/0.2 mm. (copper salt, m. p. 121°), which, with hydrocyanic acid and aqueous potassium cyanide, affords the corresponding cyanohydrin (non-crystalline

benzoyl derivative). Hydrolysis of the cyanohydrin with boiling, concentrated hydrochloric acid gives y-m-methoxyphenoxycitramalic acid,

 $OMe \cdot C_6 H_4 \cdot O \cdot CH_2 \cdot C(OH)(CO_2H) \cdot CH_2 \cdot CO_2H$ (calcium salt). m. Methoxyphenoxyacetyl chloride, b. p. 145-146.5°/15 mm., from the acid and phosphorus triand penta-chlorides, is converted by methyl sodiomalonate in benzene into methyl m-methoxyphenoxyacetylmalonate, m. p. 55-56°. 2:3-Dimethoxyphenoxyacetic acid, m. p. 102.5-103°, prepared from chloroacetic acid and pyrogallol 2:3-dimethyl ether in alkaline solution, is converted into the corresponding chloride, m. p. 162°/12 mm., which is condensed with methyl sodiocyanoacetate to methyl cyano-2: 3dimethoxyphenoxyacetylacetate, m. p. 87-88°. A mixture of phenylacetonitrile and ethyl phenoxyacetate is converted by alcoholic sodium ethoxide into y-phenoxy-a-phenylacetoacetonitrile, m. p. 126-127°, converted by methyl-alcoholic hydrogen chloride into methyl y-phenoxy-a-phenylacetoacetate, m. p. 75.5-76°; the ester reacts as a homogeneous ketone, but is partly enolised when melted. Boiling, concentrated, aqueous hydrochloric acid transforms the keto-ester into y-phenoxy-a-phenylacetone, m. p. 43-44°, which does not give a coloration with ferric chloride; the corresponding phenylhydrazone, m. p. about 94-96° after softening at about 65°, and semicarbazone, m. p. 151-152°, are described. The cyanohydrin has m. p. 94-95° after softening at about 83°. H. WREN.

Gossypol. V. Action of chromic acid on gossypol derivatives. VI. Action of boiling hydriodic acid on gossypol and derivatives; semi-micro Zeisel methoxyl method. E. P. CLARK (J. Amer. Chem. Soc., 1929, 51, 1475-1478, 1479—1483; cf. A., 1928, 208, 426, 1016).—Gossypol hexa-acetate in acetic acid is oxidised by aqueous chromic acid to bright yellow gossypolone tetra-acetate, C25H18O4(OAc)4, darkening from 210°, charring at 230° [dianil, m. p. 255-256° (corr.), softening from 250°]. This corresponds with the removal of C5H8 from, and formation of two new quinonoid carbonyl groups in, the gossypol nucleus. apoGossypol hexaacetate is oxidised in acetic acid by Kiliani's chromic acid mixture (A., 1913, i, 381) to apogossypolone tetraacelate, C22H16O2(OAc)4, m.p. 230°, sintering from 220°, which does not condense with aniline. apoGossypol hexamethyl ether is oxidised by this reagent to yellow ⁶gossypolone tetramethyl ether, C₂₈H₂₂O₄(OMe)₄, m. p. 210° (corr.). This change involves the formation of four quinonoid carbonyl groups without loss of carbon from the apogossypol skeleton. The optical properties of the new compounds are described.

The high results obtained in the determination of methoxyl in methylated gossypol derivatives by the Weishut-Zeisel method (A., 1913, ii, 78) have been traced to the formation of a volatile iodide by the action of the hydriodic acid on part of the gossypol skeleton. This iodide, which has been shown to differ from methyl iodide (cf. Willstätter and Utzinger, A., 1911, i, 659), is also obtained from gossypol derivatives which contain no alkoxyl groups. Apparatus and methods are described suitable for the determination of methoxyl in 20 mg. samples, using an ordinary balance. H. E. F. NOTTON.

Conjugated unsaturated compounds. IX. Colouring matter from alkekengi (Physalis alkekengi and P. franchetti). R. KUHN and W. WIEGAND (Helv. Chim. Acta, 1929, 12, 499-506; cf. Kylin, A., 1927, 669).-Extraction of the dry sepals with benzene and subsequent purification gives 0.9-1.8% of physalien (I), $\hat{C}_{60}H_{96}O_4$, m. p. 97° (uncorr. block), orange-red in transmitted light, also isolated from the skins of the berries (0.05% of wt. of fresh fruit). Treatment of I with iodine in ether gives a di-iodide, whilst the amount of hydrogen absorbed, during reduction in presence of platinum oxide and acetic acid, corresponds with eleven double linkings. Perhydrophysalien is colourless. Oxidation of I with potassium permanganate (cf. this vol., 425) gives 5 mols. of acetic acid showing the presence of five methyl groups. Colour reactions of I with various reagents are given. H. BURTON.

Thionaphthens. K. FRIES and E. HEMMECKE (Annalen, 1929, 470, 1-19).-Nitration of thionaphthen in acetic acid solution at 50-110° affords 2-nitrothionaphthen, m. p. 81°, reduced by stannous chloride and hydrochloric acid to 2-aminothionaphthen (I) (acetyl derivative, m. p. 168°). When I or its stannichloride (II) is heated with dilute mineral acid, 2-hydroxythionaphthen results (cf. Friedländer, A., 1907, i, 334), but when II is treated with 40% sodium hydroxide solution, or I is distilled in a vacuum, ammonia is evolved and 2: 2'-di(thionaphthenyl)amine, m. p. 117°, is obtained. Reduction of 2-nitrothionaphthen with sodium disulphide in boiling alcohol affords the sodium salt (III) of the aci-form of 2:2'dinitro-1: 1': 2: 2'-tetrahydro-1: 1'-di(thionaphthenyl) (IV), m. p. 126°. Oxidation of III with bromine water or alkaline potassium ferricyanide yields 2-nitrothionaphthen, whilst reduction with stannous chloride and hydrochloric acid gives 2:2'-diamino-1:1'-di-(thionaphthenyl), m. p. 238° (decomp.) [hydrochloride ; diacetyl derivative, m. p. 346° (decomp.)]. This is oxidised by alkaline potassium ferricyanide to di-



iminothioindigo (annexed formula), m. p. 228° (decomp.) (hydrochloride; diacetyl derivative, m. p. 285°, prepared only by similar oxidation ² of the corresponding diacetamido-

derivative): reduction of these imino-compounds regenerates the original substances. Reduction of IV with stannous chloride and hydrochloric acid yields a mixture of 2:2'-diamino-1:1':2:2'-tetrahydro-1:1'-di(thionaphthenyl), m. p. 156° (hydrochloride, decomp. 338°; acetyl derivative, m. p. 365°), 2-amino-1:2-dihydro-1:1'-di(thionaphthenyl), m. p. 83-5° (hydrochloride; acetyl derivative, m. p. 231°), and 1:1'-di(thionaphthenyl) (V), m. p. 262°. Treatment of these two amines with nitrous acid affords V. Nitration of V with nitric acid (d 1.52) in acetic acid solution below 8° gives 2-nitro-1:2-dihydro-1:2'di(thionaphthenyl), m. p. 161° (decomp.), which when reduced with stannous chloride and hydrochloric acid yields the corresponding amino-derivative, m. p. 271° [(decomp.); acetyl derivative, m. p. 225°; hydrochloride, m. p. 298° (decomp.)], together with 1:2'di(thionaphthenyl), m. p. 76°, also formed from the amine by the action of nitrous acid. The production of III from 2-nitrothionaphthen is postulated: $2 \cdot CH:\dot{C}\cdot N(:0):O+2H \longrightarrow 2 \cdots \dot{C}H\cdot\dot{C}:N(:0)\cdot OH \longrightarrow$ $|\dot{C}H\cdot\dot{C}:N(:O)\cdot OH|.$ H. BURTON.

Methoxy-derivatives of thioxanthone. K. C. ROBERTS and S. SMILES (J.C.S., 1929, 863-872).-Condensation of 2-thiolbenzoic acid and 4-iodoanisole in the presence of amyl alcohol, potassium carbonate, and copper acetate yielded 2'-carboxy-4-methoxydi-phenyl sulphide, I, m. p. 232°. 2'-Carboxy-3: 4-di-methoxydiphenyl sulphide, m. p. 212-213°, and 2'carboxy-5-methoxy-2-methyldiphenylsulphide, m. p. 176-177°, were similarly prepared by condensation of 2-thiolbenzoic acid with 4-aminoveratrole and 2-iodo-4-methoxytoluene, b. p. 252-253° (from 4-methoxy-o-toluidine), respectively. The by-product, m. p. 112°, formed in the reduction of 2-nitro-4-methoxytoluene with tin and hydrochloric acid is chloro-4methoxy-o-toluidine, and not 4-methoxy-o-toluidine (Limpach, A., 1889, ii, 698). Sulphuric acid and I afforded 2-methoxythioxanthone (*perchlorate*), m. p. 129°. Treatment of a mixture of 2-thiolbenzoic acid and 4-chloroanisole with sulphuric acid gave 1-chloro-4-methoxythioxanthone, m. p. 196°, since further treatment with p-toluidine in the presence of potassium and copper acetates readily furnished 1-p-toluidino-4methoxythioxanthone, m. p. 133°. 4-Methoxy-1-methylthioxanthone, m. p. 162°, was similarly prepared from 4-methoxytoluene. 1-Methoxy-4-methylthioxanthone, m. p. 128° (hydrochloride; perchlorate), was prepared by dehydration of 2'-carboxy-3-methoxy-6-methyldiphenyl sulphide with sulphuric acid. 1:4-Dimethoxythioxanthone (Clarke and Smiles, J.C.S., 1911, 99, 1539) yields a dihydrochloride, a chloroplatinate, a ferrichloride, and a perchlorate. Condensation of 2-bromoveratric acid and thiophenol in the presence of amyl alcohol, potassium carbonate, and copper 6-carboxy-2: 3-dimethoxydiphenyl acetate gave sulphide, which furnished 3: 4-dimethoxythioxanthone, m. p. 185° (perchlorate), with sulphuric acid. Reaction of pyrocatechol with 2-thiolbenzoic acid in sulphuric acid yielded a dihydrothioxanthone (diacetyl derivative, m. p. 191°), aqueous alkaline methylation of which yielded the dimethoxy-derivative, m. p. 172°, identical with 2:3-dimethoxythioxanthone, m. p. 172° (hydrochloride; two ferrichlorides), obtained by dehydrating 2'-carboxy-3: 4-dimethoxydiphenyl sulphide with sulphuric acid or by condensing veratrole with 2-thiolbenzoic acid in sulphuric acid. Its structure was confirmed by treatment with boroacetic anhydride and acetic anhydride, when the diacetyl derivative, m. p. 191°, and not a co-ordinated diacetoborate was obtained (cf. Dimroth, A., 1922, i, 155; 1926, 297). 1:2-Dimethoxythioxanthone, a byproduct in the preparation of the 2:3-derivative, has m. p. 143-144° (hydrochloride; perchlorate). Interaction of 1:2:3-trimethoxybenzene and 2-thiolbenzoic acid in sulphuric acid afforded 2:3:4-trimethoxythioxanthone, m. p. 150°, identical with the product obtained from 1-iodo-2:3:4-trimethoxybenzene and 2-thiolbenzoic acid (cf. Ullmann and Sone, A., 1911, i, 739, who give m. p. 153-154°). The relative stabilities of the hydrochlorides derived from the thioxanthones were investigated by a modification of Baeyer and Villiger's method (A., 1902, i,

769) and were shown to be in qualitative agreement with the tendency to salt-formation with dry hydrogen chloride at atmospheric pressure and temperature. A. I. VOGEL.

Arylamides of lævulic acid. R. LUKES and V. PRELOG (Coll. Czech. Chem. Comm., 1929, 1, 282-287).-It has been concluded that the "lævulamide" formed by the interaction of ammonia with 2-methyl-5-keto-4: 5-dihydrofuran ($\Delta^{\beta\gamma}$ -angelicalactone) (Wolff, A., 1885, 1123) cannot have a pyrrolidone structure (Beilstein, 4th ed., Vol. III, 676), since the product from methylamine and $\Delta^{\beta\gamma}$ -angelical actone is not identical with the pyrrolidone obtained from magnesium methyl bromide and N-methylsuccinimide (A., 1928, 299; this vol., 576). This conclusion is supported by the non-identity of "lævulanilide," m. p. 102° (I), prepared from $\Delta^{\beta_{\gamma}}$ -angelical actone and aniline, or from γ -acetoxy- γ -valerolactone, aniline, and water, with 2-hydroxy-1-phenyl-2-methylpyrrolid-5-one, m. p. 101° (II), which is obtained (accompanied by 1-phenyl-2: 5-dimethylpyrrole) by the interaction of magnesium methyl bromide with N-phenylsuccinimide. Aniline reacts with I in boiling toluene to yield lævulanilide anil, m. p. 145° (decomp.), which is readily hydrolysed to lævulanilide and aniline by water. Aniline does not condense with II. Hydrolysis of II by boiling, dilute sulphuric acid yields aniline and lævulic acid. The following "arylamides of lævulic acid "have also been prepared from $\Delta^{B_{\gamma}}$ angelicalactone or γ -acetoxy- γ -valerolactone: p-toluidide, m. p. 108—109°, α -naphthylamide, m. p. 105-106°, β-naphthylamide, m. p. 107-108°.

R. K. CALLOW. Acridone derivatives. W. LÉSNIANSKI (Bull. Acad. Polonaise, 1929, A, 81-88).-Condensation of 2-chloro-5-nitrobenzoic acid with p-anisidine in glycerol in the presence of anhydrous potassium carbonate and copper-bronze gave 4-nitro-4'-methoxydiphenylamine-2-carboxylic acid, m. p. 230.5° (potassium salt), which was converted into 3-nitro-7-methoxyacridone, m. p. 395°, when heated with phosphorus oxychloride at 115° (sulphuric acid is unsatisfactory). The following compounds were similarly prepared: 4-nitro-4'-ethoxydiphenylamine-2-carboxylic acid (from chloronitrobenzoic acid and p-phenetidine; ammonium salt), m. p. 213-214°, and 3-nitro-7-ethoxyacrid-one, m. p. 378° [the corresponding hydroxy-compound (sublimes above 360°) was produced with sulphuric acid at 140°]; N-4-nitrophenyl-a-naphthylamine-2carboxylic acid, m. p. 266° (from a-naphthylamine and chloronitrobenzoic acid) and 9-nitro-a-phen-naphthacridone, m. p. 382° ; N-4-nitrophenyl- β -naphthyl-amine-2-carboxylic acid, m. p. $284-285^\circ$, and 10-nitro- β -phen-naphthacridone, m. p. 440° . A. I. VOGEL.

Constitution of Guareschi's cyano-butadiene acids. Attempt to synthesise β -isopropylglutaconic acid. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1929, 1074—1080).—Various cyano-acids described by Guareschi are in reality dihydroxypyridines. The condensation of isobutaldehyde and ethyl cyanoacetate gave the animonium salt of 2:6-dihydroxy-3:5-dicyano-4-isopropylpyridine, hydrolysis of which by 60% sulphuric acid gave 2:6-dihydroxy-4-isopropylpyridine, m. p. 213—214° (hydrochloride; di-p-nitrobenzoyl derivative, m. p. 200– 201°; oxime, m. p. 123–124°), accompanied by a little 2 : 6-dihydroxy-3-cyano-4-isopropylpyridine, m. p. 273° (monohydrate, lost $1H_2O$ at 110°). Similarly, the condensation of acetaldehyde and ethyl cyanoacetate led to the ammonium salt of 2 : 6-dihydroxy-3 : 5-dicyano-4-methylpyridine and, by hydrolysis of this, to 2 : 6-dihydroxy-4-methylpyridine (Rogerson and Thorpe, J.C.S., 1905, 87, 1685).

An attempt to remove hydrogen bromide from ethyl α -bromo- β -isopropylglutarate, b. p. 178°/30 mm., by boiling with diethylaniline led mainly to the ethyl ester of the lactone of dl- α -hydroxy- β -isopropylglutaric acid, b. p. 178°/26 mm., n_{D}^{20} 1.4466, from which dl-isopropylsuccinic acid was obtained by oxidation; small quantities of ethyl isopropylglutarate were also obtained. R. J. W. LE FÈVRE.

Nitration of N-2-pyridyl-N'-ethylcarbamide. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 545— 547).—By heating 2-aminopyridine and ethyl carbimide in ether at 100°, N-2-pyridyl-N'-ethylcarbamide, m. p. 119°, is obtained. Nitration of this with either absolute nitric acid or mixed acids probably yields N-nitro-N'-2-pyridyl-N-ethylcarbamide, but on pouring the nitration mixture into water it decomposes, yielding 2-aminopyridine, ethylnitroamine, and carbon dioxide. J. W. BAKER.

Indole halogeno-ketones. I. G. SANNA (Gazzetta, 1929, 59, 169-181).-The action of chloroacetyl chloride on 2-methylindolyl magnesium bromide in anhydrous ether furnishes 3-w-chloroacetyl-2-methylindole, m. p. 220°, which gives a N-silver derivative, and a phenylhydrazone, m. p. 134°. With pyridine the chloride gives 2-methyl-3-indolacylpyridinium chloride, m. p. 332° (hydroxide prepared), and with quinoline, a quinoline derivative. Similarly, bromoacetyl chloride yields 3-ω-bromoacetyl-2-methylindole, m. p. 204° (silver, pyridine, and quinoline derivatives). Either the chloride or the bromide may be oxidised by alkaline potassium permanganate to o-acetamidobenzoic acid, with a substance, m. p. 156°, and may be converted by fusion with potassium hydroxide to 2-methylindole-3-carboxylic acid. 3-w-Iodoacetyl-2-methylindole has also been prepared. E. W. WIGNALL.

Derivatives of 8-aminoquinoline. R. P. DIKS-HOORN (Rec. trav. chim., 1929, 48, 517-544; cf. this vol., 452) .--- 8-Aminoquinoline and ethylcarbimide heated in ethereal solution at 100° yield N-8-quinolyl-N-ethylcarbamide (I), m. p. 176° (181° on remelting), which is nitrated by absolute nitric acid at -15° to N-nitro-N'-5-nitro-8-quinolyl-N-ethylcarbamide (II),m.p.145°. This, when freshly prepared, is converted by boiling with water into 5-nitro-8-aminoquinoline, m. p. 197° [the substance obtained by Claus and Hartmann (A., 1896, i, 391), not being this compound] (converted by elimination of the amino-group into 5-nitroquinoline), and 5-nitroquinoline-8-carbamic acid, m. p. about 300°. Esterification of the latter with methyl or ethyl alcohol vields, respectively, methyl, m. p. 210°, and ethyl, m. p. 115° (121° on remelting) 5-nitroquinoline-8-carbamate. The same esters are obtained by the action of the appropriate alcohol on II or V (below), and by nitration with absolute nitric acid below 0° of, respectively, methyl, m. p. 46°, and ethyl, m. p. 66°, quinoline-

8-carbamate (III), which, in turn, are obtained by the action of the alkyl chloroformate on 8-aminoquinoline in the presence of powdered potassium carbonate. By the action of N-alcoholic ammonia on II at 100° is obtained N-5-nitro-8-quinolyl carbamide, m. p. 245° (decomp.). When I is nitrated with mixed acids below 0° and the product poured on to ice it is decomposed with the formation of 5:7-dinitroquinoline-8-carbamic acid, m. p. 230° (decomp.) (the presence of ethylnitroamine is proved by the isolation of its barium salt from the aqueous liquors). This is converted by 50% sulphuric acid at 100° into 5:7-dinitro-8-aminoquinoline (Claus and Dewitz, A., 1896, i, 654) and by boiling with methyl and ethyl alcohol into, respectively, methyl, m. p. 205°, and ethyl, m. p. 195°, 5:7-dinitroquinoline-8-carbamate. When the methyl and ethyl esters III are nitrated with mixed acids they also yield methyl and ethyl 5:7-dinitroquinoline-8-carbamates, but the specimens prepared in this manner have m. p. 190° and 166-167°. respectively. Evidence is given to prove that in these pairs of esters the orientation of the nitro- and carbamate groups is identical, and it is suggested that the isomerism may be due to the existence of a quinonoid form, the nitro-group existing in its aci form, and in agreement with this view it is possible to convert the higher into the lower m. p. forms by heating with the alcoholic hydrogen chloride at 100°. When 8-aminoquinoline reacts with potassium cyanate and dilute hydrochloric acid it yields 8-quinolylcarbamide (IV), m. p. 223-224°, together with 8-quinolylbiuret. m. p. 250-252°, the amount of the latter formed being negligible if acetic acid at low temperatures is used. Nitration of IV with absolute nitric acid under special conditions yields N-nitro-N'-5-nitro-8-quinolylcarbamide (V), decomp. 190°. When 8-aminoquinoline and its nitro-derivatives are diazotised in concentrated sulphuric acid and the solution of the diazonium sulphate is poured into water or cold, dilute potassium hydrogen carbonate solution, the diazohydroxide is immediately converted into a stable product which, the author suggests, is the anti-diazohydroxide (I).

N OH N N (I.)

Thus from the appropriate 8-aminoquinoline are obtained: quinoline-, decomp. 145°, 5-nitroquinoline-, decomp. 185°, and 5: 7(I.) dinitroquinoline-, decomp. (with spontaneous ignition) 155°, -8-anti-diazohydr-

oxides. These compounds do not give the characteristic reactions of diazonium or syn-diazo-compounds, but the 5-nitro-compound is converted by 60%sulphuric acid into the reactive syn-form, which then couples with β -naphthol, whilst in 48% hydrobromic acid solution it yields 8-bromo-5-nitroquinoline by the Sandmeyer reaction. J. W. BAKER.

Quinolyl-2: 4-dinitronaphthylamines. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 548—549).— 8-Aminoquinoline condenses with 1-chloro-2:4-dinitronaphthalene in alcohol at 100° to yield N-8-quinolyl-2:4-dinitro- α -naphthylamine, m. p. 196°. The corresponding N-5-quinolyl-2:4-dinitro- α -naphthylamine, m. p. 195°, can be obtained only by fusing together the two reactants at 100—150°. J. W. BAKER.

Halogenodinitroquinolines. R. P. DIKSHOORN (Rec. trav. chim., 1929, 48, 550-559).—In agreement

with the literature, nitration of 5- and 8-bromoquinoline (obtained by the Sandmeyer reaction from the corresponding aminoquinoline) yield, respectively, a mixture of 5-bromo-6- and -8-nitroquinolines and 8-bromo-5-nitroquinoline. Attempts to introduce a second nitro-group were unsuccessful. Thus 5-bromo-6-nitroquinoline, when warmed with mixed acids yields (probably) 3:5-dibromo-6-nitroquinoline, m. p. 186° and 5-bromo-8-nitroquinoline similarly yields 3:5-dibromo-8-nitroquinoline, m. p. 195°, oxidation of a portion of the original material yielding quinolinic acid (isolated as its copper salt) and bromine, the latter attacking more of the original material to yield the dibromo-compound. The product obtained by nitration of 8-bromoquinoline (Claus and Howitz, A., 1893, i, 668), in agreement with these authors, is proved to be the 5-nitro-derivative, since the same product is obtained by the Sandmeyer reaction from 5-nitro-8-aminoquinoline (this vol., 825). 5:7-Dinitro-8-hydroxyquinoline, decomp. 325° (obtained pure by nitration of 8-hydroxyquinoline under prescribed conditions), is converted, in small yield, by the method of Ullmann and Nádai (A., 1908, i, 525), into 8-chloro-5:7-dinitroquinoline, m. p. 154°. J. W. BAKER.

Quinaldinic acid. T. W. J. TAYLOR (J.C.S., 1929, 1110—1111).—When copper quinaldinate (Reissert, A., 1905, i, 472) is boiled with sufficient 2N-sodium hydroxide to convert all copper present into copper oxide, and filtered, 85% of the product separates as sodium quinaldinate (*hydrate* with 1.5H₂O) on cooling. The salt can be recrystallised from dilute sodium hydroxide, or from 95% alcohol, and yields the acid by acidification. The hydrate is converted into the anhydrous salt at 140—150°, or in a vacuum over calcium chloride. C. W. SHOPPEE.

Synthetic drugs [quinoline and pyrazolone derivatives]. H. P. KAUFMANN.—See B., 1929, 452.

Arylamides of aromatic carboxylic and sulphonic acids. K. HELLER (J. pr. Chem., 1929, [ii], 121, 193-203).-[With H. STURM.]-The following amino-derivatives have been prepared, usually by reduction of the corresponding nitro-compounds with iron and dilute acetic acid : 1-aminonaphthalene-5-, -6-, -7-, and -8-sulphonanilides, m. p. 171°, 127-128° 146-147°, and 139-140°, respectively; the 4-sulphonanilide, m. p. 190°, is obtained by hydrolysis of the corresponding acetyl derivative (Schröter, A., 1906, i, 415) with 0.5N-alcoholic potassium hydroxide solution; 2-amino-p-toluenesulphon-p-toluidide, m. p. 128°, -o-toluidide, m. p. 148°, and -o-anisidide, m. p. 128°. 2-Nitro-p-toluenesulphon-o-anisidine has m. p. 135°. When 2-acetoxynaphthalene-6-sulphonyl chloride, m. p. 107°, is treated with aniline, and the acetyl group eliminated by Zincke's method (A., 1918, i, 220), β -naphthol-6-sulphonanilide, m. p. 104°, results. α -Naphthol-5-sulphonanilide, m. p. 200°, is prepared similarly from 1-acetoxynaphthalene-5-sulphonyl chloride, m. p. 129°. o-Chlorobenz-p-nitroanilide and p-nitrobenz-o-chloroanilide, m. p. 160°, are obtained by a slightly modified Schöpff's reaction (A., 1892, 1476). The former compound is reduced by iron and dilute acetic acid to the p-aminoanilide, m. p. 153°, and the latter by sodium hyposulphite to the amino-

derivative, m. p. 145°. 2-Amino-3-naphthanilide, m. p. 192° (β-naphthylamide, m. p. 110°), is also described. Diazotisation of the anilides containing a free amino-group and subsequent reduction with alkaline sodium pyrosulphite or sodium hydrogen sulphite affords the corresponding phenylhydrazine, isolated as the hydrochloride. Condensation of this with ethyl acetoacetate or benzoylacetate in presence of sodium acetate and acetic acid yields 1-substituted phenyl-3-methyl(or phenyl)-5-pyrazolones. Thus, 3-methylphenylhydrazine-6-sulphon-o-toluidide hydro. chloride, m. p. 199°, gives 1-m-tolyl-3-methyl-5. pyrazolone-6'-sulphon-o-toluidide, m. p. 116° (the corresponding -p-toluidide derivatives have m. p. 168° and 129°, respectively); 3-p-toluenesulphonamidophenylhydrazine hydrochloride, m. p. 179-180°, furnishes 1-3'-p-toluenesulphonamidophenyl-3-methyl-5-pyrazolone, m. p. 147° (3-phenyl derivative, m. p. 168°); 3-methylphenylhydrazine-6-sulphon-o-anisidide hydrochloride, m. p. 196°, affords 1-m-tolyl-3-methyl-5-pyrazolone-6'-sulphon-o-anisidide, m. p. 118°; phenylhydrazine-4-carboxyanilide hydrochloride, m. p. 235°, yields 1-phenyl-3-methylpyrazolone-4'-carboxyanilide, m. p. 271°; p-benzamidophenylhydrazine hydrochloride, m. p. 273°, gives the corresponding 3-methyl-, m. p. 233°, and 3-phenyl-pyrazolones, m. p. 268°; phenylhydrazine-4-carboxy-o-chloroanilide hydrochloride, m. p. about 180°, furnishes 1-phenyl-3-methylpyrazolone-4'-carboxy-o-anilide, m. p. 231° (3-phenyl derivative, m. p. 238°); β -naphthylhydrazine-3-carboxyanilide hydrochloride, m. p. 110°, affords 1-3-naphthyl-3-methylpyrazolone-3'-carboxyanilide, m. p. 179° (3-phenyl derivative, m. p. 186°) (the corresponding β-naphthylamide derivatives have m. p. 145°, 129°, and 155°, respectively); p-(2-hydroxy-3-naphthamido)phenylhydrazine hydrochloride, decomp. 295°, yields the corresponding methyl-, m. p. 310° (decomp.), and phenyl-pyrazolones, m. p. 195° (decomp.). m.(2-Hydroxy-3-naphthamido)phenylhydrazine hydrochloride, m. p. 175°, gives the corresponding methyl- and phenylpyrazolones, m. p. 203-205° and 194°, respectively. Many of the pyrazolone derivatives couple with diazocompounds to give alkali-insoluble dyes.

