

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Ballistic method of ionisation measurement with a quadrant electrometer. D. L. WEBSTER and R. M. YEATMAN (*J. Opt. Soc. Amer.*, 1928, 17, 248—253).—The method of using the quadrant electrometer by taking the reading when the needle has stopped swinging is open to the objection that the time required is long. The method described is to read the farthest point of swing. The accuracy of the method depends on (1) linearity of the differential equation of motion; (2) homogeneity, except for the term proportional to the ionisation; (3) initial values of deflexion and velocity must be zero; (4) the exposure time must be constant. In practice, the last can easily be satisfied, whilst (2) and (3) can be satisfied by introducing a constant current opposite to that of the ionisation chamber. The first condition depends on the instrument. Tests on a Compton electrometer showed that all the conditions could be satisfied and that the method has no systematic errors large enough to detect in the presence of a 1% erratic error. For large deflexions there is a deviation of 1% from linearity, but calibration by means of a potentiometer enables the comparison of ionisation currents to be carried out accurately.

A. J. MEE.

Proof of Schrödinger's theory. J. L. SNOEK, jun., and L. S. ORNSTEIN (*Z. Physik*, 1928, 50, 600—608).—Measurements have been made of the fine structure of the absorption in the H_α and H_β lines. The ratio of the total absorption of the H_α line to that of the H_β line is 5.25, a value in good agreement with that deduced theoretically from Schrödinger's theory (5.37). The ratio of the absorption maxima in the two lines also agrees with that calculated from the theory.

J. W. SMITH.

Promotion of the emission of the Balmer lines by the addition of argon. E. HIEDEMANN (*Z. Physik*, 1928, 50, 609—617).—It has been shown that the addition of argon produces a very marked effect on the relative intensities of the lines and bands in the hydrogen spectrum. The action of argon on the dissociation of the hydrogen molecule into ions and on the recombination of the latter is discussed. A theory is developed which is claimed to agree with the observed phenomena.

J. W. SMITH.

Fulcher spectrum of hydrogen. E. HIEDEMANN (*Z. Physik*, 1928, 50, 618—625).—From a discussion of the existing data the conclusion is reached that the Fulcher bands in the hydrogen spectrum are

set up by the H_2 molecule, and not by H_2^+ . It is also concluded that the continuous hydrogen spectrum is due to excited hydrogen molecules as suggested by Blackett and Franck (*A.*, 1925, ii, 1097) and not to the decomposition of H_2^+ ions as supposed by Herzberg (this vol., 1).

J. W. SMITH.

Extinction of the D-lines in flames by [the addition of] chlorine compounds. J. FRANCK and G. E. GIBSON (*Z. Physik*, 1928, 50, 691).—By observing the behaviour of a salted flame to which small amounts of carbon tetrachloride vapour were added it has been shown that a complete parallelism exists by the extinction of the emission of the D-lines and their disappearance in the absorption spectrum. This is held to indicate that the disappearance of the D-lines is due to the disappearance of the free sodium atoms which pass under these conditions into sodium chloride molecules.

J. W. SMITH.

Spectra of neon, argon, and krypton (additional lines). W. GREMMER (*Z. Physik*, 1928, 50, 716—724).—A number of new lines in the red and infra-red regions have been observed in the spectra of neon and argon. Most of these have been shown to be members of the *sp*-, *ps*-, or *pd*-series. The spectrum of krypton, like those of neon and argon, shows certain constant vibrational differences. These regularities enable a considerable number of the spectral lines of krypton to be classified.

J. W. SMITH.

Breadth of some lines of the mercury spectrum. A. CARRELLI (*Atti R. Accad. Lincei*, 1928, [vi], 7, 1014—1018).—A discussion of the results of the measurement, by the interferometer method, of the breadth of eleven lines of the mercury spectrum.

F. G. TRYHORN.

Spectra of ionised neon (Ne II) and ionised argon (A II). II. T. L. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1928, 31, 593—602).—A comparison is made between the quadruplet terms of ionised neon (Ne II) and ionised argon (A II). A table of terms is given. Nearly all the terms predicted by the theory of Heisenberg and Hund have been detected and identified. The Zeeman effect was investigated in order to check the term scheme, the calculated effect being compared with that observed.

A. J. MEE.

Intensity of reflexion of X-rays by crystals and the Compton effect. G. E. M. JAUNCEY (*Physical Rev.*, 1927, [ii], 29, 206).—A correction factor, introduced by the Compton effect, is applied

to Bragg, Darwin, and James' formula (A., 1926, 663) for the case of an ideally imperfect crystal.

A. A. ELDRIDGE.

X-Ray spectrographic measurements in the *L* and *M* series of rhenium. H. BEUTHE (Z. Physik, 1928, 50, 762—768).—The wave-lengths of a number of *L* α , β , and γ and of *M* β and γ lines of rhenium have been determined, and the corresponding term values have been calculated.

R. W. LUNT.

Intensities of *K*-series X-rays from thin targets. D. L. WEBSTER, H. CLARK, R. M. YEATMAN, and W. W. HANSEN (Proc. Nat. Acad. Sci., 1928, 14, 679—686).—Experimental data have been obtained for targets of silver so thin as to cause no appreciable retardation of most of the cathode rays. These data give the relative intensity of *K*-series X-rays, and, therefore, the relative probability of direct *K*-electron ionisation, as a function of cathode-ray energy from the excitation energy to 3.3 times that amount.

W. E. DOWNEY.

Relation between chemical constitution and *K*-absorption spectra. VII. General review. O. STELLING (Z. Physik, 1928, 50, 506—530).—Following a review of the various experimental methods now employed, the author analyses the results obtained with the compounds of phosphorus, sulphur, and chlorine. In the phosphorus compounds it is shown that the displacement of the absorption limit depends only on the nature of the atom or radical directly linked to the phosphorus, and that the displacement is proportional to the number of such atoms or radicals. The limit for sulphur shifts towards shorter wave-lengths as the valency is increased; the influence of metals in sulphides is specific to the metal, but the position of the limit is constant in organic compounds of sulphur. Metallic chlorides with water of crystallisation are characterised by a shorter wave-length limit than the corresponding anhydrous substances; the limit is constant for a number of cobaltamino-chlorides, and also constant, although different in value, for organic compounds containing chlorine. The relationship between the displacement of the absorption limit, ion distance, grating type, and electron configuration is also discussed.

R. W. LUNT.

Variation of X-ray absorption spectra in crystal gratings. K. FAJANS (Z. Physik, 1928, 50, 531—536).—The data of Stelling (cf. preceding abstract) have been used to show that the displacement of the absorption limit varies inversely as the fourth power of the ionic distance, and that therefore the absorption limit is determined by the electron configuration of the ions in the grating.

R. W. LUNT.

Ultra-violet band spectra of nitrogen. R. T. BIRGE and J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 356).—The system previously analysed (A., 1925, ii, 737) has been extended to include sixty bands between 1250 and 2025 Å. The system is not now ascribed to nitric oxide, but is the resonance system of nitrogen. Two other progressions of emission bands between 1030 and 1520 Å. have been identified.

A. A. ELDRIDGE.

Excitation of the arc spectrum of nitrogen. R. A. WOLFE and O. S. DUFFENDACK (Physical Rev., 1927, [ii], 29, 209—210).—When the arc spectrum of nitrogen was excited by an interrupted low-voltage arc in a mixture of helium and nitrogen, nitrogen arc lines were very strong in a limited region, whereas in other regions helium lines or nitrogen bands strongly predominated. Existing data are largely confirmed.

A. A. ELDRIDGE.

Absorption spectrum of antimony vapour. R. V. ZUMSTEIN (Physical Rev., 1927, [ii], 29, 209).—The arc lines 2311.50, 2175.88, and 2068.38 were strongly, and 2023.86, 2127.46 less strongly, absorbed. All five absorption lines come from the $3d_2$ state, which is doubtless the normal state of the atom.

A. A. ELDRIDGE.

Resonance glow in a hydrogen discharge tube. R. D. RUSK (Physical Rev., 1927, [ii], 29, 213—214).—A study of the blue haze obtained in a hot-filament discharge tube. A close relationship between the life of the excited molecule and its collision frequency is suggested.

A. A. ELDRIDGE.

Absorption of the mercury line 1941.5 Å. in the positive column and the optical determination of the concentration of mercury ions. W. DE GROOT (Z. Physik, 1928, 50, 559—569).—Radiation of 1941.5 Å. emitted from a low-voltage arc in a neon-mercury vapour mixture was allowed to pass through the positive column of a low-voltage discharge in a mixture of argon (16 mm.) and mercury vapour (3 mm.); the ratio of the intensity of the incident to the transmitted radiation, I_0/I , has been measured as a function of the current in the positive column. A theoretical expression for this ratio has been derived from the analyses of Lorentz, Voigt, and Minkowski in terms of the most probable velocities, assuming a Maxwellian distribution, of the ions in the light source, w_e , and in the positive column, w , of the widths of the line 1941.5 Å. in the source, ω_e , and in the positive column, ω , of the density of ionisation, N , and of the apparent temperature of the ions in the positive column T . Values of w , w_e , ω_e , and ω were then chosen so that the theoretical and experimental curves relating I_0/I with the current coincided, assuming that N is proportional to the current. Values are thus obtained for N in terms of $w\omega$, and by assuming on the basis of Langmuir's experiments (this vol., 342) that the currents used in the discharge tube correspond with values of T from 1000° to 5000° Abs. N is found to range from 1.6 to 3.2×10^{10} ions/c.c. as the current is increased from 5 to 100 ma. These values are in agreement with the recent values obtained by Compton, Turner, and McCurdy (A., 1925, ii, 86) using search electrodes.

R. W. LUNT.

Arc spectrum of iron under reduced pressure over the range 2270—3900 Å. P. MARING (Z. wiss. Phot., 1928, 26, 47—86).—A large Rowland grating was used, giving results claimed to be accurate to one thousandth of an Ångström unit. Full experimental details are given for obtaining accurate measurements of wave-length shifts.

A table is given comparing corresponding wave-lengths in air and in a vacuum, respectively, for some

hundreds of lines, and shows that the vacuum displacement, which is usually towards the red, never exceeds 1–2 Å. The vacuum lines are generally sharper than the corresponding air lines; occasionally a line is simple in the air and inverted in the vacuum spectrum. The intensity of the vacuum line is greater only when the corresponding air line is inverted. Many lines occur only in the vacuum spectrum; occasionally two apparently independent lines in the air spectrum unite to give a single line in the vacuum.

Contrary to expectation, the vacuum spectrum does not give any better results for the frequency differences between successive pairs in multiplets than the air spectrum.

In spite of the greater sharpness of the lines and the certainty of avoiding pole-effects, the vacuum spectrum of iron cannot replace the air spectrum as a standard owing to the far greater care required in operation.

S. J. GREGG.

Spectrum temperature of magnesium- and flash-light. H. ARENS and J. EGGERT (Z. wiss. Phot., 1928, 26, 95–96).—The spectrum temperatures of the magnesium flame and of flash-light are 3700° and 2900° Abs., respectively. On an Agfa colour plate flash-light showed normal distribution of intensity, whilst the magnesium flame was strong in the blue. This was confirmed by spectrum observations.

S. J. GREGG.

First spark spectrum of krypton. P. K. KICHLU (Proc. Roy. Soc., 1928, A, 120, 643–649; cf. this vol., 808).—With the aid of the data of Bloch, Bloch, and Déjardin (A., 1924, ii, 286) and of Abbink and Dorgelo (this vol., 338), an analysis has been made of the spark spectrum of krypton over the region 783.72–6768 Å. The calculated ionisation potential of the krypton ion is 26.4 volts. The discrepancy between this value and that found by Déjardin (28.25 volts) is perhaps due to the fact that the present value was calculated by taking only the first two members of a Rydberg sequence.

L. L. BIRCUMSHAW.

Absorption spectrum of caesium. (MISS) I. M. MATHEWS (Proc. Roy. Soc., 1928, A, 120, 650–654).—The light from a carbon arc was passed through caesium vapour, produced in an electrically-heated steel tube from dried caesium carbonate in the presence of powdered magnesium, and focussed on the slit of a Rowland grating. The wave-lengths and classification of the principal lines in the spectrum over the region 3888.622–3193.172 Å. are tabulated. The values are in close agreement with those obtained by Bevan (*ibid.*, 1912, A, 86, 320). As far as the *s* and *p*-terms are concerned, no support is found for the view of Sowerby and Barratt that the present accepted term values are inaccurate (cf. A., 1926, 213).

L. L. BIRCUMSHAW.

Zeeman effect for spectrum of tantalum. J. C. McLENNAN and A. M. I. A. W. DURNFORD (Proc. Roy. Soc., 1928, A, 120, 502–510).—The magnetically resolved components of 55 of the more important wave-lengths of the tantalum arc spectrum between 5548 and 6700 Å. have been determined. Several of the Zeeman patterns confirm the previous

work on atomic states and spectral terms (McLennan, McLay, and Smith, A., 1926, 874), giving the lowest spectral term for tantalum as $4F_2$, and thus indicating a quadruplet system for the arc spectrum.

L. L. BIRCUMSHAW.

New regularities in the helium band spectrum. G. H. DIEKE, T. TAKAMINE, and T. SUGA (Z. Physik, 1928, 49, 637–669).—The band spectrum of helium has been re-examined using a concave grating of 15 ft. radius leading to an accuracy of 0.008, 0.004, and 0.003 Å. in the first, second, and third orders, respectively. The helium used contained a small amount of neon; the conditions under which the spectrum was excited are not described. A large number of new bands was observed, the last members of which are $2p$ -terms; the characteristics of these bands differ widely from those of others previously recorded. The newly-observed lines have been classified and co-ordinated, and the parameters of the equations for the vibrational bands have been evaluated.

R. W. LUNT.

Mathematical relationships between fine structure and the Doppler effect. G. DOETSCH (Z. Physik, 1928, 49, 705–730).—Following an analysis of the variation of intensity throughout a spectral line due to thermal agitation, two methods are derived for the calculation of the fine structure of a line from measurements of the width and of the total intensity of a line.

R. W. LUNT.

Intensity ratios for the doublets of the principal series of the alkali metals. S. SAMBURSKY (Z. Physik, 1928, 49, 731–739).—The intensity of a number of doublets of the principal series of sodium, potassium, rubidium, and caesium have been determined. The ratio of the intensities $1s-np_1 : 1s-np_2$ ($n=2, 3, \dots$) varies linearly with the logarithm of the effective quantum number, but only in the case of sodium is the theoretical constant value of 2 attained; in the other cases the ratio increases with the logarithm of the quantum number.

R. W. LUNT.

Gurney theory of the origin of the helium lines in the spectrum of the chromosphere. W. ANDERSON (Z. Physik, 1928, 48, 749–782).—Calculations are made which show that the distance of fall of a Ca^{++} ion in the sun's gravitational field necessary to excite the 5876 Å. line of helium is in good agreement with the observed region of emission of this line relative to the sun's surface.

R. W. LUNT.

Spectrum of the hydrogen molecular ion. C. J. BRASEFIELD (Proc. Nat. Acad. Sci., 1928, 14, 686–689).—By spectroscopic examination of a luminous canal-ray beam in hydrogen, it has been found possible to separate the lines due to the hydrogen molecular ion.

W. E. DOWNEY.

Series spectra of cadmium-like atoms. J. B. GREEN and R. J. LONG (Proc. Nat. Acad. Sci., 1928, 14, 706–710; cf. Lang, this vol., 99).—The spectrum of Sb IV has been measured and analysed.

W. E. DOWNEY.

Spark spectrum of neon. A. S. GANESAN (Physical Rev., 1928, [ii], 32, 580–582).—A list of lines in the spark spectrum of neon between 2300 and

1850 Å. is given. Many of the lines seem to belong to Ne III. N. M. BLIGH.

Intensities of the lines in the spectrum of mercury. E. O. HULBERT (Physical Rev., 1928, [ii], 32, 593—599).—The total radiation in the spectral region 6000—2300 Å. from a small quartz mercury lamp was 1.85×10^{-10} erg per atom per sec. From this and the intensities of the lines, the average emission of quanta per second by each atom was found as 11.4, 8.9, 5.0, 2.3 of yellow, green, blue, and violet light, respectively. The intensities of twenty-four lines of the spectrum were measured. Plotting the logarithm of the intensity against the frequency for the lines of a series gave roughly straight lines of about the same slope for the sharp series ($2^3P_n - m^3S_1$) and for the diffuse series ($2^3P_n - m^3D_{1,2,3}$). The temperatures of the excited atoms derived from the slopes were 3900° and 2600° Abs. for the sharp and diffuse series, respectively. N. M. BLIGH.

29 and 30-Electron-system spectra of arsenic and selenium. R. A. SAWYER and C. J. HUMPHREYS (Physical Rev., 1928, [ii], 32, 583—592).—New vacuum-spark data in the extreme ultra-violet have been obtained for arsenic and selenium. Extrapolation methods are used to predict the location of and to identify the lines arising from transitions between the lowest levels in the spectra of As IV, As V, Se V, and Se VI. The ionisation potential of As V is determined as 62.4 volts, that of Se VI as 81.4 volts. The $(4P^2)^3P$ separation of the 30-electron-system spectra shows a rapid increase with respect to the separation both of $(4s4p)^3P$ term and $(4p)^2P$ term of the next ion. The theoretical significance of this effect, first observed here and not appearing in the corresponding iso-electronic spectra of the lighter elements, is discussed. The effect is believed to be due to a change of coupling of the quantum vectors with increasing nuclear charge. N. M. BLIGH.

Spectrum of potassium excited during its spontaneous combination with chlorine. L. A. RAMDAS (Indian J. Physics, 1928, 3, 31—36).—The light emitted by potassium burning in chlorine gives a spectrum showing the arc lines of potassium, an intense, broad red band due to potassium molecules, and a few feeble lines which appear to be the enhanced lines in the violet region. The possibility of thermal excitation of this spectrum is discussed.

W. E. DOWNEY.

Horizontal comparison in the location of spectra of elements. M. SAHA and K. MAZUMDAR (Indian J. Physics, 1928, 3, 67—76).—Theoretical.

W. E. DOWNEY.

Ultra-violet absorption bands of oxygen. A. S. GANESAN (Indian J. Physics, 1928, 3, 95—104).—The structure of five ultra-violet absorption bands of oxygen between 1953 and 1864 Å. has been experimentally determined. W. E. DOWNEY.

Excitation of Cu II spectrum by positive neon ions. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1927, [ii], 29, 925).—The spectra of low-voltage arcs maintained in mixtures of argon and copper and of neon and copper in a tungsten furnace were studied. The argon mixture gave no spark

lines. In neon the lines from the levels corresponding with the $(3d)^9(4p)$ and $(3d)^9(5s)$ configurations were strongly developed. The results accord with Shenstone's analysis (A., 1927, 389). A. A. ELDRIDGE.

Nature of the nitrogen afterglow. A. G. WORTHING (Physical Rev., 1927, [ii], 29, 907—908).—The observations described do not support the view that the afterglow originates in impacts of neutral unexcited nitrogen atoms and molecules.

A. A. ELDRIDGE.

Zeeman effect of the fine structure components of mercury radiation λ 2536 Å. W. A. MACNAIR (Physical Rev., 1927, [ii], 29, 915).—The five fine structure components split into triplets, the effects of a magnetic field on the components of which is recorded.

A. A. ELDRIDGE.

X-Ray absorption and valency. W. B. MOREHOUSE (Physical Rev., 1927, [ii], 29, 924).—The absorption of heterogeneous X-rays by an element depends on its valency; the effect may differ for different wave-lengths. If the screening constant changes the absorption coefficient will change. With change of valency there must be a slight change in the electronic configuration of the atom.

A. A. ELDRIDGE.

Secondary absorption edges in X-rays. B. B. RAY (Nature, 1928, 122, 771—772).—An explanation of the anomalous position of secondary edges is advanced; it is assumed that the same quantum can be absorbed successively by two or more electrons occupying different energy levels in the atom.

A. A. ELDRIDGE.

Stark effect in neon. J. S. FOSTER and W. ROWLES (Physical Rev., 1927, [ii], 29, 925).—The observed symmetrical Stark patterns for the line groups of higher order were remarkably hydrogen-like in character. Each of the lines $2p_j - 4f$ and $2p_j - 5f$ appears as a doublet, and the two members of the doublet present nearly identical Stark effects.

A. A. ELDRIDGE.

Unclassified lines of oxygen in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 923—924).—The triplet 988.67, 990.13, 990.73 Å. is possibly an unresolved group similar to the sulphur group at 1480 Å., which contains eight lines. The aurora line 5577.35 Å. is apparently related to the two ultra-violet lines of oxygen 1217.62 and 999.47 Å.; possibly the ultra-violet lines have a common initial or final state and the aurora line represents the transition between their respective final or initial states.

A. A. ELDRIDGE.

Characteristics of the neutral and of the singly- and doubly-ionised spectra of cerium. A. S. KING (Physical Rev., 1927, [ii], 29, 366).—Approximately 1600 lines between 3000 and 4700 Å. in the spectrum of neutral cerium have been measured in furnace spectrograms. More than 3000 neutral lines may now be listed. The spectrum of ionised cerium is common to the arc and spark, whilst in the ultra-violet a condensed spark discharge gives many doubly-ionised lines.

A. A. ELDRIDGE.

Series limits. A. G. SHENSTONE (Nature, 1928, 122, 727—728).—The predictions of Hund's theory

of the limits of component series are invalid, since they do not take into account the fact that a magnetic field which is, in the usual sense, strong may still be weak from other points of view. A. A. ELDRIDGE.

Fine structure of the Compton effect. M. DE BROGLIE (Compt. rend., 1928, 187, 697).—If the experiments of Davis (this vol., 1168) are considered in the light of the diffused photon theory of the Compton effect, then the continuous background diffused under the influence of an exciting source containing rays of all wave-lengths should be banded, and in the curve connecting the total absorption of an element with the wave-length, a portion of the absorption should be attributed to diffusion. J. GRANT.

Spectrum of bromine in the electrodeless discharge. N. SIRACUSANA (Atti R. Accad. Lincei, 1928, [vi], 7, 835–838).—The spectrum of bromine excited by the electrodeless discharge under unspecified electrical conditions has been examined to 2000 Å.; this is characterised by a number of lines belonging to arc spectrum many of which are new, and a faint continuous background. R. W. LUNT.

Extension of the group theory of terms. M. DELBRÜCK (Z. Physik, 1928, 51, 181–187).—Mathematical. R. W. LUNT.

Spectra of boron. R. A. SAWYER (Physical Rev., 1927, [ii], 29, 357).—Twenty-five out of ninety new "vacuum spark" boron lines have been classified. A. A. ELDRIDGE.

Stages in the excitation of the spectrum of indium. J. G. FRAYNE (Physical Rev., 1927, [ii], 29, 357).—At 3.3 volts the lines $2p_1-2s$ and $2p_2-2s$ appeared; at 4.2 volts the additional lines $2p_1-3d$ and $2p_2-3d$ appeared. At 7 volts higher members of the series appeared, whilst at 13.2 volts lines additional to the recognised series lines appeared. At this potential a second electron may have been detached from the atom, assuming that ionisation occurred at 7 volts. Most of the lines which appeared at 23 volts have been recognised as air lines. At 600–800° the lines from the $2p_1$ level were consistently stronger than those from the $2p_2$ level. A. A. ELDRIDGE.

Energy level studies on metallic vapours using a high-temperature tungsten furnace. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1927, [ii], 29, 358).—New absorption lines were observed with copper vapour at 2618.37, 2824.39, 2882.81, 2961.19, 3010.87, 3194.09, and 5782.08 Å., all originating in the metastable $2D_{3/2}$ level. The copper lines 3247, 3274, 5106, 5700, 5782 Å. originating in the $2^2P_{1/2}$ level and several copper hydride bands were obtained in emission. The $2D_{3/2}$ level is reached by thermal action and the $2^2P_{1/2}$ level by absorption of resonance radiation. A. A. ELDRIDGE.

Relations in the spectra of stripped atoms. R. C. GIBBS and H. E. WHITE (Physical Rev., 1927, [ii], 29, 359).—It has been possible to recognise the first pair of doublets in the principal series for stripped atoms as far as Mn VII in the first long period, Zr IV in the second, and Pr V in the third. The first pairs

of inverted diffuse doublets with satellite have been located for Sc III, Ti IV, and V V.

A. A. ELDRIDGE.

Two electron multiplets of the first and second long periods. H. E. WHITE and R. C. GIBBS (Physical Rev., 1927, [ii], 29, 359).—Three characteristic multiplets arising from two-valency electron systems of the first and second long periods of the periodic system follow the regular and irregular doublet laws. A. A. ELDRIDGE.

Intensity of scattered X-rays and the Compton effect. G. E. M. JAUNCEY (Physical Rev., 1927, [ii], 29, 605).—It is assumed that all the electrons in the U state in a given atom co-operate in the unmodified scattering, which therefore varies as F^2 and the modified scattering as $Z-F$, where F is Williams and Jauncey's atomic structure factor and Z is the atomic number. A. A. ELDRIDGE.

Vibrational levels in the blue-green band system of sodium. F. W. LOOMIS (Physical Rev., 1927, [ii], 29, 607).—The following assignment is made: $\nu = 20301.7 + (124.13n' - 0.84n'^2) - (158.5n'' - 0.73n''^2 - 0.0027n''^3)$. The bands to which the fluorescence lines belong can be identified approximately. A. A. ELDRIDGE.

Fine structure of the helium arc spectrum. W. V. HOUSTON (Physical Rev., 1927, [ii], 29, 749).—The sharp series line 7065 Å. and the diffuse series line 5876 Å. of the orthohelium spectrum are triple. Hence the helium spectrum is not anomalous. A. A. ELDRIDGE.