H. BURTON.

I. Benzoyl Glyoxaline fission products. derivative of diaminoethylene and its conversion into a glyoxalone. P. RUGGLI, R. RATTI, and E. HENZI (Helv. Chim. Acta, 1929, 12, 332-361).-Contrary to the statement of Oddo and Mingoia (A., 1927, 260), Bamberger and Berlé's observation (A., 1893, i, 437) that Schotten-Baumann benzoylation of glyoxaline gives dibenzamidoethylene is confirmed. The a-form (I), m. p. 202-203°, of this is converted into the β-form (II), m. p. 280-290° (decomp.), by boiling with alcohol (cf. Bamberger and Berle, loc. cit.). Reduction of I with hydrogen in presence of palladium or a nickel catalyst and aqueous alcohol yields dibenzamidoethane, whilst treatment of I or II with bromine, directly or in chloroform or tetrachloroethane solution, affords a dibromide (III), decomp. 177° after sintering at 148°. This is converted by treatment with alcohol into two forms of s-dibenzamidodiethoxyethane, m. p. 190-191° (decomp.) and 219° (decomp.), respectively. With isobutyl alcohol a corresponding diisobutoxy-derivative, m. p. 214-215° with darken-

ing, and a small amount of a substance of lower m. p., result. Treatment of III with ethylene glycol gives 2:3-dibenzamido-1:4-dioxan, m. p. 247-248° (decomp.), whilst decomposition with aqueous acetone afford's s-dibenzamidoethylene glycol, m. p. 169-170° (decomp.; diacetate, m. p. 153-154°; bisphenyl-carbimide derivative, m. p. 193-194°). This is decomposed by methyl-alcoholic potassium hydroxide. s-Dibenzamidodianilinoethane has m. p. 211-212°. When III is treated with cold pyridine an additive compound, $+3C_5H_5N$, m. p. 143—145° becoming yellow at 140°, is produced; with hot pyridine, 1-benzoyl-2-phenyl-4-glyoxalone (IV), m. p. 184° (picrate, m. p. 182-183°), results by loss of 2 mols. of hydrogen bromide. This is soluble in alkali hydroxide or carbonate, affords the double salt.

 $2C_{16}H_{12}O_2N_2$, AgNO₃, decomp. 171° after sintering at 167° and darkening at 140°, and yields a *methiodide*, m. p. 194° (decomp.). Hydrolysis of IV with cold concentrated sulphuric acid gives hippurbenzamide, m. p. 185° (lit. 179°), hippuric and benzoic acids. Bromination in chloroform solution furnishes 5-bromo-1-benzoyl-2-phenyl-4-glyoxalone, m. p. 163-164° (decomp.), and treatment of the sodium salt of IV with benzyl bromide in presence of benzene yields 1-benzoyl-2-phenyl-5-benzyl-4-glyoxalone (V), m. p. 176-177° [picrate, m. p. 128-135°; hydrochloride (VI), m.p. 180-181°; dibenzyl derivative, m.p. 111-112°]. Hydrolysis of V with 15% hydrochloric acid gives N-benzoylphenylalanine, m. p. 182-183°, and phenylalanine. 1-Benzoyl-2-phenyl-5-p-bromobenzyl-4-gly-oralone, m. p. 212-213°, is hydrolysed to p-bromo-phenylalanine, decomp. 245° after sintering at 225°. When IV is coupled with diazosulphanilic acid in presence of pyridine and sodium hydroxide an orangered compound, C22H15O5N4SNa,4H2O (free acid +3H2O, m. p. 130° resolidifying with decomp. at 195°), results. Benzyl hippurate, m. p. 91-92° (lit. 85.5-80°), and benzyl aminoacetate hydrochloride are described. When VI is heated at 190-195° for a short time, acid vapours are evolved and a substance, m. p. 257-258°, isomeric with V, is produced. Formation of IV from III occurs presumably by loss of water from the hydroxyl and substituted aminogroups of the enol form, elimination of 1 mol. of hydrogen bromide, replacement of bromine by wdroxyl, and subsequent ketonisation.

Glyoxaline fission products. II. Production a glyoxaline solution and glyoxaline fission roduct. P. RUGGLI and E. HENZI (Helv. Chim. Acta, 1929, 12, 362-364).-Glyoxal sulphate, prepared from tetrachloroethane and fuming sulphuric and (A., 1923, i, 896), is treated with formaldehyde ammonia in aqueous solution below 55°. Schotten-Baumann benzoylation of this solution ares a-dibenzamidoethylene, m. p. 202°, showing Intial formation of glyoxaline and subsequent fission. H. BURTON.

New methylcytosine. F. H. CASE and A. J. HLL (J. Amer. Chem. Soc., 1929, 51, 1590-1592).-6-Chloro 2-ethylthiolpyrimidine (Wheeler and Johnson, A., 1903, i, 526) and methylamine in absolute alcohol give at 50-60° the hydrochloride, m. p. 216°, of 6-methylamino-2-ethylthiolpyrimidine (I), m. p. 3н

58°, and at 150° the hydrochloride, m. p. 262°, of 2:6-dimethyldiaminopyrimidine, m. p. 132°. The amine, I, is hydrolysed by concentrated hydrochloric acid to the hydrochloride, decomp. 320°, of 6-methylamino-2-hydroxypyrimidine, m. p. 270° (picrate, m. p. 220-225°), which gives a purple coloration with bromine water and barium hydroxide (cf. A., 1907, ii, 826). H. E. F. NOTTON.

New aryliminoketo $-\gamma - [1:3:5]$ - triazidine derivatives. A. OSTROGOVICH and V. BENA MEDIAN (Gazzetta, 1929, 59, 181-198, 198-200).-The condensation of benzaldehyde with guanylcarbamide (A., 1909, i, 461) is repeated with substituted benzaldehydes, and the corresponding 4-imino-2-keto-6-aryl-1:3:5-triazidines (hexahydrotriazines) are obtained. Thus o-nitrobenzaldehyde and guanylcarbamide sulphate yield the sulphate, m. p. 249-250° (decomp.), of the 6-o-nitrophenyl compound, m. p. 208-209°, which darkens in daylight, and gives the salts: hydrochloride, $[+H_2O]$, m. p. 235-236° (decomp.); abnormal chloroplatinate, 235–236° (decomp.); abnormal chloroplatinate, PtCl₄(C₉H₉O₃N₅,HCl)₄ or [PtCl₈](H·C₉H₉O₃N₅)₄, m. p. 233–234°; nitrate, m. p. 216–218° (decomp.); picrate, m. p. 213–215°; dipicrate; complex silver salt, [Ag(C₉H₉O₂N₅)₂]NO₃, m. p. 200° (decomp.) (obtained by treating the base with silver nitrate); and silver salt, C₉H₈O₃N₅Ag (?) (obtained in the presence of ammonia). m-Nitrobenzaldehyde yields the sulphate, m. p. 257–258° (decomp.), of the 6-m-nitrophenyl compound, m. p. 222°, which is less sensitive to light, and gives : hydrochloride, m. p. 268°: normal chloroplatinate, m. p. 255–256° ress sensitive to high, and gives *high* 255-256° (decomp.); nitrate, m. p. 250° (decomp.); nitrate, m. p. 250° (decomp.); picrate, $[+H_2O]$, m. p. 210-211°; dipicrate; and silver salts, $[Ag(C_9H_9O_3N_5)_2]NO_3$ and $C_9H_8O_3N_5Ag$; and p-nitrobenzaldehyde the sulphate, m. p. 253-254° (decomp.), of the 6-p-nitrophenyl compound, m. p. 180° (decomp.), which gives : hydrochloride, m. p. 250° (decomp.); normal chloroplatinate, m. p. 230— 231° (decomp.); picrate, m. p. 212—213°; dipicrate (?); and silver salts as above.

The reaction between p-dimethylaminobenzaldehyde and guanylcarbamide gives rise to a sulphate, $(\tilde{C}_{11}H_{15}ON_5)_2, H_2SO_4$, m. p. 252–253° (decomp.), which when heated in dilute sulphuric acid passes into a sulphate, C₁₁H₁₅ON₅,H₂SO₄, m. p. 208-210° (decomp.), and when dissolved in concentrated sulphuric acid gives the *sulphate*, C₁₁H₁₅ON₅,2H₂SO₄, m. p. 120-122°, giving a cloudy mass which becomes green at 180-190°, and then completely melts. The base, 4-imino-2-keto-6-p-dimethylaminophenyl-1:3:5triazidine, $[+H_2O]$, m. p. 220–221° (decomp.), gives : hydrochloride, m. p. 212–214°; dihydro-chloride, m. p. $[+H_2O]$ 222–223° (decomp.), $[+2H_2O]$ 200°; nitrate, m. p. 215° (decomp.); acetate, m. p. 202-203° (decomp.); formate, m. p. 213° (decomp.). According to conditions of preparation, a semipicrate, m. p. 205-206°, a monopicrate, m. p. 220°, and a tripicrate, m. p. 190°, are formed; hydrolysis of the picromonohydrochloride, m. p. 190° (decomp.), obtained from the monopicrate, gives also a dipicrate, m. p. 190° (decomp.). A picrodihydrochloride, m. p. about 176°, is formed from the picrotrihydrochloride, m. p. 153-155° (decomp.), obtained from the monopicrate,

which also yields, in gaseous hydrogen chloride, a colourless picrotetrahydrochloride.

E. W. WIGNALL. Three isomeric 1-tolyl-3:5-dimethyl-1:2:4triazoles and their salts. F. HERNLER (Monatsh., 1929, 51, 267-276).-By condensation of the appropriate tolylhydrazine hydrochloride and diacetamide in the presence of crystalline sodium acetate, the three isomeric 1-tolyl-3: 5-dimethyl-1:2:4-triazoles have been prepared, and characterised by the preparation of several of their salts. 1-o-Tolyl-3: 5-dimethyl-1: 2: 4-triazole, m. p. 25°, b. p. 141—145°/11 mm. (hydrochloride, subliming, m. p. 214—216°, in a sealed tube; picrate, m. p. 192-193°; chloroplatinate, m. p. 158-162°; mercurichloride, m. p. 136-137°), is obtained in 40% yield. Similarly, from *m*-tolylhydrazine in acetic acid is obtained a 57% yield of 1-m-tolyl-3:5-dimethyl-1:2:4-triazole, b. p. 147-149°/11 mm. (hydro-chloride, m. p. 206-207° in a sealed tube; picrate, m. p. 138-139.5°; chloroplatinate, +2H₂O and anhydrous, m. p. 220-223°; mercurichloride, m. p. 181°; hydrochloride of mercurichloride, m. p. 215-220°, with previous sintering at 180°). 1-p-Tolyl-3:5-dimethyl-1:2:4-triazole, m. p. 47-49°, b. p. 151-153°/11 mm. [hydrochloride, m. p. 233-235°; picrate, m. p. 128-129°; chloroplatinate, m. p. 223-225° (decomp.); mercurichloride, m. p. $150-152^{\circ}$; double salt, $(C_{11}H_{13}N_3)_4$, $3HgCl_2$, m. p. $144-147^{\circ}$], is obtained in 45% yield. J. W. BAKER.

2-Nitrophenyl- $\alpha\beta$ -naphtha - 1 : 2 : 3-triazolequinones. M. GALLOTTI [with A. ERCOLI] (Gazzetta, 1929, 59, 207—211).—Oxidation of 2-o-, 2-m-, and 2-p-nitrophenyl- $\alpha\beta$ -naphtha-1 : 2 : 3-triazoles (Meldola and Hughes, J.C.S., 1891, 59, 373 : the 2-m-compound has new m. p. 226.5°) by chromic acid in acetic acid yields the corresponding triazolequinones, m. p. 267°, 237—238°, and 297°, respectively (cf. Charrier and others, A., 1926, 848), which react with o-phenylenediamine to give the phenazines, I, m. p. 277—278°, 328°, and 312°, respectively, with phenylhydrazine hydrochloride to give the hydroxyazoderivatives, II, m. p. 229°, 255°, and 240°, respectively,



and with alkaline potassium permanganate solution, or with chromic acid in acetic acid, to give 2-o-, 2-m-, and 2-p-nitrophenyl-4-o-carboxyphenyl-1:2:3triazole-5-carboxylic acids, m. p. 260°, 274°, and 267°, respectively, which are also obtained by oxidation of the corresponding m-nitrobenzeneazo- β -naphthylamines. E. W. WIGNALL.

5-Aminotetrazole. R. STOLLÉ [with E. SCHICK, F. HENKE-STARK, and L. KRAUSS] (Ber., 1929, 62, 1119—1126).—5-Aminotetrazole monohydrate, m. p. 199°, is conveniently prepared by the action of azoimide on dicyanodiamide; the nitrate, decomp. 174° after softening, and hydrobromide, m. p. 118° after softening at 110°, decomp. about 150°, are described. Anhydrous 5-aminotetrazole is converted

by phenylcarbimide at 100° into N-phenyl-N'-5-tetr. azolylcarbamide, m. p. 245° (decomp.), and by ethyl chloroformate into 5-tetrazolylurethane, m. p. 256° (decomp.). Acetyl chloride transforms 5-amino. tetrazole into 5-acetamidotetrazole, m. p. 269° (decomp.), whereas boiling acetic anhydride affords 5-acetamido-2-methyl-1:3:4-furodiazole, m. p. 180°. Appropriate treatment of a diazotised solution of 5-aminotetrazole yields the following compounds: 5-hydroxytetrazole, m. p. 254°; tetrazole; 5-chloro-tetrazole, m. p. 73° after softening, decomp. 120°, and the copper compound $C_2N_3Cl_2Cu$; 5-bromotetrazole, m. p. 156° (decomp.), and the corresponding copper salt; 5-iodotetrazole, decomp. about 190°, reduced by sulphurous acid or sodium sulphite to tetrazole and converted by 60% sodium hydroxide into 5-hydroxytetrazole. N¹-5-Tetrazolyl-N³-p-nitrophenyltriazine, decomp. about 169°, is derived from diazotised 5-aminotetrazole and p-nitroaniline or p-nitrophenyldiazonium chloride and 5-aminotetr-N¹-5-Tetrazolyl-N³-phenyltriazine, decomp. azole. 97°, is described. Treatment of dicyanodiamide with azoimide in presence of nitric acid yields 5-guanylaminotetrazole nitrate, decomp. about 183° after soften. ing. 5-Guanylaminotetrazole, not molten below 300°, is converted by water at 200° into 5-aminotetrazole. H. WREN.

Action of diazo-compounds on tetrazolyl disulphides. R. STOLLÉ, F. HENKE-STARK, and H. PERREY (Ber., 1929, 62, [B], 1112-1118).—The action of diazomethane, diazoethane, and ethyl diazoacetate on 1-substituted di-5-tetrazolyl disulphides affords the methylene compounds,

CHR: $\left[N < N=N \\ CS \cdot NR'\right]_2$ (I), which yield apparently non-uniform additive compounds with silver nitrate, and mercaptals, CHR: $\left[S \cdot C < NR' \cdot N \\ N-N \end{bmatrix}_2$ (II), which

do not give precipitates with alcoholic silver nitrate. The mercaptals are also prepared from the requisite dihalogeno-derivatives and the sodium salts of the 5-thioltetrazoles. The following compounds are de-scribed : methylenedi-1-phenyl-4:5-dihydro-5-tetrazolyl disulphide (I, R=H, R'=Ph), m. p. 124°, decomp. about 160°; methylene di-1-phenyl-5-letr-azolyl disulphide (II, R=H, R'=Ph), m. p. 136°, decomp. about 175°; ethylene di-1-phenyl-5-tetrazolyl disulphide, m. p. 150°; methylenedi-1-p-tolyl-4:5-di-hydro-5-tetrazolyl disulphide, m. p. 108°, decomp. about 160°; methylene di-1-p-tolyl-5-tetrazolyl disulphide, m. p. 136°, decomp. 145°; methylenedi-1-0tolyl-4: 5-dihydro-5-tetrazolyl disulphide, m. p. 118°, decomp. 160°; methylene di-1-o-tolyl-5-tetrazolyl disulphide, decomp. 161°; methylenedi-1-m-xylyl-4:5dihydro-5-tetrazolyl disulphide, m. p. 106°; methylene di-1-methyl-5-tetrazolyl disulphide, m. p. 157°; ethylidenedi-1-phenyl-4: 5-dihydro-5-tetrazolyl disulphide, decomp. 177°; ethylene di-1-phenyl-5-tetrazolyl disul-phide, m. p. 93°; carbethoxymethylenedi-1-phenyl-4:5dihydro-5-tetrazolyl disulphide, m. p. 104°, decomp. about 150°; carbethoxymethylenedi-1-phenyl-5-tetrazolyl disulphide, m. p. 110°; carbomethoxymethylenedi-1-phenyl-4: 5-dihydro-5-tetrazolyl disulphide, decomp. 139°. Di-1-phenyl-5-tetrazolyl disulphide is converted by mercury into the mercury compound of 1-phenyl-5-thioltetrazole, decomp. 223°. Tetraphenylthiocarbamide and alcoholic silver nitrate afford the compound, $C_{25}H_{20}N_2S$, AgNO₃, m. p. about 240° (decomp.). H. WREN.

Oxidation of uric acid in presence of hydrogen acceptors. S. DOBROWOLSKA (Compt. rend. Soc. Biol., 1928, 99, 1022—1023; Chem. Zentr., 1929, i, 102). —At p_{ii} above 8, in presence of methylene-blue, uric acid (1 in 5000) at 37° decomposes to the extent of 50% in 6 days, with production of allantoin and earbon dioxide. Uric acid in dilute solution is oxidised by thioglycollic acid in presence of air. Small amounts of copper facilitate the reaction. Methylene-blue stimulates, whilst potassium cyanide depresses, the oxidative action of sulphur compounds. It is possible that thioglycollic acid is concerned in uricolysis in vivo. A. A. ELDRIDGE.

Chlorophyll group. L. MARCHLEWSKI and A. SZYMANSKI (Bull. Acad. Polonaise, 1929, A, 119– 129).—Copper neochlorophyll, copper allochlorophyll, and copper prophyllotaonines were prepared by interaction of the chlorophyll with copper acetate in acetic acid. Copper neochlorophyll is decomposed by methyl-alcoholic potassium hydroxide into copper neo- β -prophyllotaonine (soluble in 10% disodium hydrogen phosphate solution) and copper neo- α -prophyllotaonine. The absorption spectra of phytol, copper allo- and copper neo-chlorophyll, copper alloand copper neo- β -prophyllotaonine in alcohol-chloroform solution have been measured. A. I. VOGEL.

Structure of furazan oxides. II. C. R. KINNEY (J. Amer. Chem. Soc., 1929, 51, 1592-1600).p-Methoxybenzoin, conveniently obtained by condensing benzaldehyde and *p*-anisaldehyde in presence of potassium cyanide in aqueous alcohol, is oxidised by copper sulphate and pyridine to p-methoxybenzil, m. p. 62-63°. This is converted by hydroxylamine bydrochloride and sodium hydroxide in boiling water into a mixture of dioximes which is oxidised by sodium hypochlorite (cf. Meisenheimer and others, A., 1925, i, 1073) to a mixture of furazan oxides (phenylanisylfuroxans) from which a pure α -isomeride (approx. 90% of the product), m. p. 108-109°, and a nearly pure β -isomeride, m. p. 104-105°, softening from 102°, were isolated by fractional crystallisation. The latter was also obtained by oxidising the p-methoxybenzil 8-monoxime, prepared from phenyl p-methoxybenzyl ketone, amyl nitrite, and sodium ethoxide. Ozonisation of the a-isomeride, followed by hydrolysis with cold 10% sodium hydroxide, gives anisic acid and a product which is hydrolysed by boiling alkali b benzoic acid. The β -isomeride gives the same scids in the reverse order. Diphenylfuroxan with ozone gives benzoic acid only, whilst diphenylfurazan reacts slowly and does not give acids. These results confirm the formulæ assigned by Meisenheimer to the oximes and furoxans derived from *p*-methoxybenzil (cf. A., 1927, 367). H. E. F. NOTTON.

Aminobenzthiazoles. XII. Mobility of 1-amino-3:5-dimethylbenzthiazole. A case of complete reactivity in the aminothiazole form. R. F. HUNTER and W. E. PRIDE (J.C.S., 1929, 943-

946).-Interaction of stable acetyl-m-xylylthiocarbamide, m. p. 181-182°, with bromine in chloroform gave 1-acetamido-3: 5-dimethylbenzthiazole hydrotribromide, m. p. 167° (decomp.), converted by sulphurous acid into acetamidobenzthiazole, m. p. 259-260°, also obtained from 3:5-dimethylbenzthiazole and acetic anhydride. Methyl iodide converts 1-amino-3: 5-dimethylbenzthiazole into the hydriodide of the iminomethyl base I, m. p. 265° (decomp.), which with alkali yielded 1-imino-2:3:5-trimethyl-1:2-dihydrobenzthiazole, m. p. 105-106°, the hydriodide, m. p. 274° (decomp.), of which was identical with I. Methyl iodide in benzene solution converted 1-amino-3:5-dimethylbenzthiazole into a substance, m. p. 156-157°. 1-Methylamino-3: 5-dimethylbenzthiazole, m. p. 124-125°, prepared by reducing the bromoadditive compound obtained from s-in-xylylmethylthiocarbamide (from m-xylylthiocarbimide and methylamine), m. p. 152°, and bromine in chloroform, furnished an acetyl derivative, m. p. 156-157°, and a hydriodide, m. p. 225-227° (decomp.). 1-Amino-3: 5-dimethylbenzthiazole methosulphate, m. p. 216-217°, is obtained when 1-amino-3: 5-dimethylbenzthiazole is heated with methyl sulphate in benzene solution. The intermediate bromo-additive compound obtained in the interaction of m-xylylthiocarbamide and bromine in chloroform has m. p. 273° A. I. VOGEL. (decomp.).

Ketosulphonic acids. I. Synthesis of 1:2:3thiodiazole derivatives. P. MAZAK and J. SUSZKO (Bull. Acad. Polonaise, 1929, A, 131-142).—Interaction of equimolecular quantities of potassium sulphite and chloroacetone gave a 40-45% yield of potassium acetonesulphonate, m. p. 193-194° (corresponding sodium salt, m. p. 180-181°). This reacted with phenylhydrazine to give the phenylhydrazine of acetonesulphonic acid (sinters and decomposes above 260°), which yielded 4-methyl-2-phenyl-SO :CH

dihydro-1:2:3-thiodiazole-1:1-dioxide, NPh $<_{N=CMe}^{SO_2 \cdot CH_2}$

(I), m. p. 84—58°, when heated with phosphorus trichloride at 100°. I reacted with 1 mol. of bromine in acetic acid to give the 5(?)-bromo-derivative, whilst with 2 mols. of bromine I gave the 5:5(?)-dibromo-derivative, m. p. 95—96° (decomp.). Nitrie acid (d 1.4) and I furnished the 5(?)-nitro-derivative, m. p. 170—172°. Attempts to prepare β -ketopropanesulphonic acid were unsuccessful.

A. I. VOGEL.

Microchemical reactions of piperine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 405–406). —Crystallisation from dilute acetic acid and from acetone give characteristic forms. S. I. Levy.

New reaction of hydrastine and papaverine. C. A. ROJAHN and F. STRUFFMANN (Pharm. Zentr., 1929, 70, 277).—Whilst hydrastine and papaverine separately give poorly characterised colour reactions with alkaloid reagents, mixtures of the two alkaloids give intense colorations, and this fact may be utilised in their identification. R. K. CALLOW.

Diastereoisomerism. I. Configuration of ephedrine. II. Steric rearrangement of ephedrine with hydrochloric acid. III. Chloro- and bromo-analogues of ephedrine. IV. Steric rearrangement of ephedrine with sulphuric acid. H. EMDE (Helv. Chim. Acta, 1929, 12, 365— 376, 377—384, 384—399, 399—405).—I. Natural (—)-ephedrine base (I), m. p. 39—40°, is a monohydrate (the anhydrous base is obtained only as an oil and has $[M]_{0}^{r}$ +18.5° in water), whilst natural (+)- ψ -ephedrine base (II), m. p. 118°, $[M]_{0}^{r}$ +87.5° in alcohol, is anhydrous. The higher m. p. of II suggests a betaine-like saturation of the residual valencies of the hydroxyl and methylamino-groups, indicating that these groups are in close spatial proximity (cf. Späth and Göhring, A., 1921, i, 45). The optical configuration of I,

OH-CHPh-CHMe-NHMe, is $-\alpha + \beta$, whilst that of II is $+\alpha + \beta$, where $\alpha > \beta$. (+)-Deoxyephedrine (β -methylamino - α - phenylpropane) (hydrochloride, m. p. 172°, $[M]_{17}^{**}$ +32° in water) is obtained together with dideoxyephedrine, $C_{20}H_{28}N_2$, b. p. 165°/0.6 mm., m. p. 70°, $[M]_{16}^{**}$ +78:8° in N-hydrochloric acid [chloroplatinate, m. p. 224—225° (decomp.)], by reducing α -bromo(chloro)- β -methylamino- α -phenylpropane hydrobromide (hydrochloride) with hydrogen in presence of palladised barium sulphate, acctic acid, and sodium acetate.

II. When either I or II is heated with 10 parts of 25% hydrochloric acid at 100°, the same endproduct is obtained after 60 hrs. This contains a preponderance of (+)- ψ -ephedrine hydrochloride (cf. Schmidt, A., 1908, i, 452). With 38% hydrochloric acid replacement of the hydroxyl group by chlorine occurs. Equilibration of I and II with 25% hydrobromic acid at 100° is complete after about 300 hrs., II again predominates. (-)-Ephedrine hydrobromide, m. p. 204.5°, $[M]_{10}^{\infty}$ -77.5° in water, and (+)- ψ ephedrine hydrobromide, m. p. 179°, $[M]_{341}^{\infty}$ +148.1° in water, are described.

III. Treatment of (-)-ephedrine hydrochloride (III) with phosphorus pentachloride in cold chlorogives $(+)-\alpha$ -chloro- β -methylamino- α -phenylform propane hydrochloride, m. p. 201°, $[M]_{0}^{20}$ +266° in water {free base [chloroplatinate, m. p. 188° (decomp.); chloroaurate, m. p. 128°]}, also obtained from III and (+)- ψ -ephedrine hydrochloride (IV) and thionyl chloride. The α -chlorine atom is replaced by hydroxyl when heated at 100° with water, giving a mixture of 62% of IV and 38% of III. From IV and phosphorus pentachloride, or III and fuming hydrochloric acid, (-)-α-chloro-β-methylamino-αphenylpropane hydrochloride, m. p. 197°, decomp. 199° with evolution of hydrogen chloride, $[M]_{D}$ -167° in water, is obtained. Hydrolysis of this furnishes 51% of III and 49% of IV. Treatment of (-)-ephedrine hydrobromide (V) with phosphorus pentabromide yields $(+)-\alpha$ -bromo- β -methylamino- α phenylpropane hydrobromide, m. p. 174-175° (decomp.), $[M]_{\rm b}^{20} + 385^{\circ}$ in water. This is converted by heating with chloroform almost entirely into $(-)-\alpha$ bromo-\beta-methylamino-a-phenylpropane hydrobromide, m. p. 175.5°, $[M]_{\rm p}^{\rm so} -287^{\circ}$ in water, obtained also from (+)- ψ -ephedrine hydrobromide (VI) and phosphorus pentabromide. Both these bromides are hydrolysed by water, yielding mixtures of V and VI. IV. When (-)-ephedrine hydrochloride is treated for a short time with cold concentrated sulphuric acid

(+)-ψ-ephedrine-O-sulphonic acid, m. p. $248-250^{\circ}$ (decomp.), [M]² + 322° in water (cf. Schmidt, A., 1914, i, 989), is obtained together with small amounts of ephedrine and ψ-ephedrine sulphates. Prolonged treatment with sulphuric acid gives apoephedrine (Schmidt, *loc. cit.*), which is not identical with dideoxyephedrine. This last substance is not formed from deoxyephedrine and α-chloro-β-methylamino-αphenylpropane hydrochloride in presence of acetic acid and sodium acetate solution, and is not, therefore, a sec.-tert.-amine formed by elimination of hydrogen chloride during catalytic reduction (Part I). H. BURTON.

Belladonnine, bellatropine, and chlorotropan. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1929, [iv], 45, 304-311).-Belladonnine, obtained pure by decomposing the chloroplatinate, m. p. 252°, or chloroaurate, m. p. 168° (cf. Hesse, A., 1891, 228, 748; 1892, 1498; 1894, i, 153), is hydrolysed by boiling alcoholic potassium hydroxide into tropine, together with atropic acid and polymerised atropic acid. Sulphuric acid (0.2N) similarly yields tropine and traces of tropidine. Concentrated hydrochloricacidat 140° affords 3-chlorotropan, b. p. 163-165°/760 mm. (decomp.) (hydrochloride, m. p. 232-233°, chloroplatinate, m. p. 227-228°, chloroaurate, m. p. 215°, picrate, m. p. 216-217°). The methiodide, m. p. 305-306°, is reduced by zinc and sulphuric acid to tropan methiodide. Hydrogen peroxide (30%) in acetone converts 3-chlorotropan into the N-oxide (hydrochloride, m. p. 210°, picrate, m. p. 174-175°). apo-Atropine, atropine, hyoscyamine, and tropine and other tropeines are similarly converted into 3-chlorotropan (yields 75%), and with hydrobromic acid into 3-bromotropan (hydrobromide, m. p. 219°, chloroaurate, m. p. 158°, chloroplatinate, m. p. 211°, picrate, m. p. 205°). The supposed "bellatropine" of Hesse is a mixture of bases of which chlorotropan is the chief R. BRIGHTMAN. constituent.

Sinomenine and disinomenine. VIII. Colour reactions of sinomenine and sinomenol. K. Goro (Bull. Chem. Soc. Japan, 1929, 4, 103-105; cf. A., 1926, 1160).—Colour reactions given by sinomenine with alkaline potassium ferricyanide in chloroform, and by sinomenol with ammoniacal silver in acetone closely resemble those given by thebainone and 3-methoxy -4:6-dihydroxyphenanthrene, respectively, and differ from those produced by morphothebaine and morphol, respectively. It is therefore assumed that the relative position of the hydroxy- and keto-groups in sinomenine is analogous to that in thebainone. The formula of sinomenine is discussed.

C. W. SHOPPEE. Strychnine and brucine. VIII. Action of hydriodic acid on strychnidine. Dihydrostrychnidine (B) and substances derived therefrom. W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1929, 964—1000).—When strychnidine is reduced with hydriodic acid (d 1.94) and amorphous phosphorus for 24 hrs., *dihydrostrychnidine* (B) (I), $C_{21}H_{26}ON_2$, m. p. 151°, b. p. 225—230°/0.4 mm., is obtained; it does not yield an acetyl derivative, neither does it condense with hydroxylamine or with aldehydes, and is unaffected by sodium in boiling

alcohol, or by electrolytic reduction [cf. dihydrostrychnidine (Å), Å., 1927, 1208]. It is a strong base, giving with hydrochloric acid a hydrochloride [tri-hydrate, losing $2H_2O$ at 100° to yield the monohydrate, m. p. 123° (decomp.)] from which it is regenerated by treatment with ammonia. Solutions of I in dilute mineral acids afford colour reactions with dichromate, nitrite, and ferric chloride; the acetate combines with diazobenzenesulphonic acid. The sulphate of I when treated with potassium iodide yields the dihydriodide, converted by boiling methyl alcohol into the mono-hydriodide, m. p. 235-240° (efferv.), which, when treated with silver chloride and water, affords the above hydrochloride. Treatment of I in dry benzene at 10° with methyl sulphate gives the monomethosulphate (a), converted by sodium iodide into the monomethiodide (a) (II), glistening needles becoming opaque at 100°, m. p. 340-345° (decomp.) (compound +ICHCl_a), which when treated with silver chloride and water affords the methochloride (a), m. p. 335-340° with loss of methyl chloride and conversion into I. Methylation of I with methyl sulphate in dry benzene at 30° for 24 hrs. gives the *dimethosulphate* (A), converted by sodium iodide into the *dimethiodide* (A) (III), m. p. 238-242° (decomp.), which gives II with methyl-alcoholic potassium hydroxide, and when treated in aqueous solution with silver chloride or sodium bromide furnishes the dimethochloride (A) and the dimethobromide (A), m. p. 345° (efferv.), respectively. When I is treated with methyl iodide in the cold II is obtained, but on heating a second reaction occurs, giving a mixture of II, III, and the dimethiodide (B) of I, m. p. $260-265^{\circ}$ (efferv.). The dimethiodides (A) and (B) of I do not lose methyl iodide when digested with mesitylene (cf. A., 1927, 888), but elimination takes place by treatment with hot 25% methyl-alcoholic potassium hydroxide, yielding II and the monomethiodide (b) of I, needles, which do not become opaque at 100°, shrink about 250°, and melt gradually above this temperature. The latter when treated with water and silver chloride affords the monomethochloride (b), (dihydrate), for which colour reactions are described, converted by sodium bromide into the monomethobromide (b), which blackens at 330° and effervesces at 340-345°. The base I combines with benzyl chloride in hot toluene to yield dihydrostrychnidine (B) benzyl chloride, m. p. 325° with effervescence and regeneration of I, smoothly converted by mixing with 25% methyl-alcoholic potassium hydroxide and heating at 150° into methoxybenzyltetrahydrostrychnidine (B), C29H34O2N2, m. p. 126-127°, which does not combine with methyl iodide.

Oxidation of I with powdered permanganate in mist acetone at 15° yielded mainly dihydrostrychme (B) (IV), $C_{21}H_{24}O_{2}N_2$, m. p. 196° (hydrochloride onverted by sodium iodide into the hydriodide, m. p. $50-355^{\circ}$), together with a small quantity of an acid, $C_{21}H_{24}O_7N_2$, m. p. 205° (decomp.), for which colour reactions are given. The base IV gives colour reactions reminiscent of those of strychnine; it does not couple with diazobenzenesulphonic acid, and is very readily soluble in dilute mineral acids and in dilute acetic acid. Treatment of IV with methyl iodide in boiling acetone yields a yellow methiodide, darkens about 220°, m. p. 365° (decomp.), converted by silver chloride and sodium bromide into the methochloride, m. p. 370-375° (efferv.) (colour reactions described), and the methobromide, m. p. 375° (decomp.), respectively. Benzaldehyde and IV condense readily in the presence of alcoholic sodium ethoxide to afford the benzylidene derivative, m. p. 270-275° (colour reactions; hydrochloride; sulphate), but an oxime could not be obtained. Hydrolysis of IV with sodium ethoxide at 100° yielded dihydrostrychnic acid (B), C₂₁H₂₆O₃N₂, m. p. 285° with regeneration of IV, m. p. 203°, mixed m. p. 201-202° (colour reactions; hydrochloride). Oxidation of I with hydrogen peroxide in the presence of methyl-alcoholic potassium hydroxide affords dioxydihydrostrychnic acid (B), C21H26O6N2, m. p. 300-305° (decomp.). The isomeride of I, dihydrostrychnidine (A) (A., 1927, 1208), when oxidised with powdered permanganate in hot, moist acetone yields oxydihydrostrychnidine (A), C21H24O2N2, m. p. 345° (decomp.), isomeric but not identical with IV. The substance is a feeble base, and does not combine with methyl iodide or with benzaldehyde; its colour reactions are described.

When the mono- and di-methochlorides of I are heated with methyl-alcoholic potassium hydroxide, the main product is methoxymethyltetrahydrostrychnidine (B), (V), $C_{23}H_{32}O_2N_2$, m. p. 180—181° (cf. the conversion of strychnidine methochloride into methoxymethyldihydrostrychnidine; A., 1927, 888), together with small quantities of methyl- ψ -strychnidine (B) (VI) and dihydrostrychnidine (C) (VII). The substance [cf. the isomeride methoxymethyltetrahydrostrychnidine (A), m. p. 220°; A., 1927, 888], can be distilled unchanged in small quantities, b. p. 215-225°/1 mm.; it does not combine with benzyl chloride, but dissolves in dilute mineral acids. The sulphate is converted by sodium iodide into a yellow hydriodide (VIII), which becomes colourless at 155-160°, softens and decomposes at 175-180°, solidifies immediately, effervesces again at 235°, again sets to a solid (IX), and finally decomposes at 325°. The solid IX was identified as II, and the same substance is produced more readily and completely when V is boiled with hydriodic acid (d 1.94) and amorphous phosphorus. Methyl iodide combines with V at 100° to yield a methiodide, m. p. 235-238° with regeneration of V. The methochloride, obtained from the foregoing methiodide when treated with water and silver chloride, begins to decompose at 150°, and effervesces at 170°, regenerating V; its colour reactions are described. The *dimethosulphate* is prepared with methyl sulphate in benzene at 80°, and when treated with sodium iodide gives the dimethiodide, m. p. 210°, converted by methyl-alcoholic potassium hydroxide at 100° into the above methiodide, m. p. 235-238°. When V is oxidised with powdered permanganate in moist acetone at 12° formylmethoxytetrahydrostrychnidine (B) (X), C₂₃H₃₀O₂N₂, m. p. 154°, is obtained. This is not hydrolysed by sodium ethoxide at 100°, and does not combine with methyl iodide or benzaldehyde; its colour reactions are described. When boiled with dilute sulphuric acid X eliminates formic acid, or when distilled in a vacuum gives carbon monoxide and methoxytetrahydrostrychnidine (B) (XI), $C_{22}H_{30}O_{2}N_{2}$, m. p. 150–152° (colour reactions: nitroso-derivative), which is not reducible electrolytically. Methyl iodide converts XI into the hydriodide VIII, identity being confirmed by conversion into V with ammonia. The mother-liquors from the permanganate oxidation of V, after evaporation and distillation, afford a fraction, b. p. 218-223°/1 mm., which consists of an inseparable mixture of X and XI, m. p. 137-138°, since it is completely converted into XI when boiled with dilute sulphuric acid.

The mother-liquors from the purification of V, after evaporation and distillation, yield a fraction, b. p. 220-/1 mm., from which, after removal of a quantity 225° of V, the substances VI and VII were obtained by fractional crystallisation. Methyl- ψ -strychnidine (B) (VI), C22H26ON2, m. p. 222-225° (colour reactions described), readily furnishes a dimethiodide, m. p. 275° effervescing at 280-285°, with methyl iodide in the cold; attempted preparation of the dimethochloride from the foregoing methiodide was unsuccessful and accompanied by characteristic colour phenomena. Dihydrostrychnidine (C) (VII), $C_{21}H_{26}ON_2$, m. p. 132—134, is a strong base and dissolves readily in dilute acetic acid; its colour reactions and crystallographic data are given. When heated with methyl iodide at 100°, it yields a dimethiodide, m. p. 265-270° (efferv.), converted by water and silver chloride into the dimethochloride, which with methylalcoholic potassium hydroxide regenerates VII. The substance VII is unaffected by electrolytic reduction. The foregoing results are discussed on the basis of



the structure XII for strychnine (cf. this vol., 82), but cannot be utilised in any definite manner. The preparation and properties of *benzylidenestrychnine*, m. p. 235-237°, and of *benzylidenebrucine hydrochloride* (hemihydrate), and a modified method for the preparation of

strychnidine methosulphate (cf. A., 1927, 888) are given. Strychnidine methochloride, m. p. 370° leaving a residue containing strychnidine (dihydrate), is obtained from the methiodide (cf. Tafel, A., 1898, i, 703) with water and silver chloride at 100° for 3 hrs., and is dechlorinated by silver oxide to strychnidine methohydroxide. Methylation of strychnidine with methyl sulphate in benzene at 80° for 20 hrs., and treatment of the product with sodium iodide, affords strychnidine dimethiodide, converted by water and silver chloride into the dimethochloride, which when heated with 25% methyl-alcoholic potassium hydroxide up to 140° yields methoxymethylhydrostrychnidine (A., 1927, 888). Strychnidine combines with benzyl chloride in boiling toluene to give strychnidine benzyl chloride, m. p. 330-335° (efferv.) with production of strychnidine accompanied by other substances (colour reactions described), which when heated at 150° with 25% methyl-alcoholic potassium hydroxide yields methoxybenzyldihydrostrychnidine, m. p. 92-95° (cf. A., 1927, 888). C. W. SHOPPEE.

Structure of narceine. J. J. L. ZWIKKER (Pharm. Weekblad, 1929, 66, 461-464).—The accepted formula of Freund, which postulates the existence of a \cdot CO·CH₂ · group in narceine, is improbable in view of the fact that the alkaloid does not give a coloration with alkaline nitroprusside solution. It is suggested that in alkaline solution the nitrogen becomes quinquevalent, one hydrogen atom going from the CH₂ group to the dimethylamino-group, with closing of the ring, whilst in acid solution the structure is represented by Freund's formula. S. I. LEVY.

Sensitive new reaction for ergotamine, ergotoxin, and ergotinine, and its application to the investigation and colorimetric determination of ergot preparations. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 473—481).—p.Dimethylaminobenzaldehyde gives sensitive colour reactions with the ergot alkaloids; the test is applied to ergot preparations by extracting with ether and ammonia, adding the reagent dissolved in ether, and a little sulphuric acid. The individual alkaloids cannot be differentiated. Approximate determination is possible.

S. I. LEVY. Use of vanillin as an alkaloidal reagent. A. PORTNOV (Pharm. J. Russia, 1928, 89, 453; Chem. Zentr., 1928, ii, 2271).—When an alkaloid is warmed with 2 drops of 2N-sulphuric acid and 2 drops of a solution of vanillin in glycerol (0.1 g. in 10 c.c.), a reddish-violet, becoming raspberry-red, colour is obtained. The reagent is stable. A. A. ELDRIDGE.

Structure of Boyd's chloroanhydride. A. E. ARBUZOV and B. A. ARBUZOV (J. Russ. Phys. Chem. Soc., 1929, 61, 217-253; cf. J.C.S., 1923, 123, 813; A., 1924, i, 1121; 1926, 1161).—Boyd's researches on the reaction product of triphenylmethylcarbinol and phosphorus trichloride are reviewed and his theories as to its structure and the mechanism of its reactions with reagents critically examined.

In order to determine whether the chloroanhydride formed the structure [OCPh₃]PCl₂ or CPh₃·P:OCl₂, it was treated with the sodium derivatives of different alcohols, when di-esters of triphenylmethylphosphinic acid, which were identical with those from the products of reaction of the di-esters of phosphorous acid and triphenylbromomethane, were obtained. The methyl ester has m. p. 155-156°, the ethyl 120-121°, the n-propyl 119-120°. The isopropyl ester exists in three modifications, two colourless, m. p. 122.5-128°, 216.5—217°, and one yellow, m. p. 119—120°. The isobutyl ester has m. p. 96—96.5°. By the action of the sodium derivatives of the primary alcohols on the chloroanhydride in the correct proportions, the corresponding chloro-esters are obtained. The ethyl chloro-ester has m. p. 125--126°, the isopropyl, 164-165°, and the isobutyl, 103-103.5°, and the n-propyl (by the action of the potassium derivative of propyl alcohol on the chloro-anhydride), m. P. 107-108°. The methyl chloro-esters could not be isolated in the pure condition.

The di-esters were hydrolysed by the action of hydrochloric acid in sealed tubes at 180°, triphenylmethylphosphinic acid being formed. The chloroesters were easily hydrolysed even by water alone. The chloroanhydride itself is hydrolysed at normal pressure into triphenylmethylcarbinol, but in a sealed tube at 180° triphenylmethane is formed almost quantitatively. By the action of phosphorus trichloride on triphenylmethylcarbinol a 95.2% yield of the chloroanhydride is obtained, together with a *compound*, which cannot be purified and which on hydrolysis yields triphenylmethylphosphinic acid. It is suggested that the *compound* is the triphenylmethyl chloro-ester of triphenylmethylphosphinic acid formed by the action of an excess of triphenylmethylcarbinol on the chloroanhydride.

M. ZVEGINTZOV.

Action of aromatic Grignard reagents on arsenious oxide. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 1558-1565).-Magnesium phenyl bromide and arsenious oxide in ether and benzene at 0° give diphenylarsenious oxide, m. p. 95.5-96.5°, and triphenylarsine, the latter becoming practically the sole product when excess of Grignard reagent is used in boiling solution. The intermediate product in the formation of triphenylarsine is not the oxide (cf. Matsumiya and Nakai, A., 1925, i, 1339; Sachs and Kantorowicz, A., 1908, i, 1031), since this is not formed until the reaction mixture is decomposed with water, but is probably the derivative, AsPh2.O.MgBr. Magnesium p-tolyl bromide and magnesium p-anisyl iodide behave similarly, but magnesium a-naphthyl bromide gives only di-a-naphthylarsine oxide, m. p. 250-253° (decomp.), which has the normal formula (cf. loc. cit.), and magnesium 4-diphenylyl bromide gives bis-4-phenylarsenious oxide, m. p. 150-152°. Phenylarsine and diphenylarsenious oxides are quantitatively converted by excess of magnesium phenyl bromide in boiling ether and benzene into triphenylarsine. The following are described : bromo-, m. p. 65-66°, and iodo-, m. p. 64-65°, -di-p-tolylarsines; chloro-, m. p. 83-84°, bromo-, m. p. 60-62°, and iodo-, m. p. 40-42°, -di-p-anisylarsines; bromo-, m. p. $172-173^{\circ}$, and *iodo-*, m. p. $140-141^{\circ}$, -di- α -naphthylarsines; *chloro-*, m. p. $145-147^{\circ}$, bromo-, m. p. $147-149^{\circ}$, and *iodo-*, m. p. $140-141^{\circ}$, bis-4-diphenylarsines. H. E. F. NOTTON.

Chemotherapy of some bromine derivatives of phenylarsinic acids and arsenobenzenes. A. HAYTHORNTHWAITE (J.C.S., 1929, 1011-1014).---The chemotherapeutic indices of the following organic arsenicals are less than that of salvarsan. 2-Nitro-4acetamidophenylarsinic acid, prepared from diazotised 3-nitro-4-aminoacetanilide and copper arsenite, gave m-nitroaniline when boiled with 50% sulphuric acid and 2-amino-4-acetamidophenylarsinic acid (I) when reduced with ferrous sulphate at 30°. The acid I was converted by the diazo-reaction into 2-bromo-4cetamidophenylarsinic acid, hydrolysed by dilute hydrochloric acid to 2-bromo-4-aminophenylarsinic wid. 3-Bromo-4-hydroxyphenylarsinic acid and 5bromo - 3 - acetamido - 4 - hydroxyphenylarsinic acid (hydrolysed to 5-bromo-3-amino-4-hydroxyphenylarsinic acid with alkali) were obtained from 3-amino-4-hydroxyphenylarsinic acid and 5-amino-3-acetamido-4-hydroxyphenylarsinic acid, respectively. The following arsenobenzenes were obtained from the respective phenylarsinic acids and sodium hyposulphite: 4:4'-dibromoarsenobenzene; 3:3'-dibromo-4:4'-diaminoarsenobenzene; 2:2'-dibromo-4:4'-diaminoarsenobenzene; 4:4'-diacetamidoarsenobenzene

and 2:2'-dibromo - 4:4'-diacetamidoarsenobenzene; 3:3'-dibromo - 4:4'-dihydroxyarsenobenzene; 5:5'-dibromo - 3:3'-diamino - 4:4'-dihydroxyarsenobenzene and 5:5'-dibromo - 3:3'-diacetamido - 4:4'-dihydroxyarsenobenzene. The first five of these arsenobenzenes are insoluble, the rest are soluble, in alkali.

A. I. VOGEL.

Thiolacetamide as a reagent for identifying arsinic acids. H. J. BARBER (J.C.S., 1929, 1024-1026).-Arsinic acids react with 4 mols. of thiolacetamide with the formation of di(carbamylmethyl) thioarsinites : $AsAr(OH)_2 + 4SH \cdot CH_2 \cdot CO \cdot NH_2 = AsAr(S \cdot CH_2 \cdot CO \cdot NH_2)_2 + (S \cdot CH_2 \cdot CO \cdot NH_2)_2 + 3H_2O.$ These compounds generally have sharp m. p. and can be rapidly determined by direct titration with iodine in dilute acetic acid solution at about 40° (cf. preceding abstract). The m. p. of the thioarsinites of the following arsinic acids are : phenyl-, 129-130°; o-aminophenyl-, 140°; p-aminophenyl-, 145°; o-hydroxy-phenyl-, 161-163°; p-hydroxyphenyl-, 160-162°; 3-amino-4-hydroxyphenyl-, 132-133°; 3-acetamido-4hydroxyphenyl-, 176°; 5-acetamido-2-hydroxyphenyl-, 188°; 3-amino-4-methylaminophenyl-, 141-143°; 4-chlorophenyl-, 134-136°; 4-chloro-3-nitrophenyl-, 142-143°; 3:5-diamino-4-hydroxyphenyl-, 159-161°; 2:6-diacetamido-phenoxyacetic-4-arsinic acid, 157°; 8-acetamido-3-hydroxy-1:4-benzisooxazine-6arsinic acid, 233-235°. A. I. VOGEL.

Derivatives of arylthioarsinous acids. H. J. BARBER (J.C.S., 1929, 1020-1024).-Aryl arsinoxides and aliphatic thiol compounds react with the formation of thiolarsinous acids, which are also obtained by condensation of the arsinic acids (1 mol.) with organic thiol compounds (4 mols.), the arsinic acid being intermediately reduced to the tervalent state. The following compounds are described : di(carboxymethyl) 4-aminophenylthioarsinite, m. p. 142-143° (from thiolacetic acid and 4-aminophenylarsinic acid); di(carboxymethyl) 4-aminophenyllhioarsinite (hydro-chloride, m. p. 100-105°); di(carbamyl) 4-amino-phenylthioarsinite, m. p 145° (from preceding compound and aqueous ammonia but best prepared from 4-aminophenylarsinic acid and thiolacetamide); di-(carboxymethyl) 3-amino-4-hydroxyphenylthioarsinite, m. p. 157—158° (from 3-amino-4-hydroxyphenyl-arsinic acid); di(carbamylmethyl) 3-amino-4-hydroxyphenylthioarsinite, m. p. 132-133°; di(\beta-carboxyaminoethyl) 3-amino-4-hydroxyphenylthioarsinite (from 3-amino-4-hydroxyphenylarsinic acid and cysteine hydrochloride); di(carboxymethyl) 5-acetamido-2-hydroxyphenylthioarsinite, m. p. 172-174° (from 5-acetamido-2-hydroxyphenylarsinic acid and thiolacetic acid in benzene solution); di(carboxymethyl) 4-carb-amylmethylaminophenylthioarsinite, m. p. 90° (from sodium N-phenylglycineamide-4-arsinate, thiolacetic acid, and 2N-sodium hydroxide followed by acidification); di(carboxymethyl) 8-acetamido-3-hydroxy-1:4benzisooxazine-6-thioarsinite, m. p. 212°; di(carbamyl-8-acetamido-3-hydroxy-1: 3-benzisooxazine-6methyl) thioarsinite, m. p. 233-235° (from the arsinic acid and cysteine hydrochloride); $di(\beta$ -hydroxyethyl) 8-acetamido - 3 - hydroxy - 1 : 4 - benzisooxazine - 6 - thioarsinite (from the arsinic acid in excess of aqueous ammonia and β -hydroxyethylmercaptan). The di(carboxy-

10-Chloro-5: 10-dihydrophenarsazine and its derivatives. VIII. Bromination of 10-chloro-5:10-dihydrophenarsazine and its derivatives. L. A. ELSON, C. S. GIBSON, and J. D. A. JOHNSON (J.C.S., 1929, 1080-1088) .- Treatment of 10-chloroacid. and also of 10-bromo-5: 10-dihydrophenarsazine (1 mol.) with bromine (4 mols.) in hot glacial acetic acid and other solvents in the cold (10-chloro-derivative) gave 2:4:2':4'(?)-tetrabromodiphenylamine, m. p. 186°, also obtained by brominating diphenylamine under similar conditions. Diphenylamine yields a hexabromodiphenylamine, m. p. 221-222° (lit. 218°), with 6 mols. of bromine in boiling glacial acetic acid. Similarly, 10 - chloro - 2:8 - dimethyl-5:10 - dihydrophenarsazine afforded tetrabromodi - p-tolylamine, m. p. 161-162°, or 166° (from di-p-tolylamine); 7-chloro-12:7-dihydrobenzophenarsazine gave tetrabromophenyl-a-naphthylamine, m. p. 150°; 12-chloro-7:12-dihydrobenzophenarsazine gave a tetrabromophenyl-3-naphthylamine, m. p. 205° (lit. 202-203°); 7 - chloro-9 - methyl-7 : 12 - dihydrophenarsazine gave tetrabromo-p-tolyl-β-naphthylamine, m. p. 167-170°, identical with the compound obtained from p-tolyl- β naphthylamine. Phenarsazinic acid and 4 mols. of bromine in boiling glacial acetic acid afforded chiefly tetrabromodiphenylamine together with small quantities of 2:4:6:8:10-pentabromo-5:10-dihydrophen-

> was also obtained from I and hydrogen peroxide. A. I. Vogel.

Heterocyclic systems containing selenium. I. cycloSelenobutane (tetrahydroselenophen). G. T. MORGAN and F. H. BURSTALL (J.C.S., 1929, I. 1096-1103).--- $\alpha\delta$ -Dibromobutane and sodium selenide react when heated at 80° in a current of hydrogen to give cycloselenobutane, purified by conversion into the dibromide and regenerated by treatment with sodium metabisulphite, b. p. 90–91°/172 mm., 135– 136°/770 mm., d^{10} 1.493, 1.452, γ^{10} 41.28, parachor (mean)=229.5. It is decomposed by aqueous permanganate or fuming nitric acid, but moderately concentrated nitric acid gave cycloselenobutane-1:1-dinitrate. cycloSelenobutane and mercuric chloride in alcoholic solution yielded cycloselenobutane mercuri-chloride, m. p. 146°; chlorine in carbon tetrachloride solution gave cycloselenibutane-1 : 1-dichloride, m. p. 88-89°; bromine yielded the corresponding 1:1-di-bromide, m. p. 92° (interaction of a concentrated chloroform solution of the latter and of bromine gave a perbromide, C4H8SeBr2,Br5, 5 atoms of bromine being removed by acetone), whilst interaction with iodine in carbon tetrachloride solution gave the diiodide, m. p. 99-100°. Treatment of the dibromide with 0.5 mol. of silver oxide furnished cycloselenibutane-1-hydroxy-1-bromide, m. p. 99-100° (decomp.); the corresponding hydroxy-chloride, similarly prepared, had m. p. 116° (decomp.); the 1:1-dihydroxide was produced in aqueous solution with excess of silver oxide. cycloSelenibutane 1-chloroplatinate, m. p. 230° (decomp.), is formed in dilute solution from the 1:1dichloride, whereas in warm concentrated solution containing excess of the 1:1-dichloride bis-1-chlorocycloselenibutane 1-chloroplatinate, m. p. 179° (decomp.), is produced. cycloSelenobutane and excess

arsazine (I), m. p. 275°, and 2:4:6:8-tetrabromophen-

arsazinic acid, m. p. 294° (decomp.). The last-named

methyl) arylthioarsinites react quantitatively with iodine in acid or in hydrogen carbonate solution thus : $AsAr(SR)_2+2I_2+3H_2O=AsArO(OH)_2+4HI+R_2S_2$. A. I. VOGEL.

3:4-Methylenedioxyphenylarsinic I. E. BALABAN (J.C.S., 1929, 1088-1093).-By the diazo-method 4-aminopyrocatechol methylene ether hydrochloride gave a 42% yield of 3:4-methylenedi-oxyphenylarsinic acid I, 0.75 H₂O, m. p. 270° (decomp.) (calcium, barium, and magnesium salts), reduced (sodium hyposulphite) to arsenopyrocatechol methylene ether (65% yield). Nitration of 1 at 0° yielded 6-nitro-3:4-methylenedioxyphenylarsinic acid, m. p. 231° (decomp.) (magnesium, calcium, and barium salts), identical with the arsinic acid, m. p. 228° (decomp.), ob-tained (diazo-method : 74% yield) from 5-nitro-4-aminopyrocatechol methylene ether. This acid was converted by ferrous sulphate at 70° into 6-amino-3: 4-methylenedioxyphenylarsinic acid II (magnesium and calcium salts), reduced to 6:6'-diaminoarsenopyrocatechol methylene ether; II gave 6-acetamido-3: 4methylenedioxyphenylarsinic acid (magnesium salt) when acetylated in alkaline solution. Treatment of 4-nitropyrocatechol with acetic anhydride and sulphuric acid afforded 4-nitro-1: 2-diacetoxybenzene, m. p. 98°, reduced by iron and dilute acetic acid or by moist aluminium amalgam in ether to 4-amino-1:2-di-acetoxybenzene, m. p. 114° (N-acetyl derivative, m. p. 144°). Benzylation of 4-nitropyrocatechol yielded 4-nitropyrocatechol dibenzyl ether, m. p. 97°, reduced by moist aluminium amalgam to the amine, m. p. 92° (hydrochloride, m. p. 197°; acetyl derivative, m. p. 150°). A. I. VOGEL.