Photo-electric properties of thin films of the alkali metals. N. R. CAMPBELL (Phil. Mag., 1928, [vii], 6, 633–648).—The sensitivity of a photo-electric cathode has been shown to depend on the thickness of the metallic deposit, the nature of this deposit, and the material on which the deposit is made. Potassium photo-electric cathodes produced by depositing the metal on copper, driving it off by heat, and then subjecting the remaining film to a discharge in hydrogen show remarkable and stable sensitivity to red light, the photo-electric currents obtained with a wave-length of 8000 Å. being of the same order as those obtained in normal potassium cells under a wave-length of 4500 Å. Similar but less regular effects were obtained with films of sodium, caesium, and rubidium on various other metals. It is suggested that to obtain maximum photo-electric sensitivity over the range of the visible spectrum a combination of the normal potassium cell and that with the new potassium-on-copper anode should be employed. The results indicate that the films in question consist of a succession of unimolecular layers analogous to those of caesium and oxygen on tungsten examined by Langmuir and others. A. E. MITCHELL.

Critical potentials of the spark lines of mercury. J. A. ELDRIDGE (Physical Rev., 1927, [ii], 29, 213).—From measurements of the intensities of 30 spark lines as a function of voltage, three critical values <150 volts have been found at about 18, 24, and 57 volts. A. A. ELDRIDGE.

Possible relation between radiation and ionisation potentials of iron. O. STUHLMAN (Physical

Rev., 1927, [ii], 29, 354).—Published values are considered. The critical radiation potentials can probably be attributed to multiple impact.

A. A. ELDRIDGE.

29-Volt critical potential of hydrogen. R. D. RUSK (Physical Rev., 1927, [ii], 29, 354).—The results of determinations of striking and breaking potentials of illuminated arcs in hydrogen suggest that 29 volts represents a molecular excitation level capable of sustaining intense cumulative ionisation and having a critical excitation period of the order of 10^{-8} sec.

A. A. ELDRIDGE.

Direction of ejection of photo-electrons by polarised X-rays. C. J. PIETENPOL (Physical Rev., 1928, [ii], 32, 564–569).—The lateral distribution of photo-electrons ejected by polarised X-rays was studied by means of the Geiger point counter which could rotate about the polarised beam, and results supported the theoretical relation due to Auger and Perrin (A., 1925, ii, 618).

N. M. BLIGH.

Photo-electric thresholds and fatigue. G. B. WELCH (Physical Rev., 1928, [ii], 32, 657–666).—Causes affecting threshold values were investigated, using highly purified elements the surfaces of which were prepared in a vacuum by an electromagnetic filing device. A linear relation was found between the logarithm of the photo-electric current and the logarithm of the time elapsed since polishing the surface. The rate of fatigue increases with the pressure and depends on the element used and for a given substance increases numerically as the threshold is approached. Thresholds were found as formerly (cf. A., 1927, 603) and the values obtained were: calcium 4475, iron 3155, cobalt 3165, nickel 3040, copper 2955, zinc 3180, and germanium 2880 Å. The results are in harmony with the patch theory of Richardson and Young (A., 1925, ii, 343).

N. M. BLIGH.

Distribution in space of the initial directions of photo-electrons produced by monochromatic X-rays. P. AUGER (J. Phys. Radium, 1928, [vi], 9, 225–230).—The apparatus used is described. Measurements have been made using monochromatic X-rays to excite a mixture of hydrogen with 10% of argon. The results are represented by a method previously described (cf. *ibid.*, 1927, [vi], 8, 85–112) and it is found that when ω , the angle between the emitted photo-electric ray and the incident X-ray, is plotted against the total number of emitted rays between 0 and ω , the curve closely follows that of $\sin^3\omega$. The results are discussed and it is pointed out that their difference from those given in the previous paper is due to the fact that monochromatic X-rays had not then been used.

J. L. BUCHAN.

Electric emission of incandescent platinum in an atmosphere of iodine. S. KALANDYK (J. Phys. Radium, 1928, [vi], 9, 231–235).—Both the positive and negative emission have been studied in an apparatus which is described. The latter only is influenced by the presence of iodine vapour. The intensity of the negative emission has been measured at various temperatures and pressures of the iodine vapour and for different temperatures of the emitting platinum filament. The influence of the iodine is

shown to be greater the lower is the temperature of the filament and finally disappears as the temperature is raised. The results are discussed, and the increase in intensity of emission is attributed to the formation of a film of platinum iodide on the filament.

J. L. BUCHAN.

Heat of condensation of electrons and positive ions on molybdenum. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1927, [ii], 29, 909).—The heat of electron condensation on a molybdenum sphere is 4.76 volts in argon, 4.77 or 5.01 in nitrogen, and 4.04 or 4.35 volts in hydrogen, according to the surface treatment. The heating effect of a positive ion of argon is about 1 volt.

A. A. ELDRIDGE.

Effect of oxygen on photo-electric emission from potassium. L. R. KOLLER (Physical Rev., 1927, [ii], 29, 902–903).—Variations in the effect of the admission of oxygen are ascribed to adsorption phenomena.

A. A. ELDRIDGE.

Critical potentials of copper. R. HAMER and S. SINGH (Physical Rev., 1927, [ii], 29, 901–902).—The following were observed: 3.3, 7.9, 14.2, 19.5, and 25.3 volts.

A. A. ELDRIDGE.

Simultaneous ionisation and excitation of molecules on collision with foreign ions. O. S. DUFFENDACK and H. L. SMITH (Physical Rev., 1927, [ii], 29, 914–915).—A study of the spectrum of the low-voltage arc in mixtures of helium, neon, or argon and carbon monoxide or nitrogen leads to the conclusion that an ion can ionise a molecule and excite the resulting ion to the degree represented by the difference in the ionising potentials.

A. A. ELDRIDGE.

Surface layers produced by activated nitrogen. C. KENTY and L. A. TURNER (Physical Rev., 1927, [ii], 29, 914).—The decrease in resistance of a tungsten wire in the presence of activated nitrogen is attributed to the formation of a surface layer which increases the emissivity of the filament, thereby lowering its temperature. The effect is apparently produced by a neutral substance.

A. A. ELDRIDGE.

Infra-red spectrum of mercury. V. P. LUBOVICH (Physical Rev., 1927, [ii], 29, 355).—McLennan and Shaver have ascribed higher order lines to the infra-red spectrum of mercury, photographed in the first order of a diffraction grating. Certain new lines have been observed; the line 10141 Å. is not a doublet.

A. A. ELDRIDGE.

Critical potentials of iron. R. HAMER and S. SINGH (Physical Rev., 1927, [ii], 29, 608).—Critical potentials were observed as follows:—3.7, 7.15, 11.2, 16.3, 19.4, 24.5, 29.0, 33.9, 38.8, 42.1, 45.7, 48.4, 51.4, 54.8, 61.6, 72.7, 89.6, 103.1, 111.6, 125.8 volts.

A. A. ELDRIDGE.

Ionisation of mercury vapour by 2537 Å. radiation. P. D. FOOTE (Physical Rev., 1927, [ii], 29, 609).—The relation between illumination (I) and photo-current (Δi) was of the form $\Delta i = AI^2/(1 + BI)^2$, where A and B are constants for a given vapour pressure. Admixture of nitrogen increases, and that of hydrogen effaces, the effect. Two separate excited atoms are involved in the ionisation process.

A. A. ELDRIDGE.

Excitation of mercury vapour by positive ions. E. J. JONES (Physical Rev., 1927, [ii], 29, 611).—Saturated mercury vapour at 90° was bombarded with positive potassium ions, and the lines appearing at various voltages were observed. The efficiency of excitation by positive ions is far less than that by electrons. Up to 1200 volts the probability of excitation to the $2p_2$ level is greater than that to higher levels; excitation to levels higher than $3d_{1,2,3}$ was not observed.

A. A. ELDRIDGE.

Inelastic collisions in ionised gas mixtures. G. P. HARNWELL (Physical Rev., 1927, [ii], 29, 611).—The variation with pressure of the ionisation by electron impact in mixtures of the rare gases with hydrogen and nitrogen was studied. The number of rare gas ions decreased rapidly after a pressure of about 0.05 mm. was reached. Similar effects were observed with mixtures of nitrogen and the rare gases. The results support evidence for the existence of a type of collision of the second kind resulting in ionisations by positive ions.

A. A. ELDRIDGE.

Recombination of ions in the chamber of an X-ray spectrometer. D. L. WEBSTER and R. M. YEATMAN (J. Opt. Soc. Amer., 1928, 17, 254—259).—It is shown that under proper conditions the fraction of ions lost by recombination is independent of the total number of ions produced, for any loss up to about 10%. This allows the use of a much lower chamber voltage in the comparison of ionisation currents. The fact that the fraction lost is practically constant indicates that probably the recombination is columnar, i.e., in the case of X-rays, an ion recombines only with another ion produced by the same photo-electron. This will be best satisfied with weak rays, and not with strong ones. A. J. MEE.

Reflexion of electrons from an aluminium crystal. D. C. ROSE (Phil. Mag., 1928, [vii], 6, 712—729).—An apparatus similar to a Bragg X-ray spectrograph has been used in the examination of the reflexion of electrons from the surface of an aluminium crystal. Four different orders of reflected beams were found, the positions of which agreed fairly closely with those predicted from wave theory when the refractive index of aluminium is assumed to be unity. Two other orders of another set of reflected beams, attributed to an aluminium oxide film or to some other contamination, were found. The accelerating potential, spacing constant of the crystal, and angle of reflexion are connected by the usual relationships applicable to X-rays. Similar experiments on nickel by Davisson and Germer (cf. this vol., 102) did not yield results in accordance with the wave theory, and it is suggested that the discrepancies are due to the magnetic effects of the nickel but more probably to the exhibition of a definite refractive index by the nickel.

A. E. MITCHELL.

Collisions of the second kind between zinc and mercury atoms. J. G. WINANS (Physical Rev., 1927, [ii], 29, 213).—Additional evidence (cf. A., 1926, 768) has been obtained that mercury atoms in the $2P$ state are effective in collisions of the second kind with zinc atoms. In the experiment, an excited mercury atom with an associated metastable state

was probably about twice as effective in producing collisions of the second kind as one with no metastable state near it.

A. A. ELDRIDGE.

Dependence of the free path of potassium ions in various gases on their velocity. F. M. DURBIN (Physical Rev., 1927, [ii], 29, 215).—Curves showing the dependence of the free path of potassium ions on the velocity in air, hydrogen, nitrogen, helium, oxygen, and argon show an approach to a constant high value of the free path at the higher velocities and a decrease to a kinetic theory value at the lowest velocities.

A. A. ELDRIDGE.

Secondary electron emission produced by positive caesium ions. J. M. HYATT (Physical Rev., 1927, [ii], 29, 214).

Distribution of electrons in a metal. J. E. LENNARD-JONES and H. J. WOODS (Proc. Roy. Soc., 1928, A, 120, 727—735).—Thomas (A., 1927, 290) has applied the new statistics of Fermi and Dirac to the distribution of electrons in heavy atoms. The basic idea is that the "electron gas" surrounding a nucleus is "degenerate," so that every cell of extension h^3 of a six-dimensional phase space contains two electrons, spinning in opposite directions to one another. A differential equation is obtained which has been solved by Thomas and Fermi by numerical methods. Another application of the statistics has been made by Sommerfeld to the free electrons of a metal (this vol., 467). Sommerfeld's work is criticised on the ground that he has neglected the interaction of the electrons and the atomic cores. The object of the present investigation is to find the average distribution of electrons (by the means employed by Thomas and Fermi for isolated atoms) when the metal is regarded as a whole. The same differential equation as that of Thomas and Fermi is obtained, but the boundary conditions are different. The differential equation inside a cube subject to the simple boundary conditions that $Vr \rightarrow E$ at the centre and $\partial V/\partial n = 0$ at the boundary proves to be insoluble, and the problem has been further simplified to give a kind of two-dimensional metal, where the nuclei are replaced by a series of parallel line-charges so arranged as to intersect a plane perpendicular to them in a square array. The following equation is ultimately obtained: $(\partial^2 V/\partial x^2) + (\partial^2 U/\partial y^2) = k^2 V$, where $k^2 = 16\pi^2 me^2/dh^2$, m being the mass of the electron, e the charge, and U the potential field. This is solved subject to certain conditions. By this means the work required to move an electron from any point in the crystal is obtained, and a number of equipotential lines for a crystal are plotted. Near a nucleus the equipotential lines are approximately circles, which are gradually deformed until a critical curve is reached. This extends throughout the crystal and encloses another system of closed curves. The electrons in these regions may be regarded as "shared," the "shared" electrons forming a lattice array which interpenetrates that of the nuclei. This provides some justification for the model of a metal proposed by Lindemann and Thomson.

L. L. BIRCUMSHAW.

Magnetic moment of the electron. C. G. DARWIN (Proc. Roy. Soc., 1928, A, 120, 621—631;

cf. this vol., 570).—Starting from the wave equations for an electron and the associated electric density and current, it is shown how part of the magnetic field of a moving electron can be attributed to an electric convection current and part to its intrinsic magnetisation. The relation between the wave constants and the magnetisation is shown by a geometrical construction. The formulæ are first worked out for slow motions, then generalised by relativity principles for high speeds. A comparison is made between an electron wave and a light wave; the relation of light to electricity may be loosely described by saying that a light-quantum is an electron without charge or mass. L. L. BIRCUMSHAW.

Diffraction of the magnetic electron. C. G. DARWIN (Proc. Roy. Soc., 1928, A, 120, 631–642).—The problem is solved of the diffraction of an electron wave by a line grating, supposed made out of a periodic distribution of electric or magnetic material. The electric and magnetic forces of the grating are limited in such a way that there shall only be first-order spectra on each side, two reflected and two transmitted. When a polarised electron wave falls on such a grating, the direction of magnetisation may be changed in the diffracted rays. In the case of pure electric forces and of some magnetic forces, the effect is to rotate the direction of magnetisation through a definite angle about an axis perpendicular to the incident and diffracted rays, and no polarisation can be produced by the diffraction. In cases where there are simultaneous electric and magnetic fields some polarisation may occur, but the case has not been worked out in detail.

L. L. BIRCUMSHAW.

Motion of electrons in gases. J. S. TOWNSEND (Proc. Roy. Soc., 1928, A, 120, 511–523; cf. A., 1926, 3, 878).—A reply to the criticisms of Atkinson (this vol., 809) and others of the author's work on the ionisation of gases by collision. In the method of investigation adopted by Atkinson, no account has been taken of the motion of agitation of the gas in finding the loss of energy in the simplest case where the molecules or atoms of the gas are supposed to be perfectly elastic spheres. L. L. BIRCUMSHAW.

Theory of ferromagnetism. W. HEISENBERG (Z. Physik, 1928, 49, 619–636).—Mathematical.

R. W. LUNT.

Vertical deflexion of slow electrons by gas molecules. R. KOLLATH (Ann. Physik, 1928, [iv], 87, 259–284).—The cross-section of a molecule is considered from three different points of view, a cross-section involving absorption of an electron, a cross-section involving loss of velocity with or without deflexion of the electron, and finally a cross-section involving elastic reflexion or deflexion without a change in velocity. An experimental arrangement is described whereby the last-named section can be measured in relation to the primary electron velocity for the angle range 87.1° – 92.9° to the direction of the primary beam. Over the velocity range 1–6 volt^{1/2}, helium, neon, argon, krypton, hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, and methane exhibit vertical deflexion without marked loss in velocity, and the deflexion-velocity curves show a

single maximum in all cases. When the curves are compared with those showing the effective cross-sectional area against electron velocity, the gases fall into three groups: (a) argon, neon, krypton, and methane, in which the two types of curves show maxima which are at greater velocities for the effective than for the deflexion cross-section, (b) hydrogen and helium, in which the curves run parallel, (c) the remaining gases, in which the maxima for the deflexion curves occur at the same velocity as the first maxima in the "effective" curves. R. A. MORTON.

Recombination of argon ions and electrons. C. KENTY (Physical Rev., 1928, [ii], 32, 624–635).—The afterglow of the arc spectrum of argon was investigated. Lines involving jumps from high energy levels are relatively much stronger in the afterglow than in the arc. Evidence is given for the view that the excited atoms producing the afterglow must be formed by the recombination of ions and electrons. The effect of applied potentials on the afterglow was studied. In the case of accelerating voltages of 3–10 volts, the electronic velocities are increased, and the recombination velocity is decreased, resulting in a quenching of the afterglow. Retarding after-voltages up to 90 volts had practically no effect. The intensity of the afterglow is shown to be directly related to the concentration of positive ions, and the quenching to a saving up of ions. Measurements show positive ion concentrations in the afterglow of the order 10^{12} per c.c. The mean energy of the electrons is 0.4 volt. The coefficient of recombination is approximately 2×10^{-10} . N. M. BLIGH.

Diffusion of metastable atoms in mercury vapour. J. H. COULLIETTE (Physical Rev., 1928, [ii], 32, 636–648).—The change in the rate of arrival of metastable atoms at the outer boundary of a spherical volume of gas was determined as a function of the time elapsed after a number of atoms had been formed at the centre. Detection of metastable atoms was based on the fact that they free electrons from a nickel surface. Observations were made over a vapour-pressure range of 3×10^{-9} to 0.33 mm. and a temperature range of -80° to 103° . The average duration of the metastable state is proportional to the distance travelled by the metastable atom to the walls of the tube, and this duration increased with the increase of vapour pressure of the mercury. It is also found that the effective radius of the metastable mercury atom is about 1.5 times as large as that of the normal atom, and that metastable and normal mercury atoms obey the same general laws of diffusion. Evidence of the loss of energy of excitation as the result of collision between normal and metastable mercury atoms was found. N. M. BLIGH.

Dissociation of hydrogen chloride by positive ion impact. W. M. NIELSEN (Physical Rev., 1927, [ii], 29, 907).—Positive ions from heated sodium phosphate were projected between electrodes P_1 and P_2 to P_3 . No negative current to P_1 was observed below 34 volts; above this value of the driving potential the ratio of negative current to total positive ion current increased rapidly with increase in the driving potential. The products of dissociation are not indicated. A. A. ELDRIDGE.

Magnetic moment of atomic iodine. J. B. TAYLOR and T. E. PHIPPS (Physical Rev., 1927, [ii], 29, 904).

Magnetic moment of helium and molecular hydrogen. I. H. SOLT (Physical Rev., 1927, [ii], 29, 904).—No influence of the magnetic field on a beam of atoms or molecules was observed for a gradient of 1.5×10^5 gauss/cm. A. A. ELDRIDGE.

Magnetic moment of the electron. G. BREIT (Nature, 1928, 122, 649).—Theoretical.

A. A. ELDRIDGE.

Reflexion of electrons from molybdenum. W. R. HAM (Physical Rev., 1927, [ii], 29, 908).—When the percentage of reflected electrons relative to incident electrons is plotted against the velocity of reflected electrons, a large percentage of reflexion occurs at the velocity corresponding with 2900 volts. Peaks of reflexion occur as the impressed *P.D.* passes the critical potentials for the *L*-levels and probably also the *K*-level of molybdenum.

A. A. ELDRIDGE.

Recombination of positive ions with electrons. R. D'E. ATKINSON (Z. Physik, 1928, 51, 188—203).—An attempt has been made to measure the change in intensity of a beam of caesium ions of 220 volts velocity when allowed to traverse a cloud of electrons. No change in intensity, within the limits of experimental error, was observed, from which it is deduced that the upper limit for the effective distance, measured from the centre of the ion, in which recombination can occur is 7×10^{-7} cm.

R. W. LUNT.

Metastable neon and argon. R. RUDY (Physical Rev., 1927, [ii], 29, 359—360).

Explanation of long life of metastable atoms. G. BREIT (Physical Rev., 1927, [ii], 29, 361).—Theoretical.

A. A. ELDRIDGE.

Formation of negative ions. A. P. ALEXEIEVSKY (Physical Rev., 1927, [ii], 29, 752).—Theoretical.

A. A. ELDRIDGE.

Separation of isotopes and a further separation of mercury by evaporative diffusion. W. D. HARKINS and B. MORTIMER (Phil. Mag., 1928, [vii], 6, 601—631).—The apparatus developed by Harkins and Mulliken (A., 1922, ii, 295) has been modified to allow of more rapid working and an extensive fractionation of mercury has been made. It is shown that the change in atomic weight ΔM depends largely on the separation coefficient, the cut, and the efficiency. The time required to build up any extreme fraction, allowing for the time necessary for the intermediate fractions, is $t = K(\Delta M)^3 Q_0 D E^3 B^3$, where *K* is constant, *B* the separation coefficient, *E* the efficiency, *D* the rate of production of the lighter fraction, and *Q*₀ the constant minimum mass of the intermediate fractions. It then follows that in the case of mercury, where *B* is small, the time taken to achieve large values of ΔM must be great. The extreme fractions obtained showed a difference in atomic weight of 0.189 unit, the greatest difference so far reported. This separation corresponds with changes of 27 and 20%, respectively, in the initial proportions of isotopes 204 and 198.

A. E. MITCHELL.

Isotope effect in iodine monochloride bands in the neighbourhood of the convergence limit. G. E. GIBSON (Z. Physik, 1928, 50, 692—696).—A new band series has been discovered in the iodine monochloride absorption spectrum with the same convergence limit (5144 Å.) as that previously discovered (Gibson and Ramsberger, this vol., 6). This series is attributed to the second isotope of chlorine (37). The coincidence of the convergence limits of the two series is to be expected, since the heats of dissociation must be identical. The relative positions of the corresponding vibration terms are in accordance with the theory of Sommerfeld.

J. W. SMITH.

Separation of the isotopes of chlorine. W. D. HARKINS and C. E. BROEGER (Z. Physik, 1928, 50, 537—547).—Hydrogen chloride was allowed to flow through a series of porous porcelain tubes so that only one twentieth of the original gas did not diffuse through the porous walls; this procedure was repeated on the undiffused residue twice; finally the resulting 1/8000th of the original gas was absorbed in water. Measurements of the density and of the acidity of the resulting solution gave data from which the mean value, 0.055 unit, was obtained for the apparent increase in the atomic weight of chlorine. The method is sensitive to a change of 0.002 unit of atomic weight.

R. W. LUNT.

Atom models [nucleus] for isotopes. II. G. BECK (Z. Physik, 1928, 50, 548—554).—The theoretical considerations previously advanced (cf. this vol., 344), leading to a derivation of the periodic system from the Pauli principle, have been extended to devise atomic models for isotopes.

R. W. LUNT.

Mass deficiencies and nuclear dimensions. L. STRUM (Z. Physik, 1928, 50, 555—558).—It is claimed that the recent data of Aston on mass deficiency, μ , can be related more simply to the number of protons in the nucleus, *A*, than to the atomic weight relative to oxygen; the results then fall very closely on the line $\mu = 8.4 \times 10^{-3} m_H A$, where *m*_H is the mass of a proton. By assuming point charges in the calculation of the internal energy of the nucleus and by adopting Lenz's model of the helium nucleus the value 1.4×10^{-14} cm. has been obtained for the diameter of the nucleus.

R. W. LUNT.

Experimental evidence of the existence of aggregates of active deposit atoms in gases containing radon. E. L. HARRINGTON (Phil. Mag., 1928, [vii], 6, 685—695).—The existence of aggregates of active atoms, both in the gas and on the walls of the containers, in radon-air mixtures freed from dust has been demonstrated by subjecting tubes containing them to centrifugal action, when it is found that the activity becomes greatest in regions subjected to the greatest centrifugal forces. The existence of such aggregates has been further demonstrated in the gas by the Wilson cloud method. The effects persisted in tubes which were both saturated and unsaturated with water vapour. It has been shown by a migration experiment that particles of both positive and negative sign occur in the gas. It is suggested that the aggregates originate from the combination of molecules and ions in the highly-ionised gas con-

taining radon, whilst in the case of gas saturated with water the effects will be enhanced by the droplets of water. A. E. MITCHELL.

Theory of the origin of the actinium series. T. R. WILKINS (Physical Rev., 1927, [ii], 29, 352).—The actinium series is considered to arise from an isotope of uranium-I (actino-uranium-I), the decay-constant of which is several times that of uranium-I. The parent isotopes were originally in radioactive equilibrium, but in geological time actino-uranium has largely disappeared. The ages of rocks, computed on the basis of this theory, may differ from those calculated from the lead or helium content by 40%. A. A. ELDRIDGE.

Velocity distribution of β -particles after passing through thin foils. P. WHITE and G. MILLINGTON (Proc. Roy. Soc., 1928, A, 120, 701—726).—Using the photographic method, a study has been made of the dispersion of the retardations of β -particles after passing through thin foils. The source (Ra-B and -C initially in equilibrium with Ra-A) was partly covered by a straggling foil of mica, pierced at equal distances by two or three holes adjusted to give nearly equal maximum photographic densities to each of a corresponding pair of traces. A thorough investigation was made with the three strong lines of the Ra-B spectrum 1410, 1677, and 1938 H ρ , using sheets of mica of 2.25, 2.65, 3.95, and 5.72 mg./sq. cm. The distribution of optical density along each plate was measured by means of a microphotometer. A process is worked out for computing the shape of the straggled curve which would have been obtained with an ideally fine unstraggled line, and this is applied to the experimental curves, after correction for the background due to the continuous spectrum and chemical fog and for the characteristics of the plates used (cf. Ellis and Wooster, A., 1927, 324). It is found that all the curves obtained can be summarised into a single fundamental straggling curve, for which the equation is $y = (\beta^3/\sigma)g(\beta^2x/\sigma)$, where β is the ratio of the initial velocity to the velocity of light, and σ is the thickness of the foil in centigrams per cm. The relation between most probable loss of velocity and thickness of stopping material is investigated for H ρ 1410—5904 and surface density 2—14 mg./sq. cm., and a small systematic divergence from Bohr's theory, outside the limits of experimental error, is observed. The same is found for the relation between initial velocity and most probable loss of velocity. L. L. BIRCUMSHAW.