Merequinonoid derivatives of the phenarsazine series. II. G. A. RAZUBAIEV (Ber., 1929, 62, [B], 1208-1220; cf. this vol., 585).-Treatment of 10chloro-3(1)-methyl-, 10-chloro-3:7-(1:9)-dimethyl-, and 10-chloro-3: 4-benzo-5: 10-dihydro-phenarsazine with formic acid causes addition of 1 atom of hydrogen per mol. of substance to intensely-coloured solutions which are decolorised by atmospheric oxygen. Warming the solution causes reappearance of the colour, which may be again discharged by air. The added hydrogen is determined by measurement of the carbon dioxide evolved, calculated according to the equation $H \cdot CO_2 H = CO_2 + H_2$. Addition of halogen to the reduced solutions causes disappearance of the colour after reaction of 1 atom of halogen per mol. of substance. 10-Chloro-1:2:8:9-dibenzo-5: 10-dihydrophenarsazine, 10-chloro-2: 8-dinitro-5: 10-dihydrophenarsazine, and 10-chlorophenoxarsine are not reduced by formic acid. The following are 10-bromo-3: 4-benzo-5: 10-dihydrophendescribed : arsazine, m. p. 209°, and the corresponding 10-iodocompound, m. p. 202-203°; 10-chloro-3(1)-methyl-5: 10-dihydrophenarsazine, m. p. 195-196°, from arsenic chloride and phenyl-m-tolylamine in o-di-10-bromo-3(1)-methyl-5: 10-dihydrochlorobenzene; phenarsazine, m. p. about 220° (decomp.), and the 10-iodo-compound, m. p. 188°; 10-chloro-3:7(1:9)dimethyl-5: 10-dihydrophenarsazine, m. p. 250-252° from arsenic trichloride and di-m-tolylamine; 10-iodo-3:7(1:9)-dimethyl-5:10-dihydrophenarsazine, m. p. 241-244°. H. WREN.

of $\alpha\delta$ -dibromobutane react at the ordinary temperature to give 1- δ -bromobuty/cycloselenibutane 1-bromide, m. p. 65—66°; if the mixture be heated in the presence of water at 90° tetramethylene- $\alpha\delta$ -biscycloselenibutane 1:1-dibromide, m. p. 95—96°, is obtained.

Tetramethylene- $\alpha\delta$ -diselenocyanate, m. p. 40°, is produced by heating $\alpha\delta$ -dibromobutane and potassium selenocyanate in acetone solution for several hours, and is converted by alcoholic sodium hydroxide followed by atmospheric oxidation into cyclotetramethylene diselenide (cyclodiselenobutane) (I), m. p. 41-42°, the structure of which was established by its quantitative conversion with excess of nitric acid into $\alpha\delta$ -tetramethylenediseleninic acid dinitrate, m. p. 136° (decomp.), identical with the substance obtained by treatment of tetramethylenediselenocyanate under similar conditions. When heated, I afforded cycloselenobutane and selenium, whilst bromine in chloroform solution gave cycloselenibutane-1: 1-dibromide.

A. I. VOGEL. Interaction of tellurium tetrachloride and dimethylaniline. G. T. MORGAN and H. BURGESS (J.C.S., 1929, 1103-1106).-Tellurium tetrachloride and dimethylaniline react in dry ethereal solution to give bisdimethylaniline tellurium tetrachloride (I), m. p. 144-145° (decomp.), together with a small quantity of 4:4'-tetramethyldiaminodiphenyl telluridi-chloride (II), m. p. 188-189°, more conveniently prepared by digesting the tetrachloride I with boiling water and oriented by conversion into p-nitrosodimethylaniline and tellurium dioxide on treatment with cold nitrous acid. 4:4'-Tetramethyldiaminodiphenyl telluridi-iodide, m. p. 158-159° (decomp.), is obtained by refluxing the dichloride II with sodium iedide in acetone, whilst 4:4'-tetramethyldiaminodiphenyl telluride is produced by reduction of II in dilute acctone solution with potassium metabisulphite. Trisdimethylaniline hydrochloride tellurium tetrachloride, (NPhMe2, HCl)3, TeCl4, EtOH, m. p. 119-121°, s obtained as a by-product in the preparation of the dichloride II from the tetrachloride I. Interaction of tellurium tetrachloride and N-methyldiphenylamine yielded 4: 4'-diphenyldimethyldiaminodiphenyl klluridichloride, m. p. 170-172°. A. I. VOGEL.

Mechanism of the abnormal salt formation of chromium pentaphenyl hydroxide and a peculiar bydrogen union with chromium tetraphenyl salts. F. HEIN [with O. SCHWARTZKOPFF, K. HOYER, K. KLAR, W. EISSNER, W. CLAUSS, and W. JUST] (Ber., 1929, 62, [B], 1151-1167; cf. A., 1928,In the majority of instances, chromium pentaphenyl hydroxide is converted by acids and salts into dromium tetraphenyl salts, whereby the fifth phenyl mup appears as phenol and diphenyl. The yields of plenol depend to some extent on the previous history of the base, but homogeneous chromium pentaphenyl hydroxide (as hydrate) yields with salts such as potassium bromide in presence of chloroform almost 100% of phenol and only traces of diphenyl. The base hydrate in absolute alcohol in complete absence of air affords 1 mol. of phenol from each mol. of base when acted on by potassium iodide. Production of phenol is therefore not due to oxidation, but occurs according to the scheme : CrPh5.OH+KX+H2O

 \longrightarrow CrPh₄X+Ph·OH+KOH+(H). In complete absence of water the anhydrous base yields, therefore, as expected, not more than 50% of phenol: $2 \text{CrPh}_5 \text{OH} + 2 \text{RX} \longrightarrow 2 \text{CrPh}_4 \text{X} + \text{R}_2 \text{O} + \text{PhOH} +$ (H)'+Ph·Ph. The anhydrous base does not react with gaseous or liquid ammonia and, when suspended in the last-named medium, is converted by potassium iodide or ammonium bromide into the chromium tetraphenyl salt and phenol but not aniline. The fifth phenyl group can therefore react only with a similar group or with a molecule of solvent which is united by solvation to the base. The intramolecular activity of the group explains its inability to form tetraphenylmethane with triphenylmethyl. The schemes proposed to explain the reaction indicate the production of hydrogen, the formation of which is established by decomposing the base with ammonium chloride in presence of methylene-blue, which is thereby decolorised. Addition of palladised calcium carbonate or barium sulphate or slight rise of temperature accelerates the change. Under the most favourable conditions (illumination of the solutions and presence of an excess of dye) about 33% of the theoretical quantity of methylene-blue is hydrogenated within 3 days. [Excess of dye is determined by titration with ferrous ammonium sulphate in presence of alkali tartrate and ammonia.] Chromium tetraphenyl salts therefore appear to have the ability to combine with hydrogen. Exact measurements show that chromium tetraphenyl chloride, without particular pre-treatment, absorbs 8.5-11.5% of hydrogen and that the product, after being partly dehydrogenated with methyleneblue, absorbs more active hydrogen than otherwise. Since the properties of the chromium tetraphenyl salts (colour, m. p., analytical behaviour) are not appreciably influenced by such addition, an unusual form of union is postulated. This union is so feeble that a portion of the hydrogen is lost during the isolation of the salts; the gas appears present in a form similar to that in certain metallic hydrides, notably palladium hvdride. H. WREN.

Mass and size of protein molecules. T. SVED-BERG (Nature, 1929, 123, 871).—All stable native proteins so far studied may be classed, as regards molecular mass, as hæmocyanins (M of the order 10⁶) and others (M about 35—210×10³), the latter being divisible into four sub-groups. The molecules of the first and fourth sub-groups are spherical (r 2·2 and 4·0 µµ, respectively), whilst those of the other subgroups are not. The molecules of most of the members of the fourth sub-group are easily disaggregated by increasing $p_{\rm H}$. The close relations existing between the various proteins is exemplified by the fact that a protein may, according to the $p_{\rm H}$ to which it is brought, appear with the molecular mass, size, and shape of another protein.

A. A. ELDRIDGE.

Identity of proteins. S. PEROV (Arb. staatl. Timirjasev Inst., 1925, 29 pp.; Chem. Zentr., 1929, i, 92).—Proteins, insoluble in water or 10% sodium chloride solution, functioning as "protein acids" and having the properties of animal proteins have been prepared from oats, wheat, peas, and almonds by extraction with alkali and coagulation with acetic acid. Proteins are classified according to their ionic function, and hence their equivalent weight. A.A. ELDRIDGE.

Physico-chemical properties of protein. M. LISSIZVN (Arb. staatl. Timirjasev Inst., 1925, 5 pp.; Chem. Zentr., 1929, i, 92—93).—Extraction of plant proteins is normally incomplete; it is considered that a portion of the protein is combined as insoluble calcium proteate. The whole of the protein is extracted by 0.05N-sodium hydroxide following treatment with 2% acetic acid. A. A. ELDRIDGE.

Structure of protein materials. W. BERC-MANN (Naturwiss., 1929, 17, 314—316).—The relation of arginine and its derivatives to proteins is discussed.

R. A. MORTON. Colorimetric micro-determination of chloroform. K. YODOMIGAWA (Bul. Hokuetsu Med. Soc., 1928, 43, 355—363).—The liquid to be tested is added to a heated mixture of sodium hydroxide and pyridine; the mixture is shaken and the colour compared with standards prepared from solutions containing phenolred and phosphate. CHEMICAL ABSTRACTS.

Determination of citric and tartaric acids. F. PIRRONE (Riv. Ital. Ess. Prof., 1928, **10**, 101—102; Chem. Zentr., 1928, ii, 2491—2492).—Tartaric acid (0.05 g.) or citric acid (0.0388 g.) is boiled with 0.1N-potassium iodate solution (50 c.c.), and concentrated sulphuric acid (25 c.c.) until the volume is reduced to 30 c.c.; after cooling, 100 c.c. of water are added and evaporation to 30 c.c. is repeated. To the cold solution 100 c.c. of water and 10 c.c. of 30% potassium iodide solution are added; excess of 0.1N-sodium thiosulphate is added and the excess titrated with 0.1N-iodine solution.

A. A. ELDRIDGE.

Detection and determination of methylpentose. T. FUKAI (Bul. Ferm. Tokyo, 1928, No. 100, 106– 129).—The distillate obtained from methylpentose and hydrochloric acid gives a violet-red coloration with vanillin in 0.5% sulphuric acid. Solubility differences of the phloroglucides of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde are applied to their separation. CHEMICAL ABSTRACTS.

proteins so that studied may be classed, as regards molecular mass, as hismodymins (If of the order 10%) Volumetric determination of hexamethylenetetramine. C. V. BORDEIANU (Ann. sci. Univ. Jassy, 1929, 15, 380-383).—The method proposed by Kollo and Angelescu (A., 1927, 786) gives erroneous results, mainly because of the solubility of hexamethylenetetramine picrate in water. With increasing amounts of picric acid in excess, a large negative error decreases to a minimum and finally increases to large positive errors. With hexamethylenetetramine in excess, some picric acid always remains in solution and can be titrated by sodium hydroxide owing to the solubility of the picrate in water.

L. S. THEOBALD. Diphenylamine and diphenylamine-blue. A. THIEL (Z. Elektrochem., 1929, 35, 274-278).--A method whereby diphenylamine may be determined colorimetrically with an accuracy of 1% is described. The comparison solution is made up by taking l e.e. of a 50 vol.-% solution of sulphuric acid containing 40 mg. of diphenylamine per litre, oxidising it with ferric sulphate in sufficient excess, about 100-200 mols. per mol. of diphenylamine, boiling for 5 min., making up to 10 c.e., and viewing the resulting blue solution through a layer 30 mm. thick. The colour of a solution of unknown concentration produced by oxidation with a sufficiently large excess of ferric sulphate is then matched in a colorimeter, and, assuming the validity of Beer's law, the amount of diphenylamine present is calculated.

The basic dissociation constant of diphenylamine, K_b , was found to be 7.6×10^{-14} at 15° by saturating acid solutions of known $p_{\rm H}$ with the base, and determining colorimetrically the amounts dissolved. The absorption of light by diphenylamine-blue is maximal at 5870 Å., when the molar extinction coefficient is 4.46×10^3 . The oxidation of diphenylamine is a time-reaction, but the precise order of the reaction depends on both the concentrations of diphenylamine and of ferric sulphate. The change corresponds approximately with the expression : dx/dt=k' [diphenylamine][ferric sulphate]⁹⁸, where x is the proportion changed and t is the time in min.

H. T. S. BRITTON.

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Respiration in excess of oxygen. BOUNHIOL (Compt. rend., 1929, **188**, 1340—1342).—Guinea-pigs in 80% oxygen died within two or three days; death is accompanied by increase in the soluble nitrogen compounds of the blood. The ease of obtaining oxygen retards circulation, so that the metabolic products accumulate and cause death. E. BOYLAND.

Influence of carbon dioxide tension on the oxygen dissociation curve [of hæmoglobin]. V. MENKIN and M. F. MENKIN (Science, 1928, 68, 518— 519).—The lowering of the oxygen dissociation by an increase in pressure of carbon dioxide is explained by assuming a double dissociation of oxyhæmoglobin represented by $HHbO_2 \Longrightarrow HHb+O_2$ and $HHbO_2 \Longrightarrow H'+HbO'_2$. L. S. THEOBALD. Solubility of gases in blood. A. GROLLMAN (J. Biol. Chem., 1929, 82, 317—325).—Figures are given for the solubilities of ethylene and acetylene at different temperatures in water, whole blood, bloodplasma, and solutions of hæmoglobin. Henry's law is followed by ethylene at 25° for all these fluids. The greater solubility of these gases in blood than in water is due to the lipoidal constituents of the former. C. R. HARINGTON.

Mechanism of the abnormal salt formation of chromium pentaphenyl hydroxide and a peculiar.

Manganese as a factor in hæmoglobin formation. R. W. TITUS and H. W. CAVE (Science, 1928, 68, 410).—Manganese has a beneficial effect on the formation of hæmoglobin by rabbits and rats fed on a milk-iron diet freed from copper.

L. S. THEOBALD.

Preparation of crystalline potassium salts of oxyhæmin. A. HAMSÍK (Z. physiol. Chem., 1929, 182, 117—124).—A crystalline tripotassium salt was prepared by the action of 20% methyl-alcoholic potassium hydroxide on α -oxyhæmin. It was washed with a mixture of methyl alcohol and ether. The β and ψ -modifications do not give well-crystallised salts. J. H. BIRKINSHAW.

Bile pigment content in local hæmorrhage in man. KURISHITA (Klin. Woch., 1928, 7, 1914; Chem. Zentr., 1928, ii, 2376).—Shed blood contains more bilirubin than circulating blood; it is therefore supposed that most of the bilirubin found is formed outside the liver. A. A. ELDRIDGE.

Adsorption of bilirubin by protein. O. WELT-MANN and F. JOST (Deut. Arch. klin. Med., 1928, 161, 203—226; Chem. Zentr., 1928, ii, 2493).—Of the total serum-bilirubin, 0—10% is normally adsorbable; in icterus 5—100% is adsorbable. Adsorbable bilirubin is apparently excreted only through the liver; non-adsorbable bilirubin is concerned in bilirubinuria. A. A. ELDRIDGE.

Colorimetric determination of proteins of blood-serum. D. M. GREENBERG (J. Biol. Chem., 1929, 82, 545—550).—Blood-serum is treated with sodium sulphate solution; the precipitated globulin is redissolved in dilute sodium hydroxide solution and determined colorimetrically with the phenol reagent of Folin and Ciocalteau (A., 1927, 892); the albumin in the filtrate is determined similarly.

C. R. HARINGTON.

Determination of protein and residual nitrogen in blood and urine. FISCHER (Süddeut. Apoth.-Ztg., 1928, 68, 693-695; Chem. Zentr., 1929, i, 115).—A discussion of the degradation of protein, the formation of urea, and of analytical methods. A. A. ELDRIDGE.

Isolation of a carbohydrate derivative from serum-proteins. C. RIMINGTON (Biochem. J., 1929, 23, 430-443).-The albumin and globulin fractions were prepared from the serum by the usual method of precipitation with ammonium sulphate. The proteins were hydrolysed with baryta and the hydroisate was treated with lead acctate and ammonia. The precipitate after being dissolved in acctic acid was reprecipitated several times with ammonia and decomposed with carbon dioxide. After clearing the solution with mercuric chloride the compound C12H23O10N was finally precipitated and reprecipitated with methyl alcohol and ether. The compound sa structural unit of these proteins. Glucosamine and mannose are the constituent sugars. The same prduct is obtained from serum-proteins when trypsin semployed as the hydrolytic agent. A structure is S. S. ZILVA. suggested for the compound.

Sources of error in the determination of bloodsugar by Bang's micro-method. E. RAITH (Biothem. Z., 1929, 208, 357---360).—The filter-papers used for determining blood-sugar by Bang's method reduce Fehling's solution sufficiently to cause an appreciably high result. Washing removes the reducing substance, but also decreases the absorbent power of the Paper so that it is no longer of any use for this type of determination. Blank determinations on a number of papers are therefore essential.

P. W. CLUTTERBUCK.

Distribution of reducing substances between plasma and corpuscles; a comparison of various blood-sugar methods. F. K. HERBERT and J. GROEN (Biochem. J., 1929, 23, 339-351) .-- Various methods for the determination of blood-sugar give widely different results for the distribution of "sugar" between plasma and corpuscles. The average discrepancies between methods are not great for determinations on plasma, but are considerable for those on corpuscles. Tungstic filtrates of whole blood or corpuscles produce a reduction of the Folin–Wu copper reagent in the cold, whereas filtrates from plasma give no such reaction. The reaction is not given by iron filtrates or zinc filtrates. This is most probably due to the presence of a non-dextrosereducing substance in corpuscles which is present in tungstic but not in iron and zinc filtrates. Such substances may also be responsible for the residual reduction after fermentation of blood by yeast. Uric acid, creatine, creatinine, and ergothioneine in the small amounts in which they occur in human blood have not, whilst glutathione has, an important effect on bloodsugar methods. S. S. ZILVA.

Determination of blood-sugar. I. Benedict's alkaline copper solution. M. R. EVERETT (J. Biol. Chem., 1929, 82, 369—376).—The lower values for blood-sugar obtained with alkaline copper reagents containing sulphite (e.g., the reagent employed by Benedict, A., 1925, i, 994; 1926, 984) are due to an unequal fading of the colour of the standard and unknown solution rather than to an increased specifiicity of the reagent for dextrose. The use of the acid molybdate reagent of Folin (A., 1926, 648, 1282) is therefore recommended for the determination of the true blood-sugar. C. R. HARINGTON.

Comparison of gravimetric and colorimetric methods of cholesterol determination in bloodserum. W. N. NEKLUDOV and S. S. CHALATOV (Biochem. Z., 1929, 208, 60—72).—The best gravimetric method for total cholesterol consists in heating the serum to 100° with 20 or 45% sodium hydroxide for 8 hrs. The cholesterol is extracted with ether and after removal of the ether dissolved in alcohol and precipitated and weighed as the digitonin complex. Fex's method (A., 1920, i, 697) gives 97% of the total cholesterol and offers the possibility of determining free and esterified cholesterol. Of the colorimetric methods Grigaut's gives high results and has other disadvantages; Krastelevski's method (A., 1924, ii, 127) gives 95—98% of the cholesterol present and is recommended. J. H. BIRKINSHAW.

Effect of the use of a [mercury] silica lamp on the blood-cholesterol. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1928, 99, 922—925; Chem. Zentr., 1929, ii, 255).—Irradiation of the whole body raises the blood-cholesterol by 50%, normal values being attained in 4 days. A. A. ELDRIDGE.

Oxidative determination of phospholipin in blood and tissues. W. R. BLOOR (J. Biol. Chem., 1929, 82, 273-286).—The blood or finely divided tissue is extracted with alcohol; aliquot portions of the extract are evaporated and the lipins taken up in light petroleum; the concentrated solution is treated with acetone and alcoholic magnesium chloride. The precipitated phospholipins are dissolved in moist (peroxide-free) ether; after removal of the latter by evaporation the residue is subjected to the quantitative oxidation of Bang as modified by the present author (A., 1928, 662). C. R. HARINGTON.

Phosphoaminolipins and sterols of bloodserum and plasma. II. Physical chemistry of the protein fraction richest in phospholipins and sterols. M. MACHEBEEUF (Bull. Soc. Chim. biol., 1929, **11**, 485–503; cf. this vol., 206).—The phosphoaminolipin-protein is soluble in water in either alkaline or neutral media. Extraction with ether of aqueous solutions at varying p_{π} yields only traces of a substance which consists of 50% cholesterol and 45% fatty acids, moreover addition of neutral salts to the aqueous solutions does not increase the amount of the ethereal extract. Small quantities of alcohol in neutral or more concentrated solutions yield a precipitate which is rich in phosphorus, fatty acids, and cholesterol and dissolves if treated at once in excess of alcohol or water. Prolonged treatment with alcohol of a neutral solution at 12° yields a precipitate consisting of a protein coagulum and crystalline cholesteryl esters, but in alkaline media the precipitation is incomplete. Precipitation of the protein in any solution is obtained on treatment with alcohol at 70° for 10 min.

The protein fraction forms a stable gel when the precipitate is converted into a faintly alkaline paste with 3N-ammonia. Treatment with 2N-ammonia yields a viscous mass which corresponds in all its properties with the gliode of Bottazzi (Arch. Sci. Biol., 1923, 4, 3), an independent phase intermediate between a sol and a gel. It is suggested that the protein fraction under examination is an entity and that the linkings between the constituents modify the physical properties of the individual constituents.

C. C. N. VASS.

Calcium and potassium contents of the bloodserum of fasting dogs. S. MORGULIS (Biochem. Z., 1929, 208, 257–258).—The serum-calcium for fasting dogs is 11.0 mg.-% and remains constant during rest for a long time. When the body-weight has decreased by 20% the calcium content is 10.6 mg.-%, and when the body-weight has decreased by 35–40% the serum-calcium is 9.6 mg.-%. The potassium : calcium ratio during prolonged fasting is almost unchanged, the normal value of 2.0 increasing only to 2.1. P. W. CLUTTERBUCK.

Dispersoidal properties of some salts of the plasma. B. DOGADKIN (Russ. fisiol. Zhur., 1925, 10 pp.; Chem. Zentr., 1929, i, 210).—Sol systems (protected by sodium chloride or sulphate) are formed between the following concentrations : calcium mono-hydrogen phosphate N/130-N/250; tricalcium phosphate N/700-N/1100; calcium carbonate N/100-N/180; calcium oxalate N/600-N/1200; calcium formate, citrate, and lactate do not form colloidal solutions. A. A. ELDRIDGE.

Physico-chemical behaviour of magnesium in serum. Z. STARY and R. WINTERNITZ (Z. physiol. Chem., 1929, **182**, 107—116).—The non-dialysable fraction of magnesium in serum amounts to 28%. In spite of the fact that cerebrospinal fluid shows a higher magnesium content than serum, it is shown by compensation dialysis at varying $p_{\rm H}$ values that the magnesium in serum follows the Donnan law.

J. H. BIRKINSHAW.

Determination of inorganic phosphate of blood-serum. L. GUNTHER and D. M. GREENBERG (J. Biol. Chem., 1929, 82, 551-553).—The calciumfree filtrate obtained in the determination of calcium by the method of Tisdall (A., 1923, ii, 656) is freed from protein with trichloroacetic acid; phosphate is then determined by the method of Fiske and Subbarow (A., 1926, 443), excess of oxalate being oxidised with permanganate. C. R. HARINGTON.

Determination of phosphorus in small amounts of serum and cerebrospinal fluid. K. SAMSON (Biochem. Z., 1929, 208, 230–236).—Slight modifications in Neumann's volumetric method which enable 0.01-0.15 mg. of phosphorus to be determined to 0.001-0.002 mg are described. J. H. BIRKINSHAW.

Micro-determination of chlorides in serum and cerebrospinal fluid by the method of electrical conductivities. M. DUBOUX and L. PARCHET (Bull. Soc. Chim. biol., 1929, 11, 504—516).—A conductance titration whereby the chloride content of 0.4 c.c. of serum can be determined to an accuracy of 0.05 g. per litre is described. Prolonged contact of the serum with the blood clot lowered its chloride content by adsorption. The average chloride content expressed as g. sodium chloride per litre is 5.65—5.90 in normal human serum and 6.70—7.20 in cerebrospinal fluid. C. C. N. VASS.

Determination of small amounts of iodine [in blood]. E. GLIMM and J. ISENBRUCH (Biochem. Z., 1929, 207, 368-376).—When proper care is taken, the amount of iodine contained in human blood is found to be $20-30 \gamma$ -%, a figure much higher than that usually accepted (10γ -%). P. W. CLUTTERBUCK.

P. W. CLUTTERBUCK. Anticoagulant action of antithrombin. J.O.W. BARRATT (Biochem. J., 1929, 23, 422–424).—The anticoagulant action of antithrombin on a mixture of fibrinogen and thrombin *in vitro* is exerted on thrombin alone, which becomes diminished in amount.

S. S. ZILVA. Urobilin in organs. M. ROYER (Compt. rend. Soc. Biol., 1928, 99, 1006—1007; Chem. Zentr., 1929, i, 419—420).—The liver and kidneys contain the largest, and the musculature, pancreas, and lung contain the smallest amount of urobilin.

A. A. ELDRIDGE.

Preparation of glycogen. Glycogen of the abalone, Haliotis rufescens, Swainson. L. G. PETREE and C. L. ALSBERG (J. Biol. Chem., 1929, 82, 385-395).—Glycogen was prepared from the flesh of the abalone (an edible mollusc), without the use of alkali, as follows. The finely-divided flesh was extracted with boiling water, the extract being kept neutral to litmus by addition of sodium hydroxide, and then slightly acidified with acetic acid; proteins were removed with picric acid, and the glycogen was precipitated from the filtrate by addition of alcohol.
Purification was accomplished by repeated re-dissolution in water and precipitation with alcohol, addition of a trace of ammonium acetate being necessary in the final precipitations. Glycogen prepared in this way retained small amounts of ash which could not be removed by electrodialysis, nor did the latter process separate the glycogen into fractions containing different proportions of phosphoric acid. The ash of the electrodialysed preparations contained small amounts of calcium and iron in addition to phosphoric acid.

C. R. HARINGTON.

Keratohyalin. L. NÜRNBERGER (Klin. Woch., 1928, 7, 1961—1962; Chem. Zentr., 1928, ii, 2373).— Keratohyalin is not identical with nucleochromatin. A. A. ELDRIDGE.

Cholesterol content of the human intestinal wall. M. BÜRGER and H. D. OETER (Z. physiol. Chem., 1929, 182, 141—147).—The sigmoid contains considerably more cholesterol than any other section of the intestinal tract. It was shown by bromination that coprosterol was absent, indicating that the high sterol content is due to excretion rather than resorption. J. H. BIRKINSHAW.

Phosphatide content of different kinds of muscle. K. Sorg (Z. physiol. Chem., 1929, 182, 97-106).—A method involving methyl-alcoholic extraction is described whereby the phosphatide content of small amounts of tissue (0.5—2 g.) may be determined to $\pm 1\%$. The phosphatide content of the heart muscle of the rabbit may amount to 0.430%; that of red and white muscle is much less, 0.173% and 0.128%, respectively, representing maximum values. The total acid-insoluble phosphoric acid of heart muscle and nearly all of that contained in the red and white muscle is present as phosphatides.

J. H. BIRKINSHAW. Tyramine and tyrosine content of the salivary glands of cephalopods; micro-determination of these two substances. M. HENZE (Z. physiol. Chem., 1929, 182, 227—240).—Tyramine and tyrosine terminations on the salivary glands of Octopus *reropus* were made using the apparatus of Widmark (Stand. Arch. Physiol., 1927, 48, 61) for microetraction of organic acids. The amounts present in the right and left glands from the same animal are approximately the same; the tyramine content is two to six times that of the tyrosine.

J. H. BIRKINSHAW.

lodine-containing compounds of the thyroid gland. Isolation of dl-3:5-di-iodotyrosine. C.R. HARINGTON and S. S. RANDALL (Biochem. J. 1929, 23, 373-383).-The desiccated thyroid gland Was hydrolysed with baryta and the hydrolysate precipitated with sulphuric acid at $p_{\rm H}$ 5.0. The pecipitate after having the acid-soluble iodine extracted with alkali was worked up for thyroxine. The filtrate to which the alkaline extract from the acid-insoluble fraction was added in the isolation process was treated as follows. It was precipitated with basic lead acetate, the precipitate hydrolysed again with baryta and precipitated twice with silver aitrate. The filtrate from the decomposed silver salts was then extracted with butyl alcohol. This extract was cleared with uranium acetate and after final treatment with lead acetate yielded a crystalline compound which was recrystallised from 50% acetic acid and was identical with dl-3: 5-di-iodotyrosine. The iodine content of the various fractions was followed up. Evidence is adduced that the whole of the acidsoluble iodine is present as di-iodotyrosine, whilst the whole of the acid-insoluble iodine belongs in all probability to thyroxine. S. S. ZILVA.

Occurrence of methylguanidine in the animal organism. III. Use of benzenesulphonyl chloride for separation of methylguanidine. I. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 182, 259—264; cf. this vol., 589).—The amount of methylguanidine precipitated as the benzenesulphonate by excess of benzenesulphonyl chloride is only 9—30% of the theoretical, depending on the conditions. The yield is diminished in presence of creatinine.