Absorption of β -rays. J. A. GRAY and B. W. SARGENT (Physical Rev., 1927, [ii], 29, 351—352).—The absorption of the β -rays of radium-E and uranium-X in carbon, aluminium, copper, tin, and lead has been studied. The energy lost in an atom by the β -rays of uranium-X is, on an average, proportional to the atomic number. A. A. ELDRIDGE.

Atomic disintegration with α -rays. W. BOTHE and H. FRÄNZ (Naturwiss., 1928, 16, 204—205; Chem. Zentr., 1928, i, 2232).—Experiments with beryllium, carbon, aluminium, and iron, and with aluminium, boron, magnesium, and paracyanogen, support the results of Rutherford and Chadwick rather than those

of Kirsch and Pettersson. With boron the absorption curve showed two separate groups of hydrogen particles, of differing range, possibly to be attributed to the isotopes of boron. When the Geiger counter was filled with air or argon instead of hydrogen, greater effects, ascribed to the K-rays of aluminium, iron, and zinc, excited by the α -rays, were observed.

A. A. ELDRIDGE.
Light quantum theory. T. TAKEUCHI (Z. Physik, 1928, 50, 697—700).—Mathematical. Schrödinger's wave equation is applied to the motion of photons in a gravitational field, and a relation is deduced for the dependence of the refractive index of a medium on the curvature of space. The phase and group velocities of de Broglie waves and their dependence on the curvature of space are calculated and Brewster's law is deduced. J. W. SMITH.

Synthesis and disintegration of atoms as shown by an application of the Wilson cloud-track method. W. D. HARKINS and H. A. SHAD-
DUCK (Physical Rev., 1927, [ii], 29, 207).—In two cases (in 265,000 tracks) union of a fast α -particle with a nitrogen nucleus, and release of a hydrogen nucleus, have been observed. A. A. ELDRIDGE.

Dissociation of pure mercury. R. S. BRADLEY (Nature, 1928, 122, 573).—Theoretical. It is computed that for cadmium amalgams and zinc amalgams respectively 0.13 and 0.12 of the mercury is ionised.

A. A. ELDRIDGE.
Origin of penetrating radiation. W. PERSCHKE (Z. Physik, 1928, 48, 740—751).—By assuming the validity of the Bohr model the orbital number of an electron in the nucleus of a helium atom can be shown to be 10^{-4} . If this value be inserted in the Balmer formula applied to calculate the wave-length associated with the transition of an electron from a hydrogen atom to the nucleus of a newly-formed helium atom, the value 10^{-13} cm. is obtained. This value corresponds with the lower limit for penetrating radiation, and it is therefore suggested that this may arise from the formation of helium from hydrogen.

R. W. LUNT.
Evolution of heat in the condensation of electrons on metals. R. VIOHL (Ann. Physik, 1928, [iv], 87, 176—196).—An arrangement is described whereby the heat of condensation of electrons on nickel is found to be 97,800 (\pm 9800) g.-cal. per mol.

R. A. MORTON.
Polarisation of the resonance radiations of [the] zinc [family]. P. SOLEILLET (Compt. rend., 1928, 187, 723—725).—The author's method (this vol., 930) has been used to investigate the resonance radiations of the zinc atom ($1^1S_0 - 2^3P_1$, $\lambda = 3076$, and $1^1S_0 - 2^1P_1$, $\lambda = 2139$, the polarisations obtained with the magnetic field in the directions of the exciting and observed rays being discussed from the point of view of Larmor's theory. The approximate mean life in the excited state (τ) of the zinc atom was found to be 10^{-5} sec. for the ray 3076. Comparison with the values obtained for cadmium and mercury ($\lambda = 3261$ and 2537, $\tau = 2 \times 10^{-6}$ and 1.13×10^{-7} , respectively) shows that the stability of the excited atoms increases as the atomic number decreases, i.e., as the electronic edifice becomes simpler. J. GRANT.

Life-history of an adsorbed atom of caesium. J. A. BECKER (Physical Rev., 1927, [ii], 29, 364).—The average life of an absorbed atom under equilibrium conditions is N/A , where N is the number of absorbed atoms and A the arrival rate. The behaviour of caesium adsorbed on tungsten is considered. A. A. ELDRIDGE.

Anomalies in the position of the innermost ring in pleochroic uranium haloes. F. LOTZE (Zentr. Min. Geol., 1928, A, 87—89; Chem. Zentr., 1928, i, 1754).—The anomalies are ascribed to changes in the range of α -particles owing to changes in the physical properties (cohesion) of the material. A. A. ELDRIDGE.

Current according to Dirac's electron theory. W. GORDON (Z. Physik, 1928, 50, 630—632).—Mathematical. J. W. SMITH.

Wave mechanics of an alkali metal atom in an electric field. F. RASETTI (Atti R. Accad. Lincei, 1928, [vi], 7, 1010—1014).—From a calculation of the behaviour in an electric field of an atom of the lithium type a value is obtained for the dielectric constant of the vapour which is of the same order of magnitude as approximate experimental values. F. G. TRYHORN.

Impact polarisation and spinning electron. A. ELLETT (Physical Rev., 1927, [ii], 29, 207).—A theoretical note. A. A. ELDRIDGE.

Spectroscopic interpretation of the magneton numbers in the iron group. A. SOMMERFELD and O. LAPORTE (Physical Rev., 1927, [ii], 29, 208).—A formula for the magneton number is given. A. A. ELDRIDGE.

Electronic theory of passivity. W. D. LANSING (Physical Rev., 1927, [ii], 29, 216—217).—Under normal conditions the electrons of iron are probably distributed among the energy levels as 2, 8, 14, 2; under strongly oxidising conditions this may become 2, 8, 8, 8, the iron then being passive and non-magnetic. Thin films of iron produced by cathode sputtering are passive and possibly non-magnetic, although apparently not throughout their whole thickness. A. A. ELDRIDGE.

Theory of diffraction of electrons in crystals. H. BETHE (Ann. Physik, 1928, [iv], 87, 55—129).—Mathematical. The observations of Davisson and Germer, and others, on the diffraction of electrons in crystals are treated from the point of view of wave-mechanics. It is shown that the observed difference between X-ray and electron diffraction can be explained by means of a refractive index. The dynamics of the field of the de Broglie waves in crystals and the conditions at the surface are investigated. On the basis of the theory the deviations occurring with respect to X-ray reflexion are settled. A. J. MEE.

Life period of excited mercury atom. I. ASADA (Physikal. Z., 1928, 29, 708—711).—The mean life period of the 3P_0 -state, obtained by resonance in pure nitrogen, is about 0.001 sec. at a few mm. of nitrogen. Impurities in the gas greatly reduce the intensity of the fluorescence (cf. this vol., 1065). R. A. MORTON.

Origin of the cosmic rays. R. A. MILLIKAN and G. H. CAMERON (Physical Rev., 1928, [ii], 32, 533—557).—Theoretical. Ionisation-depth curves pre-

viously found (cf. this vol., 811) indicate a band spectrum, the existence of which demands that cosmic rays originate in some nuclear act having sharply-defined energy values translatable like quantum jumps into spectral line frequencies. Quantitative arguments, based on Aston's mass spectrograph curve and Einstein's equation, are given against the possibility of the production of rays having the observed penetrating power, from any atomic disintegration process, and in support of the view that the only possible transformations capable of yielding the rays are those corresponding with the building up of abundant elements such as helium, oxygen, silicon, and iron out of hydrogen, or, in the case of the last two elements, out of helium. Calculations in these cases, for which alone sufficient mass disappears to create the observed rays, are in satisfactory agreement with the results of experimental observation, except for iron, which is less definite. Kinetic and other evidence is suggested for supposing that the rays do not originate in the stars but in interstellar space, where the atom building is favoured by extremely low temperature and density. In this connexion a theory is advanced concerning the relation of cosmic processes to the second law of thermodynamics.

N. M. BLIGH.

Duration of atomic hydrogen. J. KAPLAN (Physical Rev., 1927, [ii], 29, 920).—The Welsbach mantle test was observed 3 sec., and infected spots on the glass 6 sec., after the discharge was discontinued.

A. A. ELDRIDGE.

Evolution of the chemical elements. B. CABRERA (Anal. Fis. Quím., 1928, 26, 186—205).—A discussion of atomic evolution in the light of Aston's work on atomic structure. H. F. GILLBE.

Experimental test of Schrödinger's theory. E. GAVIOLA (Nature, 1928, 122, 772).

Quantum mechanics and chemical combination. F. HUND (Z. Elektrochem., 1928, 34, 437—442).—The importance of the new quantum mechanics in chemistry is discussed with particular reference to the recent work of London (this vol., 344).

S. K. TWEEDY.

Wave mechanics of alkali metal atoms in an electric field. F. RASETTI (Atti R. Accad. Lincei, 1928, [vi], 7, 839—844).—Mathematical.

R. W. LUNT.

Calculation of M -terms from the statistical atomic potential. F. RASETTI (Atti R. Accad. Lincei, 1928, [vi], 7, 915—918).—Mathematical.

R. W. LUNT.

Degeneration of electron gases in the interior of stars. W. ANDERSON (Z. Physik, 1928, 50, 874—877).

A possible generalisation of the Planck radiation law. L. STRUM (Z. Physik, 1928, 51, 287—291).

System of structures for atomic nuclei. W. W. NICHOLAS (Physical Rev., 1927, [ii], 29, 612—613).—A theory is based on a "neutron" structure, the evolution of light elements from complex to simple, and a geometrical structure in which protons and neutrons are on alternate cube corners in a cubic lattice. A. A. ELDRIDGE.

King's classical theory of atomic structure. B. PODOLSKY (Physical Rev., 1927, [ii], 29, 750).—King's theory ("A classical theory of atomic structure and radiation," Montreal) is criticised.

A. A. ELDRIDGE.

Absorption spectra of liquid crystals. D. VORLÄNDER (Naturwiss., 1928, 16, 759—760).—Whilst there is a considerable difference between the absorption spectra of substances in the crystalline state and in the liquid crystalline state, there is practically no difference between them for the substance in the liquid crystalline state and the amorphous liquid state.

A. J. MEE.

Collisions of the second kind between molecules. Excitation of the Lyman band and non-combination of symmetrical with asymmetrical term systems in the hydrogen molecule. H. BEUTLER (Z. Physik, 1928, 50, 581—599).—The hydrogen spectrum is discussed from the point of view of wave mechanics.

J. W. SMITH.

Band fluorescence of mercury vapour. S. MROZOVSKI (Z. Physik, 1928, 50, 657—690; cf. Wood and Gaviola, this vol., 1065).—Further investigations have been made on the conditions of excitation and the structure of the mercury fluorescence bands. It has been shown that any spectral line which lies in the absorption region of mercury vapour will excite fluorescence, but that the structure of the fluorescence spectrum so obtained depends markedly on the mode of excitation. The change in intensity of certain bands with changing density of mercury vapour is attributed to reabsorption in the vapour. The bands in the short-wave ultra-violet region have been studied in detail and their series structure has been partly elucidated. The destruction of certain fluorescence bands on superheating the vapour is shown to be due to a diminished absorption of the exciting radiation. The $2P$ series bands have been classified, and from their convergence limits the heat of dissociation of the mercury molecule has been calculated as about 15 kg.-cal. The effect of adding water vapour and other gases to the fluorescing vapour has also been investigated.

J. W. SMITH.

[Absorption spectra of] potassium ferro- and ferri-cyanides. S. H. C. BRIGGS (J. Physical Chem., 1928, 32, 1422).—In view of Getman's conclusions (this vol., 345), attention is directed to the author's previous work (J.C.S., 1920, 117, 1026).

L. S. THEOBALD.

Fluorescence spectra in metallic vapours excited by the light of the mercury arc. J. C. McLENNAN and I. WALTERSTEIN (Physical Rev., 1927, [ii], 29, 208).—Sulphur vapour gives a set of bands extending over the visible spectrum. Selenium at 325° gives a fluorescence spectrum from 2200 to 6500 Å., whilst at 425° it gives nine broad bands between 4178 and 4829 Å., this latter spectrum disappearing at high temperatures. The fluorescence spectrum of tellurium consists of regularly spaced bands in the visible region. Bismuth emits a band spectrum in the region 4400—4900 Å. The fluorescence of tellurium vapour was produced by mercury radiation between 2536 and 3655 Å.

A. A. ELDRIDGE.

Some hydrocarbon bands. F. C. McDONALD (Physical Rev., 1927, [ii], 29, 212).—Two new bands, 2264 and 2367 Å., observed when methane was introduced into a Wood tube and excited by a condensed discharge, and when acetylene mixed with helium was excited by a transformer discharge, have been analysed. The possibility of a CH ion as carrier is considered.

A. A. ELDRIDGE.

Fine structure of three infra-red absorption bands of ammonia. G. A. STINCHCOMB and E. F. BARKER (Physical Rev., 1927, [ii], 29, 213).—The fine structure of bands at 1.98, 2.2, and 3.0 μ has been studied.

A. A. ELDRIDGE.

Titanium bands. R. T. BIRGE and A. CHRISTY (Physical Rev., 1927, [ii], 29, 212).—Twenty-eight of the well-known titanium bands have been arranged in one system, and vibrational quantum numbers have been assigned. The bands are attributed to TiO.

A. A. ELDRIDGE.

Fluorescence and chemiluminescence of cod-liver oil. J. W. WOODROW and G. M. WISSINK (Physical Rev., 1927, [ii], 29, 219).—Faint bluish-green chemiluminescence of cod-liver oil has been obtained by oxidation of the heated vapour. The fluorescence spectrum of cod-liver oil illuminated by light from a quartz mercury-vapour arc is of maximal intensity at about 5000 Å.

A. A. ELDRIDGE.

Quenching of mercury vapour fluorescence by the addition of other gases. O. OLDENBERG (Z. Physik, 1928, 49, 609—618).—The quenching produced by the addition of nitrogen or of argon has been investigated at the ordinary temperature and at 750° . In the former case the quenching disappears as the temperature is raised to 750° , whilst for argon the quenching increases with rise of temperature. It is thought that the behaviour in the case of nitrogen is due to a resonance phenomenon between the first vibrational frequency of the nitrogen molecule, 0.29 volt, and the transition $2^3P_1 \rightarrow 2^3P_0$ of the mercury atom, 0.218 volt. In support of this view it has been observed that an addition of carbon monoxide, the first vibrational frequency of which corresponds with 0.265 volt, produces an increase of fluorescence as the temperature is raised. The increased quenching in the case of argon can be explained by postulating that the probability of collisions of mercury atoms in the 2^3P_1 state with argon atoms, resulting in the transition of the mercury atoms to the normal state, increases with the kinetic energy of the colliding argon atoms. This assumption is discussed at length and held to be in general accord with current theory and experiment.

R. W. LUNT.

Absorption spectra of iron carbonyl. I. DRECHSLER (Arb. Hemiju, 1928, 2, 175—197).—See this vol., 1075.

Ultra-violet absorption spectra of simple benzene derivatives. F. W. KLINGSTEDT (Z. physikal. Chem., 1928, B, 1, 74—93).—The ultra-violet absorption spectrum of acetanilide in hexane and ethyl alcohol, up to 2060 Å., has been examined and compared with the spectra of aniline and aniline salts. The normal absorption spectrum of acetanilide in hexane, like that of aniline, has two

regions of selective absorption in the ultra-violet. The one of longer wave-length, between 2900 and 2630 Å., is made up of a succession of narrow bands. Only two of these bands could be measured, because the outer absorption region overlaps the inner. Not only the long-wave band system, but also the outer broad band, which is present in a number of aromatic amines, appears to be due to the amine radical. In alcoholic solution a marked change occurs, resulting in the disappearance of the narrow bands and indicating a disturbance of the vibrations of the nucleus. The change of spectrum cannot be ascribed to the isomeric form, but must depend on a solvent influence of another kind. The introduction of acetyl into the amino-group results in a very definite change in the aniline spectrum. The selective absorption of the anilide begins at much shorter wave-lengths. The longer wave absorption region is shifted towards the shorter and the short wave in the opposite direction. The frequency of the nuclear vibrations increases from 450 to about 950 cm^{-1} and reaches a value characteristic for several other mono-derivatives of benzene. The intensity of the selective absorption in the longer-wave ultra-violet falls by about 20%, whilst in the short-wave region, on the contrary, it is doubled. Acetylation apparently causes a closer union in a phenyl radical combined with an amino-group, but not to the same extent as salt formation. This behaviour is probably connected with the polar nature of the nitrogen atom in combination in the benzene nucleus. The atom acquires a polarity through dissymmetry in the distribution of its charge within the molecule. This will be greater in aniline salts than in the anilide.

M. S. BURR.

Absorption spectrum of nitrogen dioxide. L. HARRIS (Proc. Nat. Acad. Sci., 1928, 14, 690—694).—The absorption spectrum of single nitrogen dioxide molecules consists of bands between 6000 and 2250 Å. The absorption due to double molecules, N_2O_4 , in the gaseous phase is continuous. W. E. DOWNEY.

Relation of hydrolysis to the validity of Beer's law. R. C. GIBBS and C. V. SHAPIRO (Proc. Nat. Acad. Sci., 1928, 14, 694—700).—It has been found experimentally that, with substances of the phenolphthalein type, the hydrolysis which occurs at low concentrations results in a complete modification of the absorption spectrum. This modification invalidates Beer's law. W. E. DOWNEY.

"Line" absorption of crystalline chrome alums. H. SAUER (Ann. Physik, 1928, [iv], 87, 197—237; cf. Joos, this vol., 345).—The absorption spectra at 18°, -78°, and -190° of crystals of the types $\text{R}^1\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ($\text{R}^1 = \text{K}, \text{Rb}, \text{Cs}, \text{Ti}^{\text{II}}, \text{NH}_4, \text{NH}_2\text{OH}$, and NH_2Me) and $\text{R}^1\text{Cr}(\text{SeO}_4)_2 \cdot 12\text{H}_2\text{O}$ ($\text{R}^1 = \text{K}, \text{Rb}, \text{Ti}^{\text{II}}$, and NH_4) have been studied in the visible region, using a continuous light source and a registering microphotometer. Solid chrome alums show considerable absorption throughout the visible region except at 6300—6800 Å. The unresolved absorption (König-Martens photometer) shows a maximum near 5700 Å. and a flat minimum near 4750 Å., followed by a region of rapidly increasing absorption extending beyond the blue limit of visibility. The intensity of absorption is about 50% greater for crystals than for

solutions. In the region 6300—6900 Å., crystals of the chrome alums exhibit selective absorption showing a high degree of resolution, especially at very low temperatures. The positions and intensities of the component bands vary with the cations and anions, but the absorption is fundamentally unaltered in type, since corresponding lines can be identified in the different alums. The caesium and methylamine alums are anomalous. Most of the alums investigated exhibit sequences of sharp bands separated by constant frequency differences, e.g., in the potassium chromium selenate $\Delta\nu = 43 \text{ cm}^{-1}$ and for the rubidium analogue $\Delta\nu = 44.2 \text{ cm}^{-1}$. The vibration is attributed to a normal lattice constituent giving an oscillation corresponding with a residual ray of 232 μ . Raising the temperature shifts the band towards the red and causes a loss in definition. The changes in wave-length are irregular, but the half-breadth increases as $T^{\frac{1}{2}}$. The alums show a well-defined doublet band near 6700 Å. For different alums $\Delta\nu$ varies from 2.0 to 24.0 cm^{-1} .

The number of absorbing centres is very small but approximately constant. The ratio absorbing/total chromium atoms (or complexes) is 3×10^{-8} for the characteristic doublet and not more than 10^{-3} for the unresolved absorption in the visible and ultra-violet. The conclusion is reached that the absorbing entity for the banded structure is a non-electrostatically bound, homopolar $\text{Cr}-(\text{H}_2\text{O})$ complex.

R. A. MORTON.

Wide absorption bands among the halogens. P. BOVIS (Ann. Physique, 1928, [x], 10, 232—344).—Methods are described of obtaining extremely thin layers of bromine and iodine between quartz plates and of the measurement of their thickness by an interferometric method. The absorption of such films and of aqueous solutions of copper sulphate, copper chloride, copper acetate, cobalt sulphate, cobalt chloride, nickel sulphate, nickel chloride, potassium chromate, and of certain mixed solutions of these substances has been measured between 2000 and 4500 Å. These solutions are suggested for photometric standards. With rise of temperature the opacity of liquid bromine decreases, the decrease being seven times as great as would be anticipated from the thermal expansion of the liquid. Absorption curves were determined for solutions of bromine in water, chloroform, carbon tetrachloride, ethyl alcohol, and carbon disulphide. The positions of the two bands of bromine do not vary greatly in these solutions, the maxima of the violet and characteristic ultra-violet solution bands being in the neighbourhood of 0.414 and 0.260 μ , respectively. The ultra-violet band is narrow but very persistent. Thin films of solid iodine showed a wide band with a maximum at 0.255 μ which appears to be related to the wide absorption near 0.206 μ of iodine vapour. F. G. TRYHORN.

Beryllium hydride band spectra. W. W. WATSON (Physical Rev., 1928, [ii], 32, 600—606).—Measurements were made at high dispersion of two new band systems appearing in a beryllium arc in hydrogen, one in the green from 4800 to 5120 Å., the other from 3700 to beyond 2200 Å. in the ultra-violet. The quantum analysis is given. The green band group

belongs probably to the ${}^2P \rightarrow {}^2S$ class due to BeH molecules, and consists of the 0—0, 1—1, etc. bands, degrading to the violet, but all branches exhibit a marked shift to the red for $j > 30$. The analysis gives $I_0' = 2.6833 \times 10^{-40}$ g.-cm.² and $I_0'' = 2.7212 \times 10^{-40}$ g.-cm.² for the moments of inertia, $r_0' = 1.35 \times 10^{-8}$ cm., $\omega_0' = 2053.4$, $\omega_0'' = 2025.7$. The ultra-violet system consists of singlet P, R branch bands degrading to the red. For this system $I_0' = 3.85 \times 10^{-40}$ g.-cm.² and $I_0'' = 2.50 \times 10^{-40}$ g.-cm.², $r_0' = 1.29 \times 10^{-8}$ cm. The probable electronic transition for the ultra-violet bands is discussed. N. M. BLIGH.

Less refrangible bands in the spectrum of tin monochloride. W. F. C. FERGUSON (Physical Rev., 1928, [ii], 32, 607—610).—Four groups of bands previously obtained by Jevons (A., 1926, 222) in a discharge through stannic chloride vapour are now found also in streaming active nitrogen. Two groups, α and β , were classified by Mulliken (A., 1926, 1079) as a ${}^2S \rightarrow {}^2P$ transition in SnCl. It is concluded from new measurements and from an examination of the band structure that the other two groups, λ 3500 and 3800, are a ${}^2D \rightarrow {}^2P$ transition with the same 2P state as the α and β bands. The chlorine isotope effect confirms the identity of the emitter as SnCl, and confirms the vibrational quantum number assignments. The vibrational intensity distribution (intensity concentrated in $\Delta n = 0$ sequence) is in qualitative agreement with theory, for the ratio of ω_0'' to ω_0' . No new bands were obtained in an attempt to obtain analogous bands by introducing stannic iodide vapour into active nitrogen.

N. M. BLIGH.

Absorption band spectrum of iodine monochloride. E. D. WILSON (Physical Rev., 1928, [ii], 32, 611—617).—The visible spectrum has been photographed and measured, and eight new members have been located in the two series described by Gibson and Ramsperger (this vol., 6) as corresponding with $n'' = 1$ and $n'' = 2$. The convergence limit of the former series is at $\nu = 17430 \pm 5$ cm.⁻¹, making the heat of dissociation 49650 ± 15 g.-cal. per mol. Four members of a new series, $n'' = 3$, have been found, also a further series of five members. The ratio c_p/c_v for gaseous iodine monochloride is calculated as 1.30, in agreement with empirical results. The fine structure of three consecutive bands has been measured. Approximate values for the moment of inertia have been computed. N. M. BLIGH.

Absorption spectrum of liquid benzene. J. BARNES and W. H. FULWEILER (Physical Rev., 1928, [ii], 32, 618—623; cf. this vol., 458).—A precision method is described for measuring the wave-lengths of radiation in the near infra-red region of the spectrum using a 6-ft. Rowland concave grating with a Thalofide cell. The wave-length of a further outstanding absorption band was determined as 0.6060μ . The absorber of these radiations is considered to be a linear anharmonic oscillator, the energy states of which are represented by odd multiples of half quanta.

N. M. BLIGH.

Potential of photo-active cells containing fluorescent electrolytes. H. W. RUSSELL (Physical Rev., 1928, [ii], 32, 667—675).—A theory is developed

and expression obtained for the variation of potential with time of illumination for the photo-active cell. It is assumed that the exciting light produces a chemical change in the electrolyte. Experiments made with a cell containing rhodamine-*B* gave results in good agreement with the theory, and diffusion was shown to play an important part. N. M. BLIGH.

Fluorescence and photo-chemical change. K. G. MATHUR and S. S. BHATNAGAR (Indian J. Physics, 1928, 3, 37—52).—From a study of the decay of fluorescence of certain fluorescent solutions when exposed to sunlight in the presence of air it is concluded that this photo-decomposition is probably an oxidation phenomenon which may have nothing to do with fluorescence. W. E. DOWNEY.