J. H. BIRKINSHAW.

Tetradecenoic acid from Tetradenia glauca, Motsum. M. TSUJIMOTO (Bull. Inst. Tokyo Ind. Res. Lab., 1928, 23, No. 3, 53-60).—" TSUZUIC acid," from the oil of Tetradenia glauca, is Δ^3 -tetradecenoic acid; Δ^5 -tetradecenoic acid, from the oil of the whale Physeter macrocephalus is named physeteric acid. CHEMICAL ABSTRACTS.

Rufin, the epidermal pigment of Arion Rufas. C. DHÉRÉ and C. BAUMELER (Compt. rend. Soc. Biol., 1928, 99, 492—496; Chem. Zentr., 1928, ii, 2479— 2480).

Histochemical detection of urea. W. LAVES (Wien. klin. Woch., 1928, 41, 1403—1404; Chem. Zentr., 1928, ii, 2493).—The section is immersed for 6 hrs. in a 6% solution of xanthhydrol in acetic acid, whereby crystals of dixanthylcarbamide are formed. A. A. ELDRIDGE.

Use of mercurochrome and modified mercurochrome as biological stains. J. D. HERR-MANN, W. DENNIS, and D. D. DEDRICK (Univ. Oklahoma Bull., 1928, [ii], No. 409, Sudies ser. 29, 132-133).

Adrenaline and choline in lymph. G. VIALE (Compt. rend. Soc. Biol., 1928, 99, 1009-1010; Chem. Zentr., 1929, i, 96).-10-35 Mg. of choline per g. of lymph, and adrenaline, were detected.

A. A. ELDRIDGE.

Excretion of nucleoproteins in the bile. P. CARNOT and Z. GRUZEWSKA (Compt. rend. Soc. Biol., 1928, 99, 598—600; Chem. Zentr., 1929, i, 103).— The cholenucleins are obtained by treating the bile with an equal volume of alcoholic chloroform and washing the precipitate with ether. The moist substance is readily soluble in dilute alkali solutions. The cholenuclein content of dog's bile is reduced by large doses of sodium hydrogen carbonate from 1 to 0.3%. A. A. ELDRIDGE.

Absorption and secretion in the small intestine. I. Secretion of electrolytes. S. KUCZKOWSKI (Acta Biol. Exp., Warsaw, 1929, **3**, 57-80).—The fluid found in an intestinal loop after the introduction of water, neutral salts, acids, or alkalis has the same mineral content, viz., sodium 32.5, potassium 2.4, calcium 1.1, magnesium 0.15, chlorine 26.7, and phosphorus 0.3 mg.-%. A comparison of this fluid with that normally found indicates that the mineral constituents of the latter are secreted by intestinal glands. Sodium and potassium salts, phosphates, and above all hydrogen carbonates are absorbed freely, whilst calcium and magnesium undergo resorption R. TRUSZKOWSKI. relatively very slowly.

Simultaneous determination of pepsin and lipase in gastric juice. L. Gózony and F. HOFFEN-REICH (Biochem. Z., 1929, 208, 259-261).-The gastric juice is brought to p_{μ} 5.6 and a saturated solution of monobutyrin in physiological saline added to a series of dilutions. After keeping, sodium caseinogenate is added; the amount of caseinogen precipitated by the freed fatty acids is determined nephelometrically and forms a measure of the activity of the lipase. The caseinogen is then completely precipitated by addition of a drop of 0.1N-hydrochloric acid, and, after keeping, the activity of the pepsin is determined by the decrease in the amount of caseinogen precipitated. P. W. CLUTTERBUCK.

Urea and chlorine in the cerebrospinal fluid in retention of both substances. P. SAVY and H. THIERS (Compt. rend. Soc. Biol., 1928, 99, 516-518; Chem. Zentr., 1928, ii, 2376) .- Determination of urea and chlorine in cerebrospinal fluid docs not suffice for a decision concerning their retention. Both substances take at least 53 hrs. to reach equilibrium with the blood-chlorine and -urea.

A. A. ELDRIDGE.

Ch'an Su, the dried venom of the Chinese toad. Isolation of adrenaline. H. JENSEN and K. K. CHEN (J. Biol. Chem., 1929, 82, 397-401).-Finelypowdered Ch'an Su was extracted with dilute acetic acid, the extract was cleared by addition of alcohol and centrifuging, and then concentrated; it was further cleared with lead acetate and extracted with chloroform; the residual aqueous solution, on concentration and treatment with ammonia, yielded adrenaline (0.35 g. from 150 g.). C. R. HARINGTON.

Determination of amino-acids in urine. L. TIXIER (Bull. Sci. pharmacol., 1928, 35, 570-571; Chem. Zentr., 1929, i, 419).-Use is made of the sensitivity of phenolphthalein, and the insensitivity of litmus, towards amino-acids. A. A. ELDRIDGE.

Detection of alcohol in urine. P. LIEBESNY (Klin. Woch., 1928, 7, 1959-1960; Chem. Zentr., 1928, ii, 2388).-With the chromic acid method, 0.5 c.c. of alcohol ingested per kg. body-weight can be detected within 6 hrs.; 3 c.c. per kg. can still be detected after the seventh hour. A. A. ELDRIDGE.

Citric acid content of normal urine. 0. Öst-BERG (Biochem. Z., 1929, 208, 352-353).-The presence of citric acid is detected and its amount determined in normal urine in terms of the increased velocity of decolorisation of methylene-blue in presence of the citric acid dehydrogenase of cucumber seeds. The total amount of citric acid excreted daily by a man varies from 0.23 to 1.85 g

P. W. CLUTTERBUCK. Effect of the blood-serum of the healthy and alcaptonuric individual on homogentisic acid. F. LANYAR and H. LIEB (Z. physiol. Chem., 1929, 182, 218-226).-Free homogentisic acid in aqueous solution is not oxidised by air at 37°; if the acid is neutralised or the solution contains free alkali oxid. ation occurs. When mixed with healthy serum there is a small loss of acid due to adsorption by the protein. Oxidation occurs when the acid is brought to the $p_{\rm H}$ of serum. The same phenomena were observed with alcaptonuric serum. J. H. BIRKINSHAW,

Changes of cholesterol content of serum in anaphylaxis. J. M. GOLDBERG and W. N. NEKLT. Dov (Biochem. Z., 1929, 208, 285-287).-In experiments with sensitised rabbits and guinea-pigs, the serum-cholesterol content during the period of anaphylactic shock increased, fell, and then increased again, remaining high when the shock was greatest. P. W. CLUTTERBUCK.

Reaction of the blood in cancer. H. MILLET (J. Biol. Chem., 1929, 82, 263-267) .- No change from the normal was observed in the $p_{\rm H}$ of the blood of patients suffering from cancer. C. R. HARINGTON.

Carbohydrate metabolism of tumours. H.G. CRAETREE (Biochem. J., 1929, 23, 536-545).-Determinations of the carbohydrate metabolism of several strains of mouse tumours are recorded. In many cases there were great deviations from the standard value found for tumours of rat, fowl, and a limited series of human tumours. There were also variations between tumours of different strains and also between those of the same strain. There was a number of cases of high respiration both in its absolute value and in its relation to the acrobic and anacrobic glycolysis. This respiration is ineffective in checking the aërobic glycolysis. The respiratory quotients with one exception were found to be below unity. Xylose was not metabolised by tumour tissue. Evidence is brought forward which suggests that the glycolytic activity of tumours exerts a checking effect on their respiration. The carbohydrate metabolism of tumours is to some extent influenced by the environment in which they grow. The respiration of the subcutaneous growths was on the average 50% higher than that of the intraperitoneal growths. The majority of these subcutaneous tumours do not exhibit a positive value for the excess fermentation.

S. S. ZILVA.

Reaction of neutral-red in cancerous sera and its relation to other dyes. A. ROFFO and H. DEGIORGI (Z. Krebsforsch., 1927, 25, 136-140; Chem. Zentr., 1929, i, 272).—Cresol-red and rosaniline also react. Since the three dyes belong to different groups, the constitution of the dye appears to be unconcerned in the reaction. A. A. ELDRIDGE.

A peculiar disturbance of carbohydrate metabolism. R. SCHÖNHEIMER (Z. physiol. Chem., 1929, 182, 143-150).-The liver and kidney of a child which, having shown curious symptoms from birth, succumbed to influenza, were found to be enormously enlarged and contained about 35% of glycogen (on dry weight). The liver was incapable of metabolising its own glycogen. J. H. BIRKINSHAW.

Potassium : calcium ratio and magnesium content of cerebrospinal fluid. B. EISLER (Z. ges. exp. Med., 1928, 61, 549-559; Chem. Zentr., 1928, ii, 2660).-A study of pathological conditions. A. A. ELDRIDGE.

Behaviour of the lactic acid of the cerebrospinal fluid in normal and pathological conditions. G. MARGRETH (Folia Clinica, 1929, 3, 397-405).—In normal individuals the proportion of lactic acid in the cerebrospinal fluid is 16-18 mg. per 100 c.c., that in the blood being 10-14 mg. per 100 c.c. In cases of tubercular meningitis the proportion is 41-60, in those of meningo-myelitis and tabes it is slightly above the normal, and in a case of lues cerebri normal. The leucocytes doubtless play a considerable part in the transformation of sugar into lactic acid during the course of meningitis, and bacteria possibly help in the glycolysis in the inflammatory processes of the meninges. T. H. POPE.

Action of insulin and pituitrin on the elimination of urine and especially on carbonuria in diabetes insipidus. G. MARINESCO, O. KAUFFMAN-COSLA, and S. DRAGANESCO (Compt. rend. Soc. Biol., 1928, 99, 911—913; Chem. Zentr., 1929, i, 97).— Pituitrin reduces to normal the quantity of urine, but does not affect the carbonuria. Insulin does not reduce the quantity of urine, but abolishes deoxidative carbonuria. A. A. ELDRIDGE.

Action of guanidine derivatives in diabetes. M. R. CASTEX and M. SCHTEINGART (Compt. rend. Soc. Biol., 1928, 99, 999—1000; Chem. Zentr., 1929, i, 101).—Glycosuria is influenced more strongly than glycæmia by synthalin or "glukhorment." In combination with insulin a greater effect is produced than by either type alone. In normal subjects "glukhorment" causes hyperglycæmia.

A. A. ELDRIDGE.

Decreased diastatic action of the urine in kidney diseases and in diabetes. F. SCHMEREL (Biochem. Z., 1929, 208, 415-427).—The small diastatic action of diabetic urine is not due to decreased diastase content of blood and cannot be accounted for solely in terms of the medium (since bringing back the urine to optimal conditions of $p_{\rm fl}$ and salt content for diastase action does not bring tack the diastatic value to normal), but is in part due to the lowered permeability of the kidney to diastase.

P. W. CLUTTERBUCK. Cutaneous and venous blood-sugar curves. II. Benign glycosuria and diabetes. M. FRIEDENSON, M. K. ROSENBAUM, E. J. THALHEIMER, and J. P. PETERS (Arch. Int. Med., 1929, 43, 633-652).—The cutaneous and venous blood-sugar curves have been studied in cases of benign glycosuria and diabetes after the administration of dextrose or mixed meals both with and without insulin therapy. In 14 cases of benign glycosuria all the patients developed distinct positive arterial-venous differences. The differences may be so great that the venous curves fail to show hyperglycamia. In 15 studies on diabetic patients, all but the two least severe cases showed large differences after meals; consequently such differences cannot be taken as a measure of the severity of the disease nor can much guidance be obtained from a study of the arterial-venous curves in differentiating benign from diabetic glycosuria. In extreme hyperglycæmic reactions the ability of the tissues to remove sugars is not entirely lost, but it is limited, rapidly exhausted, and occurs at a higher blood-sugar

level. Insulin-treated patients with diabetes of variable severity gave arterial-venous differences during fasting with far greater frequency than normal persons, and after meals at a reduced blood-sugar level. F. C. HAPPOLD.

Inorganic salts and the acid-base equilibrium of the blood in fever. M. AKIYA (Z. klin. Med. 1928, 109, 312—341; Chem. Zentr., 1929, i, 253).— Determinations on rabbits and man are recorded. A. A. ELDRIDGE.

Lacticæmia, spontaneous and induced, as a test of hepatic function. G. MARGRETH (Folia Clinica, 1929, 3, 381-396).-The liver plays the principal part in the re-synthesis of lactic acid to glycogen and dextrose, although the muscles also appear to participate in these changes. Experiments made by administering lactic acid to healthy individuals and patients with liver disease kept without food and in a state of complete rest for the previous 12 hrs. show that only very serious alterations of the hepatic cells are accompanied by marked increase in the lactic acid content of the blood. With healthy subjects this lactic acid content increases slightly 1-2 hrs. after ingestion of the acid, but reverts to the normal value after 3 hrs., whereas with those suffering from diseased livers the increase still persists after 3 hrs. and usually T. H. POPE. becomes more marked.

Fat metabolism. II. Character of bloodlipins in hepatic disorders, including migraine. C. W. MCCLURE and M. E. HUNTSINGER (Arch. Int. Med., 1929, 43, 715-730).-The blood of normal subjects and patients suffering from migraine, gallstones, cirrhosis of the liver, toxic jaundice, hæmo-chromatosis, and cancer of the liver has been examined both in the fasting state and after ingestion of olive oil, oleic acid, egg-white, and dextrose. The lecithin-phosphorus, cholesterol, total fatty acids, and the iodine number of the two latter have been determined. The variations in cholesterol concentrations from the fasting level after ingestion of food were not great, but changes in the iodine numbers and in the concentrations of the blood-lipins followed. In particular an increased iodine number of the bloodcholesterol in these pathological conditions was fairly general, and suggests differences in the chemical constitution of the cholesterol in disease and that of normals. The lecithin-phosphorus concentration was not demonstrably influenced. F. C. HAPPOLD.

Distribution of lipins in normal and abnormal liver. III. Effect of disease on human liver. E. R. THEIS (J. Biol. Chem., 1929, 82, 327-334).— The lipins of normal human liver are closely similar in the proportion of phospholipins (60% of the total) and in the distribution of fatty acids to the lipins of ox and rabbit liver (A., 1928, 319, 676). In pathological degeneration of the liver the proportion of phospholipins shows a progressive decease.

C. R. HARINGTON.

Blood-bilirubin in catarrhal and salvarsan icterus. D. SIMICI and M. POPESCO (Compt. rend. Soc. Biol., 1928, 99, 1084—1085; Chem. Zentr., 1929, i, 97).—In icterus the maximal blood-bilirubin is 0.4 g. per litre (normally 1 in 3500—7000); in salvarsan icterus bilirubinæmia is more prolonged. Insulin has a favourable effect in reducing the value. A. A. ELDRIDGE.

Action of iron on the resting metabolism of rachitic rats. H. SEEL (Biochem. Z., 1929, 208, 295—298).—The decreased oxygen utilisation in rachitic rats may be increased almost to normal by administration of ferrous sulphate or better of ferrous hydrogen carbonate, but this has no beneficial effect on the rachitic condition of the bone.

P. W. CLUTTERBUCK.

Hexosediphosphatase in hens with leg weakness. M. SCHECHTER (Biochem. Z., 1929, 208, 443— 444).—Hens kept in a small darkened cage for several months became unable to walk or stand. In this condition, the plasma-calcium content is slightly lower (mean for 4 hens, 11·1, for 6 normals 16·8 mg.-%) whilst the inorganic phosphorus content is somewhat increased (mean 5·0, in controls $3\cdot9$ mg.-%). The hydrolysis of hexosediphosphate is investigated with material from the limiting cartilage of the distal joint of the phalanx of the second and third toes. The tissue from hens in the above condition hydrolysed hexosediphosphate more strongly than tissue from normal hens. P. W. CLUTTERBUCK

Prevention of tetany in parathyroidectomised dogs. I. Cod-liver oil; effect on calcium assimilation. II. Lactose. I. GREENWALD and J. GROSS (J. Biol. Chem., 1929, 82, 505-530, 531-544).-I. The power of cod-liver oil to protect parathyroidectomised dogs against the development of tetany is not so regular or so considerable as has been claimed by other workers; the effect of codliver oil is increased if it be administered in conjunction with a source of calcium. The variability of the results is explained on the assumption that most animals possess more or less accessory parathyroid tissue which escapes removal at operation, and that it is through the stimulation of parathyroid tissue that cod-liver oil exercises its effect. The development of tetany is due not only to the final degree of reduction of the blood-calcium, but also to the rapidity with which this reduction is brought about. Irradiated ergosterol was without effect, even in conjunction with calcium. The theory that the parathyroids are stimulated by cod-liver oil is supported by the increased excretion of calcium following the substitution of cod-liver oil for maize oil in the diet of a dog on normal diet.

II. Administration of lactose prevents the development of tetany in parathyroidectomised dogs only when the diet contains large amounts of calcium (cf. Dragstedt and Peacock, Amer. J. Physiol., 1923, 64, 424). C. R. HARINGTON.

Tuberculous pus. R. ZANOLI (La Chir. Org. Mov., 1927, 11, 26 pp.; Chem. Zentr., 1929, i, 419).— Organic and inorganic constituents, and the enzyme content, of tuberculous pus have been determined. A. A. ELDRIDGE.

Chloride metabolism and alkalosis in alkali treatment of peptic ulcer. H. A. WILDMAN (Arch. Int. Med., 1929, 43, 615-632).—The alkali treatment of cases of peptic ulcer is studied and its effect on chloride metabolism and alkalosis discussed. Hypo-

chloræmia is accompanied by a marked decrease in

the urinary chlorides, an early sign of approaching alkalosis; when decreased gastric secretion is concurrent the ratio of cell to plasma-chlorides is reduced. A normal carbon dioxide capacity of the plasma may occur in hypochloræmia with symptoms of alkalosis, consequently such capacity cannot be taken as a trustworthy index of alkalosis. F. C. HAPPOLD,

Course of [biological] oxidation processes. H. WIELAND (Anal. Eds. Quím., 1929, 27, 181–191). —A lecture. R. K. CALLOW.

Respiratory quotient of nerve at rest and during activity. O. MEYERHOF and F. O. SCHMITT (Biochem. Z., 1929, 208, 445-455).—The mean respiratory quotient for frog's resting nerve is 0.69 (varying from 0.64 to 0.73) and the resting respiration (mm.³ of oxygen per g. moist wt. per hr.) 14.5 (varying from 14.4 to 18.0). During stimulation the respiratory quotient is 0.79 (0.71-0.85) and the mean respiration 28 (21-39.6). The respiratory quotient of resting nerve therefore corresponds with the oxidation of fat and on stimulation is increased to a small extent, whilst the respiration is doubled.

P. W. CLUTTERBUCK.

Chemistry of the micelle and its application to biochemical and biological problems. K. H. MEYER (Biochem. Z., 1929, 208, 1-31).—A general discussion of the reactions of colloids from the point of view of micellar structure.

J. H. BIRKINSHAW.

Iodine metabolism. III. Iodine metabolism of the thyroidectomised dog. A. STURM. IV. Iodine distribution in the human and animal organism in relation to the thyroid gland. A. STURM and B. BUCHHOLZ (Deut. Arch. klin. Med., 1928, 161, 129—142, 227; Chem. Zentr., 1928, ii, 2484—2485).—III. After thyroidectomy in dogs the blood-iodine falls from 12—17 γ -% to 3—10 γ -%; the urinary elimination of iodine markedly increases, becoming normal again after 10 days. During hunger the iodine elimination falls only slightly in the normal dog, but disappears almost completely in the thyroidectomised dog. The thyroid gland is regarded as the centre of the mechanism of iodine regulation.

IV. The iodine contents of the more important organs of man, dogs, and guinea-pigs have been determined. Iodine was always detected; the endocrine organs, skin, and hair are richest in iodine, but in the testicles and pancreas the iodine content does not exceed that of the general tissue. The human spleen contained in 7 cases 14.4-129 y-% and the skeletal muscle 8-111.5 γ -%. The total iodine content markedly rises in the spring; this cannot be ascribed to increased consumption of green vegetables. Only active ovaries have a high iodine content (30-160 y-%); in the menopause ovarial iodine is frequently not observed. The musculature contains 0.33-0.5 of the total iodine of the organism, and the thyroid gland 0.2-0.1. Removal of the thyroid gland causes the iodine content of the endocrine organs to fall whilst the iodine of the other tissue remains unaltered; hence only the "endocrine iodine" is regulated by the thyroid gland. The thyroid gland of tuberculous guinea-pigs was very

poor in iodine. Infective diseases appear to cause a diminution of iodine in almost all organs. A. A. ELDRIDGE.

Influence of ration of salts on nitrogen retention during growth. E. F. TERROINE and T. REICHERT (Compt. rend., 1929, 188, 1268-1271).-In continuation of previous work (Terroine and Mahler-Mendler, Arch. int. Physiol., 1927, 28, 101). in which a mixture of salts containing the elements chlorine, sulphur, phosphorus, sodium, potassium, calcium, magnesium, and iron was found to promote nitrogen retention and growth of young pigs, the effect of certain single salts has been investigated. Sodium or potassium chloride, dipotassium hydrogen phosphate, or calcium citrate separately have no promoting effect. The reality of the better utilisation of nitrogen with the complex salt mixture is shown by the persistence of better nitrogen retention when the ration is discontinued. R. K. CALLOW.

Does feeding with cabbage increase the calcium of rabbit's blood-serum. R. KAPSINOW and F. P. UNDERHILL (J. Biol. Chem., 1929, 82, 377-384).—In experiments on variations in the calcium of the blood-serum of rabbits, the effect of frequent withdrawal of blood cannot be neglected. Definite support could not be obtained for the suggestion of Culhane (A., 1927, 904) that feeding with cabbage produces a rise in the serum-calcium of rabbits. C. R. HARINGTON.

Copper content of plant and animal foods. C. W. LINDOW, C. A. ELVEHJEM, and W. H. PETER-SON [with H. E. HOWE]. Copper content of feeding stuffs. C. A. ELVEHJEM and E. B. HART [with H. E. HOWE] (J. Biol. Chem., 1929, 82, 465-471, 473-477).—Figures are given for the copper content of 160 human foods of vegetable and animal origin, and of 47 vegetable feeding stuffs commonly given to domestic animals. In no case was copper absent.

C. R. HARINGTON. Physico-chemical phenomena during regeneration. III. Determination of the hydrogen-ion concentration of the regenerating extremity of the crab (*Paralithodes camtschatica*). N. OKUNEV (Biochem, Z., 1929, 208, 328–333).—During regeneration of the crab's extremity, a shift of $p_{\rm H}$ to the acid side is obtained, similar to that obtained during regeneration of the extremity of the axolotl (A., 1928, 96), the displacement in the two cases being almost identical (0.24 and 0.28 $p_{\rm H}$).

P. W. CLUTTERBUCK.

Metabolism of sulphur. XV. Relation of protein and cystine content of diet to growth of hair in the white rat. H. D. LIGHTBODY and H. B. LEWIS (J. Biol. Chem., 1929, 82, 485-497).—Rats which show deficiency of growth on diets containing inadequate amounts of protein and particularly of cystine exhibit also a deficiency in the production of hair of a still greater magnitude. This indicates that the demand for cystine for the growth of hair is secondary to the demand for this amino-acid for other more essential tissue formation.

C. R. HARINGTON. Tryptophan and growth. I. Growth on a tryptophan-deficient basal diet supplemented at 3 1 intervals with tryptophan. C. P. BERG and W. C. ROSE (J. Biol. Chem., 1929, 82, 479–484).—In order satisfactorily to supplement a tryptophan-deficient diet for growing rats by separate administration of tryptophan, the doses of the latter must be given at least as frequently as every 12 hrs.

C. R. HARINGTON.

Formation of creatine from proteins [in diet]. E. F. TERROINE and P. DANMANVILLE (Compt. rend., 1929, 188, 1439—1441).—By simultaneous determinations of excreted creatine and the amount of nitrogen retained by young, growing pigs fed on diets in which only the protein constituent was varied it is shown that during growth the larger was the amount of nitrogenous material retained by the animal the smaller was the amount of creatine excreted. Thus the order of creatine formation of proteins is exactly the reverse of that of their nutritive value. J. W. BAKER.

Origin of creatine. E. ABDERHALDEN (Naturwiss, 1929, **17**, 293—294).—Creatine can be formed from arginine and choline in the presence of arginase. Adenine and guanine, hydantoin, methylhydantoin, and histidine are likewise bases from which creatine may arise. The processes involved in the Abderhalden reaction for pregnancy are shown to be fermentation reactions. Investigations on the nature of fermentation lead to the view that an enzyme-substrate compound is formed at a definite hydrogen-ion concentration, the nature of the entire molecule being by this time so changed that a hydrogen-ion concentration, which results in negligible hydrolysis for the substrate as such, is now quite effective. R. A. MORTON.

Benzoylated amino-acids in the animal organism. IV. Origin of glycine. W. H. GRIFFITH (J. Biol. Chem., 1929, 82, 415-427).—After administration of benzoic acid to rats, 66-95% was excreted in the urine in the form of hippuric acid. A satisfactory basal diet for the growth of rats could be impaired by addition of 3% of sodium benzoate, the limiting factor being the supply of glycine, since addition of the latter neutralised the effect of the benzoate. This effect of benzoic acid on the rate of growth of rats affords therefore a method for the investigation of the presence or absence of glycine or its precursors in the diet. C. R. HARINGTON.

Behaviour of aromatic amines in the organism. H. WEBER and C. HEIDERRIEM (Zentr. Gewerbehyg. Unfallverh., 1928, 15, 269—272; Chem. Zentr., 1928, ii, 2662).—Naphthylamine and dimethylaniline, when injected subcutaneously into dogs, are partly eliminated unchanged in the urine, partly hydroxylated. Benzidine is eliminated unchanged. Dimethylaniline poisoning produced methæmoglobin. A. A. ELDRIDGE.

Decomposition of creatinephosphoric acid in relation to the activity of muscle. II. D. NACH-MANSOHN (Biochem. Z., 1929, 208, 237—256; cf. A., 1928, 917).—The isometric coefficient K_m (kg. tension \times cm. muscle-length/mg. phosphoric acid split off) and the isometric time-coefficient K_t (kg. tension \times cm. muscle-length \times sec. tetanus/mg. phosphoric acid split off) were determined. K_t is about 15 for 2 sec. tetanus, 32 for 5 sec., 50 for 10 sec. The anaërobic resynthesis for periods of varying length is about 30% of the amount hydrolysed. In curarised muscle K_7 is relatively high for 2 sec., and changes little with number or length of period. It falls with submaximal and increases with excessive stimulation. Muscle in phosphate solution resynthesises creatine-phosphoric acid up to 95% of the creatine present. The K_m value at 4° is 70—100, at 24° 40—60.

J. H. BIRKINSHAW.

Significance of guanidinephosphoric acids (phosphagens) for muscle activity. O. MEYER-HOF (Naturwiss., 1929, 17, 283-287).—Creatininephosphoric acid (phosphagen) is decomposed to a measurable extent as a result of a muscular contraction lasting 5 sec. The phosphagen is resynthesised anaërobically to the extent of 30% during the first 30 sec. after the contraction. The process has been studied with normal muscle and curarised muscle in relation to the time of contraction. The decomposition of phosphagen bears a very close relationship to the velocity of response to stimulus.

R. A. MORTON.

Muscular contraction. III. Change in glycogen during contraction produced by tetanus toxin. H. A. DAVENPORT, H. K. DAVENPORT, and S. W. RANSON (J. Biol. Chem., 1929, 82, 499—504).— Contraction of rabbit and guinea-pig muscles under the influence of tetanus toxin was accompanied by reduction of the glycogen content; this was not the case in the rat, nor did contraction caused by section of the dorsal roots of the spinal nerves influence the glycogen content. Tetanus toxin had no effect on the glycogen of denervated muscles.

C. R. HARINGTON.

Lactic acid excretion in urine and sweat in various sports. I. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1929, 208, 212—220).—After football on cold days and rowing, more than 60 mg. of lactic acid was found in the urine of the majority of contestants. Football on warm days led to high lactic acid and chlorine excretion (468 and 846 mg.) in the sweat. After long-distance running there was little lactic acid excretion in the urine, the "steady state" is reached after 9 min. After swimming (5 and 20 min.) there was much lactic acid in the urine (maximum 1.76 g.). Albuminuria frequently occurs after swimming, glucosuria occasionally after football and swimming. J. H. BIRKINSHAW.

Relation between phosphoric acid and carbohydrate metabolism in isolated liver. W. A. ENGELHARDT and A. N. PARSHIN (Biochem. Z., 1929, 208, 221—229).—Surviving isolated rabbit's liver was perfused with Ringer's solution. With well-fed animals the phosphoric acid eliminated shows a steady increase, with fasting animals a constant value or slight decrease. Addition of dextrose to the perfusion liquid decreases the phosphoric acid excretion. Fluoride and calcium nullify the effect of dextrose, although inactive in its absence.