New phenomenon of light scattering in crystals. G. LANDSBERG and L. MANDELSTAM (Naturwiss., 1928, 16, 772).—A better photograph of the dispersed light and comparison spectra (this vol., 936) is given. J. W. BAKER.

Raman spectra of scattered radiation. R. W. WOOD (Phil. Mag., 1928, [vii], 6, 729—743).—Results similar to those obtained by Raman and Krishnan for the spectra of light scattered by transparent media have been obtained for ten liquids and for quartz. Both Stokes and anti-Stokes lines have been observed. The scattered light shows, in addition to lines of the illuminating radiation, other bright lines having constant differences in frequency from the exciting lines. These frequency differences correspond with frequencies in the infra-red, and in some cases agree closely with observed infra-red absorption bands. The experimental arrangements are fully described. The results are in accordance with the quantum theory, the incident light quantum giving up a portion of its energy to the molecule, thus raising it to an excited state, and then passing off with diminished energy exhibited in lines of greater wave-length. The results obtained with calcite do not correspond with the known infra-red absorption bands. No modified lines were obtained with sodium chloride.

A. E. MITCHELL.

Raman effect in glycerol and glycerol-water mixtures. S. VENKATESWARAN (Indian J. Physics, 1928, 3, 105—122).—When light from a quartz-mercury lamp is diffused through glycerol, the spectrogram of the scattered light contains a bright continuous spectrum and a number of modified lines, including one of enhanced frequency. The shifts of frequency of the modified lines correspond with certain characteristic infra-red frequencies of the molecule.

W. E. DOWNEY.

Raman effect in xylene. C. E. BLEEKER (Z. Physik, 1928, 50, 781—786).—The wave-lengths and intensities of the Raman lines excited by the light from a mercury arc have been determined. The frequency differences correspond with a number of infra-red frequencies, many of which lie very close to those observed by Coblentz. R. W. LUNT.

Influence of temperature on the Raman effect. K. S. KRISHNAN (Nature, 1928, 122, 650).

Raman effect in crystals. I. R. RAO (Indian J. Physics, 1928, 3, 123—135).—The Raman effect has

been studied in the cases of ice and quartz. Compared with water, the bands observed with ice are sharper and of shorter wave-length. This result is in agreement with the corresponding infra-red absorption data. W. E. DOWNEY.

Raman effect in gases and vapours. L. A. RAMDAS (Indian J. Physics, 1928, 3, 131—136).—The Raman effect has been obtained with ether vapour and with liquid ether at the ordinary temperature. The intensity of the modified radiation is smaller in the case of the vapour than in that of the liquid. Some experiments have been made on the effect in carbon dioxide liquid and vapour at and near the critical temperature. W. E. DOWNEY.

Raman effect in organic liquids. P. PRINGSHEIM and B. ROSEN (Z. Physik, 1928, 50, 741—755).—The Raman spectra of the following liquids, in addition to quartz, have been examined using a mercury arc as light source: methylene chloride, chloroform, carbon tetrachloride, dichloroacetylene, tetrachloroethylene, acetylene tetrachloride, benzene, chlorobenzene, toluene, and silicon tetrachloride. For each liquid every observed Raman line has been identified as corresponding with a known infra-red frequency, although the converse does not hold. No similarity can be traced between the spectra of carbon and silicon tetrachlorides. A number of lines have been observed for quartz, but only some of these appear to be related to the known infra-red frequencies; fused quartz does not give a Raman spectrum. R. W. LUNT.

Cause of the luminescence of phosphorus. A. PETRIKALN (Naturwiss., 1928, 16, 205; Chem. Zentr., 1928, i, 2235—2236).—The excitation of phosphorus trioxide vapour yields the same band spectrum as is obtained by the oxidation of phosphorus and phosphorus trioxide. Absorption experiments also support the view that the luminescence spectrum of phosphorus is to be attributed to the trioxide. With the pentoxide the spectrum of the glow of phosphorus, either in emission or in absorption, was not obtained. Emeléus and Purcell's band, 3270 Å. (A., 1927, 497), arises from impure phosphorus pentoxide.

A. A. ELDRIDGE.

Spectra of intermetallic compounds. J. M. WALTER and S. BARRATT (Nature, 1928, 122, 684—685).—Most of the "mercury-thallium" spectrum described by Waring (this vol., 603, 1166) is identical with that listed by Mohler and Moore (A., 1927, 917) as the "cadmium" molecular spectrum; the true origin of the system appears to be the molecule of thallium chloride. Similarly, Waring's "indium-cadmium" spectrum appears to coincide with another set of cadmium bands found by Mohler and Moore; these appear to arise from an association of cadmium and oxygen, although they may be totally unconnected with cadmium. A. A. ELDRIDGE.

Chemiluminescence of aminophthalic hydrazide. H. O. ALBRECHT (Z. physikal. Chem., 1928, 135, 321—330).—The strong chemiluminescence observed when 3-aminophthalic hydrazide and its diacetyl derivative are oxidised in alkaline solution has been investigated. Most oxidising agents which

may be used in alkaline solution are active, especially hypochlorites and ferricyanides. The action of hydrogen peroxide alone is feeble, but the maximum effect is obtained with a mixture of hydrogen peroxide and hypochlorite or ferricyanide. The luminescence is visible even at concentrations of $10^{-8}M$. Of the various cyclohydrazides and hydrazine derivatives investigated, only those related in some manner to phthalic acid exhibit this highly developed luminescence. H. F. GILLBE.

Vitamin-D and isoergosterol. A. VAN WIJK and E. H. REERINK (Nature, 1928, 122, 648).—Similarities in the absorption curves of ergosterol, isoergosterol, and vitamin-D suggest that ergosterol has two types of absorption bands connected with different parts of the molecule. On irradiation and formation of vitamin-D the first system (293, 281, 270 μ) gives place to the characteristic absorption band of isoergosterol, indicating constitutional change, whilst another part of the molecule is unchanged constitutionally, since the bands 262, 250 μ are permanent.

A. A. ELDRIDGE.

Intensity relations and band structure in bands of the violet CN type. R. S. MULLIKEN (Physical Rev., 1927, [ii], 29, 923).—Theoretical intensity formulae applicable to bands of the violet CN ($^2S \rightarrow ^2\bar{S}$) type are obtained, assuming Hund's case *b*. Their predictions are verified with CaH, N_2^+ , and violet CN bands.

A. A. ELDRIDGE.

Infra-red reflexion spectra of some carbonates. E. K. PLYLER (Physical Rev., 1927, [ii], 29, 923).—A study of the structure of the band of selective reflexion of calcium carbonate indicated maxima at 6.36, 6.54, and 6.62 μ . These maxima are probably due to the isotopes of calcium. Iron carbonate and dolomite showed two maxima. A. A. ELDRIDGE.

Infra-red spectrum of ammonia. W. F. COLBY and E. F. BARKER (Physical Rev., 1927, [ii], 29, 923).—The ammonia absorption band consists of two overlapping bands with zero branches at 10.3 μ and 10.7 μ . About 12 lines have been observed in each branch, the spacing differing somewhat. Ammonia bands are interpreted in terms of two different types of transition: one in which the second rotational quantum number changes, and the other in which it does not change. A. A. ELDRIDGE.

Shift in a near infra-red absorption band of some benzene derivatives. J. BARNES (Physical Rev., 1927, [ii], 29, 922).—The following wave-lengths (Å.) are recorded: benzene 8741, toluene 8758, ethylbenzene 8772, *o*-xylene 8781, *m*-xylene 8793, *p*-xylene 8808, diethylbenzene 8799, mesitylene 8844.

A. A. ELDRIDGE.

Ultra-violet absorption and emission spectra of carbon monoxide. J. J. HOPFIELD and R. T. BIRGE (Physical Rev., 1927, [ii], 29, 922).—Nine absorption systems between 920 and 2064.5 Å. have been obtained, representing transitions from the normal level to all of the previously known excited electronic levels, and to four new levels. Other absorption systems do not permit of definite analysis. Certain band systems are also found in emission.

A. A. ELDRIDGE.

Band structure and intensities, atomic and molecular electronic states, in diatomic hydrides. R. S. MULLIKEN (Physical Rev., 1927, [ii], 29, 921).—Theoretical intensity formulæ applicable to $^2P \rightarrow ^2S$ and $^2S \rightarrow ^2P$ molecular electronic transitions have been obtained for Hund's case *b*. Observations on CaH, MgH, OH, and CH (λ 3900) bands are in agreement with the theory. A. A. ELDRIDGE.

Structure and isotope effect in the α -bands of boron monoxide. F. A. JENKINS (Physical Rev., 1928, [ii], 29, 921).—New observations on the α -bands of boron monoxide support Mulliken's interpretation of the structure as due to a $^2P \rightarrow ^2S$ transition. The 2P doublet is inverted. The origins of the ($\frac{1}{2}$, $\frac{1}{2}$) bands of B¹⁰O and B¹¹O are separated by 1.547 Å., the amount required for half-integral vibrational quantum numbers. Analysis of the B¹⁰O band gives smaller moments of inertia than those obtained for B¹¹O, but identical internuclear distances, $r_0' = 1.352 \times 10^{-8}$ and $r_0'' = 1.208 \times 10^{-8}$ cm. A. A. ELDRIDGE.

Theoretical relation between infra-red and ultra-violet bands. R. T. BIRGE and J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 365–366).—Measurements with carbon monoxide show that the frequency of infra-red (vibration-rotation) bands of a diatomic molecule can be calculated from the measured frequencies of certain ultra-violet (electronic) bands correlated with the normal state of the molecule.

A. A. ELDRIDGE.

Fluorescence of mercury vapour under low excitation. (LORD) RAYLEIGH (Nature, 1928, 122, 725).—When dense mercury vapour is excited by radiation of wave-length 3000 Å., the spectrum shows, besides the visual maximum, the broad maximum at about 3300 Å. The fluorescence can be distilled away from the place of origin (cf. this vol., 935).

A. A. ELDRIDGE.

Absorption of ultra-violet light by organic vapours. A. W. SMITH, C. E. BOORD, and C. S. PEASE (Physical Rev., 1927, [ii], 29, 355).—The characteristics of bands observed with benzene, diethyl ether, methyl *n*-amyl ether, and ethylene chlorohydrin are described.

A. A. ELDRIDGE.

New series in the spectrum of fluorescent iodine. F. W. LOOMIS (Physical Rev., 1927, [ii], 29, 355).—The constants *d* and γ of new series in Wood's spectra of fluorescent iodine afford nearly integral values of the vibrational quantum number of the fluorescent molecule before excitation. Values of *n'* and *n''* are obtained for each doublet in the series.

A. A. ELDRIDGE.

Absorption spectra in the extreme ultra-violet. J. J. HOPFIELD (Physical Rev., 1927, [ii], 29, 356).—Nitrogen, air, acetylene, and carbon monoxide show selective absorption and a region of continuous absorption on the short wave-length side. Acetylene shows band absorption beginning at 2300 Å. Nitrogen shows Spöner's bands and continuous absorption beginning at 990 Å. The principal lines of the four ultra-violet series of N I and a group of lines at 1085 Å. due to ionised nitrogen were observed. Some carbon lines (probably resonance), the Cameron bands (arising from the normal state) of carbon

monoxide, and some bands of a new system in carbon monoxide were observed with that gas.

A. A. ELDRIDGE.

Quantitative test of Hund's theory of doublet bands of the OH type. E. C. KEMBLE and F. A. JENKINS (Physical Rev., 1927, [ii], 29, 607).—A study, for doublets, of the effect of molecular distortion on the rotational term formula, and an application of the results to NO β -bands confirm Hund's theory.

A. A. ELDRIDGE.

Activation of hydrogen by the contact action of palladium. M. POLJAKOV (Naturwiss., 1928, 16, 131; Chem. Zentr., 1928, i, 1743).—When hydrogen is circulated over a palladium plate which has been heated in hydrogen at 700–800° and cooled at 1–5 mm. to 300–400°, a violet luminescence is observed beyond the palladium towards the pump and at the walls of the tube.

A. A. ELDRIDGE.

Absorption and fluorescence of iodine vapour. P. PRINGSHEIM (Naturwiss., 1928, 16, 131–132; Chem. Zentr., 1928, i, 1750).—In view of Wychodil's observation that iodine vapour under suitable conditions exhibits surface fluorescence, the supposition that all collisions between excited and unexcited iodine molecules cause extinction of fluorescence is invalid. Also a resonance spectrum was obtained in iodine vapour at 100 mm. above 600° by mercury radiation 2537 Å.; it consisted of twelve positive and four anti-Stokes members. Between 2100 and 3000 Å. and below 500°, iodine vapour is almost completely transparent. On progressive rise of temperature increasingly strong absorption bands appear.

A. A. ELDRIDGE.

Striking potentials of metallic arcs in a vacuum. S. H. ANDERSON (Physical Rev., 1927, [ii], 29, 750–751).—The striking potential is dependent on a gaseous atmosphere as well as on the nature of the electrodes (cf. Simeon, Phil. Mag., 1923, 46, 816).

A. A. ELDRIDGE.

Carbon monoxide band excitation potentials. A. B. HEPBURN (Physical Rev., 1927, [ii], 29, 212).—Birge's computation that the lines 4511, 4880, 2190, and 3794 Å. should be produced by electrons having a minimum velocity corresponding with 10.7, 16.7, 19.8, and 19.8 volts, respectively, is experimentally confirmed within 0.1 volt.

A. A. ELDRIDGE.

Relation between dipole moment and constitution. J. ERRERA (Physikal. Z., 1928, 29, 689–690).—Chloroiodoethylene forms compounds in which the iodine is tervalent; *cis*- and *trans*-dichloro-derivatives of this type have been prepared and their molecular polarisations determined. The results confirm the view that the iodine atom is positively charged relative to the chlorine atom, since the dipole moment of the *trans*-derivative is more than twice that of the *cis*-derivative.

R. A. MORTON.

Electrical symmetry of the molecular structure of methane derivatives. L. EBERT, R. EISENSCHITZ, and H. VON HARTEL (Z. physikal. Chem., 1928, B, 1, 94–114).—The physical methods for the determination of the symmetry of molecules in gaseous form or in dilute solution are discussed. By measurements of the change in dielectric constant when

solution is substituted for pure solvent, determinations of the molecular polarisation of derivatives of $C(OH)_4$, $C(CH_2OH)_4$, and $C(CO_2H)_4$ of the form CX_4 have been made in benzene and carbon tetrachloride solutions. In a number of cases it was found that the orientation polarisation, as measured by the difference between the molecular polarisation in the dissolved and solid states, respectively, had a value far beyond the limits of experimental error. This is regarded as indicating that the following substances examined possess a fixed dipole moment: $C(OMe)_4$, $C(OEt)_4$, $C(CH_2CO_2Me)_4$, $C(CH_2O\cdot NO_2)_4$, $C(CO_2Me)_4$, and $C(CO_2Et)_4$. These substances appear to possess a normal mol. wt. in solution as determined by Beckmann's f.-p. method. The results supplement Weissenberg's theory (A., 1926, 934) that the molecule CX_4 shows greater variety of form than is in accordance with the requirements of classical stereochemistry, since if it is to be regarded as a symmetrical pyramid it could not have a dipole moment. M. S. BURR.

Dielectric constants and dispersion of some organic compounds and shattering of light by the molecules. W. LAUTSCH (Z. physikal. Chem., 1928, B, 1, 115—133).—The degree of depolarisation of the Tyndall beam, diffracted by the molecules of pure liquid, has been determined for 15 organic liquids. In order to determine whether a large depolarisation is due to a departure of the simple molecule from the spherical form or to association, the influence of temperature on the function $(\epsilon-1)/(\epsilon+2)d$, where ϵ is the dielectric constant and d the density, has been determined in a number of cases. From the constancy of this expression for the liquid hydrocarbons, diphenyl, dibenzyl, triphenylmethane, and decalin, these appear to possess no dipole moment, but its existence is indicated in the case of the ethyl esters of stearic, palmitic, lauric, and oleic acids. For the last the moment increases with diminishing length of chain. The double linking in the oleic ester apparently increases the moment. When hydrocarbons are arranged in the order of degree of depolarisation certain conclusions with regard to the influence of molecular structure are indicated. The closed ring is not necessarily productive of large depolarisation, but a double linking appears to give a certain amount of rigidity to the molecule which tends to make the value high. The position of the substituents in the benzene nucleus may have a marked influence, the depolarisation by *o*-xylene being much less than by *p*- and *m*-xylene. The value for dibenzyl is distinctly less than for diphenyl, which is similar to the value for naphthalene. Possibly the benzene rings in the two last compounds lie more nearly in the same plane. For triphenylmethane the value is relatively small, which may be explained by the arrangement of the groups round the methane carbon atom. From the dispersion in the visible region the ultra-violet and the ultra-red portion of the characteristic frequency of the molecules may be calculated. M. S. BURR.

Electrical dipole moment of organic molecules. J. ESTERMANN (Z. physikal. Chem., 1928, B, 1, 134—160).—The methods employed for the calculation of the electrical dipole moment from dielectric constant measurements are discussed and

it is shown that the error obtained by employing the molecular refraction or the polarisation in the solid state, instead of the deformation or dielectric fraction of the molecular polarisation, may be considerable. In non-associated liquids the dipole moment may be determined from the variation of dielectric constant with temperature. This method has been employed for a number of ethers, diphenyl derivatives, and esters of amino-acids in dilute benzene solutions. Symmetrical ethers have all, apparently, the same dipole moment, so that its value must depend on the oxygen atom. The asymmetric ethyl amyl ether has a larger moment. The mixed ethers, anisole and phenetole, have different values of molecular polarisation according to whether they are in the pure liquid state or in solution. Diphenyl, which has a small moment, is not much influenced by the introduction of a CH_3 group, but the O, NH, and CO groups give an increasingly larger moment. The methyl esters of amino-benzoic acids contain a positive group and a negative group, and it is found that the moment of the *o*-compound is less than that of either aniline or methyl benzoate, whereas the moment of the *p*-ester is approximately equal to the sum of the two. The moments of the methyl esters of α - and δ -aminovaleric acid appear to indicate that a straight aliphatic chain is obtained and not a curved one. M. S. BURR.

Electrical dipole moments of organic molecules by the molecular ray method. J. ESTERMANN (Z. physikal. Chem., 1928, B, 1, 161—169).—The method of comparison of electrical dipole moments by the deviation of a molecular ray in a non-homogeneous electric field has been improved. The relationship between the dipole moments of the series diphenyl, diphenylmethane, benzophenone, and diphenyl ether, and also of *o*-, *m*-, and *p*-amino-benzoic esters obtained by this method agrees with that found by measurements of the dielectric constant. M. S. BURR.

Anomalous dispersion in calcium, strontium, and bromine vapour. V. PROKOFIEV (Z. Physik, 1928, 50, 701—715; cf. this vol., 577).—The anomalous dispersion in calcium, strontium, and bromine vapours has been investigated with respect to the changes $1^1S_0 \rightarrow 2^1P_1$ and $1^1S_0 \rightarrow 2^3P_1$. The ratio of the number of dispersion centres of these two lines diminishes very strongly with increasing atomic number. When the probability of the spontaneous transition $2^1P_0 \rightarrow 1^1S_0$ is taken as unity, the probability A_2 of the spontaneous combination change $2^3P_1 \rightarrow 1^1S_0$ is given by $A_2 = (\Delta\nu/\delta\nu)^{2.44}$, where $\Delta\nu$ and $\delta\nu$ indicate the term differences $2^3P_2 - 2^3P_0$ and 1^1S_0 —centre of gravity of the $2^3P_{0,1,2}$ term in cm^{-1} . The results obtained by other investigators for cadmium and mercury also follow this relation. Predictions of the relative probabilities for the intercombination lines of magnesium and zinc are also made from this relation. J. W. SMITH.

Reflecting power of carbon between the ordinary temperature and 1500°. K. WARMUTH (Wiss. Veröff. Siemens-Konz., 1928, 7, 307—320).—The reflecting power of carbon for light of wavelengths 0.538 and 0.663 μ has been determined by Pirani's method with an accuracy of 4—5%. The

results show that the reflecting power of carbon varies only slightly between 20° and 1470° from 0.034 to 0.028. Assuming that the latter value remains constant for higher temperatures, the true temperature of the positive crater of the carbon arc is 3740° Abs. On this basis a new vapour-pressure curve for carbon has been constructed from which the mean heat of vaporisation of carbon at 3900° Abs. under 1–5 atm. pressure has been calculated as 125.54 kg.-cal./g.-mol. A. R. POWELL.

Molecular theory of diffusion of light in fluids.

I. Without consideration of the intermolecular field. II. The intermolecular field. Y. ROCARD (Ann. Physique, 1928, [x], 10, 116–179, 181–231).—I. A mathematical consideration of the diffusion of light by a hypothetical atom built up of isotropic oscillating ions.

II. The previous treatment of the problem is modified by taking into account the effect of the intermolecular field on the diffusion of light, and it is shown that the results predicted by the author's theory are in closer accord with experiment than those deduced from the Einstein-Gans theory.

F. G. TRYHORN.

Refractive index of sodium vapour and the width of the *D*-lines in absorption. J. Q. STEWART and S. A. KORFF (Physical Rev., 1928, [ii], 32, 676–680).—A theoretical relation is developed by classical methods between the refractivity of sodium vapour near the *D*-lines and their observed width in absorption. The theory is approximately verified by preliminary results of experiments described, involving observation of the wave-lengths of interference fringes produced by sodium vapour, using a Michelson interferometer in conjunction with a spectroscope and a source of white light.

N. M. BLIGH.

Anomalous magnetic rotation in excited neon. R. N. JONES (Physical Rev., 1928, [ii], 32, 681–688).—Measurements were made of the angle of rotation for different frequencies of light near strong lines in the yellowish-red region of the neon spectrum. These lines show anomalous dispersion, and the dispersion constants are calculated from the angle of rotation using Kuhn's formula; hence the relative transition probabilities were found. N. M. BLIGH.

Internal field of polarisation. R. DE MALLE-MANN (Compt. rend., 1928, 187, 720–722).—The author's general method for the calculation of the internal field of the molecules of a substance (this vol., 1172) indicates that the field is essentially a heterogeneous effect. This contradicts the classic reasoning of Lorentz, and a new expression is derived for the refractive power (n) of a spherical isotropic body in which the Lorentz or Gladstone factor is replaced by $3K/(2K+1)$, where K is the inductive power of the medium. The new factor gives values of n in close agreement with experimental values and with those derived from Gladstone's formula. J. GRANT.

Chemical constitution and rotatory power.

III. S. BERLINGOZZI (Atti R. Accad. Lincei, 1928, [vi], 7, 925–929).—Measurements have been made of the specific rotatory power and the dissociation constant of a number of aminosuccinic acid mono-

amides in which an acyl group is introduced into the amino-group. The following derivatives were examined: anisoyl, cuminoyl, *p*-toluoyl, *p*-chlorobenzoyl, *p*-nitrobenzoyl, *m*-toluoyl, *m*-nitrotoluoyl, *o*-chlorobenzoyl, *o*-bromobenzoyl, *p*-toluenesulphonyl, and 2-nitrotoluene-3-sulphonyl. The data are thought to show that a diminution in rotatory power is associated with an increase in the dissociation constant. R. W. LUNT.

Anomalous dispersion of lithium and mercury.

E. SEGRÈ and E. AMALDI (Atti R. Accad. Lincei, 1928, [vi], 7, 919–921).—The ratio of the intensity of the lithium lines 6708 (2*S*–2*P*) and 3232 (2*S*–3*P*) and that of the mercury lines 2537 (6S_0 – 6P_1) and 1849 Å. (6S_0 – 6P_1) has been determined from measurements of the anomalous dispersion of these lines by the interferometer method of Rasetti. The data obtained show that the ratio of the number of "dispersion" electrons associated with 6708 to that associated with 3232 Å. is 135 ± 27 , and that the ratio for the mercury lines 2537, 1849 Å. is approximately 100. R. W. LUNT.

Variation with state of the optical constants of caesium. J. B. NATHANSON (Physical Rev., 1927, [ii], 29, 369–370).—For liquid caesium at 33° values of the coefficient of absorption, the refractive index, and reflecting power are, for 5400 Å., respectively, 3.66, 0.310, 0.588, whilst for solid caesium (23°) corresponding values are: 3.74, 0.308, 0.595.

A. A. ELDRIDGE.

Covalency, the paramagnetism of oxygen, and stereochemistry. H. F. BIGGS (Phil. Mag., 1928, [viii], 6, 659–664).—London's theory of covalency (cf. this vol., 344) is shown to be applicable to the structure of oxygen, since if his model be accepted and one Bohr magneton be assigned to each *p*-orbit, the calculated value of the paramagnetic susceptibility accords with the accepted observed value. Van Vleck's theory (cf. this vol., 572), whilst requiring only slight modification for oxygen and nitrogen, is not applicable to nitric oxide when tested on the susceptibility criterion. London's theory is used to explain some points in the structures of graphite, diamond, and the aliphatic compounds, whilst it accounts also for the apparent anomaly that the addition of two extra hydrogen atoms to benzene leads to a more unsaturated substance, since such addition, displacing the hexagonal symmetry of the carbon atoms, destroys the unstrained plane structure of the ring and leads to a reversion of the carbon atoms from trivalent to quadrivalent. By analogy with the results for oxygen and nitric oxide, the effect of adsorbed hydrogen in diminishing the paramagnetism of palladium (Biggs, A., 1916, ii, 412) is attributed to the neutralisation of two palladium magnetons per molecule of hydrogen adsorbed. A. E. MITCHELL.