J. H. BIRKINSHAW. Carbohydrate metabolism. IV. Action of hydroxymethylglyoxal on normal and hypoglycæmic animals. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem. J., 1929, 23, 410-415).—Hydroxymethylglyoxal in its dimeric

form is highly toxic to mice and rabbits, and in sublethal doses produces symptoms similar to those of insulin hypoglycamia. In its monomeric form the toxicity is reduced by 75°_{ϕ} and the same train of symptoms is not produced. Hydroxymethylglyoxal in either the dimeric or monomeric form is unable to cause recovery from insulin hypoglycamia.

S. S. ZILVA.

Carbohydrate metabolism. V. Effect of administration of dextrose and of dihydroxyacetone on glycogen content of muscle in depancreatised cats. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem, J., 1929, 23, 416-421). -Small quantities of dihydroxyacetone administered intravenously to decerebrated cats from which the pancreas has been removed tend to increase, whilst large quantities tend to decrease, the muscle-glycogen. Similar results are obtained with dextrose except that the relation between the amount of dextrose administered and the change in glycogen may not be so great. High initial blood-sugars before pancreatectomy appear to cause an increase in muscle-glycogen. Muscle-glycogen is not more readily formed from dihydroxyacetone than from dextrose in presence of the liver. S. S. ZILVA.

Action of acid on glycogen in the cell. H. ELLAS and S. WEISS (Wien. med. Woch., 1928, 78, 1351—1352; Chem. Zentr., 1928, ii, 2571).—With increasing hydrogen-ion concentration of the surrounding liquid, the glycogen content of frog-spawn gradually diminishes. A. A. ELDRIDGE.

Inhibiting action of polysaccharides on dertrose hyperglycæmia. G. SOLARINO (Boll. Soc. Ital. Biol. sper., 1927, 2, 1039—1042; Chem. Zentr. 1928, ii, 2375).—Soluble rice or cereal starch (25 g.) in warm water causes in fasting dogs a hyperglycæmia of 0.012—0.048%. Soluble starch, when administered after dextrose, inhibits the hyperglycæmia, the values being between those for dextrose alone and those for starch alone. A. A. ELDRIDGE.

Changes in metabolism during irradiation. V. Changes in carbohydrate metabolism. II. L. PINCUSSEN and T. KAWAKAMI (Biochem. Z., 1929, 208, 185—190; cf. A., 1928, 918).—Rats exposed to the light of a mercury lamp for 30 min. showed an increase in glycogen in the liver and muscle and a decrease in lactic acid content; the heart showed no change. The effect is compared with that of insulin. J. H. BIRKINSHAW.

Pentose metabolism. III. Rates of disposal of d- and l-arabinose in the rabbit. R. C. COBLET (J. Biol. Chem., 1929, 82, 269—272).—Following intravenous administration of d- and l-arabinose to rabbits the rates of disappearance of the two sugars from the blood are closely similar, that of the d-isomeride being possibly slightly more rapid: the conclusion of Neuberg and Wohlgemuth (A., 1902, ii, 336) is therefore not confirmed. C. R. HARINGTON.

Scyllitol in selachian ontogeny. J. NEEDHAM (Biochem. J., 1929, 23, 319-323).—The yolks of the undeveloped eggs of Acanthias vulgaris contain only insignificant quantities of scyllitol, whilst the embryos contain greater amounts. The dogfish therefore synthesises most of its scyllitol. The yolk and jelly of Scyllium canicula eggs also contain only traces of scyllitol. S. S. ZILVA.

Influence of work on the fat content of frog muscle. W. NIEMIERKO (Acta Biol. Exp., Warsaw, 1929, 3, 143—164).—The fat contents of symmetrical gastrocnemius muscles are identical; individual values for different animals vary by 300%. During the winter the fat content declines progressively from an average value of 0.74% in the autumn to 0.30% in June. The destruction of cell structure, as well as heat tetanus, does not affect the fat content of muscle-tissue. The fats present in frog muscle are not utilised until glycogen reserves have been considerably exhausted. R. TRUSZKOWSKI.

Body fats. Physiology of fat deposition. W. SPEANGER (Biochem. Z., 1929, 208, 164-178).-The viscosity of a number of emulsions was determined as a measure of the dispersion. The viscosity of Ringer solution is scarcely changed by sodium or calcium oleate, lecithin, cholesterol, and cholesteryl ester present in physiological amounts. Albumin, lecithin, and sodium oleate act as oil-in-water emulsifiers. The effect is increased by cholesterol, cholesteryl ester, and calcium oleate at low concentrations and diminished at higher concentrations : these substances cause phase inversion when the amount of fat is increased. Cholesterol and its ester when present together (optimum ratio 1:2), however, favour an oil-in-water emulsion. The phase-inverting action of cholesterol, but not of the ester, depends on the amount of the water phase. A water-in-oil emulsion exists in fatty deposits. J. H. BIERINSHAW.

Phosphatide content of organs after administration of large amounts of phosphatide. II. B. REWALD (Biochem. Z., 1929, 208, 179—184; cf. A., 1928, 1154).—A dog receiving 30 g. of phosphatides per day for 15 months showed practically the same increase in the lipin content of various organs as occurred in a previous experiment lasting 6 months. The glands—ovaries, thyroid, pancreas, etc.—showed wy large increases, two to three times normal.

J. H. BIRKINSHAW.

Asymmetric utilisation of *p-iso*butylphenol in the animal body. C. FROMAGEOT (Biochem Z., 1929, 208, 490—492).—When optically inactive *p-iso*mutylphenol is fed to rabbits and the urine hydrolysed, *iso*butylphenol is obtained. P. W. CLUTTERBUCK.

Parenteral absorption of colloids. II. S. HAVA-SH (Biochem. Z., 1929, 208, 361-367).—By intrarenous injection of urease, a considerable concentration of the enzyme is obtained in the serum and is maintained for several hours. Intraperitoneal injection a larger amounts also causes urease to accumulate in the serum, but more slowly. Subcutaneous injection results in the appearance gradually of traces of urease in the serum. Intraperitoneal absorption of the enzyme is dependent on the medium, on its $p_{\rm H}$, on the ions present, and their concentration.

P. W. CLUTTERBUCK.

Increase in the calcium content of the organs of rabbits on feeding with naphthalene. A. CADE and P. BARRAL (Compt. rend. Soc. Biol., 1928, 99, 520-522; Chem. Zentr., 1928, ii, 2479). Effect of ethyl alcohol on dehydrogenation and on the oxygen demand of muscle. G. DI MACCO and P. FORMICOLA (Riv. Pat. sper., 1928, 3, 44—51; Chem. Zentr., 1929, i, 410).—Small doses of alcohol, on injection into frog's muscle, have an inhibitory, and large doses an activating, action. The decomposition of alcohol in the tissue is accomplished by an enzyme. A. A. ELDRIDGE.

Blood anti-coagulant in peptone. B. E. BRÜDA (Klin. Woch., 1928, 7, 1742; Chem. Zentr., 1928, ii, 2482).—Witte's peptone, on precipitation with acetone, extraction with methyl alcohol, taking up with water, filtering, and evaporating, affords a substance which renders blood non-coagulable, and is similar to Howell's heparin. A. A. ELDRIDGE.

Neutralising power of soaps for cobra venom. M. RENAUD (Compt. rend. Soc. Biol., 1928, 99, 496-498; Chem. Zentr., 1928, ii, 2480).—Detoxication of cobra venom by soaps is slower than that of tetanus, diphtheria, or *B. coli* toxins. A. A. ELDRIDGE.

[Electrostatics in biochemistry.] K. SPIRO (Koll.-chem. Beih., 1929, 28, 208–219).—A lecture on the relations between electrical phenomena and the phenomena of life. E. S. HEDGES.

Cell- and tissue-potentials. K. UMRATH (Koll.chem. Beih., 1929, 28, 259-262).—The relation between electrical potential and susceptibility to staining in tissue is discussed, and also the variation in potential according to whether the cell is living or dead. E. S. HEDGES.

Electrostatics as a special domain in biochemistry. R. KELLER (Koll.-chem. Beih., 1929, 28, 219–234).—A lecture, in which qualitative and quantitative methods of determining electrical potential in living cells are discussed.

E. S. Hedges.

Physical foundations of electrical potential in the organism and direct methods of measurement. R. FURTH (Koll.-chem. Beih., 1929, 28, 235— 245).—The measurement of electrical potential in organisms is discussed and a practical potentiometric method is described in detail. E. S. HEDGES.

Comparative cardiovascular action of two stereoisomerides, tropanol and ψ -tropanol. M. POLONOVSKI and R. HAZARD (Compt. rend., 1929, 188, 1441-1443).-Whilst intravenous injection of tropanol (cis) into a dog lowers the blood-pressure, large doses causing a decrease in the regularity and amplitude of the contractions of the heart, the transisomeride, 4-tropanol, similarly injected, raises the blood-pressure, seemingly due to peripheral vascular contraction. The action is complex (closely resembling that produced by nicotine) and consists of two phases: (1) one of inhibition which is suppressed by atropine; (2) one of relative acceleration and increased blood-pressure. Normal conditions are subsequently restored and the effects produced diminish with each J. W. BAKER. successive injection.

Biological assay of ergot preparations. G. L. PATTEE and E. E. NELSON (J. Pharm. Exp. Ther., 1929, 36, 85—105).—The assay of ergot by the cock's comb method and the adrenaline reversal method of Brown and Clark have been compared. The results are practically identical. Ergotoxin is found to be slightly but distinctly stronger than ergotamine. F. C. HAPPOLD.

Reagent for detection and determination of quinine. E. G. STERKIN and G. I. HELFGAT (Biochem. Z., 1929, 207, 8-24).-The reagent consists of a mixture of equal volumes of 0.12% sodium arsenate solution, 2% ammonium molybdate solution, and 2% hydrochloric acid. It can be preserved in the dark for 4-5 months and under certain conditions it will detect quinine hydrochloride at a dilution of $1 \text{ in } 2 \times 10^6$. For the determination 1 c.c. of the reagent is added to 5 c.c. of a slightly acid, suitably diluted portion of the liquid to be tested and after a certain time a nephelometric measurement is made. A method for the extraction of quinine from blood is described. At a dilution of 1 in 1.5×10^5 quinine hydrochloride can be determined in such extracts with an error not exceeding 5%. At higher dilutions the error is greater. Caffeine, morphine, apomorphine, cocaine, atropine, and plasmoquin are precipitated by the reagent, but their presence in sufficient quantity to interfere with the determination of quinine is not likely to occur. Potassium mercuric iodide cannot be used for the nephelometric determination of quinine.

W. MCCARTNEY.

Regulation of the hydrogen-ion concentration of the blood. III. Effect of strychnine on the acid-base equilibrium. IV. Action of strych-nine on the blood. VI. Effect of synthalin on the acid-base equilibrium. VII. Respiratory regulation. S. K. LIU and R. KRÜGER. VIII. Effect of acids, bases, and other toxic substances on the acid-base equilibrium of the blood. S. K. LIU (Z. ges. exp. Med., 1928, 61, 757-766, 767-774, 780-786, 787-793, 794-807; Chem. Zentr., 1929, i, 97-99).-With rabbits, intravenous or intramuscular administration of large doses of strychnine causes acidosis which can be suppressed by chloral hydrate. Strychnine and lactic acid accelerate the reduction by hydrogen of oxalated whole blood, and retard its oxidation in air. Intravenous, but not intramuscular or subcutaneous, administration of small doses of synthalin often causes a temporary rise in $p_{\rm H}$, whilst large intravenous doses cause a fall in $p_{\rm H}$. The acidosis is ascribed to increased combustion of sugar and considerable formation of acid. The effect of synthalin is very similar to that of insulin. Small quantities of lactic acid momentarily reduce the p_n of the blood, but the acid is rapidly neutralised and the acid-base equilibrium readjusted. Large quantities of lactic acid momentarily reduce the $p_{\rm H}$ of the blood; after some time the blood may have an alkaline reaction. Small quantities of sodium hydroxide raise the $p_{\rm H}$ only momentarily. A study of the relation between the acid, sodium hydroxide, or other toxic substance administered and the buffer mixture of the blood shows that the change in $p_{\rm H}$ of the blood is directly proportional to the administered hydrogen-ion concentration, and inversely proportional to the total buffering. The toxic reactions (oxidation, reduction) between the substance administered (quinhydrone, salvarsan, neosalvarsan) and the

blood appear to be retarded or diminished by the buffer mixture of the blood. A. A. ELDRIDGE.

Quantitative micro-detection of morphine. I. Determination of morphine in pure solution. II. Determination of morphine in serum and in whole blood. P. FLEISCHMANN (Biochem. Z., 1929, 208, 368-391, 392-414).-I. A method for the determination of morphine, which depends on the precipitation of the alkaloid with phosphomolybdic acid with colorimetric determination in terms of the colour formed on solution in concentrated sulphuric acid, is described. 0.02-2 Mg. of morphine hydrochloride in 5 c.c. of water may then be determined, the error with amounts over 0.6 mg. being less than 1%, with amounts between 0.2 and 0.5 mg. up to 3%, and with smaller amounts as much as 10%.

II. Morphine hydrochloride (up to 0.01 mg. per 5-7 c.c. of blood) in the whole blood of sheep, rabbits, and guinea-pigs may be determined without extraction and purification by deproteinising with 145% uranyl acetate, eliminating the excess of uranium with concentrated phosphate solution, and applying the colorimetric method above. With serum of these animals and of man, much smaller concentrations of uranyl salts can be used, and elimination of the excess is unnecessary. The error in the determinations in blood and serum are the same as in pure P. W. CLUTTERBUCK. solution.

Opium addiction. IV. Blood of the addict during morphine administration. W. G. KARR, A. B. LIGHT, and E. G. TORRANCE (Arch. Int. Med., 1929, 43, 684-690).- A comprehensive study of the blood of addicts receiving morphine sulphate hypodermically has been made. There is a tendency for a low red and a high white cell count. The cholesterol content was usually increased and the phosphates were diminished; the lactic acid content was uniformly high. F. C. HAPPOLD.

[Toxicity of] arsenic. F. WASMUTH (Arch. exp. Path. Pharm., 1929, 142, 17-40).—Small quantities of arsenious oxide reduce the power of suitably prepared extracts of animal tissues to oxidise reduced phenolphthalcin. It is concluded from this and other observations that the toxic action of arsenic on the animal organism is a result of its inhibitory action on the oxidative enzyme.

W. O. KERMACK.

Toxicity of arsenic. Comparative study of injections of solutions of sodium arsenate and of arsenical mineral waters of the Bourboule. J. GODONNECHE (Bull. Soc. Chim. biol., 1929, 11, 477-484).-Intraperitoneal injections of guinea-pigs with synthetic Bourboule water, or with the bottled natural water, or with the natural water direct from the spring, showed that whilst the first two possessed the same toxicity, the water obtained direct from the spring possessed a much greater toxicity. C. C. N. VASS.

Mercury poisoning and its chemical detection. FRIEDERICH and BUHR.—See this vol., 784.

Buffer antiseptics. III. Silver ion buffers. J. K. GJALDBAEK (Dansk Tidsskr. Farm., 1929, 3, 133-172).-Solutions of simple silver salts have all their silver in a therapeutically active form, but they injure the tissue and tend to produce merely local effects. The optimum concentration of silver nitrate to obtain a deep effect below the surface of the tissue is 0.01-0.02%. Diffusible silver complexes are effective at greater depths. Sodium citrate does not form complexes with silver ions, and does not depress ionisation more than any other salts. Colloidal silver preparations produce very few silver ions, even in the presence of iodide. Ammoniacal silver nitrate solutions and silver nitrate solutions with hexamethylenetetramine contain 97–98% of their silver in a complex form. These solutions should be valuable for the therapeutic administration of silver.

E. BOYLAND. Fermentative formation of allantoic acid from allantoin. R. Fosse and A. BRUNEL (Compt. rend., 1929, 188, 1067—1069).—The occurrence of an enzyme capable of converting allantoin into allantoic acid is reported in the following : frog, eel, pike, carp, conger-eel, herring, dab, whiting, plaice, thorn-back, dog-fish, salmon, crab, shrimp, lobster, cray-fish, star-fish, and sea-urchin. E. A. LUNT.

Biochemical determination of allantoin in presence of carbamide. R. Fosse, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, **188**, 1418—1421). —The determination of allantoin as xanthylcarbamide (A., 1927, 891) in the presence of carbamide (or substances generating it such as ureides etc.) may be effected if *Soja hispida* is used as a hydrolysing agent in place of alkali. The urease present destroys the carbamide and creates the correct degree of alkalinity required by a second enzyme, allantoinase, which converts allantoin into allantoic acid. The latter is then determined as xanthylcarbamide as in the previous process. J. W. BAKER.

Influence of formaldehyde on dilute malt extracts. O. MÜLLNER (Biochem. Z., 1929, 208, 354– 356).—When formaldehyde is added to dilute (2%) solutions of malt extract, the diastatic power is considerably decreased. P. W. CLUTTERBUCK.

Activation of certain oxidase preparations. C. E. M. PUGH (Biochem. J., 1929, 23, 456-471).-The apparent activation by peroxidases of a con-stituent of the oxidase of the fungus Lactarius tellereus separable from it by 40% alcohol observed by Bach and Chodat (A., 1902, ii, 344, 522; 1903, i, 377) has been confirmed. Peroxidase from horseradish and various species of Lactarius fungi were employed. No evidence was, however, obtained to support Bach and Chodat's view of the dual constitution of oxidases. The most probable interpretation of the phenomenon is the presence in the fungus of an autoxidisable substance. The phenomenon is not due to the formation of hydrogen peroxide or to the presence of an inhibitory substance (cf. Szent-Györgyi, this vol., 98). The addition of boiled peroxidase or of glycine does not produce the activation. Dialysed peroxidase activates. Unless excess of substrate be present the rate of action cannot be assumed to be a measure of activity of the enzyme. Preparations from potatoes were not activated by peroxidase. The action of tyrosinase on tyrosine and on p-cresol is shown to be autocatalytic, the lag being eliminated by addition of a

small amount of pyrocatechol or of dihydroxyphenylalanine. The lag can also be eliminated by boiled tyrosinase preparations. S. S. ZILVA.

Peroxidase of phanerogams. D. MICHLIN and P. KOPELIOVITSCH (Biochem. Z., 1929, 208, 288— 294).—A peroxidase is prepared from the bark of fir trees which is thermolabile and sensitive to cyanide but contains no iron and does not give an aldehyde reaction. The optimum $p_{\rm H}$ for its action is from 3.8 to 5.6. P. W. CLUTTERBUCK.

Specificity of intracellular dehydrogenases. II. Effect of poisons on dehydrogenase systems of frog and fish muscle. M. E. COLLETT and M. F. CLARKE. III. Dehydrogenases of frog muscle. M. E. COLLETT, M. F. CLARKE, and J. McGAVRAN (J. Biol. Chem., 1929, 82, 429–434, 435–437).— II. Selenite, arsenite, phenol, and benzoate show similar degrees of toxicity towards the dehydrogenase of fish muscle regardless of the nature of the hydrogen donator; in the case of frog muscle, however, the relative toxicity varies with the donator, from which it appears that frog muscle must possess at least three specific dehydrogenases.

III. Five different donators exhibit mutually accelerating effects on the rate of dehydrogenation by frog's muscle; the latter therefore contains a specific dehydrogenase for each of the donators (succinic, citric, malic, lactic, and glycerophosphoric acids).

C. R. HABINGTON.

Influence of $p_{\rm H}$ on glycerophosphatase. K. INOUVE (J. Biochem. Japan, 1928, 10, 133-145).— The preparation of glycerophosphatase from takadiastase is described. Purification with kaolin shifts the point of optimal activity from $p_{\rm H}$ 5.6 to $p_{\rm H}$ 2.7— 3.0. The activity- $p_{\rm H}$ curve is a typical dissociation curve, pK 4.8. The X-substance affects only that portion of the curve which corresponds with the dissociation curve of a base. The unit of X-substance is the quantity necessary to shift the optimum $p_{\rm H}$ of the reaction from 3.0 to 5.6, 0.5 unit to 5.0, and 0.25 unit to 4.5, the enzyme activities of these optima being 60, 30, and 20%, respectively, of that of the purified enzyme at $p_{\rm H}$ 3.0. CHEMICAL ABSTRACTS.

Cataphoresis of glycerophosphatase. H. KOBAYASHI (J. Biochem. Japan, 1928, 10, 147— 155).—Glycerophosphatase from taka-diastase contaminated with the X-substance migrated to the anode on the alkaline side of its optimum reaction ($p_{\rm H}$ 5.56), and to the cathode on the acid side. The enzyme, when free from X-substance, has its optimum reaction at $p_{\rm H}$ 3—4, but migrates to the anode over the entire $p_{\rm H}$ range 3.8—6.7. The difference is due to the greater protein content of the crude enzyme.

CHEMICAL ABSTRACTS.

Kidney glycerophosphatase. K. ASAKAWA (J. Biochem. Japan, 1928, 10, 157—175).—The preparation of glycerophosphatase from pig's kidney is described. At $p_{\rm H}$ 8.9 the kidney phosphatase has the same activity as the phosphatase of taka-diastase at $p_{\rm H}$ 2.8—3.0. The kidney glycerophosphatase has a basic dissociation constant pK_b 4.8; for the acid dissociation constant the values of pK are 10.8 and 9.0, respectively. CHEMICAL ABSTRACTS. Sulphatase. XI. Stereochemical specificity of sulphatase. C. FROMAGEOT (Biochem. Z., 1929, 208, 482–489).—The sulphatase of the mould Aspergillus oryzæ and that of pig's liver hydrolyse potassium *p*-isobutylphenyl sulphate, giving in both cases d-*p*-isobutylphenol, the highest rotation obtained being $[\alpha]_{10}^{30}$ +13·3°. In both cases the portion of the sulphate not attacked was hydrolysed with hydrochloric acid and gave a phenol with the opposite rotation. P. W. CLUTTERBUCK.

Effect of various substances of the quinine group on the enzymic functions of the organism. XI. Comparison of the influence of potassium, sodium, and quinine chlorides on the peptic digestion of protein. J. A. SMORODINCEV and E. A. SVESCHNIKOVA (Biochem. Z., 1929, 208, 151– 163; cf. this vol., 97).—The chlorides of sodium and potassium and quinine hydrochloride in 0.025 molar concentration inhibit the peptic digestion of eggalbumin. Lower concentrations have no effect. The effect of quinine hydrochloride is due to the reduced acidity of the medium which it produces; there is no inhibition when the $p_{\rm H}$ is kept constant.

J. H. BIRKINSHAW. Factors influencing tryptic digestion in the intestine. H. J. VONK and H. P. WOLVEKAMP (Z. physiol. Chem., 1929, 182, 175-200).-Since the average $p_{\rm H}$ of the intestinal contents is about 7 (not 8 as stated in the earlier literature), tryptic digestion does not take place at the optimum reaction (about $p_{\rm H}$ 8). However, two factors were found either of which would nullify the disadvantage due to the displacement of the $p_{\rm H}$. (1) The movement of the intestinal contents. The digestion of fibrin in vitro is about twice as fast when the substrate is stirred. (2) The activation of tryptic digestion by the bile (or bile salts). To compensate for a displacement of $p_{\rm H}$ from 8 to 6 would require only 5% of bile in the intestinal contents. Digestion of peptone is not activated in this way, but here the $p_{\rm H}$ optimum is very broad. J. H. BIRKINSHAW.

Formation of urocanic acid in the tryptic digestion of edestin. E. ABDERHALDEN, W. IRION, and H. SICKEL (Z. physiol. Chem., 1929, 182, 201— 204).—A small amount of urocanic acid was isolated from the products of a 50 days' tryptic digestion of edestin. This may have arisen by bacterial action, although the usual precautions were taken to avoid contamination. J. H. BIRKINSHAW.

Enzymatic fission of proline peptides. W. GRASSMANN, H. DYCKERHOFF, and O. VON SCHOENE-BECK (Ber., 1929, 62, [B], 1307—1310).—Prolylglycine and prolylglycylglycine, like the peptides of other amino-acids, are rapidly hydrolysed by the glycerol extracts of intestinal mucous membrane, less readily by pancreas extract or crude yeast autolysate. Solutions of intestinal erepsin, freed from trypsin by adsorption with aluminium hydroxide, decompose both peptides rapidly, frequently at a greater rate than the corresponding leucyl peptides. Unexpectedly, dry, purified preparations of dipeptidase and polypeptidase from yeast or intestine, preparations of pancreas trypsin, yeast proteinase, or activated papain are completely or nearly inactive

towards both peptides. The enzyme responsible for the hydrolysis of prolyl peptides is therefore not identical with any of the previously described peptidases of yeast or intestine. H. WREN.

Intestinal erepsin. K. LINDERSTROM-LANG (Z. physiol. Chem., 1929, **182**, 151–174).—Erepsin from the intestinal mucosa of the pig contains two dipeptidases. For one the optimum $p_{\rm R}$ is 7.3, it hydrolyses leucylglycine and glycylglycine at about the same rate. The other has optimum $p_{\rm R}$ 8.1; it hydrolyses leucylglycine some 20 times as fast as glycylglycine. A partial separation can be effected by fractional extraction or adsorption by aluminium hydroxide. J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on the inactivation of urease by some heavy metal salts. M. KITAGAWA (J. Biochem. Japan, 1928, 10, 197-205).-In the presence of acctate buffer mixtures the action of urease is partly inhibited at $p_{\rm H}$ 7.3 by small quantities of zinc ions, but this inhibition becomes less as the $p_{\rm H}$ is decreased and has almost disappeared at $p_{\rm H}$ 6.0. Practically complete inhibition of urease activity is effected at $p_{\rm R}$ 7.0-7.5 by small quantities of cupric or mercuric ions. In the case of cupric ions the inhibition becomes less as the $p_{\rm H}$ is decreased, but in the case of the mercuric ions it is still almost complete at $p_{\rm H}$ 6.0. The quantities of sodium chloride, potassium chloride, or potassium iodide necessary to effect appreciable inactivation are considerably greater than those of the heavy metal salts. The inhibiting action of sodium or potassium chloride does not change much when the $p_{\rm H}$ is varied. whereas that of potassium iodide increases as the W. O. KERMACK. $p_{\rm H}$ decreases.

Auxo-substances in the urease reaction. M. KITAGAWA (J. Biochem. Japan, 1928, 9, 347–352).-The activating action of glycine, starch, or fibrin (auxo-substances) on pure urease solutions is apparently due to their removing from combination with the urease some inhibitory substance present even in ordinary distilled water. Treatment of urease solutions by insoluble fibrin followed by removal of the fibrin is sufficient to effect activation. From adsorption experiments with alumina it appears that the activating mechanism does not consist of combination of the enzyme with the activator.

W. O. KERMACK.

[Biochemical factors in] heredity. H. VON EULER, H. HELLSTRÖM, and D. RUNEHJELM (Z. physiol. Chem., 1929, 182, 205-217).—In the first 6—16 days of germination, the catalase content of chlorophyll-defective and chlorophyll-normal strains of barley representing Mendelian mutants was in the ratio 1:2 to 1:3. No marked difference was observed in the peroxidase action.

J. H. BIRKINSHAW.

Quantitative enzyme studies with respect to Mendelian factors. H. von EULER and H. NILSSON (Naturwiss., 1929, 17, 289—290).—Studies on the crosses of chlorophyll-defective and chlorophyll-normal barley in respect of the action of catalase for 6—12 days at 18° show that the green is a dominant and the white a recessive Mendelian factor. The green and white barley differ definitely in respect of the action of catalase and of xanthophyll content. The Mendelian effect has been experimentally detected for the first time for a concentration of enzyme. R. A. MORTON.

Mechanism of alcoholic fermentation. A. J. KLUYVER (Bull. Soc. chim., 1929, [iv], 45, 311-312; cf. A., 1925, ii, 1173).—A claim for priority over Kostytschev (A., 1926, 756) and others in reply to a statement by Favorski (*ibid.*, 500).

R. BRIGHTMAN. Interchange of ions between yeast-cells and ammonium chloride solutions. P. GENAUD (Compt. rend., 1929, 188, 1513-1514).-If brewer's yeast is immersed in a solution of ammonium chloride $(p_{\rm H}, 7)$, whilst the concentration of the chloride ion remains unchanged, the initial concentration (n_0) of the ammonium ions decreases to a value n_1 which is approximately independent of the amount of yeast. Simultaneously potassium and calcium ions are found in the ammonium chloride solution, their total concentration being approximately equal to that of the ammonium ions which have disappeared $(n_0 - n_1)$, whilst an equal quantity of potassium and calcium disappears from the yeast. These results confirm the conclusions of Devaux (A., 1916, i, 457), the living yeast-cell acting like an insoluble salt of which the anion is always insoluble, but with which a partial and reciprocal interchange of cations with those of the saline solution occurs. The ratio n_1/n_0 is independent of the initial concentration of the saline solution when the interchanging ions are of the same valency, but it increases with concentration when the ion of the saline solution has a lower valency than that of the ion replaced, the equilibrium being governed by the law of mass action. J. W. BAKER.