Electronic symmetry and polyatomic molecules. P. VINASSA (Atti R. Accad. Lincei, 1928, [vi], 7, 975–979).—To account for the inactivity of the nitrogen molecule compared with that of the chlorine molecule it is suggested that in these molecules the centre consists of the pair of nuclei, each carrying the two electrons of the innermost orbit, and that the residue of the electrons is distributed

in orbits about this centre. Thus the electron distribution of the fluorine molecule is (2+2).2.8.2.2, and of the chlorine molecule (10+10).2.8.2.2. These molecules possess perfect electronic symmetry, but not that typical of the inert gas atoms, and in consequence exhibit chemical activity. The distributions in the oxygen and nitrogen molecules are, respectively, (2+2).2.8.2 and (2+2).2.8. The inertness of the latter molecule is due to the fact that the two nuclei, each possessing the stability of the helium type, are surrounded by electrons having the stable neon configuration. Ozone is regarded as a compound of molecular and atomic oxygen, since its electronic formula, based on the assumption of a molecule O_3 , (2+2+2).2.8.8, possesses the symmetry of an inert gas and is not in accord with the properties of ozone. Sulphur is assumed to form true allotropes, e.g., S_8 , (10+10+10).2.8.8, with an electronic symmetry similar to that of argon. The probable constitution of a number of more complex molecules is discussed from this point of view. F. G. TRYHORN.

Co-ordination and atomic structure. P. RAY (Z. anorg. Chem., 1928, 174, 189—192).—The main factors governing complex formation are: (1) the volume occupied by the central ion, and its charge; (2) the tendency of the central ion to assume the atomic structure of the next higher inert gas; (3) the electronic arrangement in the central atom; (4) the co-ordinating group must be of such a nature that for each co-ordinated linking two electrons must be transferable to the central ion. H. F. GILLBE.

Constitution of hydrated crystals. M. A. RAKUZIN (Bull. Soc. chim., 1928, [iv], 43, 984—988; cf. A., 1927, 948).—The nature of the linkings which hold the molecules of water of crystallisation in a hydrate is considered from the point of view of the theory of Wurtz (1879), according to which the water molecules are joined in a closed chain directly to the metallic atom of the salt. The importance of distinguishing between water of crystallisation and water of constitution is emphasised. O. J. WALKER.

Desiccation and the density of magnesium nitrate. L. LE BOUCHER (Anal. Fis. Quím., 1928, 26, 223—227).—Dehydration of magnesium nitrate hexahydrate over sulphuric acid at the ordinary temperature yields a stable dihydrate without loss of nitric acid. The densities and m. p. of the hexa- and di-hydrates are 1.6363, 89°, and 2.0256, 120—125°, respectively. The density of the hexahydrate as given in the literature is thus erroneous. H. F. GILLBE.

Rule of additive volumes. E. MOLES (Anal. Fis. Quím., 1928, 26, 228—233).—Satisfactory calculated values for the molecular volume of lanthanum, cerium, praseodymium, neodymium, and samarium nitrates are obtained if the general formulæ $[M^{III}(\text{NO}_3)_2(\text{H}_2\text{O})_6]_3$ and $[M^{III}(\text{NO}_3)_2(\text{H}_2\text{O})_3]_2$ be employed. Insufficient data are extant for the calculation to be applied to gadolinium. For the trivalent rare-earth metals there is a systematic decrease of molecular volume as the atomic weight of the central atom increases. H. F. GILLBE.

Magnetic moments of iron in complex salts. L. A. WELO and O. BAUDISCH (Physical Rev., 1927,

[ii], 29, 612).—Iron salts are grouped according to the magnetic moment of the iron atoms.

A. A. ELDRIDGE.

Effective cross-section of gas molecules in the presence of alkali ions of 1—30 volts velocity. C. RAMSAUER and O. BEECK (Ann. Physik, 1928, [iv], 87, 1—30).—The magnetic method already used for the determination of the effective cross-section of gas molecules in the presence of slow electrons is here applied to slow alkali ions. The ions were obtained from a platinum or platinum-iridium filament coated with alkali-metal amalgam. The alkali metals used were lithium, sodium, potassium, rubidium, and caesium, and the gases used were helium, neon, argon, hydrogen, oxygen, and nitrogen. It was found that for all combinations the effective cross-section of the gas molecule in the presence of alkali ions increases as the velocity of the ions is reduced at first slowly and then more rapidly. There is a turning point in the cross-section-voltage curve between 1 volt and 2 volts. The alkali ions show an increasing cross-section with increasing atomic number. The same behaviour was obtained with hydrogen, oxygen, and nitrogen as with the rare gases. Here the effective cross-section increased with the gas-kinetic size of the molecule. The results obtained were compared with those obtained using electrons instead of alkali ions. The ionic radius was also compared with the radius of the outer electron shell. A. J. MEE.

Temperature of the cathode as a factor in the sputtering process. L. R. INGERSOLL and L. O. SORDAHL (Physical Rev., 1928, [ii], 32, 649—656).—Cathodic sputtering was investigated over an extreme temperature range of 150—1350° and a relatively low potential of 500—800 volts. Gold, platinum, and nickel show an increase in the rate of sputtering in argon with rise in cathode temperature. The lower the sputtering voltage the more pronounced is the effect. Films sputtered from a hot cathode suffer less change in resistance on baking and show a more definite crystal structure than those from a cold cathode. Results are consistent with the explanation of sputtering as essentially a vaporisation process. N. M. BLIGH.

Effect of molecular form and association on light scattering in liquids. I. Fatty acids and alcohols. II. Some aromatics. S. R. RAO (Indian J. Physics, 1928, 3, 1—30).—The variations of intensity of the transversely scattered light, the depolarisation factor, and the optical molecular anisotropy have been determined in the cases of four primary alcohols, three fatty acids, and four polar aromatic compounds. W. E. DOWNEY.

Magnetic properties of some substances in the adsorbed state. S. S. BHATNAGAR, K. N. MATHUR, and P. L. KAPAR (Indian J. Physics, 1928, 3, 53—66).—Iron, nickel, cobalt, and manganese lose their paramagnetism and become diamagnetic when adsorbed on charcoal. Adsorption is not analogous to mixing, but would appear rather as a chemical combination. Adsorption by silica gives a slight increase in paramagnetism in the case of iron. W. E. DOWNEY.

Types of [chemical] combination. H. G. GRIMM (Z. Elektrochem., 1928, 34, 430—437).—A

general account. The characteristics of the individual types of combination are discussed and the various types compared and contrasted. S. K. TWEEDY.

Significance of atom models [in the types of chemical combination]. A. SOMMERFELD (Z. Elektrochem., 1928, 34, 426—430).—A general account of the recent theories of atom mechanics.

S. K. TWEEDY.

Crystal structure and the types of chemical combination. V. M. GOLDSCHMIDT (Z. Elektrochem., 1928, 34, 453—463).—A general account in which previous work on crystal structure is collated from the point of view of chemical combination.

S. K. TWEEDY.

X-Ray absorption spectra and chemical combination. O. STELLING (Z. Elektrochem., 1928, 34, 520—522).—The author summarises his work on the subject (cf. A., 1927, 391).

S. K. TWEEDY.

Inversion point of the second order. W. JAZYNA (Z. Physik, 1928, 51, 292—307).

Close agreement between the X-ray spectra of a substance in the liquid and liquid crystalline states. J. R. KATZ (Naturwiss., 1928, 16, 758—759).—The X-ray spectra of various substances were investigated just above and just below the transition from the liquid to the liquid crystalline state. It was found that there were no characteristic differences between the two diagrams. The molecules in the liquid must therefore be arranged in the same way as in the liquid crystals of the same substance.

A. J. MEE.

K-Series X-ray absorption spectrum of potassium in various compounds. O. STELLING (Z. Physik, 1928, 50, 626—629).—The investigations of Lindh (Arkiv Mat. Astron. och Fysik, 1924, 18, No. 14) on the dependence of the X-ray absorption spectrum of potassium compounds on the nature of the anion have been confirmed and extended, data for 27 potassium salts having been obtained. It has been shown that the compounds cannot be divided into groups, according to the wave-length of the absorption line observed, as suggested by Lindh, but that there is a continuous transition from metallic potassium to potassium hydrogen tartrate, in which the change in wave-length is most marked (5.5 X-units). The normal halides all show the same wave-length, which is surprising in view of the great differences in atomic distances to be observed in this group. There is a great difference in many cases between the values given by the normal and acid salts, but the phenomenon is not general.

J. W. SMITH.

X-Ray coloration of kunzite and hiddenite. P. L. BAYLEY (Physical Rev., 1927, [ii], 29, 353).—A spectrographic study. The green colour in both minerals is probably due to a similar physical cause.

A. A. ELDRIDGE.

K β_2 -Lines of the elements potassium to manganese. T. WETTERBLAD (Z. Physik, 1928, 49, 670—673).—In view of the doubt thrown by the work of Druyvestyn (A., 1927, 804) on the values of β_1 — β_2 given by Hjalmar (cf. A., 1920, ii, 655), new determinations of this difference have been made, with an estimated accuracy of 0.3X-unit, for the

elements potassium to manganese. The difference β_1 — β_2 , determined for the oxides, shows a maximum at 21 (scandium) when plotted against the atomic number; this relationship is similar to that already traced for the difference α_{12} — β_1 (Wetterblad, A., 1927, 491). The spectrograms show that in the case of calcium the β_2 line occurs as a doublet in the metal, and only the longer wave-length member of this doublet in the oxide. The difference between the doublet members is 3.3X-units, corresponding with 4.4 volts. This value agrees well with that previously observed by the author for the influence of oxygen in the elements sodium to chlorine, 4.3 volts. Druyvesteyn has recorded a β''' -line for calcium and potassium; these values cited are now shown to be but mean values of doublets of wave-length 3404.5, 3396.3 and 3047.6, 3043.9, respectively. R. W. LUNT.

Theory of X-ray diffraction in liquids. G. W. STEWART (Physical Rev., 1928, [ii], 32, 558—563).—The assumption of myriads of non-crystalline and non-permanent molecular groupings in liquids at any instant, a condition termed cybotaxis, makes possible the use of the crystal powder theory as an idealised one for liquids, and is shown to give a simple explanation of a number of experimental results in the diffraction of X-rays in liquids not otherwise adequately explained by a single theory. N. M. BLIGH.

Thermal degeneration of the X-ray haloes in liquids and amorphous solids. S. S. RAMASUBRAMANYAM (Indian J. Physics, 1928, 3, 137—149).—X-Ray diffraction in cyclohexane, pentane, and glycerol at different temperatures has been studied. On raising the temperature a contraction of the ring, a broadening of the ring and diffuseness at the edges, and a large amount of internal scattering occur. The theory of these changes is discussed.

W. E. DOWNEY.

Diffraction of cathode rays by calcite. S. NISHIKAWA and S. KIKUCHI (Nature, 1928, 122, 726).—The pattern obtained by reflexion of cathode rays at a cleavage face of calcite is described. The structure factor for X-ray reflexion appears to have a similar influence on cathode-ray reflexion, since the relative intensities of lines due to different orders are similar in the two cases. Similar patterns were obtained with mica, topaz, zinc blende, and quartz.

A. A. ELDRIDGE.

Polarisation of ions in a crystal lattice. A. E. VAN ARKEL (Z. Physik, 1928, 50, 648—656).—On the supposition that an ion is equally polarisable in all directions, the energy of polarisation in different crystal forms is calculated. Among binary compounds, this energy is least in the caesium chloride lattice and increases with decreasing co-ordination number. This accounts for the decreasing readiness of polarisation in passing from the caesium chloride type to the sodium chloride type and thence to the zinc-blende type. Among alkali halides the caesium chloride type is found only with compounds of very low polarisation energy. Potassium fluoride and caesium fluoride appear to be somewhat anomalous cases.

J. W. SMITH.

Crystal structure of calcium. C. D. NIVEN (Phil. Mag., 1928, [vii], 6, 665—666).—Calcium has

been crystallised by condensation of the vapour and the crystals have been shown to be rhombic dodecahedra and not hexagonal as concluded by Moissan (A., 1898, ii, 578).

A. E. MITCHELL.

Symmetry and structure of the cubic nitrates of calcium, strontium, barium, and lead. F. M. JAEGER and F. A. VAN MELLE (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 651—655).—There are a number of discrepancies in the crystal structure of the cubic nitrates of calcium, strontium, barium, and lead. In order to settle some of these, rotation spectrograms, as well as Laue spectrograms of the nitrates, were made. The great majority of diffraction spots obtained were compatible with holo-cubic symmetry. Vegard's conclusion that these nitrates have a dyakisdodecahedral symmetry is confirmed.

A. J. MEE.

Arsenides of magnesium and zinc. G. NATTA and L. PASSERINI (Gazzetta, 1928, 58, 541—550).—An investigation of the physico-chemical properties of the compounds As_2Zn_3 and As_2Mg_3 . The densities are 5.578 and 3.165, respectively. The magnesium compound melts at 800° . X-Ray investigations by the powder method show that both substances have a cubic lattice containing two molecules of As_2M_3 in the unit cell, the side of which is 5.81 Å. ($d_{\text{calc.}}$ 5.854) in zinc arsenide and 6.10 Å. ($d_{\text{calc.}}$ 3.26) in magnesium arsenide. The arrangement of the atoms in the lattice represents a new type of structure defined by the co-ordinates: As ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), ($\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$), ($\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$), ($\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$); M ($\frac{1}{2}, 0, 0$), ($0, \frac{1}{2}, 0$), ($0, 0, \frac{1}{2}$), ($0, \frac{1}{2}, \frac{1}{2}$), ($\frac{1}{2}, 0, \frac{1}{2}$), ($\frac{1}{2}, \frac{1}{2}, 0$). The structure is not ionic. This is confirmed by the low heat of formation, which in the case of zinc arsenide is found to be 30.3 g.-cal.

O. J. WALKER.

Symmetry of the pentaerythritol nucleus. H. SEIFERT (Z. anorg. Chem., 1928, 174, 318—320).—Polemical (cf. Schleele and Hettich, this vol., 694).

H. F. GILLBE.

Solid solutions of chromium and nickel and of iron and nickel. F. C. BLAKE, J. LORD, and A. E. FOCKE (Physical Rev., 1927, [ii], 29, 206—207).—Chromium enters the nickel lattice up to 63% Cr; from 63 to 100% Cr the nickel is in the face-centred chromium lattice. This lattice is metastable at the ordinary temperature, and most of the chromium separates in the body-centred form. Iron distorts the nickel lattice up to 74% Fe; from 74 to 100% Fe the nickel is in the face-centred iron lattice which is stable only at high temperatures.

A. A. ELDRIDGE.

Theory of the mechanism of crystal growth. W. P. DAVEY (Physical Rev., 1927, [ii], 29, 206).—Experimental evidence is quoted in support of the view that crystallisation proceeds along a three-dimensional lattice structure, which is later filled in with crystalline material, instead of uniformly along a plane surface.

A. A. ELDRIDGE.

Crystal structure of potassium chloroplatinate. W. A. FREDERIKSE and H. J. VERWEEL (Rec. trav. chim., 1928, 47, 904—908).—By means of the powder method the distance between the chlorine and platinum ions in the compound K_2PtCl_6 has been found to be 2.29 Å.

O. J. WALKER.

Crystal structure of copper-gold alloys. C. S. SMITH (Min. and Met., 1928, 9, 458—459).—The lattice parameters of gold-copper alloys, annealed at 600° and quenched to retain the homogeneous solid solution, lie on a smooth curve slightly concave to the axis of composition and rising from 3.603 Å. for pure copper to 4.064 Å. for pure gold. Very slow cooling from 400° to 365° results in a gradual decomposition of alloys containing 50 at.-% Au with the separation of the compound CuAu which has a tetragonal lattice. Evidence of the non-existence of Cu_3Au is afforded by X-ray examination of an alloy containing 24.36 at.-% Au which on annealing shows only the face-centred cubic lattice of copper and traces of the tetragonal lattice of CuAu.

A. R. POWELL.

Lattice constants for the mixed crystal series KCl-KBr. F. OBERLIES (Ann. Physik, 1928, [iv], 87, 238—258).—The lattice constants d 3.1362 and 3.2952 Å. have been found for potassium chloride and bromide, respectively. The change in d with changing composition has been followed for the mixed crystal series, and Vegard's additivity formula found to reproduce the data accurately. No new interference lines (corresponding with a regular distribution of the components) were detected.

R. A. MORTON.

Positions of adjacent rings in carbocyclic and heterocyclic molecules. H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1928, 40, 233—242).—The position of the rings in two-ring compounds is discussed with reference to the views of van 't Hoff (symmetrical distribution of carbon valencies) and of Weissenberg (symmetrical structure of the whole molecule independent of symmetrical carbon valency distribution; cf. A., 1926, 934). According to X-ray measurements the elementary cells of anthracene and naphthalene have the following respective dimensions: 8.58, 6.02, 11.18 Å., and 8.34, 6.05, 8.69 Å. They thus differ in length only and by an amount 2.5 Å. which is the length of the additional benzene ring. Hence in anthracene all three rings lie in one plane, the 9 and 10 carbon atoms being bent out of it. In the combination of quinol and benzoquinone to quinhydrone the salt formation of the substances in alkaline solution of increasing p_{H} has been determined colorimetrically, using borate buffer solutions of known p_{H} and working in an atmosphere of hydrogen. With quinol, a yellow colour appears which increases in intensity up to p_{H} 10 and then remains constant at 3.0 Lovibond units. Benzoquinone gives a yellow which increases fairly rapidly with increasing p_{H} , being 3.3 Lovibond units at p_{H} 9.40 and 20 at p_{H} 10.6. The colour of quinhydrone increases much more rapidly with increasing p_{H} , being 4.4 at p_{H} 8.07, 34 at p_{H} 9.40, and undeterminable at p_{H} 10.6. Thus quinhydrone forms a salt in alkaline solution giving ions which possess a characteristic absorption in the visible which is stronger than that of the quinol ions. Thus quinhydrone is not a mere molecular compound, but probably has a diplanar formula. The position of the rings in dihexoses and their derivatives is discussed in the light of the X-ray data and is confirmed by reference to the structure of the anhydrides (glucosans and cellobiosans).

S. J. GREGG.

Strongly birefringent crystal species. P. TERPSTRA (*Physica*, 1928, 8, 95—100).—1 : 6 : 8-Tri-nitro-2-ethylaminonaphthalene, monoclinic, has $a : b : c = 2.2913 : 1 : 1.1027$, $\beta 106^\circ 29'$; $n_a 1.5177$, $n_\beta 1.854$, $n_\gamma 2.316$.
CHEMICAL ABSTRACTS.

Oscillation method of X-ray analysis of crystals. Analcite. J. W. GRUNER (*Amer. Min.*, 1928, 13, 123—141, 174—193).—Analcite has a cubic holohedral lattice, space-group O_h^2 . The unit cube of edge 13.64 Å. contains 16 mols. of $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$.
CHEMICAL ABSTRACTS.

Determination of the magnetic saturation of iron carbide. F. STÄBLEIN and K. SCHROETER (*Z. anorg. Chem.*, 1928, 174, 193—215).—A ballistic method of saturation determination is described, whereby the test-piece is removed from the field and from the induction coil by withdrawal through a hole of about 10 mm. diameter bored centrally through the pole pieces of the field magnet. The necessary corrections have been experimentally determined. By filling a copper tube of the requisite dimensions with a ferromagnetic powder, magnetic data for the latter may be obtained. Iron carbide powder, obtained by dissolving Swedish iron in cold *N*-sulphuric acid, and having d 7.15 and composition 91.0% Fe, 6.7% C (combined), 0.5% C (free), has a saturation value of about 12,400 gauss, as compared with 12,300 gauss obtained for Fe_3C by extrapolation from the values obtained for two specimens of carbon steel containing, respectively, 0.46 and 0.95% of carbon.
H. F. GILLBE.

Piezoelectricity of crystal quartz. L. H. DAWSON (*Physical Rev.*, 1927, [ii], 29, 216).—The piezoelectric charge of quartz is maximal at 60° and disappears at 576° . The piezoelectric charges on surfaces variously oriented with respect to the optical axis show an unexplained distribution.
A. A. ELDRIDGE.

Magnetic susceptibility of rare-earth metals. E. H. WILLIAMS (*Physical Rev.*, 1927, [ii], 29, 218).—The susceptibilities of cerium, lanthanum, praseodymium, and yttrium range from 20 to 50×10^{-6} dyne/cm./g.; the value decreases as the magnetic field is increased from 10 to 4000 gauss.
A. A. ELDRIDGE.

Magnetostriction. A. SCHULZE (*Z. Physik*, 1928, 50, 448—505).—An exact method for determining the magnetostriction coefficient, $\Delta l/l$, is described based on the Whiddington heterodyne method for determining small changes in spacings. The coefficient has been measured for iron and nickel of various purities, cobalt, bismuth, manganese steels, iron-nickel alloys, permalloy, iron-silicon, iron-aluminium, and iron-manganese alloys. No general relationship between magnetostriction and other physical properties could be traced.
R. W. LUNT.

Magnetic properties of evaporated films of nickel. K. J. MILLER (*Physical Rev.*, 1928, [ii], 32, 689—690).—A supplementary note to previous work (*A.*, 1927, 299). Nickel films were tested in fields up to 167 gauss. The coercive force reached a value approximately three times that for hard-drawn wire, and decreased with decreasing deposit temperature and

increasing thickness. Retentivity as high as 65% was observed.
N. M. BLIGH.

Magnetic susceptibility of single-crystal metals. C. NUSBAUM (*Physical Rev.*, 1927, [ii], 29, 905).—The magnetic susceptibility for bismuth and antimony, respectively, in a direction parallel to the principal axis is 1.13×10^{-6} and 0.497×10^{-6} dyne cm., and in a perpendicular direction 1.32×10^{-6} and 1.38×10^{-6} dyne cm.
A. A. ELDRIDGE.

Electrical conductivity in solid sodium chloride at the ordinary temperature. J. GINGOLD (*Z. Physik*, 1928, 50, 633—643).—The electrical conductivity of solid sodium chloride has been measured with the salt in the forms of single natural crystals, blue rock salt, artificially prepared crystals, and compressed blocks of different types. Charge and discharge currents through the salt have also been investigated. The phenomena are explained on the supposition that the conductivity is occasioned by defects in the space lattice.
J. W. SMITH.

Electrical conductivity of arsenic and antimony at low temperatures. J. C. MCLENNAN, C. D. NIVEN, and J. O. WILHELM (*Phil. Mag.*, 1928, [vii], 6, 666—672).—A convenient method for crystallising arsenic by subliming the substance into a furnace tube which is not at an even temperature over its whole length is described. The crystals grow on the cooler portions of the tube. The electrical conductivities of an arsenic crystal, a crystal of antimony, and a piece of massive antimony have been measured down to 2.42° Abs. The two samples of antimony gave almost identical results. Both arsenic and antimony gave resistance-temperature curves similar to those of pure metals. Both showed evidence of maintaining definite residual resistances at low temperatures and neither showed superconductivity. Arsenic behaves similarly to most pure metals except that its resistance is by no means proportional to the absolute temperature. Neither arsenic nor antimony exhibits the abnormally high residual resistance found by Clay for bismuth.
A. E. MITCHELL.

Resistance of caesium, cobalt, and chromium at low temperatures. J. C. MCLENNAN, C. D. NIVEN, and J. O. WILHELM (*Phil. Mag.*, 1928, [vii], 6, 672—677).—Caesium appears to be unique amongst the alkali metals in that its resistance continues to decrease at temperatures below 4° Abs., whilst those of sodium, potassium, and rubidium examined by McLennan and Niven (*A.*, 1927, 925) reach constant values close to that temperature. The metal is not superconducting down to 2.2° Abs. It is suggested that the persistence of the temperature gradient of electrical resistance in the case of caesium is due to the fact that if the valency electron is stripped off, the fourteen 4_s electrons are missing, whilst in the other alkalis the core is left complete. Neither chromium nor cobalt is superconducting down to 2.5° Abs., whilst below the temperature of liquid hydrogen the resistance of each is practically independent of temperature. Calculations of specific resistance at 20.6° Abs. indicate that although iron is a poorer conductor than either cobalt or nickel at the ordinary temperature, it is superior at low temper-

atures. From electronic structural considerations it is suggested that for a metal to be a good conductor the electron systems of the core must be completed and the relative conductivities must depend on the relative stabilities of the electronic arrangements of the cores. A. E. MITCHELL.

Effect of cadmium as an impurity in lead on the conductivity of lead. J. C. MCLENNAN, C. D. NIVEN, and J. O. WILHELM (Phil. Mag., 1928, [vii], 6, 678—685).—Measurements of the electrical conductivities of lead-cadmium alloys, containing up to 5.19% of cadmium, have been made at low temperatures. The specific resistances of the alloys at constant temperatures show a general increase with increasing proportions of cadmium except in the case of the cadmium-richest alloy, where irregularities were observed. The resistance of each alloy falls suddenly at the superconductivity temperature of lead (7° Abs.), but they do not become superconducting until 0.2 — 0.4° below this temperature. Considerable differences were found in the specific conductivities determined before and after cooling to the lowest temperatures. These are attributed to the "ageing" of the alloys at the low temperatures. The persistence, in its cadmium alloys, of the superconductivity phenomenon of lead and its inception at or close to the superconductivity temperature of lead are probably due to the existence of a continuous chain of lead atoms in the superconducting state of the alloy. A. E. MITCHELL.

Electrophoretic mobility formula. M. MOONEY (Physical Rev., 1927, [ii], 29, 217).—The formula, which accords approximately with experiment only below $0.01N$, is based on the observation that with oil drops immersed in water there is a definite variation in mobility with the diameter of the drop. A. A. ELDRIDGE.

Rate of evaporation of molten cadmium in a high vacuum. A. A. SUNIER (J. Physical Chem., 1928, 32, 1516—1521).—The average rates of evaporation of molten cadmium in a vacuum over the range 340 — 425° are recorded, and are compared with the theoretical rates calculated from the equation of Herz (Ann. Phys. Chem., 1882, 18, 177). The low experimental results are attributed to a contaminated surface. Two types of apparatus are described. L. S. THEOBALD.

"Alteration of the legal temperature scale." The international temperature scale (Paris, 1927) and the Physikalisch-Technische Reichsanstalt (1924) scale. F. HENNING and J. OTTO (Z. Physik, 1928, 48, 742—748).—The temperature scale of Physikalisch-Technische Reichsanstalt established in 1924 has been compared with the international scale adopted at Paris in 1927. It is shown that throughout the range -190° to 1063° and up to 4000° the difference between the two scales is less than the experimental error. R. W. LUNT.

Rotational and vibrational specific heat of a diatomic gas, the molecules of which have a doublet P normal state. E. E. WITMER (Physical Rev., 1927, [ii], 29, 918).—In addition to the initial rise in the neighbourhood of the absolute zero, the specific heat curve shows a secondary rise at temper-

atures at which molecules begin to exist in the upper component of the doublet in appreciable numbers. The curve thereafter falls, tending towards the value R . A. A. ELDRIDGE.

Critical temperature measurements on carbon dioxide in small capillaries. H. T. KENNEDY and C. H. MEYERS (Refrigerating Eng., 1928, 15, 125—130).—The critical temperature of carbon dioxide, measured in capillary tubes of diameter 0.004 and 0.060 mm., respectively, is $30.96 \pm 0.01^{\circ}$. CHEMICAL ABSTRACTS.

Equation of state of a perfect gas. R. D. KLEEMAN (Phil. Mag., 1928, [vii], 6, 743—744).—Alternative deductions are indicated of the equation of state of a perfect gas, $pv = MRT\xi$, where p is the pressure and ξ is a function of the volume v , the absolute temperature T , and the mass M (cf. this vol., 955). A. E. MITCHELL.

Entropy of vaporisation of non-associated liquids. J. CHIPMAN (J. Physical Chem., 1928, 32, 1528—1531).—Equations of previous investigators connecting the entropy of vaporisation of a normal liquid with its b. p. are compared graphically with recent experimental data. Kistiakovski's equation (J. Russ. Phys. Chem. Soc., 1921, 53, 256) holds over a wide range of temperature and is considered to be the best. It accords with Hildebrand's rule (A., 1915, ii, 416). L. S. THEOBALD.

Volume isobars of water up to the melting curve. G. TAMMANN and W. JELLINGHAUS (Z. anorg. Chem., 1928, 174, 225—230).—New measurements have been made of the specific volume of water at pressures up to 1500 kg./cm.² and temperatures from -14° to $+15^{\circ}$. Bridgman's values at 1500 kg./cm.² and temperatures below 0° are considerably too high, as are those at 500° and 1000 kg./cm.²; his results for the temperature of maximum density at various pressures are therefore incorrect. H. F. GILLBE.

Entropy and thermodynamic potentials of real gases and mixtures of real gases and a mass-action law for chemical reaction between real gases. II. Integrated equations. III. Relations for pure gases, and the equilibrium pressure of a gas in a mixture. J. A. BEATTIE (Physical Rev., 1928, [iii], 32, 691—698, 699—705; cf. this vol., 589).—II. Mathematical. The general thermodynamic equations previously derived are integrated by means of a new equation of state for gas mixtures.

III. Mathematical. Assuming that the pressure of a real gas approaches nRT/V as the volume approaches infinity, the general thermodynamic equations are developed for a pure gas, and integrated by a new equation of state. General expressions are obtained for the density and pressure of a gas in equilibrium at constant temperature through a semipermeable membrane with a mixture containing the gas in question. N. M. BLIGH.

Thermal expansion of beryllium. P. HEDNERT and W. T. SWEENEY (Physical Rev., 1927, [ii], 29, 616).—The coefficients of expansion of beryllium in ten temperature ranges between -120° and $+700^{\circ}$ are recorded; those between -50° and $+20^{\circ}$, and

between 20° and 100° are 9.8 and 12.3×10^{-6} , respectively. A. A. ELDRIDGE.

Molecular cohesion. G. A. TOMLINSON (Phil. Mag., 1928, [vii], 6, 695—712).—Experiments are described in which the forces of adhesion between glass or quartz fibres and between glass spheres have been measured. It is assumed that in such contacts only the surface molecules exert cohesive attraction. An attempt is made to interpret the results on the basis of a simple inverse law of attraction and it is found that they are best satisfied by an inverse fourth power relationship between the forces and the distances between the molecules. The calculated value of the tenacity of drawn glass is in good agreement with the observed values of Griffith, but is considerably higher than those usually found by tensile methods. The results are not inconsistent when the law is applied to the calculation of the tenacities of some metals. A. E. MITCHELL.

Elastic constants of single-crystal aluminium wire. G. SUBRAHMANYAM (Nature, 1928, 122, 650).—The values γ 6.779×10^{11} , n 2.432×10^{11} , obtained at 28°, are slightly smaller than those given by ordinary specimens. A. A. ELDRIDGE.

Compressibility and pressure coefficients of resistance of ten elements. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1927, 62, 207—226).—Values are recorded for the compressibility of praseodymium, lanthanum, cerium, beryllium, barium, thorium, chromium, vanadium, sulphur, and phosphorus (red and black), and for the electrical resistance of the first six elements. Cerium is polymorphic at high pressures. Beryllium has d^{20} 1.820. Lanthanum has m . p. 826°. CHEMICAL ABSTRACTS.

Viscosity of mercury under pressure. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1927, 62, No. 8, 187—206).—The absolute viscosities at 30° and 75°, respectively, are: 1 kg./cm.², 0.01516, 0.01341; 2000, 0.01588, 0.01399; 4000, 0.01663, 0.01463; 6000, 0.01742, 0.01528; 8000, 0.01825, 0.01599; 10,000, 0.01913, 0.01675; 12,000, 0.02008, 0.01757. Some kind of interlocking mechanism between the molecules of a liquid is postulated.

CHEMICAL ABSTRACTS.

Internal friction and flow-point in lead. W. D. KUSNETZOV (Z. Physik, 1928, 51, 239—262).—A number of experiments on the tensile strength and mechanical deformation of lead are described, together with an analysis of the conditions most appropriate to the determination of the coefficient of inner friction. R. W. LUNT.

Molecular association. Relation between the vapour pressures of binary liquid mixtures and the polarity of the molecules of the constituents. J. ERRERA (Compt. rend., 1928, 187, 727—730).—The vapour pressures of liquids afford a measure of the total association, whilst polarity measurements indicate only dipolar association, homopolar association being an effect of the second order. When the azeotropism is negative, or the vapour-pressure curve concave, the two components are always polar or partly ionised, but when one or both of the two

components are non-polar, the vapour-pressure curve can be only a straight line or convex, and azeotropism, if it exists, is positive. The curves indicate that the forces of association diminish with rise in temperature. J. GRANT.

[Formation of] solid solutions by precipitation. G. NATTA and L. PASSERINI (Gazzetta, 1928, 58, 579—618).—Solid solutions can be obtained by the simultaneous precipitation of metallic hydroxides from aqueous solution by means of alkalis. The formation of solid solutions is shown by an X-ray examination of the precipitates. The following systems have been studied: $\text{Ni(OH)}_2\text{--Co(OH)}_2$, $\text{Ca(OH)}_2\text{--Cd(OH)}_2$, $\text{Cd(OH)}_2\text{--Ni(OH)}_2$, $\text{Mg(OH)}_2\text{--Co(OH)}_2$, $\text{Mg(OH)}_2\text{--Ni(OH)}_2$, $\text{Cd(OH)}_2\text{--Mn(OH)}_2$, $\text{Zn(OH)}_2\text{--Mg(OH)}_2$, $\text{Zn(OH)}_2\text{--Ni(OH)}_2$, and $\text{Zn(OH)}_2\text{--Co(OH)}_2$. The lattice constants of the pure hydroxides and of mixtures have been measured. Solid solutions are formed only in those cases where the cations of the two hydroxides do not differ widely in radius. For example, nickel hydroxide forms solid solutions with the hydroxides of magnesium, zinc, and cobalt, but not with those of cadmium and calcium. The lattice constants of the solid solutions vary directly with the composition and therefore obey Vegard's law. The method of obtaining solid solutions by simultaneous precipitation may be applied to other types of compounds. O. J. WALKER.

Electrolytic solution tensions and the ionic state. III. Solubility and solvent forces, solvent and ionising powers. K. FREDENHAGEN (Z. physikal. Chem., 1928, 134, 33—56; cf. A., 1927, 936).—Mainly theoretical. The solubility of a substance is related to the distribution between gas and liquid phases, and the distribution numbers (cf. *loc. cit.*) measure the solution forces concerned between the solvent and solute. Solution forces are independent of concentration only at low concentrations. With binary compounds, three distribution numbers, viz., those of the undissociated compound and the dissociated components, must be taken into account. When electrolytic dissociation occurs in the liquid state, the distribution numbers of the neutral products of decomposition in the gaseous phase in relation to their ions are given by the electrolytic distribution numbers. The ionic product of a compound AB is given by the expression $c'_{(A^+)} \cdot c'_{(B^-)} = c_A c_B P_A P_B$, where c_A and c_B are the concentrations of the dissociation products in the gaseous phase, and P_A and P_B are the electrolytic distribution numbers previously defined (*loc. cit.*). These latter have been calculated for a number of elements in various solvents, and their sequence differs from that of the normal potentials of the elements. The ionic products calculated for various compounds in different solvents agree with the values obtained when the Nernst heat theorem is used to calculate the dissociation constant in the gaseous phase. Generalisations concerning the magnitude of the distribution numbers of undissociated compounds cannot yet be made, but in all cases it appears that the order of magnitude is far less than that indicated by the electrolytic numbers.

L. S. THEOBALD.

Charcoal as an adsorbent. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1928, 60, 859—869).—Nitric acid, ammonium, potassium, and barium nitrates, chloric acid, and sodium hydroxide solutions remove adsorbed chlorine ions almost quantitatively from charcoal. This is not due to preferential adsorption, for acetic acid, which is more strongly adsorbed than nitric acid, does not show this effect. A very highly adsorbent charcoal, containing practically no adsorbed acid, is prepared by heating ordinary charcoal at 850° for 1 hr., and then wetting it with 4*N*-nitric acid. After 3—4 hours excess of nitric acid is removed by filtration, and the charcoal boiled for 2 hrs. with 2 litres of water. The product is dried and heated on the blow-pipe for half an hour in a closed porcelain crucible, when the adsorbed nitric acid is decomposed with oxidation of part of the charcoal. The resulting product strongly adsorbs acid and neutral salts, but not alkalis. R. TRUSZKOWSKI.

Expansion of charcoal accompanying sorption of gases and vapours. D. H. BANGHAM and N. FAKHOURY (Nature, 1928, 122, 681—682).—The expansion of charcoal on sorption of water vapour is not directly proportional to the quantity of vapour sorbed; the curve obtained on plotting the variables is concave to the expansion axis. This result supports the chemical theory of sorption at the pressures employed, and indicates that the mechanical disturbance suffered by the solid during the sorption of a given quantity of gas becomes greater as the absorption proceeds. In experiments with water and carbon dioxide the expansion was directly proportional to the square of the sorption value. The difference in the expansion caused by equal numbers of molecules of water and carbon dioxide is not proportional to the difference of molecular size. A. A. ELDRIDGE.

Absorption of mercury, mercury oxide and chloride, bromine, and carbon disulphide by chabasite. O. WEIGL and E. BEZNER (Sitzungsber. Ges. Naturwiss. Marburg, 1927, 62, 57—108; Chem. Zentr., 1928 i, 2168).—In presence of air, mercury vapour at 400° is absorbed by chabasite. Mercuric chloride and bromine are absorbed at 360—370° and 90—95°, respectively, to equilibrium values. Carbon disulphide at 100—135° reacts with residual water: $\text{CS}_2 + 3\text{H}_2\text{O} = 2\text{H}_2\text{S} + \text{H}_2\text{CO}_3$; unchanged carbon disulphide colours the crystals yellow. If too high a temperature is employed sulphur is obtained. A. A. ELDRIDGE.

Dipolar nature of adsorbed gas molecules. A. MAGNUS (Z. Elektrochem., 1928, 34, 531—533).—If gas adsorption which does not follow Henry's law, $\pi S = RT$ (π is surface pressure of the adsorbed layer and S area on which one mol. is adsorbed), is represented by a van der Waals equation ($\pi - \alpha/s^2$)($s - \beta$) = RT , α being a repulsion constant and β double the total cross-section of the molecules in one mol., the constant α may be calculated on the assumption that the adsorbed molecules consist of vertically disposed dipoles, and is found to be of the order of 10^{20} , in agreement with the value obtained from the adsorption isotherms and heat of adsorption. This and other evidence show that the adsorbed gas molecules are dipolar in nature; conversely, strongly

adsorbed vapours, e.g., water and ammonia, are all dipolar. S. K. TWEEDY.

Adsorption of gases by sodium chloride and aqueous sodium chloride solution. F. DURAN (Ann. Physik, 1928, [iv], 87, 307—384).—The sodium chloride was purified by melting in a vacuum and powdered in an atmosphere of nitrogen. Measurements were made at 0.4 mm. and at atmospheric pressure. Adsorption isotherms for nitrogen, hydrogen, carbon dioxide, oxygen, and nitric oxide were measured for unheated salt. The adsorption of carbon dioxide by salt outgassed at 480° was less than that by unheated salt. The adsorption increases with the b. p. of the adsorbed substance. Sulphur dioxide is the only gas which is adsorbed to the extent of the formation of a complete unimolecular layer. W. E. DOWNEY.

Adsorptive combination. H. CASSEL (Z. Elektrochem., 1928, 34, 536—538).—The behaviour of the molecules of a solid adsorbent in the interfacial layer between the solid and the gas is considered. According as repulsive or attractive forces are exerted between the different surface molecules there appear to be two extreme limiting cases in which either the adsorbent molecules are partly turned out of the layer into the solid surface or *vice versa*. In general, both these effects will occur simultaneously. This conception is discussed very briefly. S. K. TWEEDY.

Detection of protons in metals. A. COHEN (Naturwiss., 1928, 16, 183—184; Chem. Zentr., 1928, i, 2232).—It is said that hydrogen adsorbed in palladium, iron, etc. is partly dissociated into electrons and protons. Diffusion experiments support this view. A. A. ELDRIDGE.

Influence of quartz lamp irradiation on adsorptive power of certain adsorbents. E. V. ALEKSEEVSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1173—1178).—The irradiation of active charcoal and of Patrick's silica gel, using a quartz lamp, slightly enhances the adsorptive power of these substances. R. TRUSZKOWSKI.

Thermal and magnetic researches on adsorbed gases. F. SIMON (Z. Elektrochem., 1928, 34, 528—530).—The adsorption isotherms for argon on dehydrated chabasite at 90° Abs., and magnetic susceptibility measurements with chabasite containing adsorbed oxygen, show that the gas molecules are evenly distributed over the cells in the adsorbent. The specific heat of hydrogen adsorbed in this material suggests that the molecules within each cell are in a comparatively free state, although the possibility of their passing from one cell to another is very small.

According to Sommerfeld's theory the specific heat of electron gas in iron should equal the specific heat of the metal at about 6° Abs.; experimental results agree with theory only if the latter is modified to take into account the forces between the electrons and the metal ions. S. K. TWEEDY.

Adsorption and constitution: adsorption of organic acids on animal charcoal. K. M. GRIFFIN, H. L. RICHARDSON, and P. W. ROBERTSON (J.C.S., 1928, 2705—2709; cf. A., 1925, ii, 383).—The adsorption of aliphatic and aromatic acids from

ethyl-alcoholic solution by animal charcoal has been determined. Since the activity of different samples of charcoal was found to vary, the results are expressed in terms of a standard acid (acetic for the aliphatic series, benzoic for the aromatic). In general the relative adsorption tends to increase with mol. wt., but this increase is subject to marked constitutive effects. In the normal fatty acid series the odd-numbered members are less adsorbed than the even. Aromatic acids are much more strongly adsorbed than aliphatic acids; substitution, especially in the *para*-position, increases the adsorption.

R. N. KERR.

Adsorption of mixtures of electrolytes from dilute aqueous solution. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1928, 60, 951—963).—A linear relation is found for solutions containing two electrolytes, viz., $y = b - kx$, where b and x measure the adsorption of each electrolyte alone, and y is that of one of them when in solution with the other. This expression holds for solutions containing hydrochloric or nitric and oxalic acids, and hydrobromic or hydrochloric and nitric acids, and is also applicable to such mixtures as hydrochloric or acetic acid and acetone. Practically no adsorption of the chlorine ion takes place from solutions containing nitrates and chlorides in equivalent proportions, although when nitrates are replaced by nitric acid the adsorption of chlorine ion is little less than normal.

R. TRUSZKOWSKI.

Adsorptive power of aluminium silicates used pharmaceutically. R. PORTILLO (Anal. Fis. Quím., 1928, 26, 271—286).—The percentage of silica and water and the adsorptive power for methylene-blue have been determined for a number of commercial preparations of kaolin. There is no apparent connexion between chemical composition and adsorptive power. The adsorptive power falls to a low value, which is practically the same for all the samples examined, when the kaolin is dehydrated by heating, and in general decreases on treatment with alcohol.

R. K. CALLOW.

Absorption phenomena. J. RATELADE and M. TSCHETVERGOV (Rev. gén. Mat. col., 1928, 32, 302—305).—The absorption of dyes from mixed solvents by filter-paper and by artificial silk has been investigated with reference to the percentage composition of the solvent. With "direct diamine" dyes on filter-paper, minima were found using water-methyl alcohol, water-ethyl alcohol, and water-pyridine mixtures, but not with ethyl alcohol-methyl alcohol or ethyl alcohol-pyridine mixtures. In the case of diphenylmethane and triphenylmethane dyes no minima were found. Similar results were obtained with viscose. The extraction of direct colours from filter-paper by water-alcohol and water-pyridine mixtures also showed a minimum (cf. Schilov and Pevsner, A., 1926, 238).

C. W. GIBBY.

Adsorption of iron from ferric hydroxide sols and ferric chloride solutions by kaolin and by talc. A. FODOR and A. ROSENBERG (Kolloid-Z., 1928, 46, 91—95).—Kaolin and talc adsorb ferric hydroxide from colloidal solutions and also from hot solutions of ferric chloride, but do not adsorb aluminium hydroxide from a colloidal sol or from a hot

solution of aluminium chloride. Pulverised sand does not adsorb ferric hydroxide under these conditions. A separation of iron and aluminium may be effected by the preferential adsorption by kaolin or talc of iron from a hot solution of the mixed chlorides. The colloid content of ferric chloride solutions was checked by measuring the rate of hydrolysis of sucrose by the hydrolytically produced hydrochloric acid. Kaolin adsorbs iron hydrolytically from a ferric chloride solution and the free acid remains behind. On the other hand, the adsorption of iron from a hot ferric chloride solution by talc is mainly a secondary process; the first process is an exchange-adsorption between magnesium and hydrolytically formed hydrogen ions, magnesium ions gradually appearing in the solution. The amount of colloidal ferric hydroxide subsequently adsorbed is proportional to the amount of adsorbed hydrochloric acid.

E. S. HEDGES.

Adsorption and swelling. II. V. KUBELKA and J. WAGNER (Kolloid-Z., 1928, 46, 107—114; cf. Kubelka and Taussig, A., 1926, 900).—The gross adsorption of hydrochloric acid by hide powder is characterised by a maximal value of the equilibrium adsorbed amount (x/m) in very dilute solutions (0.06 millimol.). With increasing concentration of acid the value of x/m remains practically constant. The gross adsorption of sulphuric acid does not exhibit such a maximum, but a steady rise with increasing acid concentration. The swelling of hide powder in water has a maximal value at which 7 g. of water are taken up by 1 g. of the air-dried substance. In hydrochloric acid, the swelling is considerably greater than in pure water and reaches a maximal value in quite dilute solutions. A swelling maximum was not observed in sulphuric acid solutions; in dilute solutions, the degree of swelling is approximately the same as in pure water, and at higher concentrations the swelling is less than that in water. The corrected adsorption curves have the characteristic form of the adsorption isotherm, but show that for both acids the logarithmic adsorption equation holds only for a definite range of concentrations.

E. S. HEDGES.

Adsorption at crystal-solution interfaces. III. Individual macroscopic ammonium alum crystals grown in the presence of gelatin and dyes. G. W. BENNETT and W. G. FRANCE (J. Amer. Ceram. Soc., 1928, 11, 571—581; cf. this vol., 358, 472).—Preliminary qualitative experiments showed that striking "hour-glass" figures are obtained when potassium alum coloured with diamine-sky-blue is recrystallised from hot water, and that adsorption of the dye takes place only during the growth of crystals. All quantitative experiments were conducted in an air-thermostat at $30.0 \pm 0.1^\circ$. The crystallisation cell was filled with ammonium alum solution, saturated at 30° , and weighed quantities of the desired foreign material, i.e., dyes, gelatin, or amino-acids, were added to it. A carefully selected seed crystal, fastened to a platinum wire, was introduced into the solution, and an initial exposure of the film immediately made. Photographic records were continued every half hour over periods of 20—30 hrs., and the distances between cube faces and between octahedral

faces were measured on the magnified film. The ratio between the corresponding perpendicular displacements of the cube and the octahedral face, which for the pure ammonium alum crystal was found to be 1.53, varies with the extent of adsorption. Thus, diamine-sky-blue, oxamine-blue, and anthraquinone-green are adsorbed on the cube faces only and at the same time repress the displacement of these faces.

The hydrogen-ion concentrations of the solutions were practically constant. The dyes, both in pure water and in alum solutions, were examined for state of dispersion. Some colloid particles were detected, but there appeared to be no relationship between the number of particles and the action of the dye in repressing face displacement. It is, therefore, suggested that individual dye molecules rather than colloidal aggregates of them are responsible for the observed effects. The mechanism of adsorption is explained on the basis of residual valencies, polar groups in the adsorbed material, and interionic distances in the lattice. This explanation is extended to include the specific nature of the adsorption.

A. T. GREEN.

[Adsorption and crystallisation.] **Calcite and aragonite.** C. H. SAYLOR (J. Physical Chem., 1928, 32, 1441—1460).—It is shown that foreign substances are adsorbed preferentially on certain crystal faces, the adsorption retarding the growth perpendicular to the faces, and resulting ultimately in their enlargement. All crystalline substances adsorb from the mother-liquor ions of electrolytes, molecules of solvent and of dissolved non-electrolytes. The preferential adsorption of a cation on one face species is accompanied by a similar adsorption of the anion on the other principal crystal faces. The development of octahedral faces on sodium chloride is favoured by the presence of sodium, potassium, and ammonium hydroxides, and sodium carbonate. Mercuric chloride, antimony chloride in hydrochloric acid, and carbamide act similarly. Ethyl alcohol, which is known to decrease the adsorption of anions, counteracts the tendency to form octahedra when added to the mother-liquor in the above-mentioned cases. No true octahedral faces could be observed on crystals of sodium chloride grown from pure salt solutions, or from solutions containing nickel or ferric chloride, or hydrochloric acid, as has been claimed by previous investigators. The adsorption of anions on the cubic faces of the alums and on the end forms of sodium nitrate favours their enlargement, and that of cations on the cubic faces of barium nitrate, and on the side forms of sodium nitrate acts in a similar way. Experiments with acidic and basic dyes are also recorded. Preferential adsorption on an allotropic modification may spoil each crystal nucleus as a centre for crystal growth, and will tend to suppress the modification, allowing an unstable form to be temporarily stabilised. This view is supported by crystallisations of the three forms of calcium carbonate from solutions of potassium carbonate and calcium chloride, and is shown to explain various findings of previous workers. Aragonite and μ -calcium carbonate are capable of existence because certain ions, e.g., the hydrogen carbonate and acetate ions, carbamide; the high-

temperature form of water, and organic material (in the case of molluscs) are preferentially absorbed on calcite and prevent its growth. L. S. THEOBALD.

Passivity of metals. W. J. MÜLLER (Z. Elektrochem., 1928, 34, 571—586).—A general account of the previously published work of this author and his co-workers (cf. this vol., 714). A consequence of the author's theory is that the "passivating" power of an electrolyte may be expressed numerically. It is proposed to call "coating passivity" that kind of passivity which is characterised by the metal passing into solution at stronger polarisation with the valency of the active metal.

S. K. TWEEDY.

Surface energy of solid sodium chloride. III. Heat of dissolution of finely-ground sodium chloride. S. G. LIPSETT, F. M. G. JOHNSON, and O. MAASS (J. Amer. Chem. Soc., 1928, 50, 2701—2703; cf. A., 1927, 954).—Finely-ground sodium chloride has a smaller (negative) heat of dissolution than the coarsely ground salt. Results obtained with finely-ground material are not suitable for the calculation of surface energy.