Species of yeast stable towards boiling. J. RENNING (Ber., 1929, 62, [B], 1267-1270).-Technical "Südwein" yeasts (yeasts which are capable of producing at least 15% of alcohol) or their spores resist the temperature necessary to expel the alcohol formed by them in a sugar solution since fermentation occurs when the residue from the distillation, including the yeast, is mixed with a boiled 20% sugar solution so as to give about a 10% sugar solution, which is covered with a layer of oil. The new fermentation begins after 4-6 days and hence cannot be due to enzymes but must be attributed to the spores, since its incidence occurs after precisely the necessary period of incubation. Under similar conditions, the yield of alcohol by the second fermentation is of the same order of magnitude as by the first. Similar resistant spores appear to be derived from various fruits. H. WREN.

Co-zymase. H. VON EULER and K. MYRBACK (Naturwiss., 1929, 17, 291—293; cf. this vol., 472).— A stage has been reached in the purification of co-zymase in which the activity appears to have reached a maximum (0.01 mg. gives a fermentation velocity of 0.8 c.c. carbon dioxide per hour). The preparation appears to consist of an adenine nucleotide of a special type. A carbohydrate is present in the molecule and the phosphorus content corresponds with one atom in a mol. wt. of 400—500. Inactivation by means of a pancreas preparation discloses a 33% decrease in activity when the phosphate is set free to the extent of 31%, from which it would seem that the phosphorus is an essential constituent of the co-zymase molecule. The yeast preparations used in the determination of co-zymase activity are described. R. A. MORTON.

Growth and fermentative power of wine yeasts at low temperatures. K. KROEMER and KRUMB-HOLZ (Landw. Jahrb., 1928, 68, Suppl. I, 445-446; Chem. Zentr., 1929, i, 159).—A selective study of wine yeasts for fermentation at 7--8°.

A. A. ELDRIDGE.

Effect of alcohol and sulphur dioxide on the fermentability of wine yeasts. KRUMBHOLZ and Soós (Landw. Jahrb., 1928, 68, Suppl. I, 451-452; Chem. Zentr., 1929, i, 159).—An examination of wine yeasts for resistance to alcohol and carbon dioxide. A. A. ELDRIDGE.

Influence of iodine on the growth and metabolism of yeasts. J. E. GREAVES, C. E. ZOBELL, and J. D. GREAVES (J. Bact., 1928, 16, 409-430).---Iodine (1 in 10⁶) as the element or combined with sodium, potassium, or calcium accelerates the growth of yeast; iodine appears to be essential for yeast growth. Iodine compounds may possibly be the cause of the phenomena attributed to Wildier's bios. CHEMICAL ABSTRACTS.

Accelerating action of very small quantities of lanthanum salts on fermentation. C. RICHET and L. BRAUMANN (Compt. rend., 1929, 188, 1198-1199).—In presence of 10⁻⁷ to 10⁻⁸ g. per litre of lanthanum sulphate the production of acid in lactic fermentation after 48 hrs. was increased by about 30%. R. K. CALLOW.

Enzymes secreted by Hymenomycetes; alkaloids and the anti-oxygenic function. L. LUTZ (Compt. rend., 1929, 188, 1342—1344).—Alkaloids with free phenol or quinol groups inhibited slightly the oxidation of guaiacol and α -naphthol, and the reduction of methylene-blue, by Hymenomycetes. Other alkaloids, particularly those with an esterified phenolic group, are inactive in these respects.

E. BOYLAND.

Action of colloidal calcium fluoride and mercurous chloride on Aspergillus niger. E. WEDE-KIND and E. BRUCH (Biochem. Z., 1929, 208, 279-284).—Calcium fluoride and mercurous chloride in colloidal solution inhibit the growth of Aspergillus niger, the latter more strongly than the former. Increasing the concentration especially with calcium fluoride increases the fungicidal action, but the increase is not in proportion to the concentration. Addition of a solution containing calcium fluoride and mercurous chloride in equal proportions gave the same inhibition as the mercurous chloride alone. The inhibition is due solely to the ionised portion of the solutions of these substances.

P. W. CLUTTERBUCK.

Allelocatalytic substances in cultures of Colpidium colpoda, Ehrbg. E. GRINWALD (Acta Biol. Exp. Warsaw, 1929, 3, 81–100).—The rate of multiplication of Colpidium is greater when a single individual is placed in the same volume of culture medium (1—90 c.mm.) than when several are introduced. The velocity of division is less in small drops $(<12.5 \text{ mm}.^3)$ than in large ones; above $12.5 \text{ mm}.^3$ the volume of the culture medium is immaterial. Washing members of depressed cultures with fresh hay infusion does not affect the rate of division. The presence of Robertson's allelocatalyst cannot be demonstrated for the above infusorium, the rate of multiplication of which depends on the nutritive value of the medium, its volume, and its liquid-air interface. R. TRUSZKOWSKI.

Biological decomposition of pectin. A. G. NORMAN (Ann. Bot., 1929, 43, 233-243).-The rate of decomposition of pectin and its degradation products by various bacteria is determined in suitable media, containing peptone, potassium dihydrogen phosphate, magnesium sulphate, and precipitated chalk. The most convenient concentration of pectin was 1%, and its destruction was followed by determinations of furfuraldehyde and calcium pectate. The former, which is determined as its insoluble phloroglucinol compound, gives the amount of pectin and its degradation products; the latter gives pectin alone. The author considers that, if the two values are close together, the organism in question utilises the degradation products more readily than pectin itself, and if, on the other hand, the difference is large, the organism contains an enzyme which decomposes pectin. B. carotovorus, B. atrosepticus, B. solanisaprus, and *B. subtilis* were shown to contain such an enzyme. P. G. MARSHALL.

Enzymes in B. coli communis which act on fumaric acid. B. WOOLF (Biochem. J.), 1929, 23, 472-482).—B. coli contains a considerable quantity of fumarase. In the presence of propyl alcohol the same equilibrium between fumaric acid and *l*-malic acid is attained as that given by muscle-fumarase. In the absence of inhibitors such as propyl alcohol the action of this enzyme is masked by an irreversible anaërobic destruction of malic acid. The equilibrium between aspartic acid, fumaric acid, and ammonia (cf. Quastel and Woolf, A., 1926, 868) is really a complex malic-fumaric-aspartic acid equilibrium. When the fumarase of the organism is destroyed by treating it with cyclohexanol the true aspartic-fumaric acid equilibrium is obtained. The change of fumaric acid to aspartic acid is catalysed by a distinct enzyme for which the name *aspartase* is suggested.

S. S. ZILVA.

Participation of micro-organisms in the dissolution of insoluble phosphates. K. DREWES (Zentr. Bakt. Par., 1928, II, 76, 102–113; Chem. Zentr., 1929, i, 432).—Bacillus coli aërogenes, B. amylobacter, B. prodigiosus, Torula, and Penicillium are most active in dissolving tricalcium phosphate. The quantity of phosphoric acid dissolved is parallel with that of the acid formed by the organism from dextrose. A. A. ELDRIDGE.

Diphtheria toxin. Biological and chemical analysis. A. LEULIER, P. SEDALLIAN, and (MME.) CLAVEL (Bull. Soc. Chim. biol., 1929, 11, 413-436).--Diphtheria toxin is precipitated as an amorphous substance from filtered Martin's broth at $p_{\rm H}$ 4.7. Rapid centrifuging within 4 hrs. of precipitation enables a toxin to be obtained possessing 95-100% of its original toxieity. It can be dissolved in slightly alkaline solutions and from its phosphorus content is considered to be of the nucleoprotein type. Pepsin causes incomplete decomposition. Dialysis of the toxin removes the inorganic salts and destroys the toxicity. After 2 days' growth the amount of toxin produced is strictly proportional to the weight of the bacteria, up to 6 days' growth. Formaldehyde at 37° causes inactivation of the toxin, whether it is dissolved in a faintly alkaline solution, in peptone solution, in aqueous gelatin solution, or in Martin's broth. C. C. N. VASS.

Purification of vaccine virus by adsorption on kaolin. H. YAIO and H. KASAI (Proc. Imp. Acad. Tokyo, 1929, 5, 179—181).—Vaccine virus was purified by adsorption on kaolin in slightly acid solution. The sediment containing the virus is washed with distilled water, suspended in 0.04N-ammonia, shaken for 10 min., and centrifuged. The supernatant fluid which contains the virus is neutralised to phenolphthalein with acetic acid and the preparation made up to its original volume. The resultant preparation when concentrated gives a weak biuret, but no Molisch, reaction. F. C. HAPPOLD.

Interrelationship between hormones and immune bodies. Y. TOKUMITSU (Acta Med. Keijo, 1929, 12, 34-50) .- Immunised rabbits at the stage of constant immune titre were injected intravenously with hormones, kidney extract, muscle extract, bovine serum, peptone, pilocarpine, and physiological salt solution, and the variation of the agglutinin titre was recorded during 24-48 hrs. after the injection. Increase of the agglutinin titre was observed with the extracts of the suprarenal cortex, testicle, throud. liver, ovary, corpus luteum, and insulin whilst adrenaline, thymus, pituitary, parathyroid, and renal extract showed a decrease. Injection of pilocarpine always gave a temporary increase even on removal of endocrine organs. The effect on the agglutinin titre of the extirpation of endocrine organs either singly or in various combinations, or their transplantation, or the blockade of the reticulo-endothelial system, in the injected animal was measured. The decrease in agglutinin titre caused by peptone and also by the renal extract was shown to be non-hormonal by extirpation experiments. Muscle extract, bovine serum, and physiological salt solution caused no C. C. N. VASS. variation in agglutinin titre.

Heart hormone. G. KATZ and E. LEIBENSON (Compt. rend. Soc. Biol., 1928, 99, 695—696; Chem. Zentr., 1929, i, 96).—An active solution was obtained by emulsifying mixed alcoholic and aqueous extracts of secretory glands, heart, blood-vessels, liver, and kidneys with physiological salt solution.

A. A. ELDRIDGE.

Female sexual hormone, Menoformon. X. E. LAQUEUR and S. E. DE JONGH (Klin. Woch., 1928, 7, 1851—1853; Chem. Zentr., 1928, ii, 2480).— Experiments with rabbits and mice are described. A. A. ELDRIDGE.

Effect of ovarian hormone on the blood-sugar of the normal dog. F. RATHERY, R. KOURILSKY, and S. GIBERT (Compt. rend. Soc. Biol., 1928, 99, 529-532; Chem. Zentr., 1929, i, 96).-In the fasting dog injection of ovarian hormone causes a rise in blood-sugar. Rise of blood-sugar on oral administration of dextrose is intensified or prolonged if the hormone is simultaneously administered.

A. A. ELDRIDGE. Action of folliculin on the blood-sugar of depancreatised bitches. F. RATHERY, R. KOURIL-SKY, and Y. LAUBENT (Compt. rend. Soc. Biol., 1928, 99, 679-682; Chem. Zentr., 1929, i, 96).—A considerable rise in blood-sugar follows injection of ovarian hormone. A. A. ELDRIDGE.

Physiology of the isolated pancreas. I. External secretion. B. GOLDSTEIN (Z. ges. exp. Med., 1928, 61, 694—699; Chem. Zentr., 1928, ii, 2660— 2661).—Secretin in large, but not in small, concentrations increased the quantity and enzyme content of the secretion. Pilocarpine was less effective in increasing the amount of secretion, which contained much trypsin. A. A. ELDRIDGE.

Crystalline insulin. VIII. Isolation of crystalline insulin from fish islets and pig's pancreas. Activity of crystalline insulin. H. JENSEN, O. WINTERSTEINER, and E. M. K. GEILING (J. Pharm. Exp. Ther., 1929, **36**, 115—128).—Crystalline insulin from the islets of the cod and pollock is identical in shape, in physiological activity, and in its sulphur and nitrogen content with crystals prepared from bovine insulin. Difficulties have been encountered in the preparation of crystalline pig's insulin, and such material differs in physiological activity and sulphur content from bovine and fish insulin, probably because it is not quite pure. The physiological activity of bovine and fish insulin is about 24 international units per mg. F. C. HAPPOLD.

Insulin. I. Chemical observations. C. R. HARINGTON and D. A. SCOTT. II. Physiological assay. K. CULHANE, H. P. MARKS, D. A. SCOTT, and J. W. TREVAN (Biochem. J., 1929, 23, 384–409). -Active crystals were obtained from crude preparations of insulin by a modified Abel's method (A., 126, 1063) and by a method devised by the authors. hthe latter method an acetic acid solution of insulin is treated with saponin and ammonia, centrifuged, sijusted to $p_{\rm R}$ 5.6, and the insulin allowed to separate a micro-crystalline precipitate on keeping. The temolytic index of saponin is a better indication of its theiency of promoting crystallisation than is its bothing power. By the use of digitonin active crystals ay also be obtained by a procedure similar to the love. Although the addition of butyl alcohol yields a other crop of crystalline material from the saponincontaining mother-liquors the preparation of active critals by the application of this reagent and of bile alt did not meet with success. Potentially crystalline material inactivated by alkali could not be regenerated making the reaction acid. Four batches of crystals prepared by the two methods and assayed by four different workers showed no significant difference of activity, which was 23.3 international units per mg.

S. S. ZILVA.

Comparison of the effects of sodium hydrogen carbonate and insulin on the exoretion of ketonic substances in the urine of dogs on a water diet. F. MAIGNON and E. KNITHAKIS (Compt. rend. Soc. Biol., 1928, **99**, 604—606; Chem. Zentr., 1929, i, 97).—A water diet does not lead to ketosuria in dogs; the β -hydroxybutyric acid is so much reduced that in spite of the appearance of a small amount of acetone the total quantity of ketonic substances falls. Administration of sodium hydrogen carbonate or acetone reduces the elimination of acetone and usually also of β -hydroxybutyric acid. A. A. ELDRIDGE.

Effect of insulin and synthalin on the glycogen content of the liver and muscle. P. RUBINO, B. VARELA, and I. A. COLLAZO (Klin. Woch., 1928, 7, 2186—2190; Chem. Zentr., 1929, i, 405).—When administered subcutaneously to rabbits, small doses of synthalin prevent the accumulation of glycogen in the liver, and diminish that already present, whilst the glycogen content of muscle is not markedly changed. A. A. ELDRIDGE.

Effect of thyroid feeding on protein and fat metabolism. B. KOMMERELL (Biochem. Z., 1929, 208, 112—126).—Two fasting experiments were carried out on a dog at an interval of 5 weeks; during the second experiment 5 g. of thyroid-gland powder were administered daily. Thyroid produced a 30.5%increase in the basal metabolism; this was covered by an increase in protein combustion of 31.3% and in fat combustion of 68.7%. Feeding of thyroid during fasting about doubles the nitrogen excretion. Certain improvements in the technique of the Haldane method of gas analysis are described.

J. H. BIRKINSHAW.

Specific dynamic action of meat on animals receiving thyroid gland. F. MEYER (Biochem. Z., 1929, 208, 127—150).—Thyroid preparation administered to dogs considerably lowers the specific dynamic action of a protein diet; the oxidation curve rises more sharply but the level is much lower than normal. The view is held that the specific dynamic calories are placed at the service of the increased metabolism due to thyroid. The specific dynamic action is evidence of a chemical change involving loss of energy in the food materials. J. H. BIRKINSHAW.

Rôle of the iodo-components in the thyroxine molecule. B. ZAVADOVSKI, N. RASPOPOVA, T. ROLITSCH, and E. UMANOVA-ZAVADOVSKAJA (Z. ges. exp. Med., 1928, 61, 526-538; Chem. Zentr., 1928, ii, 2662).—Metamorphosis of axolotls is brought about by iodine, which is one eightieth as effective as thyroxine. Di-iodotyrosine had an even smaller effect, and is probably not an intermediate product in the formation of thyroxine from iodine and tyrosine. A. A. ELDRIDGE.

Antimony trichloride reaction of fish oils. H. VON EULER, M. RYDBOM, and H. HELLSTRÖM (Biochem. Z., 1929, 208, 73-78).—The vitamin-A content as measured by the antimony trichloride reaction of a 96% alcohol extract of cod-liver oil after removal of the alcohol is greater than that of the extracted oil. The difference between the two is more marked at the second extraction of the same oil. The extract, treated with antimony trichloride, gives an absorption band at 322—317 mµ, maximum 320 mµ. J. H. BIRKINSHAW.

Oryzatoxin theory. M. MIURA (Bull. Inst. Phys. Chem. Res., 1929, 8, 311-318).-Using nervous 852

symptoms, particularly the convulsions and the rapid fall of body temperature, as a criterion of the onset of polyneuritis, and the effect of subsequent vitamin-Badministration as a check, a large number of dietetic experiments have been carried out on pigeons, Uroloncha domestica, and albino-rats. Typical polyneuritis can be caused by a diet of alcohol-extracted polished rice or alcohol-extracted potato-starch, and can be cured or prevented by administration of vitamin-B. With Simonnet's diet pigeons suffered from convulsions, the onset of which was remarkably delayed in some cases, and death from marasmus was occasioned by removal of fats and alcohol-soluble matter from the diet; the incubation period of polyneuritis in U. domestica was similarly affected. Although the addition of a very minute amount of vitamin-B, vitamin-A, irradiated or non-irradiated ergosterol in a vitamin-B-free dict, did not affect the onset of polyneuritis, the possible presence of some specific non-toxic substance (or substances), in alcoholic extract of polished rice, which increases the requirement of vitamin-B, is admitted. The alcoholic extract of polished rice shows slight protein reactions, and contains a little vitamin-B and a large amount of fats; potato-starch extract contains much less vitamin-B. These results are not in agreement with those of Teruuchi on chickens, and the existence of oryzatoxin in alcoholic extract of polished rice is considered unproved. An excessive dosage of irradiated ergosterol is poisonous for U. domestica.

C. W. SHOPPEE.

Purification of the antineuritic water-soluble vitamin-B by fractional precipitation. A. DE CUGNAC (Bull. Soc. Chim. biol., 1929, 11, 443-465).-The vitamin-B concentrates obtained by the method of Scidell (A., 1926, 644) from brewer's yeast after absorption on fuller's earth with subsequent liberation by sodium hydroxide and immediate neutralisation with dilute sulphuric or acetic acids were used. Assay of vitamin-B content was carried out on pigeons as described by Seidell. Aqueous solutions of vitamin-B, both "acetate" and "sulphate" concentrates, were precipitated successively with 70%, 80%, 87% alcohol and with acctone. In every experiment the activities of the precipitates, which contained decreasing amounts of inorganic substances, were approximately equal to that of the original product, whereas the residue obtained on removal of the solvents had lost the greater portion of its activity. Acetic acid solutions of the "sulphate" concentrates on successive treatment with acetic acid and ether gave precipitates the activities of which equalled that of the original, but the residue, contrary to the findings of Levine, McCollum, and Simmonds (A., 1922, i, 975), showed no activity. Anhydrous or aqueous ethyl acetate did not dissolve the active constituent of the vitamin-B concentrates, but they dissolved in the cold in pure formic acid, and less readily in dilute formic acid. Treatment of the formic acid solution successively with acetone and ether yielded a white and a brown precipitate of almost equal activity; the residue contained none of the active principle.

Ĉ. C. Ñ. VASS.

Water-soluble vitamins and their relation to each other. W. KOLLATH (Arch. exp. Path. Pharm., 1929, 142, 86—110).—Rats fed on a diet deficient in the vitamins-B die of symptoms which are characteristic of the absence of both the pellagra-preventive and the anti-beriberi factors, whereas when alkaline hæmatin is added to the diet in sufficient quantities the symptoms are those of beriberi only. It therefore appears that alkaline hæmatin can function as the pellagra-preventive factor. W. O. KERMACK.

Sparing action of fat on the antineuritic vitamin. H. M. EVANS and S. LEPKOVSKY (Science, 1928, 68, 298).—The presence of fat appears to favour the action of the antineuritic vitamin.

L. S. THEORALD. Vitamin requirements of nursing young. VI. Anhydræmia of rats suffering from deficiency of vitamin-B. B. SURE, M. C. KIK, and D. J. WALKER (J. Biol. Chem., 1929, 82, 287-306).-A marked concentration of the blood was observed in nursling rats the mothers of which were kept on a diet deficient in the vitamin-B complex.

C. R. HARINGTON. Effect of vitamin deficiencies on carbohydrate metabolism. I. Hypoglycæmia associated with anhydræmia in young rats suffering from deficiency of vitamin-B. B. SURE and M. E. SMITH (J. Biol. Chem., 1929, 82, 307—315).—Coincidently with the anhydræmia already described (cf. preceding abstract) young rats suffering from vitamin-B deficiency develop marked hypoglycæmia; both conditions are immediately relieved by administration of vitamin-B. C. R. HARINGTON.

Nutrition. IX. Comparative vitamin-B values of pulses and nuts. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J. 1929, 23, 546-557).—Taking the vitamin-B value of dried yeast to be 100, the following are the relative activities: split peas 13, whole dried green peas 13, lentils 13, haricot beans 10, soya beans 13, peanuts 20, ground almonds 10, whole almonds 10, hazel nuts 20, dried chestnuts 10, coconut 0, green coffee less than 13, roasted coffee 0. The tests were carried out on pigeons. More vitamin is required for hatching and rearing of young pigeons than for maintenance.

S. S. ZILVA.

Assay of the antineuritic vitamin- B_1 in which the growth of young rats is used as a criterion. H. CHICK and M. H. ROSCOE (Biochem. J., 1929, 23, 498-503).-The unit is the minimum dose necessary to restore normal growth when growth has failed in a diet deficient only in this vitamin. Vitamin- B_2 is supplied in the basal diet in the form of fresh eggwhite or of yeast autoclaved at 120° for 5 hrs. Although by using autoclaved yeast there is a risk of traces of vitamin- B_1 escaping destruction, it is preferable to egg-white, because when the latter is used normal growth is frequently maintained for only a few weeks after weaning ; after this period growth is subnormal. This is possibly due to the absence of a third hypothetical dietary factor in the vitamin-B S. S. ZILVA. complex.

Attempt to separate vitamin- B_2 from vitamin- B_1 in yeast and a comparison of its properties with those of the antineuritic vitamin- B_1 . H. CHICK and M. H. ROSCOE (Biochem. J., 1929, 23,

504-513).-About one half to three quarters of the vitamin-B, present in the original yeast is carried down in the precipitation with lead acetate at $p_{\rm H}$ 4.7 in Peter's scheme of fractionation (Kinnersley and Peters, A., 1925, i, 1516; A., 1927, 904). The vitamin- B_2 can be recovered from the lead fraction (maintenance dose=0.03 g., equivalent to 0.5 g. of the original yeast). This preparation contains more or less vitamin- B_1 depending on the reaction at which precipitation took place and probably on the amount contained in the original yeast. Vitamin- B_2 is insoluble and vitamin- B_1 is soluble in 92 wt.-% alcohol. Concentrated alcohol destroys vitamin- B_2 in the process of fractionation. Both vitamins dialyse freely through cellophan. Ultra-violet light exerts a destructive action on both vitamins, vitamin- B_2 being destroyed at a quicker rate than vitamin- B_1 (cf. Hogan and Hunter, A., 1928, 1059).

S. S. ZILVA.

Distribution of vitamin- B_2 in certain foods. W. R. AYKROYD and M. H. ROSCOE (Biochem. J., 1929, 23, 483–497).—The vitamin- B_2 value of wheat and maize is poor, that of maize being on the whole lower. The vitamin content of germ and bran of wheat is about equal and is lower than that of the endosperm. In maize the germ is not so rich a source, but whole maize is better than maize endosperm. Dried peas have a low vitamin- B_2 content, whilst dried ox liver, yeast, and fresh whole milk are excellent sources of this vitamin. Dried meat and egg yolk are not as good as the preceding substances, but are richer than cereals. The distribution of vitamin- B_2 , Goldberger's "P.P." factor, and the factor preventing black-tongue in dogs is identical. Chick and Roscoe's method (A., 1928, 800) was employed for determining vitamin-B₂. S. S. ZILVA.

Effect on vitamin- B_2 of treatment with nitrous acid. H. CHICK (Biochem. J., 1929, 23, 514-516). -Levene's observation (A., 1928, 1405) that the activity of vitamin- B_2 is destroyed by the action of ultrous acid is not confirmed. S. S. ZILVA.

Antirachitic potency of biosterin. S. HAMANO Bull. Inst. Phys. Chem. Res., 1929, 8, 293-296).--Ibino-rats were made to suffer from rickets after aving been fed on Steenbock's diet No. 2965 for -5 weeks. The regular daily dose, 0.1, 0.05, 0.01, -5 weeks. The regular daily dose, 0.1, 0.05, 0.01, -5 weeks. The regular daily dose, 0.1, 0.05, 0.01, -5 weeks. The regular daily dose, 0.1, 0.05, 0.01, -5 weeks. The regular daily dose, 0.1, 0.05, 0.01, -5 weeks, and then animals were examined by radiograph. Six -5 size of observations on 88 rats showed that a daily -6 0.01-0.05 mg. of biosterin was necessary to produce healing or curative effects.

C. W. SHOPPEE. Effects [on animals] of large doses of irradiated "gosterol. J. C. HOYLE and H. BUCKLAND (Biothem. J., 1929, 23, 558—565).—The incorporation of 1% of ergosterol, irradiated in oil, in the diet had to lethal effect on rats subsisting on this diet for a period of more than 50 days. There was a persistent or marked loss in weight and urinary calculi were found post mortem. There was also persistent diuresis without any increase in the total phosphate and chloride passed per day and without any significant change in the reaction of the urine. This confirms Dixon and Hoyle's previous observations (cf. Brit. Med. J., 1928, ii, 832). S. S. ZILVA.

Growth of rats on fat-free diets. A. J. MCAMIS, W. E. ANDERSON, and L. B. MENDEL (J. Biol. Chem., 1929, 82, 247—262).—Good, but not optimal, growth was obtained in rats kept on a diet freed as far as possible from fat; addition of a small amount of fat produced a definite improvement, but it is not certain whether this was due to the fat as such or to the vitamins associated with it. C. R. HARINGTON.

Deficiency disease due to exclusion of fat from the diet. G. O. BURR and M. M. BURR (J. Biol. Chem., 1929, 82, 345—367).—Rats kept on a diet almost completely free from fat, but containing all vitamins except vitamin-E, developed a deficiency disease chiefly characterised by caudal necrosis but involving lesions on other parts of the body also. The condition is relieved by addition of 2% of fatty acids to the diet, but not by addition of glycerol or of the unsaponifiable fraction from cod-liver oil.

C. R. HARINGTON.

A. Relation between maximum rate of photosynthesis and concentration of chlorophyll. B. Photosynthesis as a function of light intensity and of temperature with different concentrations of chlorophyll. R. EMERSON (J. Gen. Physiol., 1929, 12, 609-622, 623-639).-(A) By growing Chlorella vulgaris in media containing various quantities of ferric sulphate, cells were obtained differing in the content of chlorophyll per unit volume of cell. The maximum rate of photosynthesis with suspensions of such cells is a smooth function of the chlorophyll content provided uniform conditions are observed. (B) The depressing effect of hydrogen cyanide on the rate of photosynthesis increases as the chlorophyll content of the cells decreases, but the effect of temperature on the reaction and also the light intensity at which the maximum rate is attained are independent of the chlorophyll content.

W. O. KERMACK.

Energetic metabolism of germination (Helianthus annuus). Z. KRASINSKA (Acta Biol. Exp., Warsaw, 1929, 3, 101-141).-Sunflower seeds germinating in the dark at 25° lose during the first 6 days 0.362 g. of fat per g. of dry substance, the original fat content being 58.2%. Over the same period the heat of combustion of 1 g. of dry substance falls from 7330 to 5275 g.-cal., corresponding with a loss of 60% of the calorific value of the fats utilised. The respiratory quotient is 0.523, pointing to the retention of the greater part of the oxygen by the organism. 93% of the energy requirements of the processes of germination are covered by fats, and the remainder by proteins and carbohydrates. About 44% of the fats undergoes complete combustion, 56% being converted into carbohydrates, whence it follows that 23% of the energy supplied by fats is due to the latter reaction and 77% to the former. Respiration attains a maximum on the fourth day of germination, by which day the value of the respiratory quotient has fallen from 0.928 to 0.488, to rise again R. TRUSZKOWSKI. to 0.644 on the seventh day.

Variations in the intensity of respiration and fermentation in the tissues of peas. L. GENEVOIS (Compt. rend., 1929, **188**, 1338—1340).—Sterile anaërobic soaking of peas increased their power to ferment; this was reduced by mincing the material. On the other hand, mincing increased the respiration, which could be inhibited with potassium cyanide, without effect on the fermentation. E. BOYLAND.