S. K. TWEEDY.

Permeability of metals towards gases. V. LOMBARD (J. Chim. phys., 1928, 25, 587—604; cf. this vol., 1085).—Using the apparatus described previously, measurements have been made of the permeability, d , of nickel membranes for nitrogen, argon, and helium, and of iron and platinum for hydrogen (d =number of c.c. of gas measured at 0° and 760 mm. passing per hour through a membrane 1 cm.² in area). With nickel membranes at about 500° the permeabilities for nitrogen and argon are very small—about one hundredth of the permeability for hydrogen; the permeability for helium is somewhat greater, but the results for this gas are untrustworthy. The diffusion of hydrogen through iron and platinum follows the same general laws as in the case of nickel. For these three metals the relationship between permeability towards hydrogen, temperature (t), and pressure (p) is $d=k\sqrt{p/h}\times a^{\alpha}$, where h =thickness of membrane, a is an arbitrary number, and k and α are constants characteristic of the metal. The temperature ranges studied were for nickel 350—750°, for iron 350—520°, and for platinum 400—700°.

O. J. WALKER.

Permeability of membranes. V. Diffusion of non-electrolytes through the dried collodion membrane. A. A. WEECH and L. MICHAELIS (J. Gen. Physiol., 1928, 12, 55—81).—The rates of diffusion of acetone, carbamide, glycerol, and dextrose through dried collodion membranes decrease in the order given. For each substance the rate of diffusion varies directly with the difference in concentration between the solutions on either side of the membrane.

E. A. LUNT.

Permeability of gelatin membranes. R. COLLANDER (Protoplasma, 1927, 3, 213—222).—Experiments with substances such as lævulose and methyl citrate indicate that molecular size, as measured by molecular refraction, is the main factor governing the rate of diffusion through gelatin membranes 0.8—1 mm. thick. The results are considered in relation to those obtained with protoplasm; they support the lipid theory.

CHEMICAL ABSTRACTS.

Pore size of compressed carbon and silica membranes. F. E. BARTELL and H. J. OSTERHOF (J. Physical Chem., 1928, 32, 1553—1571).—Methods for the determination of membrane pore radii based on capillary rise and on Poiseuille's law are discussed. Experimental work with membranes formed by the compression of finely-powdered carbon and silica show that when certain conditions are satisfied both methods give results which are in close agreement. The capillary rise method is more convenient for finding pore radii in determinations of the adhesion tension of a solid against a liquid by the pressure displacement method. L. S. THEOBALD.

Light absorption in solution and the transition between different types of combination. G. SCHEIBE (Z. Elektrochem., 1928, 34, 497—502).—The absorption of light by solutions of some organic compounds including ethyl iodide and of metal iodides in water, alcohols, and hexane is described. The two maxima exhibited by the iodide ion in water are attributed to an iodine atom and also a metastable iodine atom, formed by the iodide ion losing its electron. Solvation has also an influence on the absorption in this case. Observations on solutions of cadmium bromide in alcohol support this theory. Zinc, cadmium, and mercury halides may contain both homo- and hetero-polar linkings, between which, in solution, an equilibrium exists. S. K. TWEEDY.

Molecular state of salts in solutions. H. ULICH and E. J. BIRR (Z. angew. Chem., 1928, 41, 443—446, 467—472, 1075—1078, 1141—1144).—In the first place, infinitely dilute solutions are considered and the application of Stokes' law to the calculation of ionic radii is examined. With reference to the solvation of ions in non-aqueous solutions it is pointed out that for alkali ions, as well as for halogen ions, the solvation number falls with increasing ionic weight, a fact which may be accounted for by supposing that the dipole group of the solvating molecule can get nearer to the centre of a lighter and smaller ion, and that therefore the attractive force will be greater. For sodium and potassium the solvation numbers are approximately the same for all solvents, but for halogen ions they are greater in solvents which contain the hydroxyl group. This must be connected with the dipole nature of the solvent. It is not the solvent molecule as a whole which influences the ion, but only certain atoms or groups which have a semi-polar character, e.g., hydroxyl in alcohol, and carbonyl oxygen in acetone. In considering the interaction of ions and solvent molecules, and that between the ions themselves, it is possible to distinguish between an "electrical" and a "chemical" interaction. In very dilute salt solutions there is a region in which the effect of electrical interaction between free ions greatly exceeds the chemical effect. This region is that in which the Debye-Hückel theory holds. This theory is considered in its relation to activities, and the influence of the electric force on the osmotic effect is investigated. When moderately dilute solutions are investigated, the Debye-Hückel theory shows considerable deviations. Three reasons are given for these deviations. The properties of these solutions, and indeed those of concentrated

solutions, can be made clear by assuming that for "weak" salts as the concentration is increased undissociated molecules predominate in solution, and for "strong" salts free, but largely associated, ions are formed. The relationship between the dielectric constant of the solvent and the osmotic coefficient for "strong" salts is considered. The dielectric constant of the solution increases for a "strong" salt, but does not when a "weak" salt is dissolved, as a rule. This is in agreement with the presence of undissociated molecules in the solution of a "weak" salt. Finally, molten salts are considered. Salts which are "strong" as regards solutions are also "strong" when molten. The same is true for "weak" salts. Thus, it should be expected that a "strong" salt is very nearly completely dissociated when melted. A. J. MEE.

Influence of neutral salts on the rotatory power of tartaric acid and the tartrates. E. DARMOIS (Ann. Physique, 1928, [x], 10, 70—115).—Measurements of the rotatory power of mixed solutions of tartaric acid, calcium chloride, and hydrochloric acid of varying p_H value indicate that the degree of ionisation of the acid determines its specific rotation. For a given wave-length the specific rotation of the normal alkali tartrates varies regularly with the atomic weight of the metal. The curves obtained by plotting the specific rotation of the alkali tartrates against concentration form a pencil converging approximately at the value 42.5° for zero concentration. With increasing concentration the specific rotation of the lithium and sodium salts diminishes, whilst that of the potassium, rubidium, and caesium salts increases. The effect of the addition of numerous salts on the rotatory power of the normal tartrates was investigated. The variation in specific rotation is attributed partly to the dehydration of the tartrate ion in the presence of the cations and partly to the deformation of the electronic orbits in the ion by the field of the cations. The rotatory power of the alkaline-earth and rare-earth tartrates was measured in solutions containing other salts of the respective metals and further evidence of deformation of the ion was then obtained. The extent of this increases with the charge on the ion for those cations which possess the electronic structure of the inert gases. The limits of increase of this deformation are determined by the formation of ionic complexes in the more concentrated solutions. F. G. TRYHORN.

Refractometric behaviour and the state in solution of ammonium salts and concentrated acids. K. FAJANS (Z. physikal. Chem., 1928, 137, 361—382).—It is assumed that the far-reaching analogies between NH_4^+ and OH_3^+ and the rubidium ion, as regards the fields of force in the lattice, apply also to the deforming influence exerted on the anion in the molecule, and further, that the formation of OH_3Cl is accompanied by only a small change in the refraction. Observations of the volatility and ease of decomposition of ammonium chloride and OH_3Cl indicate that the deformation of NH_4^+ and OH_3^+ ions by an anion, together with the converse effect, depends on whether the anion is symmetrical or asymmetric. In the latter case there results a dis-

placement of the hydrogen nucleus in the NH_4^+ or OH_3^+ ion and an increased tendency to deformation by the cation. The large variations with concentration of the refraction of ammonium chloride, and the even greater variations in the case of hydrogen chloride, compared with that of rubidium chloride, are thus explicable. H. F. GILLBE.

Interferometric measurement of particles visible in the ultra-microscope. U. GERHARDT (Ann. Physik, 1928, [iv], 87, 130—144).—The apparatus used for the determination is described, and the most important results of theory and experiment for both self-luminous and particularly for non-self-luminous particles are discussed. By the use of a sufficiently small azimuth-shutter both ends of the particle of which the diameter is to be measured can be seen as separate bright points. The influence of coherence is also investigated. A. J. MEE.

Preparation of gold sol. O. WUTH (Münch. med. Woch., 1928, 75, 472—473; Chem. Zentr., 1928, i, 2192).—The optimal hydrogen-ion concentration is p_{H} 7.1—7.2 for preparation and 6.1—6.3 for the reaction. A. A. ELDRIDGE.

Preparation of negatively charged sols by means of tartaric acid. III. Adsorption of sodium tartrate and succinate by aluminium hydroxide. A. DUMANSKI and A. IAKOVLEV (Bull. Soc. chim., 1928, [iv], 43, 969—977; cf. this vol., 584).—The adsorption of sodium tartrate by aluminium hydroxide in the form of hydrosol, newly-formed precipitate, and a four months' old precipitate can in each case be expressed by the ordinary adsorption isotherm $x/m = kc^{1/n}$. The value of k increases with increasing degree of dispersion, whereas $1/n$ remains constant. The adsorption of sodium succinate by aluminium hydroxide sol is much weaker than that of the tartrate; the presence of the hydroxyl groups in the acid has apparently a strong influence on the adsorbability. This is to be expected from the results previously obtained in the use of hydroxy-acids for the preparation of metallic hydroxide sols. O. J. WALKER.

Preparation of negatively charged sols by means of tartaric acid. IV. Formation of lead hydroxide sols and gels from alkali tartrates. A. V. DUMANSKI and A. P. BUNTIN (J. Russ. Phys. Chem. Soc., 1928, 60, 933—949; cf. preceding abstract).—Solutions prepared by dissolving lead sulphate and lead hydroxide in alkali tartrate solutions in presence of excess of alkali or lead tartrate in alkalis contain the complex $\text{C}_4\text{H}_2\text{O}_6\text{R}_2\text{Pb}$, where R is K, Na, or NH_4 . When the alkalinity of the solution is small, colloidal solutions of lead hydroxide may form, passing into vitreous, transparent gels if the solution contains more than 3% Pb. Lead alkali tartrates may be isolated by adding alcoholic alkali to solutions of lead tartrate. Solutions of this salt are alkaline and levorotatory, and on dilution their conductivity changes considerably, indicating a high degree of hydrolysis. On dialysis, colloidal solutions of lead hydroxide are obtained. These sols are made up of negatively-charged particles, readily coagulable by electrolytes and of the composition expressed by $\text{Na}[\text{C}_4\text{H}_2\text{O}_6\text{Pb}, n\text{Pb}(\text{OH})_2]$. R. TRUSZKOWSKI.

Preparation of negatively charged sols by means of tartaric acid. V. Physico-chemical properties of tungstate-tartaric acid colloids. A. V. DUMANSKI and S. I. DIATSKOVSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1053—1068).—The addition of sodium tungstate to *d*-tartaric acid solutions gives rise to the formation of a series of colloidal double salts, which undergo hydrolysis on dilution; the degree of dispersion increases with the tungsten content. These colloidal solutions exhibit mutarotation; on concentration they yield vitreous gels, which become blue on exposure to light. R. TRUSZKOWSKI.

Colloidal carbon solutions. H. LACHS and K. GESTEL (Z. physikal. Chem., 1928, 137, 193—200).—Carbon hydrosols prepared by Sabbatini's method exist as definite systems containing probably carbo-hydrates and their decomposition products. The X-ray spectrograph yields no evidence of crystalline structure, nor is double refraction to be observed. Approximately 70% of the sol particles have a diameter of about $141 \mu\mu$, 15% $71 \mu\mu$, and 15% $4.4 \mu\mu$. Despite the large average particle size, the sols are very stable, probably on account of the high degree of hydration. Depolarisation measurements indicate that the sol particles are approximately spherical. H. F. GILLBE.

Action of light on silver hydrosols containing particles of uniform magnitude. A. GALECKI and R. SPYCHALSKI (Rocz. Chem., 1928, 8, 394—404).—The velocity of decolorisation of silver hydrosols subjected to ultra-violet illumination increases with diminution in the size of the silver particles. Such decolorised solutions possess greater conductivity and smaller viscosity than the original sols, pointing to the conversion of the colloidal silver particles into ions. If the illumination be continued after decolorisation the above effects are reversed, and a hydrosol is again obtained. R. TRUSZKOWSKI.

Dependence of the stability of carbon suspensions on the gas charge and the composition of the solution. N. BACH-NIKOLJEVA and A. FRUMKIN (Kolloid-Z., 1928, 46, 89—90).—A preliminary communication in which the following results are recorded. Platinised carbon (prepared by mixing carbon with platinum chloride and heating in a stream of hydrogen) in hydrochloric acid gives the most stable suspension in air and the least stable in hydrogen; unplatinised carbon in air occupies an intermediate position. The suspension in potassium hydroxide is more stable in an atmosphere of hydrogen than in an atmosphere of air. The stability of suspensions saturated with air is much less in sulphuric acid than in hydrochloric acid. E. S. HEDGES.

Dielectric properties and structure of the hydrophilic colloids. N. MARINESCO (Compt. rend., 1928, 187, 718—720).—The fall in ϵ with increase in the concentration of the sol may be used to determine the water fixed by a hydrophilic colloid, the dipoles of the adsorbed water being subjected to the influence of an external field just as in the case of the solidification of a liquid. The amounts of water adsorbed by methæmoglobin, soluble starch, and gum arabic were determined, and indicate that the dispersing medium plays an important rôle in fixing the structure of

the micelles of which it constitutes the principal portion. J. GRANT.

Formation of gels. Vulcanised oils. B. C. J. G. KNIGHT and P. STAMBERGER (J.C.S., 1928, 2791—2798).—The products obtained by heating triolein with sulphur (B., 1928, 23) have been examined by means of X-rays; the diagrams obtained show only an amorphous circle of the same diameter for all the products. The behaviour of the products as thin films on a water surface has also been examined. All give unimolecular films. In the acetone-soluble product which is a viscous, sticky liquid, the mode of orientation of the molecules is not altered from that in triolein and the dimensions are only slightly affected. The benzene-soluble product, a more viscous fluid, gives a film of approximately the same thickness, but the area per molecule is twice that of the acetone-soluble product. When kept this product changes to an elastic, sticky solid which has a very high mol. wt., indicating that the molecule contains at least seven of vulcanised triolein. This product gives a slightly thicker film which is still unimolecular but much less expanded. A sulphurised oleic acid obtained from this solid by saponification had no elastic properties. It is suggested that sulphur first unites with triolein, the sulphur atoms forming a chain which connects the double linkings of the adjacent oleic acid chains. Double molecules are then formed by the linking together of two such molecules with the glyceryl groups combined by means of sulphur. The more highly polymerised elastic products are then formed by the linking of further molecules in the same manner. The significance of this polymerisation and orientation for the theory of gel structure (McBain, A., 1927, 1022) is briefly discussed. R. N. KERR.

Coagulation of strongly-solvated sols with organic substances and salts. II. B. JIRGENSONS (Kolloid-Z., 1928, 46, 114—128; cf. this vol., 839).—The following results have been obtained in the coagulation of sols of casein, hæmoglobin, and albumin with organic substances and solutions of electrolytes. In small or medium concentrations, mixtures of organic compounds and inorganic salts coagulate the sol more rapidly than either constituent of the mixture alone. At higher concentrations (e.g., 30—60 vol.-% of *n*-propyl alcohol and 0.3 mol. of calcium chloride per litre) stabilisation occurs in virtue of the capillary-active nature and small dielectric constant of the organic compound (e.g., *n*- and *iso*-propyl alcohol, allyl alcohol, ethyl alcohol); this behaviour was observed with both positive and negative hæmoglobin and also with both acid and basic egg-albumin. At still higher concentrations of the capillary-active material (above 60 vol.-%), flocculation is again observed. Glycerol has a sensitising influence on the coagulation of a casein sol by magnesium chloride. The degree of adsorption of alcohols by both hæmoglobin and albumin particles is in the order *n*-propyl alcohol > ethyl alcohol > methyl alcohol, the adsorbability thus being parallel to the sensitising or stabilising effect. Colloids produce a greater increase in the viscosity of alcohol-water-salt mixtures than in pure water. Sensitisation is ascribed

to the dehydrating effect of the organic compound and to the alteration of the dielectric properties of the medium. Stabilisation is due to the peptising effect of the salt through the formation of adsorption complexes of hydrated colloid particles and molecules of the salt and of the organic compounds. The rôle of the organic compound is to diminish the dielectric constant in the vicinity of the colloid particle, enabling easily adsorbable complexes of salt molecules to be formed. Thus, only those organic substances which have a low dielectric constant and can be strongly adsorbed by the colloid can have a stabilising effect. The flocculating effect observed at concentrations above 60 vol.-% is due to excessive dehydration of the complexes. Viscosity measurements support the view that the particles in the stabilised mixtures are more strongly solvated than particles of the sols in water. E. S. HEDGES.

General theory of rapid coagulation. Coagulation of rod-like and plate-like colloids; theory of general polydisperse systems and streaming coagulation. H. MÜLLER (Kolloidchem. Beihefte, 1928, 27, 223—250).—Smoluchowski's theory of rapid coagulation is characterised by three conditions: (a) the spherical nature of the particles, (b) isodispersity of the colloid, and (c) neglect of sedimentation and other movements of the particles. The present paper is a general theoretical investigation of rapid coagulation where these conditions are not fulfilled. The theory involves three postulates: (1) for the coagulation of two micelles, contact of the surface is essential, (2) the frequency of collision of the particles is determined by the temperature movements and streaming of the particles, and (3) the coagulation of a given particle is determined only by the stationary distribution of particles. The application of these principles to isodisperse systems free from streaming has led to a theory of the coagulation of colloids with disc- and rod-like particles and shows that sols with disc-like particles are coagulated in a similar way to those with spherical particles, whereas sols with rod-like particles have a greater coagulation velocity. The influence of polydispersity of the sol is considered, and a relation between the initial tangents of the coagulation curve and the distribution curve of radii of the spherical particles of a sol has been derived. Approximately isodisperse systems must coagulate in accordance with Smoluchowski's rule within the limits of experimental error, but polydisperse systems coagulate more rapidly. The influence of sedimentation and of stirring is discussed, and it appears that these effects influence only the coagulation of the larger particles; a formula has been derived, expressing the minimal radius of particles where such an effect is observed. E. S. HEDGES.

Precipitation of mixtures of colloids of the same sign. M. A. BOUTARIC and (MLLE.) M. DUPIN (Bull. Soc. chim., 1928, [iv], 43, 1059—1062).—The precipitating action of potassium, lithium, and barium chlorides on mixtures of sols of gamboge and arsenious sulphide has been studied by the spectrophotometric method. The minimum quantity of electrolyte required for precipitation of any mixture is less than that expected from the mixture rule. In

the case of mixtures of sols of mastic-resin and gamboge, the required quantity of electrolyte varies nearly linearly with the composition.

R. N. KERR.

Salting-out of gelatin into two liquid layers with sodium chloride and other salts. J. W. McBAIN and F. KELLOGG (*J. Gen. Physiol.*, 1928, 12, 1—15).—The concentrations of salt and of hydrogen ion necessary to bring about the separation of gelatin into two liquid layers have been studied in the case of sodium chloride, potassium chloride, sodium sulphate, ammonium sulphate, sodium nitrate, and potassium nitrate. The system gelatin-sodium chloride-hydrogen ion-water behaves as a true quaternary system.

E. A. LUNT.

Formation of Liesegang rings as a periodic coagulation phenomenon. E. S. HEDGES and (Miss) R. V. HENLEY (*J.C.S.*, 1928, 2714—2726).—Experiments have been made to test the view that the occurrence of periodic bands is a secondary coagulation effect which takes place after the chemical change. The behaviour of silver dichromate and magnesium hydroxide in gelatin and of lead iodide in agar has been studied. When a concentrated solution of silver nitrate was superimposed on a colloidal solution of silver dichromate in gelatin which had been allowed to set, periodic rings exactly similar to those prepared in the normal way by chemical action were obtained. Bands were also obtained by diffusion of a concentrated ammonia solution into a gelatin gel of magnesium hydroxide. In the case of an agar gel of lead iodide diffusion of either reactant caused ring formation. Periodic structures were also obtained by the diffusion of an electrolyte other than one of the reactants. With sols of arsenious sulphide these were produced by ferric chloride and aluminium sulphate and with colloidal ferric hydroxide by sodium arsenite and ammonium carbonate. In both cases a decrease in the distance apart of successive rings throughout the diffusion was observed.

When gradually increasing concentrations of silver nitrate solution were added to colloidal silver dichromate, precipitation was not found to vary periodically with the concentration, but a critical concentration of silver nitrate was found necessary for coagulation.

The relative amounts of product in the bands and in the clear spaces (cf. Ostwald, *A.*, 1925, ii, 530) were determined for a magnesium hydroxide gel by chemical analysis. The ratio of magnesium hydroxide in the band to that in the clear space was about 12 : 1, and the corresponding ratio for ammonium chloride (produced in the reaction) about 1 : 3.

Certain anomalous periodic structures are noted.

R. N. KERR.

Theory of the colloid reactions of cerebro-spinal fluid. J. K. MAYR (*Kolloidchem. Beihefte*, 1928, 27, 347—348).—Polemical against Schmitt (this vol., 477).

E. S. HEDGES.

Behaviour of caseinogen in partial solution in calcium hydroxide. V. PERTZOFF (*J. Biol. Chem.*, 1928, 79, 799—813).—Purified caseinogen was brought into equilibrium with calcium hydroxide in aqueous solution. The quantity of dissolved caseinogen can be expressed by $K_2/\{1/\text{Ca}(\text{OH})_2 - (K_1 - K_2)/C\}$, where

C is the total caseinogen in the system, K_1 is the equivalent combining weight of caseinogen, and K_2 the maximum base-binding power of caseinogen (*A.*, 1927, 895). The solubility therefore depends on the total amount of caseinogen present as well as on the base added; a linear relationship was observed between the calcium hydroxide bound and the dissolved protein. Similar relationships hold for the solubility of caseinogen in large amounts of sodium hydroxide at 5°.

C. R. HARINGTON.

Titration curves of coagulated and uncoagulated egg-albumin. B. M. HENDRIX and V. WILSON (*J. Biol. Chem.*, 1928, 79, 389—403).—Comparison of the electrometric titration curves of coagulated and uncoagulated egg-albumin shows that the latter has a greater acid- and base-binding power, the difference being more marked if the coagulated protein has been dried before being brought into equilibrium with acid or alkali; the results are in accordance with the view that coagulation involves a decrease in the number of free amino- and carboxyl groups owing to internal condensation.

C. H. HARINGTON.

Filterability of hydatid "antigens." C. H. KELLAWAY, N. H. FAIRLEY, and F. E. WILLIAMS (*Austral. J. Exp. Biol.*, 1928, 5, 189—204).—When hydatid fluid is filtered through collodion membranes of various permeabilities the ultra-filtrates for the less permeable membranes do not act as an antigen towards serum from animals immunised to the parasite, although the ultra-filtrates for the more permeable membranes give a positive reaction when tested by intradermal injection into a sensitised animal, by the sensitised guinea-pig uterus, or, in some cases, by means of the complement fixation test. These ultra-filtrates remain active after boiling and fail to give most of the ordinary tests for protein.

W. O. KERMAK.

Cataphoresis and the electrical neutralisation of colloidal material. S. MATSON (*J. Physical Chem.*, 1928, 32, 1532—1552; cf., *A.*, 1922, i, 800).—An ultramicroscopic cell which permits the rapid determination of the cataphoretic movement of colloidal particles before and after flocculation and also of the isoelectric point is described. A study of the electrical neutralisation of electro dialysed clay suspensions by aluminium chloride alone and after treatment with acid and alkali shows the products of hydrolysis of the aluminium salt to be more active than the trivalent cations, and that the greatest efficiency is obtained at p_H 5.2. In the case of neutralisation of the clay by methylene-blue, the isoelectric ratio dye/clay is increased by the presence of anions and decreased by that of cations, the magnitude of the effect increasing with valency. The amount of methylene-blue required to neutralise the electronegative proteins in milk decreases with an increase in acidity of the latter, thus affording a means for determining its freshness.

Barium sulphate, by itself and in the presence of an excess of barium, is electropositive, whilst with an excess of sulphate ions it is electronegative. The conditions cause a decrease and an increase, respectively, in the p_H of the solution. An explanation based on a difference in solution tension of two ions for the former,

and one based on the assumption of adsorption of the hydroxyl and hydrogen ions of the water for the latter, are offered.

The behaviour of certain electrolytes, *e.g.*, sodium ferrocyanide, in forming a transient turbidity before dissolution has been studied. The crystalline chips which in water break away from the larger crystals carry a high electronegative charge.

It is pointed out that all electrolytes in water may give rise to a dissociation *P.D.* at the phase boundaries, the sign of the charge being determined by the solution tension and osmotic pressure of the respective ions, and that the electronegative charge of inert materials is due to an adsorbed layer of oriented water molecules.

L. S. THEOBALD.

Influence of salts on the isoelectric behaviour of proteins. K. KONDO and T. HAYASHI (Mem. Coll. Agric. Kyōtō, 1928, No. 5, 1—29).—The optimum p_H value for the flocculation of rice glutelin is 5.38—5.08 in a 0.1*N*-sodium acetate solution which is 0.02—0.04*N* in acetic acid (*cf.* A., 1927, 269). The influence of the presence of a number of salts on such an apparent isoelectric solution had been studied. The presence of a chloride shifts the point of maximum precipitation to the acid side, and at the same time decreases the precipitability of rice glutelin up to a certain concentration of salt, which varies with the salt. The precipitability then increases until, at a still higher concentration, it again decreases. The first change of direction of the curve is explained by the formation of an insoluble complex compound of the protein molecule with the cations of the salt, and the second by the formation of a soluble complex compound. The higher the valency of the cation the more pronounced are the effects. The influence of the cations of the same valency decreases in the following order: $Li^+ > Na^+ > K^+ > Rb^+$; $Cu^{++} > Ni^{++} > CO^{++} > Mg^{++} > Ca^{++} > Ba^{++}$; and $Fe^{+++} > Al^{+++}$. The poisoning action of cupric ions on the organism and the sterility of acid soil due to the presence of iron and alumina in the soil, may result from the inhibition of the living cell metabolism by the formation of a complex compound in which cupric, ferric, or aluminium ions combine with the protoplasmic protein. The effect of inorganic potassium salts, other than carbonate, is similar to that of the chloride, and the influence of the anion also is specific. The carbonate and the acetate, tartrate, and citrate, but not the oxalate, shift the apparent isoelectric point to the alkaline side, their influence being in the order of the dissociation constants of the acids. Potassium oxalate has no influence, owing to the relatively high dissociation constant of oxalic acid. They all decrease the precipitability of the salt. The effect of salts on the isoelectric point is said to be explainable in terms of the ionisation of the protein, each ion giving rise to a protein ion of opposite charge, and of the relative magnitudes of these ionising agencies.