Respiration and geotropism in Vicia faba. I. A. E. NAVEZ (J. Gen. Physiol., 1929, 12, 641-667).— The rate of excretion of carbon dioxide by a single seedling of Vicia faba (brown Windsor bean) is constant over a considerable range of time provided the temperature and other conditions remain uniform. When the seedling is rotated so as to excite the geotropic response an increase in the rate of excretion of carbon dioxide occurs which is a measure of the geotropic activity. Observations have been made on the basic rate of respiration as well as on the geotropic response at various temperatures.

W. O. KERMACK.

Changes in chemical composition of pears stored at different temperatures (with special reference to pectic changes). A. M. EMMETT (Ann. Bot., 1929, 43, 269—307).—Determinations of total pectic substances, and acidity, viscosity, and pectic substances of the juice of Conference pears were made on pears stored at 12° and 1°. In a further series of experiments at 4°, 5°, and 1° the same determinations were made together with the following determinations : (a) hardness of fruit, (b) dry weight, (c) residue after alcoholic extraction, (d) total sugars, (e) reducing sugars, (f) acidity, and (g) specific gravity of juice.

Carre's method of determination of pectic compounds was used, whilst the pectin plus protopectin were determined by the calcium pectate method after extraction of the pulp with N/75-hydrochloric acid. It was found necessary, for the determination of soluble pectin, to centrifuge the extracts, as otherwise results nearly 100% too high were obtained. Pectin of the juice was determined as calcium pectate, and its viscosity was measured by the Ostwald method at 25°. The alcohol-insoluble residue was determined by extraction with 95% alcohol. Archbold's method of determination of the "dry weight" of the juice was employed for the later determinations and was more accurate than the high temperature method originally employed. Determinations of sugars were carried out by Evans' methods and of the acidity by titration with N/10-sodium hydroxide, using phenolphthalein as indicator. Errors of sampling were estimated on the individual pears and, except in the case of the acidity, errors of weight were found to be not more than 2%. The changes occurring during storage were determined, the loss of weight being due almost entirely to transpiration.

Whereas fruit stored at 5° ripened in 3 weeks, that stored at 1° showed only slight signs of ripening in 6 months as determined by penetration of the skin by methylene-blue. The different rates of ripening at different temperatures were accompanied by differences in the rate of change in pectic content; in nearly all cases, however, the protopectin was converted into soluble pectin according to the exponential law, and the rate of decomposition of the soluble

pectin after the period of full ripeness followed the same law. During the early stages of ripening, the viscosity increased according to the amount of soluble pectin present, but later decreased more rapidly than the soluble pectin disappeared, possibly owing to demethoxylation of the pectin. Evidence was obtained showing that the "hardness" depended on the amount of soluble pectin present.

The inversion of sucrose took place at a greater rate than the utilisation of sugars in respiration. Unsound pears appeared to have a smaller content of all constituents except acid and reducing sugars than sound pears. In pears and apples of low acidity the pectic changes are considered to be controlled mainly by the enzymes present.

P. G. MARSHALL.

Transport of nitrogenous substances in the cotton plant. I. Downward transport of nitrogen in the stem. E. J. MASKELL and T. G. MASON (Ann. Bot., 1929, 43, 205-231).-A preliminary examination of the variations in total nitrogen content of the tissues of the cotton plant is undertaken using the salicylic-thiosulphate method of determination as modified by Ranker (Ann. Miss. Bot. Gard., 1925, 12, 367-380). The diurnal variations in total nitrogen of leaf and bark are determined, the results being expressed in most cases as g. of nitrogen per 100 g. residual dry weight (dry weight less total carbohydrates). In the case of the leaf there is a fall in total nitrogen during the night, organic nitrogen being presumably drawn from it during that period. The deviation (expressed as a percentage of the mean) is about 3.9%. In the case of the bark there is no evidence of any real change of nitrogen content.

The effect of ringing the stem is to cause accumulation of nitrogen in the wood and bark above the ring. The transport of nitrates to the leaves is not obstructed, thus showing that they travel by way of the wood and not the bark. Separation of the bark and wood produces no variation in the mean nitrogen content of the bark, thus showing that contact between wood and bark is unnecessary for normal transport of organic nitrogen from leaf to root.

The effect of a constriction (produced by partial removal of the bark) is to reduce the rate of transport, although not in proportion to the cross-sectional area. The increase in rate per unit area is not as great as in the transport of carbohydrate, a fact which suggests variable diffusibility of the nitrogen compounds. The deviation for nitrogen is 36% of the mean rate of transport, compared with 71% for carbohydrate. The bark and wood contain approximately equal amounts of nitrogen, but the wood is more sensitive to changes than the bark (average change is 8.48%of the mean content for the wood and only 4.74% for the bark).

The rate of transport of organic nitrogen compounds downwards is greatly in excess of that due to diffusion. P. G. MARSHALL.

Influence of a complete [inorganic] fertiliser on the osmotic pressure in cultivated plants. Special action of potassium fertilisers. E. BLANCHARD and J. CHAUSSIN (Compt. rend., 1929, 188, 1515—1517).—The effect of a complete inorganic fertiliser on growing oats and beetroot, and of a potassium fertiliser on wheat, has been investigated by methods similar to those used for wheat (A., 1925, i, 623) grown in the same plot. The results are similar to those previously obtained, the extracts of the various portions of the fertilised plant having a larger proportion of ash of smaller mean mol. wt. than those of the unfertilised plant. The results support the earlier conclusion that the increase in growth promoted by the fertiliser coincides with an increased internal osmotic pressure in the plant, this effect being due largely to the potassium salts in the fertiliser. J. W. BAKER.

Effects on Pisum sativum of a lack of calcium in the nutrient solution. D. DAY (Science, 1928, 68, 426—427).—Plants deprived of calcium show less growth, chlorotic lower leaves, and tough curled upper leaves; death occurs in 9—10 weeks. The anatomical structures of stem and root remain practically constant except for a change in elongation. Rapid recovery to normal accompanies the addition of calcium after 5 weeks' growth. Calcium stored in seed is used for early growth. L. S. THEOBALD.

Titanium in phanerogamic plants. G. BER-TRAND and C. VORONCA-SPIRT (Compt. rend., 1929, 188, 1199-1202).-The titanium content of a variety of phanerogamic plants, mostly foodstuffs, has been determined after careful removal of dust. All the plants examined have been found to contain titanium up to a maximum of 6 mg. per kg. of fresh material. As in the case of zinc (this vol., 362), the amount of titanium increases, in general, with the chlorophyll content of the part examined. Grains of cereals contain 0.7-1.5 mg. per kg., almost entirely in the husks, whilst leguminous seeds contain about 3 mg. per kg. Reserve material such as the flesh of fruits and potato tubers is poor in titanium. The aerial portions of flowering annuals contain about 1 mg. per kg. R. K. CALLOW.

Tobacco. I. Water in tobacco. N. J. GAV-BLOV and B. B. EVSLINA (Biochem. Z., 1929, 208, 19-90).—Water in tobacco was determined by various methods. The methods of Marcusson (distillation in bluene) and of Tausz and Rumm (distillation in tetrachloroethane) gave concordant results somewhat bwer than the figure obtained by drying at 95°. brying in a current of dry air at the ordinary temperture gave results about 30% lower. It is suggested that this method gives the true "hygroscopic water," rest is chemically bound. Zerevitinov's method pes only a small fraction of the "hygroscopic Tar." J. H. BIRKINSHAW.

Effects of the absence of boron and of some ther essential elements on the cell and tissue structure of the root tips of *Pisum sativum*. A. L. SOMMER and H. SOROKIN (Plant Physiol., 1928, 3, 237-254).—Experiments with culture solutions containing or lacking boron, magnesium, sulphur, manganese, potassium, nitrogen, iron, phosphorus, and calcium are described.

CHEMICAL ABSTRACTS. Effect of boron deficiency on the growth of tobacco plants in aërated and unaërated solutions. J. E. McMurtrey (J. Agric. Res., 1929, 38, 371-380).—Tobacco plants do not develop to maturity in the usual nutrients in the absence of boron. Addition of 0.5 part per million of boron to the culture solutions is sufficient to produce normal growth. In the absence of boron the growth of the stem is restricted and there is a well-marked injury to the bases of the young leaves forming the terminal bud. The improved root development and subsequent top growth due to aëration of the culture solution is not merely the result of mechanical mixing of the nutrient. A. G. POLLARD.

Seeds of Euphorbia Paralias, L. P.GILLOT (Bull. Sci. pharmacol., 1928, **35**, 561–564; Chem. Zentr., 1929, i, 402).—The seeds contained : water 7-08, fat 38-05, protein 22-43, sugar 2.58, mineral substances 5-39, cellulose 24.47%. The oil showed an absorption band at 675 $\mu\mu$, complete absorption below 520 $\mu\mu$; $\alpha + 4^{\circ}$ 30', d_{15}° 0.9368, n^{22} 1.4819, n^{15} 1.4845; Crismer value 62°, f. p. -25°; Chemical constants of the oil are recorded. A. A. ELDRIDGE.

Water-soluble phosphatide and the Nadi oxidase reactions. M. GUTSTEIN (Biochem. Z., 1929, 207, 177-185).—The water-soluble iron-free phosphatide prepared from peas and from yeast according to the method of Cranner (cf. Grafe and Magistris, A., 1926, 1280) in amounts as small as 0.00004 g. gives a positive oxidase reaction *in vitro* and also reduces dyes and permanganate, being, in these respects, twenty times as active as an equal weight of yeast. The oxidase action, which is entirely specific, is not inhibited by heat or by cyanide. W. MCCARTNEY.

Composition of spinach fat. J. H. SPEER, E. C. WISE, and M. C. HART. Unsaponifiable fraction of spinach fat. F. W. HEYL, E. C. WISE, and J. H. SPEER (J. Biol. Chem., 1929, 82, 105--110, 111--116). —From 68 kg. of spinach there were obtained 550 g. of fatty acids of which 47% were present in the form of neutral fat. The solid acids, forming a small proportion of the total, consisted of palmitic and stearic acids with a small amount of cerotic acid. The liquid fraction contained 12.7% of linolenic, 34.7% of linoleic, and 26.3% of oleic acids; volatile acids were practically absent. The unsaponifiable fraction of the spinach fat yielded a hydrocarbon, $C_{20}H_{42}$, m. p. $67.5-68.5^{\circ}$, a sterol, $C_{27}H_{46}O, H_2O$, m. p. $165-167^{\circ}$, $[\alpha]_{1}^{\infty} + 1.7^{\circ}$ in chloroform, two alcohols, (a) $C_{22}H_{46}O$, m. p. $76-77^{\circ}$, (b) $C_{24}H_{50}O_{2}$, m. p. $87-88^{\circ}$, and an unsaturated compound, $C_{27}H_{54}O$, b. p. 172-188%

C. R. HARINGTON.

Seed fats of the Umbelliferae. II. Seed fats of some cultivated species. B. C. CHRISTIAN and T. P. HILDITCH (Biochem. J., 1929, 23, 327–338; cf. A., 1928, 560, 1059).—The seeds of fennel (Foeniculum capillaceum, Gilib.), carrot (Daucus Carota, Linn.), coriander (Coriandrum sativum, Linn.), celery (Apium graveolens, Linn.), parsnip (Pastinaca sativa, Linn.), chervil (Chaerophyllum sativum, Gartn.), and caraway (Carum Carvi, Linn.) have been examined and it has been found that $\Delta^{6:7}$ -octadecenoic (petroselic) acid is present in quantity in all cases. The other components of the mixed fatty acids are palmitic acid in small quantity (1–8%) together with $\Delta^{9:10}$ -octadecenoic (oleic) acid and linoleic acid in somewhat varying proportions. The fatty oils are accompanied in all cases by considerable amounts of unsaponifiable and resinous matter. S. S. ZILVA.

Sterols from vegetables. M. SUMI (Bull. Inst. Phys. Chem. Res., 1929, 8, 228–233).—Sitosterol has been isolated from Enteromorpha compressa, Cytophyllus fusiforme, Harv., Digenea simplex, C., Osmunda regalis, L., spores of Lycopodium clavatum, pollen of Typha japonica, Miq., seeds of Gingko biloba, L., and oil of rice-bran. Stigmasterol was not obtained in any case. The uncrystallisable portion of the unsaponifiable matter from the first three, after precipitation with digitonin, has antirachitie properties. H. BURTON.

Pine-wood lignin. E. HÄGGLUND and H. URBAN (Biochem. Z., 1929, 207, 1-7).—Lignins obtained from resin-free pine wood by the action, for a short time, of hydrochloric acid still contain carbohydrates which can be removed without damage to the material by boiling for 1-2 days with 4-5% mineral acid. Continued hydrolysis with such acid and with periodical washing out of the lignin produces gradual rise of the methoxyl content to 17% without important loss of material. Simultaneously the amount of formaldehydo which can be eliminated by the Tollens method falls to 0.4%. Lignosulphonic acids, according to the method of preparation, give, in the Tollens distillations, varying amounts of substances which condense with barbituric acid. In these distillations no formaldehyde is eliminated from naphthylamine compounds, from lignin produced by the action of amyl or propyl alcohol containing 0.4-0.5% of hydrogen chloride on wood or on lignin prepared by the hydrochloric acid method, or from lignin derived from the action of glacial acetic acid containing 0.4% of hydrogen chloride on lignin. Piper-onylic acid yields no formaldehyde when treated with amyl alcohol or glacial acetic acid under the conditions used in the preparation of lignin. Paraformaldehyde, when boiled with amyl alcohol and hydrogen chloride is converted into diamylmethylal.

W. MCCARTNEY.

Nature of the sugars in liquorice root (Glycyrrhiza glabra). A. GIAMMONA (Annali Chim. Appl., 1929, 19, 110—127).—Fresh liquorice root contains 1.38% of dextrose and 3.183% of sucrose, the same root, air-dried and after 3 months, containing 2.373%and 5.40%, respectively, of these sugars. Thus, the dextrose of the fresh root is co-existent with the sucrose, which does not undergo scission during its natural drying. Possibly, as in the barley embryo, dextrose is converted into sucrose by enzyme action. T. H. POPE.

Preparation of gentianose from gentian root dried in the air without fermentation. M. BRIDEL and M. DESMAREST (J. Pharm. Chim., 1929, [viii], 9, 465-479).—By the authors' percolation process (cf. B., 1928, 491) 95.95% of the total gentianose is extracted by 90% alcohol and 36.5% by 95% alcohol from air-dried gentian powder containing 24% of gentianose. Cold percolation gives supersaturated solutions from which the gentianose crystallises on keeping. This may be due to the presence of

an unstable complex in the root which is more soluble than the gentianose and on decomposition the gentianose crystallises. By this method 5 g. of pure gentianose can be easily extracted from 100 g. of dry gentian powder. E. H. SHARPLES.

Nature of the carbohydrates found in the Jerusalem artichoke. A. C. THAYSEN, W. E. BAKES, and B. M. GREEN (Biochem. J., 1929, 23, 444-455).-Autumn-gathered tubers and the unripe pith of the Jerusalem artichoke contain considerable proportions of an insoluble non-fermentable carbohydrate apparently identical with inulin. This carbohydrate disappears almost completely from the tubers towards the spring with the formation of the more soluble carbohydrates which are already present in the autumn tubers. At the same time there is an increase in the dextrorotatory compounds, part of this being most probably due to the formation of sucrose. Comparatively mild autoclaving without acid hydrolysis renders inulin fermentable. The observation that inulin may be fermented by yeast when present in a solution of already fermenting carbohydrates has been confirmed. S. S. ZILVA.

Sweetening components of astringent "kaki" (varieties of Dispyros Kaki, L.). M. Iwara (Bull. Inst. Phys. Chem. Res., 1929, 8, 220—222).—d-Mannitol is shown to be a constituent of "kaki," in addition to dextrose, lævulose, sucrose, and a small amount of pentose. H. BURTON.

Carrageen (Chrondrus Crispus). IV. The hydrolysis of carrageen mucilage. P. HAAS and B. RUSSELL-WELLS (Biochem. J., 1929, 23, 425– 429).—The loss of gelatinising power resulting from mild hydrolysis of carrageen is not accompanied by production of free sugars although reducing properties are developed. The products of hydrolysis contain two ethercal sulphates. One of these is retained in dialysis and possesses reducing properties, the other dialyses and does not reduce. Alkaline hydrolysis of an aqueous extract breaks down completely the carbohydrate complex. Quantitative separation of the sulphate could not be effected by this means. Carrageen mucilage contains dextrose.

S. S. ZILVA.

Chemical constitution of the gums. I. Nature of gum arabic and the biochemical classification of the gums. A. G. NORMAN (Biochem. J., 1929, 23, 524-535).—The acid group of gum arabic is of the "uronic" type. The presence of galactose and arabinose as the only sugars in the molecule is confirmed and analytical figures for these are given for the untreated gum and for its products of hydrolysis. Gum arabic is not a substance of definite empirical formula. It is most probably composed of a nucleusacid consisting of galactose and a uronic acid, probably galacturonic acid, to which is attached arabinose by glucosidic linking. S. S. ZILVA-

Properties of lamarin from Laminaria. H. COLIN and P. RICAED (Compt. rend., 1929, 188 1449—1451).—The isolation of lamarin (cf. Kylin, A., 1915, i, 931), $[\alpha]_D = -11.5^\circ$ (solubility 21 g. 100 g of water at 15°; 16.5 g./100 g. 60% alcohol) (optical data by GAUDEFROY) from Laminaria flexicause by successive precipitation with alcohol from the aqueous extract previously boiled with barium hydroxide and purified by means of lead, is described (yield, 400 g. from 38 kg.). On hydrolysis, in confirmation of earlier results, it yields only dextrose in almost quantitative yield in accordance with the equation $(C_6H_{10}O_5)_n+nH_2O=nC_6H_{12}O_6$, cryoscopic measurements showing that n=6 or 7. J. W. BAKER.

Variation of colour of plants during desiccation. Glucoside of Lathraea clandestina, L., is aucubin. M. BRIDEL (Compt. rend., 1929, 188, 1182—1184).—The crystalline glucoside extracted by 86% alcohol from L. clandestina, L. (yield, 1.66 g. per kg. fresh plant), is not, contrary to the conclusion of Goris (A., 1924, i, 815), meliatin, but is proved by direct comparison of its crystalline form, optical rotation, reducing power, and quantitative enzymolysis to be identical with aucubin isolated from Aucuba japonica, L. (A., 1921, i, 840).

J. W. BAKER.

Presence of monotropitin in Gaultheria procumbens, L., after drying. M. BRIDEL and S. GRILLON (Bull. Soc. Chim. biol., 1929, 11, 466-474). -See this vol., 613.

Methyl salicylate glucoside of Gaultheria procumbens, L., identical with monotropitin. M. BRIDEL and S. GRILLON (J. Pharm. Chim., 1929, viii], 9, 5-16).—See A., 1928, 1224.

Constituents of corn-cockle seed. II. Githagenin and githaginic acid. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1929, 182, 72-81; cf. A., 1926, 982).—The acid obtained by chromic acid oxidation of githagenin in glacial acetic acid and formulated as $C_{28}H_{42}O_5$ is now, from an analysis of its methyl ester, m. p. 206—207° [dioxime, m. p. 200° (decomp.)], shown to be $C_{29}H_{42}O_5$, a diketo-monobasic acid containing a lactone ring. Pure githagenin can be sublimed at 0.01 mm. at temperatures below 260° and is now formulated as $C_{29}H_{44}O_4$, a hydroxytetolactone. C. C. N. VASS.

Reproductive organs of plants. III. Constituents of the pollen-grains of the sugar-beet. A. KIESEL and B. RUBIN (Z. physiol. Chem., 1929, 182, 241-250; cf. A., 1926, 440).—A quantitative analysis of pollen grains from the sugar-beet gave foures differing considerably from analyses made to be years ago. The ether extract yielded $5\cdot38\%$ crude fat" which contained phosphorus equivalent $b12\cdot6\%$ of lecithin and about 30% of a hydrocarbon corresponding closely with heptacosane. The alcohol ethact following the ether extraction was treated with light petroleum and gave $5\cdot54\%$ of a material containing 40% of lecithin. The phosphotungstic acid precipitate of the aqueous extract of the residue gave adenine and betaine (0.04% and 2.96% on original pollen) and traces of choline.

J. H. BIRKINSHAW.

Alkaloidal constituent of Artabotrys suaveolens, Blume. J. M. MARAÑON (Philippine J. Sci., 1929 38, 259-265).—A physiologically active alkaloid, arbotrine, C₃₆H₅₅NO₆, m. p. 187°, was isolated from an extract of the bark of the stem and root of A. suaveolens. The alkaloid is soluble in chloroform, alcohol, ether, and acetone; it is precipitated by the usual alkaloid reagents, and gives colour reactions with nitric acid and Fröhde's reagent.

B. W. ANDERSON.

Histology and microchemistry of the bark and leaf of Artabotrys suaveolens, Blume. J. K. SANTOS (Philippine J. Sci., 1929, 38, 269–280).—A detailed description of the structure of A. suaveolens is given. Microchemical tests with gold chloride, palladium chloride, and other reagents showed that the alkaloid is located in the bark of the stem and root, and is absent from the wood and leaf.

B. W. ANDERSON.

Glutelins. V. Glutelins of rye (Secale cereate) and of barley (Hordeum vulgare). F.A. CSONKA and D. B. JONES (J. Biol. Chem., 1929, 82, 17-21).-Rye and barley flour respectively were extracted with 50% alcohol containing 0.2% of sodium hydroxide, and the filtered solutions adjusted to $p_{\rm H}$ 6.8 with hydrochloric acid; after subjection to a second similar treatment the precipitated proteins were dissolved in 0.2% aqueous sodium hydroxide and treated with ammonium sulphate; the rye extract yielded a single glutelin and the barley extract an α -glutelin precipitating at 1-3% saturation with ammonium sulphate followed by a β -glutelin at 18% saturation. Figures are given for the nitrogen distribution of the rye glutelin and of the a-glutelin from barley, both of which resemble the a-glutelin of wheat. C. R. HARINGTON.

Symbiotic fungi of cereal seeds and their relation to cereal proteins. S. L. JODIDI and J. PEKLO (J. Agric. Res., 1929, 38, 69—91).—A prolamine has been isolated both from English ryegrass and from the symbiotic fungus identified as "smuts" which occurs on it. The percentages of prolamine-nitrogen in the seed are 0.52 and 28.35 of the dry weight and total nitrogen, respectively. The corresponding percentages in the fungi are 0.43 and 9.51, respectively. E. A. LUNT.

Method for making aceto-carmine smears permanent. B. MCCLINTOCK (Stain Tech., 1929, 4, 53-56).—Anthers are placed in a mixture of 1 part acetic acid and 3 parts alcohol. The contents of the anther are squeezed out on a slide in a drop of Belling's iron-aceto-carmine solution and a cover-slip is placed over the drop. The slide is heated for a second in a flame, this is repeated four or five times. The slide is then placed in 10% acetic acid and the cover-slip removed. The slide and the cover-slip are then passed through the following liquids: 1 part acetic acid+1 part alcohol; 1 part acetic acid+3 parts alcohol; 1 part acetic acid+9 parts alcohol; absolute alcohol; 1 part xylene+1 part alcohol. The cover-slip is then replaced on the slide in xylene-balsam. H. W. DUDLEY.

Staining fungal mycelium in wood sections. K. ST. G. CARTWRIGHT (Ann. Bot., 1929, 43, 412– 413).—A combination of safranine and picro-anilineblue was found to be satisfactory for differentiation of the lignified walls and the fungus mycelium which are stained red and blue, respectively.

P. G. MARSHALL.

Effect of partial decay on the alkali solubility of wood. W. G. CAMPBELL and J. BOOTH (Biochem. J., 1929, 23, 566—572).—The effect of partial decay caused by *Trametes serialis*, Fr., on the wood of Sitka spruce is typical of the "brown rot" type. The effect of partial decay on the alkali solubility of the wood of Sitka is of the same order as that produced in the same species of wood by acid hydrolysis and consequently it should be regarded as an acid hydrolysis. S. S. ZILVA.

Plant hæmagglutinins ; the navy bean. V. R. GODDARD and L. B. MENDEL (J. Biol. Chem., 1929, 82, 447-463).-The defatted meal prepared from the navy bean (Phaseolus communis) was extracted with 3% sodium chloride solution; the dialysed and filtered extract was salted out with ammonium sulphate and the solution of the precipitate again dialysed and evaporated. The albumin so obtained was non-toxic, and produced agglutination of rabbit's red blood-corpuscles (in 2.5% suspension in 0.89% sodium chloride solution) at a dilution of 1: 6,000.000. The agglutinating activity was reduced by the presence of traces of egg-albumin and of blood-serum, or by exposure of the protein to dilute hydrochloric acid or to pepsin; it was increased by the presence of sodium chloride. The general behaviour of the plant agglutinin therefore resembles that of agglutinating blood-sera, and suggests that the protein is itself the agglutinating factor. C. R. HARINGTON.

Acetone as a control substance for respiration and gas analysis apparatus. T. M. CARPENTER, E. L. FOX, and A. F. SEREQUE (J. Biol. Chem., 1929, 82, 335–343).—Acetone is recommended as an alternative to alcohol as a test substance for gas analysis apparatus, and the technique of its employment is described. C. R. HARINGTON.

Anaërobiosis and the use of alkaline solutions of pyrogallol. H. NICOL (Biochem. J., 1929, 23, 324—326).—A study of the absorption by Rockwell's solution containing pyrogallol of oxygen from commercial oxygen and from the atmosphere with the production of carbon dioxide and carbon monoxide. S. S. ZILVA.

[Dialysis and extraction] apparatus. III. H. J. FUCHS (Biochem. Z., 1929, 207, 405-409).— The apparatus of Gutbier and Ottenstein (A., 1926, 647) is modified for rapid dialysis of physiological solutions. In a second apparatus by attaching a vacuum pump to a Soxhlet extraction apparatus, the extraction is carried out at temperatures below the b. p. of the extraction fluid.

P. W. CLUTTERBUCK. Micro-apparatus for conductivity measurements in small volumes of liquid. I. REMESOV (Biochem. Z., 1929, 207, 66—79).—The apparatus described enables accurate conductivity measurements at constant temperature to be carried out on volumes of liquid (including biological fluids) as small as 0.05 c.c. The method employed is a modification of that of Kohlrausch. W. MCCARTNEY.

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Preparation of micro-electrodes for measurement of potential. J. GICKLHORN (Koll.-chem. Beih., 1929, 28, 252—258).—The essential features of micro-electrodes suitable for measurements of electrical potential in biochemical systems are discussed, and a method of preparing such electrodes is given. E. S. HEDGES.

Potential measurements. K. UMRATH (Koll. chem. Beih., 1929, 28, 245—251).—A discussion of the practical methods of measuring potential as applied to biochemical systems, especially when the potential varies with time. E. S. HEDGES.

Foundations and limitations of biological $p_{\rm fl}$ determinations. F. LEUTHARDT (Koll.-chem. Beih., 1929, 28, 262–280).—Methods of measuring the hydrogen-ion concentration of cells and tissues are summarised and the results discussed in connexion with the influence of neutral salts and of buffer mixtures. E. S. HEDGES.

Dielectric constants. R. FÜRTH (Koll.-chem. Beih., 1929, 28, 322-328).—Theoretical.

E. S. HEDGES.

Relations of dielectric constants to physiology. J. GICKLHORN (Koll.-chem. Beih., 1929, 28, 328– 332).—Some relations between dielectric constant and other properties of molecular and colloidal solutions are summarised. E. S. HEDGES.

Methods of measuring dielectric constants applicable to biology. R. FÜRTH (Koll.-chem. Beih., 1929, 28, 314—322).—Whereas measurements of dielectric constants are usually carried out on insulating materials, the measurements required in biology are on substances of relatively good electrical conductivity. Only certain methods of measurement are therefore applicable and a description of these methods is given. Results are given for a number of substances present in animal and plant organisms. E. S. HEDGES.

Application of the iodometric method to the determination of small amounts of aldoses. M. MACLEOD and R. ROBISON (Biochem. J., 1929, 23, 517-523) .- Satisfactory results are obtained using three to four times the theoretical quantity of iodine with sodium carbonate as the alkali and allowing the oxidation to proceed during 30 min. at 21 Under these conditions, the oxidation of dextrose is complete, whilst lævulose and sucrose are oxidised only to a very small extent. Values obtained for galactose, maltose, lactose, barium dextrosemonophosphate, barium lævulosemonophosphate, and barium laevulosediphosphate are also given. The extent to which laevulose is oxidised by iodine in presence of excess of sodium hydroxide is much greater than can be explained by the Lobry de Bruyn and van Ekenstein transformation, unless it is assumed that the change from ketose to aldose is largely increased owing to the rapid and continuous S. S. ZILVA. removal of the latter by oxidation.

Determination of halogens in organic substances. W. ROMAN.—See this vol., 713.