M. S. BURR.

Isoelectric point of glutenin. K. KONDO and T. HAYASHI (Mem. Coll. Agric. Kyōtō, 1928, No. 5, 31—47).—Glutenin free from gliadin, and containing 17.17% of Kjeldahl nitrogen, has been obtained by a method which is described. The apparent isoelectric point is p_H 5.15—5.39. This value is independent of

the concentration of glutenin, but the proportion of glutenin flocculated increases with increasing concentration of the protein owing to the fact that the solubility of the protein at its maximum flocculation point is constant in a solution of fixed salt concentration. Dehydration of the glutenin with alcohol and ether has no effect on its isoelectric point, but addition of rubidium chloride to the buffer solution shifts the isoelectric point of the glutenin to the acid side and reduces the precipitability. The varying values obtained for glutenin from different flours by other investigators may possibly be explained by failure to remove completely the gliadin, which has an influence on the isoelectric point. M. S. BURR.

Equilibrium in the reaction $C_2H_6 = C_2H_4 + H_2$. R. N. PEASE and E. S. DURGAN (J. Amer. Chem. Soc., 1928, 50, 2715—2718).—Equilibrium may be approached from either side at 600°, 650°, and 700° (*cf.* Bone and Coward, J.C.S., 1908, 93, 1197; Sabatier and Senderens, A., 1905, i, 333), although the results are rendered uncertain by the methane formed in increasing quantities with rising temperature. When approximately equilibrium mixtures are heated, the equilibrium constants, K_p (atm.), at the temperatures indicated are 0.0310, 0.082, and 0.20 respectively, and the heat of dissociation of 1 mol. of ethane is —31,244 g.-cal.

H. E. F. NOTTON.

Equilibrium between hydrogen-carbon monoxide and methane-carbon dioxide in the corona discharge. G. L. WENDT and G. M. EVANS (J. Amer. Chem. Soc., 1928, 50, 2610—2621).—The effect of corona discharge (10,000—20,000 volts) on the reaction $2H_2 + 2CO = CO_2 + CH_4$ has been investigated, one of the electrodes being a wire along the axis of the discharge tube. After the initial "corona expansion" the volume (corrected for temperature influence) passes through a maximum when carbon dioxide and methane are the initial gases; otherwise an immediate contraction takes place. The equilibrium mixture always contains 13.3% CO_2 , 37.1% CO , 8.7% CH_4 , and 37.6% H_2 , and is not influenced by the presence of phosphoric oxide. This equilibrium corresponds with that obtained at a temperature between 900° and 950°. The volume contraction, which continues beyond the equilibrium point, is due to a second reaction, as is evidenced by the deposition of carbon suboxide. A little aldehyde seems to be produced also. The end products are probably carbon and water.

S. K. TWEEDY.

New high-temperature fixation reactions of nitrogen. N. W. KRASE and B. MACKEY (J. Physical Chem., 1928, 32, 1488—1494).—Theoretical. A thermodynamic investigation of nitrogen fixation using the data of Lewis and Randall has been made. In the case of oxygen and nitrogen, only a small increase in the concentration of nitric oxide can be produced in the arc process, by the use of stoichiometric proportions of these gases in place of air, but the reaction between nitrogen and carbon dioxide should double the concentration of nitric oxide. Nitrogen, hydrogen, and carbon should yield concentrations of hydrogen cyanide greater than 15% at the usual arc temperature, whilst nitrogen and acetylene should yield a product containing 70%

of hydrogen cyanide. The establishment of equilibrium in the reaction between nitrogen and methane at 2000° Abs. or above should result in a gas containing 40% of hydrogen cyanide and 60% of hydrogen.

L. S. THEOBALD.

Compound formation in ester-water systems. J. KENDAL and L. S. HARRISON (Trans. Faraday Soc., 1928, 24, 588—596).—To determine the influence of the radicals R, R' in esters of the type R·CO₂R' on compound formation in aqueous solutions, measurements have been made of the f.p. depression and miscibility curves for systems of water and the following: methyl propionate, *n*-propyl formate, ethyl formate, methyl acetate, and methyl oxalate. An analysis of the results shows that the course of the miscibility curves depends primarily on the internal pressure of the ester. Esters with low internal pressures are only slightly soluble in water and exhibit retrograde solubility with rise of temperature. The solubilities of esters with higher internal pressures are either almost independent of, or increase with, temperature. Compound formation is extensive in all systems and increases with the strength of the acid radical of the ester. The nature of the alcohol radical appears to be of little influence in this respect.

F. G. TRYHORN.

Active volume. F. DOBRZYŃSKI (Rocz. Chem., 1928, 8, 369—375).—The law of mass action is not applicable to esterification reactions; for these the relative volume and not the mass of the reacting substances is of importance. The expression $z = mf \pm c/V$ is derived, where z is the active volume, m the number of mols. of the given reagent, c the dilatation or contraction constant, and V the total volume of the system. The conception of active volumes explains the steady increase in the equilibrium constant as the relative concentration of alcohol to acid rises, and shows why a greater yield of ester is obtained when the relative concentrations of alcohol and acid are as $n:1$ than when they are as $1:n$. Finally, it explains why the esterification does not proceed to completion even when the concentration of alcohol is infinitely great.

R. TRUSZKOWSKI.

Equilibrium state for esterification reactions in the liquid phase. S. POZNAŃSKI (Rocz. Chem., 1928, 8, 377—393).—The equilibrium constant for the reaction between acetic acid and ethyl alcohol varies from 2.45 in a mixture containing 3 mols. of acid to 1 mol. of alcohol to 4.73 when these proportions are reversed. The law of mass action does not therefore apply to the above reaction.

R. TRUSZKOWSKI.

Theory of acidity. L. P. HAMMETT (J. Amer. Chem. Soc., 1928, 50, 2666—2673).—The influence of the solvent on the acidity of an acid is investigated mathematically, and the following conclusions are reached. Decreased basicity of the solvent means greater acidity and also less ionisation of the acid. The hydrogen-ion activity of a weakly ionised acid is independent of the dielectric constant of the solvent, but in the case of a highly ionised acid it is greater in solvents of low than in solvents of high dielectric constant. Decrease in the dielectric constant has little effect on salt formation when the ionisation is large, but decreases salt formation when the ionisation

is small. For all except very highly ionised solutions the result of decreasing dielectric constant is a decrease in apparent acidity as measured by a basic indicator, but the latter change does not run parallel with the hydrogen-ion activity. The same scale of activities in all solvents is adopted throughout the discussion. The predictions of the theory are in agreement with the results of Hantzsch (A., 1927, 525) and of Hall and Conant (cf. this vol., 129) and of Hall and Werner (*ibid.*, 1188).

S. K. TWEEDY.

Partition of nitric acid between sodium and potassium hydroxides. V. I. NIKOLAIIEV (J. Russ. Phys. Chem. Soc., 1928, 50, 893—904).—A phase diagram for the quaternary system K₂O—Na₂O—N₂O₅—H₂O is described.

R. TRUSZKOWSKI.

Influence of neutral salts on acid-base equilibria. V. First and second dissociation constants of succinic, tartaric, and adipic acids, and the influence of neutral salts on the p_H of a mixture of the acid and its acid salt, and the acid salt and normal salt, respectively. VI. Dissociation constants of acetic, hexoic, and benzoic acids and the influence of neutral salts on the dissociation constants of weak acids. I. M. KOLTHOFF and W. BOSCH (Rec. trav. chim., 1928, 47, 861—872, 872—882; cf. this vol., 954).—V. The following values have been found from p_H measurements for the first and second dissociation constants of the three dibasic acids: succinic 6.6×10^{-5} and 2.7×10^{-6} , adipic 4.6×10^{-5} and 3.6×10^{-6} , tartaric 9.6×10^{-4} and 2.8×10^{-5} . These results are extrapolated for infinite dilution. Neutral salts increase the activity of the undissociated acid; the dissociation constant of the acid is not increased. The Debye-Hückel equation does not completely represent the effect of neutral salts on the ratio of the activity coefficients of the uni- and bi-valent anions of the weak dibasic acid. A specific ionic interaction has to be taken into account.

VI. The dissociation constants of the three monobasic acids at 18° are found to be: acetic 1.70×10^{-5} , hexoic 1.44×10^{-5} , benzoic 7.0×10^{-5} . In this case also, there is no evidence that neutral salts increase the dissociation constant of weak acids.

O. J. WALKER.

Electrochemical study of the action of acids on solutions of some zinc salts. J. GUÉRON (Compt. rend., 1928, 187, 599—601).—The variation of p_H in solutions of zinc salts on addition of acid has been investigated in the cases of zinc acetate-acetic acid, zinc acetate-hydrochloric acid, and zinc sulphate-sulphuric acid.

C. W. GIBBY.

The equilibrium $2K_3Fe(CN)_6 + 2KI \rightleftharpoons 2K_4Fe(CN)_6 + I_2$ in aqueous potassium chloride solutions. V. K. LA MER and K. SANDVED (J. Amer. Chem. Soc., 1928, 50, 2656—2665).—The system was investigated in water and in potassium chloride solutions (0—2 molar). The ionic strength is not an entirely satisfactory measure of the electric environment (cf. La Mer and Mason, A., 1927, 314). The data confirm the view that the law of mass action holds for ionic systems when sufficient neutral salt is present to maintain constant electrical environment, although this law fails completely in the absence of

excess of neutral salt. The acidity of the solution is without influence up to a p_H value of 3.5. Thermodynamic equilibrium constants for the ionic reaction, and the reaction in which I_3^- is produced, are calculated with the aid of *E.M.F.* data. S. K. TWEEDY.

Effect of the position of substitution on the ionisation constants of some organic acids. D. A. MACINNES (J. Amer. Chem. Soc., 1928, 50, 2587—2595).—If K is the dissociation constant of a substituted acid, and if d represents the position of the substituent (*i.e.*, $d=1$ for α position, 2 for β position, etc.), then, for many series of acids, $\log K = k_1 + k_2/d$, where k_1, k_2 are constants. This relation holds even better for series of acids in which substitution is always on the final carbon atom of the chain. k_1 may be the logarithm of the ionisation constant of a hypothetical acid in which the chemical change of substitution has occurred, but in which the substituent is at an infinite distance from the carboxyl group. The term k_2/d is then a measure of the potential energy involved in bringing the two negative groups near to each other. Apparently d is the distance between the polar linking joining the carboxyl to the carbon chain and the polar linking joining the other substituent to the chain. The chlorobenzoic acids conform accurately to the equation if a "puckered" ring structure is assumed for benzene and if the " α -distance" in the fatty acid is equal to the "*ortho*-distance" in the aromatic acid. Evidence is adduced that the benzene ring is a stable system, whereas aliphatic chains are comparatively flexible. Bromine- and iodine-substituted aliphatic acids show small, systematic deviations from the equation with which, however, the corresponding aromatic acids agree closely. S. K. TWEEDY.

Effect of salts on weak electrolytes. II. Calculation of overlapping constants. H. S. SIMMS (J. Physical Chem., 1928, 32, 1495—1515).—In continuation of a previous paper (this vol., 1093), the potentiometric titration data are given, and the method of calculating the titration indices of multivalent acids with overlapping constants is explained.

L. S. THEOBALD.

Acid dissociation of aquo-ions. II. J. N. BRÖNSTED and K. VOLQVARTZ (Z. physikal. Chem., 1928, 134, 97—124; cf. this vol., 18).—The acid dissociation constants at 15° have been found for the tervalent aquopentammino-, diaquotetrammino-, triaquotriammino-, and tetra-aquodiammino-cobalt ions, aquopentammino-rhodium ion, hexa-aquo-aluminium-, chromium-, and -ferric ions by means of the determination of (i) the hydrogen-ion concentration by the diazoacetic ester method, (ii) the solubility of the salts in solutions of different acidities, and (iii) the hydrogen-ion concentration from the velocity of decomposition of the nitrate-aquotetrammino-cobalt salts. In the case of the first two ions, the values of the dissociation constant decrease with increase in the concentration, and the deviations from the theoretical values can be represented by an equation similar to that found for the hexa-aquochromic ion (*loc. cit.*). The extrapolated values of the acid dissociation constants at infinite dilution for the above ions are 2.04×10^{-6} , 6.2×10^{-6} , 2.0×10^{-5} , 4.0×10^{-4} , 1.38×10^{-6} ,

1.3×10^{-5} , 1.26×10^{-4} , and 6.3×10^{-3} , respectively. The methods and results are discussed.

L. S. THEOBALD.

Hydrolytic scission of succinimide. H. VON EULER and A. OLANDER (Z. physikal. Chem., 1928, 137, 393—398).—Electrometric measurements of the hydrogen-ion concentration in acid solution of succinimide gave a value $K_a = 2.6 \times 10^{-10}$ at 25° for the first ionisation constant. Efforts to determine the second ionisation were unsuccessful. Similar measurements with succinamic acid gave an acid ionisation constant of 2.72×10^{-5} at 25°. Unsuccessful attempts were made to measure the basic ionisation constant, which is smaller than that of acetamide. Determinations were made in solutions of varying alkalinity of the velocity of hydrolysis of succinimide to succinamic acid. In the region p_{OH} 3 the rate of increase of the velocity coefficient becomes greater, but falls almost to zero at p_{OH} 2.5. Thence onwards the rate of increase becomes much greater, reaching 0.00418 at p_{OH} 0.083. No satisfactory theoretical explanation can be advanced for these irregularities.

The hydrolysis of succinimide is much slower in acid solutions at the ordinary temperature, but at 90° a mean value corresponding with 2.9×10^{-4} H^+ was found in 0.118—0.05*N*-hydrochloric acid.

F. G. TRYHORN.

Partial osmotic pressures and membrane equilibria, with special reference to the application of Dalton's law to hæmoglobin solutions in the presence of salts. G. S. ADAIR (Proc. Roy. Soc., 1928, A, 120, 573—603; cf. A., 1926, 21).—By means of the method previously described (A., 1925, ii, 965), the osmotic pressures of hæmoglobin solutions in equilibrium with solutions of diffusible salts have been measured and correlated with determinations of the membrane potentials, and the distribution of diffusible ions. The relations between the activities of diffusible ions and the membrane potentials are in accordance with Donnan's theory, but his assumptions with regard to osmotic pressures do not appear to be applicable to protein solutions of finite concentration. Experiment shows that, even if the concentration of diffusible ions is only 0.01 equiv. per litre, the margin of uncertainty in the partial pressures of the diffusible ions is of the same order of magnitude as the observed osmotic pressures of the protein. The formula $p_p = p_{obs} - p_i$, where p_p is the partial osmotic pressure of the protein ions and p_i the diffusible ion pressure difference, yields a provisional value for the partial osmotic pressure, which is approximately correct within a limited range of hydrogen-ion, salt, and protein concentrations. The application of Dalton's law to protein systems can be verified by determinations of the mol. wt. of a protein. Systematic experimental investigations of the partial pressures indicate that certain variations in the osmotic pressure, formerly attributed to actual changes in the aggregation of the protein, are really due to deviations from the ideal solution laws. In solutions of p_H 5.0—9.0, and with sodium chloride concentrations from 0.01 to 4.0 mols. per litre, and in solutions with different kinds of ions, including K, Na, NH_4 , Mg, Cl, HCO_3 , SO_4 , H_2PO_4 , HPO_4 , the degree of aggregation of hæmoglobin appears to be constant. Methods are developed for determin-

ing the mol. wt. of proteins in non-ideal solutions containing salts, use being made of the formula $M_a = 170,330/k_m$, where k_m is an empirical constant. The value 67,000 obtained for hæmoglobin in physiological salt solutions agrees with that previously determined for hæmoglobin in distilled water.

L. L. BIRCUMSHAW.

Activity of univalent ions. H. MUELLER (Physical Rev., 1927, [ii], 29, 216).—It is shown that Debye's theory is in accord with the experimental results for small ions without the assumption of partial association.

A. A. ELDRIDGE.

Application of the method of partition coefficients to the determination of the activity coefficients of the dissociated and undissociated fractions of salicylic acid in neutral salt solutions. B. VON SZYSZKOWSKI and A. VON SKAPSKI (Z. physikal. Chem., 1928, 137, 238—262).—The partition coefficients of salicylic acid between benzene and aqueous solutions of sodium chloride, chlorate, nitrate, and sulphate, barium chloride, and magnesium sulphate over the concentration range 0.005—2.0M have been determined, and the activity coefficients of the undissociated and dissociated acid have been calculated. From thermodynamical considerations the equation $c'/c = 1 - \alpha/f_0 + \alpha/f$ has been derived, where c' is the solubility, c and α are the solubility and degree of ionisation in water, and f_0 and f the activity coefficients of the undissociated and dissociated molecules, respectively. The formula yields values of c' which are in close agreement with those determined experimentally, and accounts satisfactorily for the maxima which exist in all cases in the solubility curves.

H. F. GILLBE.

Activity coefficients of sodium and potassium hydroxides in their corresponding chloride solutions at high constant total molality. H. S. HARNED and J. MCA. HARRIS, jun. (J. Amer. Chem. Soc., 1928, 50, 2633—2637).—The *E.M.F.* at 25° of cells of the type $H_2|MOH(c_1), MCl(c_2)|M_xHg|MOH(c_0)|H_2$ are recorded, in which $M=Na$ or K , and c_1+c_2 is kept constant (3, 3.5, or 5M) throughout a given series of measurements. The logarithms of the activity coefficients of the hydroxides in the chloride solutions, calculated from these results, are not a linear function of the concentration of the hydroxide, although the deviation is small.

S. K. TWEEDY.

Molecular statistical thermodynamics. E. SVENSEN (Ann. Physik, 1928, [iv], 87, 424—460).—Mathematical.

W. E. DOWNEY.

Hydrodynamics and the kinetic theory of gases. Y. ROCARD (Ann. Physique, 1928, [x], 10, 345—348).—A correction (cf. A., 1927, 826).

Second law of thermodynamics in general relativity. R. C. TOLMAN (Proc. Nat. Acad. Sci., 1928, 14, 701—706).—Mathematical.

W. E. DOWNEY.

Thermodynamics of irreversible reactions. Evolution of physical and chemical systems in time. N. A. KOLOSOVSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1079—1115).—The time factor is introduced as an independent variable into De Donder's thermodynamic theory of chemical reactions (Mém. Acad. Roy. Belg., 1927, 9) and a series of

expressions for velocity of reaction is derived from an exclusively thermodynamical point of view. Further equations are given expressing uncompensated heat of reaction in gaseous systems, which represent a generalisation of the ordinary conditions of equilibrium in such systems.

R. TRUSZKOWSKI.

[Polymorphism and solubility of] triglycerides. K. LOSKIT (Z. physikal. Chem., 1928, 134, 135—155).—The polymorphism and the solubility of tristearin, tripalmitin, trimyristin, trilaurin, tricaprin, tricaprylin, tricaproin, tributyrin, and triacetin have been investigated. The velocity of crystallisation in all cases is small, the maximum speed (1.2 mm./min.) being shown by tristearin. The spontaneous crystallisation has also been studied. The first three glycerides mentioned above show three modifications, two unstable and one stable; the next three show two, one stable and one unstable, and the last three solidify to a glassy state. The unstable forms exist at the ordinary temperature, and change to the stable forms only at temperatures near the m. p. Solubility data for the triglycerides in benzene, ether, chloroform, and carbon disulphide are tabulated. In general, no depression of the m. p. of the solvent is to be observed, and the solubility curves for benzene as solvent consist of two parts and indicate the simultaneous existence of stable and unstable modifications. The results suggest that the triglycerides are polymerised and are colloidal in character and that a reversible equilibrium between the crystalline and colloidal states exists. Polymorphism is considered to be due to different degrees of polymerisation.

L. S. THEOBALD.

Polymorphism. K. LOSKIT (Z. physikal. Chem., 1928, 134, 156—159).—The solubility curves for the systems resorcinol—water, benzophenone—benzene, phenylsalicylate—benzene have been determined by the method previously described (preceding abstract). A sharp break in the curves occurs at 41.6% of resorcinol, 48% of benzophenone, and 49.7% of phenyl salicylate, respectively. This is the case with many monotropic, polymorphous substances. The cause of polymorphism, it is considered, lies in polymerisation, and, contrary to the views of Smits (A., 1927, 1027), the modifications of a substance are not co-existent and do not form mixtures with each other. Polymerisation and depolymerisation are analogous to electrolytic dissociation.

L. S. THEOBALD.

Relation between deviations of the vapour-pressure curves of binary mixtures of normal substances from the linear law, and the heats of mixing in the liquid phase. J. J. VAN LAAR (Z. physikal. Chem., 1928, 137, 421—446).—Theoretical. Expressions are deduced on a thermodynamical basis for the vapour pressure, heat of mixing, and for the volume changes of binary mixtures. The calculated values of the above quantities are compared with the experimental values of Schmidt (A., 1926, 787) for 21 binary mixtures.

F. G. TRYHORN.

Structure of copper-tin alloys. W. BRONIEWSKI and B. HACKIEWICZ (Compt. rend., 1928, 187, 651—654).—Copper-tin alloys of varying composition were annealed for prolonged periods at temperatures between 200° and 620°, and measurements were

then made of (1) electrical conductivity at 0°, (2) temperature coefficient of resistance between 0° and 100°, (3) thermo-electric power against lead at 0°, and its variation between -78° and +100°, (4) solution potential, (5) coefficient of expansion at 0°, and its variation between -186° and +218°, (6) Brinell hardness. The results are given in abstract only, and indicate that the compound Cu_3Sn_2 dissolves about 1% of copper and 5% of tin. The compound Cu_3Sn dissolves about 1% of each constituent according to the curves for thermo-electric power, but the other curves are less clear. The component Cu_4Sn is of fixed composition. W. HUME-ROTHERY.

Equilibrium diagram of the copper-tin system. T. ISIHARA (Sci. Rep. Tôhoku, 1928, 17, 927—937).—A redetermination of the solubility of tin in copper by microscopical examination and electrical resistance measurements following very prolonged annealing shows that the saturated solid solution contains 14% Sn between 0° and 510° and 12% Sn at the triple point at 790°. The existence of a narrow range of solid solution between 68 and 70% Cu could not be confirmed. At the composition corresponding with the compound Cu_3Sn the solidus and liquidus lines do not coincide, but a freezing interval exists between them. A. R. POWELL.

Equilibrium diagram of the molybdenum-carbon system. T. TAKEI (Sci. Rep. Tôhoku, 1928, 17, 939—944).—The system contains one compound only, Mo_2C , m. p. 2307°. This forms a limited range of solid solutions with molybdenum containing 5.5—6% C and a eutectic with about 4% C (m. p. about 2300°). The solubility of carbon in molybdenum is about 0.3%. The carbide may be isolated as a greyish-white powder by electrolytic dissolution of an alloy containing 5% C in hydrochloric acid; it has a hexagonal close-packed lattice with the constants $a=2.995 \text{ \AA.}$, $c=4.723 \text{ \AA.}$ A. R. POWELL.

Equilibrium diagram of the iron-iron sulphide system. K. MIYAZAKI (Sci. Rep. Tôhoku, 1928, 17, 877—881).—The equilibrium diagram of the iron-ferrous sulphide system has been redetermined by thermal analysis and by measurements of the electrical resistance, the constituents being melted together in an electric furnace under a layer of calcium chloride. The eutectic contains 83% FeS and melts at 985°; no solid solutions are formed at either end of the system. Pure ferrous sulphide melts at about 1190° (extrapolated). A. R. POWELL.

Equilibrium diagram of the iron sulphide-manganese sulphide system. Z. SHIBATA (Tech. Rep. Tôhoku, 1928, 7, 39—49).—The system iron sulphide-manganese sulphide has been investigated by thermal analysis and microscopically. The two components melt at $1163 \pm 2^\circ$ and $1610 \pm 3^\circ$, respectively. $\text{Fe}_3\text{Mn}_2\text{S}_5$ does not exist (cf. Röhl, A., 1912, ii, 1059). Solid iron sulphide and manganese sulphide are partly miscible and give rise to a eutectic at 1164°. C. W. GIBBY.

System LiCl-CoCl_2 . A. FERRARI (Atti R. Accad. Lincei, 1928, [vi], 7, 848—853).—The m.-p. curve for mixtures of lithium and cobalt chlorides shows a maximum corresponding with the formation of the double salt $2\text{LiCl} \cdot \text{CoCl}_2$. R. W. LUNT.

F. p.-solubility relations of geometrical isomerides. I. β -Chlorocrotonic acids. E. L. SKAU and B. SAXTON (J. Amer. Chem. Soc., 1928, 50, 2693—2701).—The f. p.-solubility diagram for the system β -chlorocrotonic acid- β -chloroisocrotonic acid was determined. The system is of the simple eutectic type. The molal heats of fusion of the separate acids are $\Delta H=20,300-94.15T+0.1426T^2$ and $\Delta H(\text{iso})=11,660-61.26T+0.1085T^2$, which yield values at the m. p. differing somewhat from those calculated from the f.-p. measurements. The system is not entirely ideal; complex and mixed crystal formation are probably absent. The existence of a slight heat of mixing would account for the observed results.

In the region of the m. p. the molal heat of fusion of crotonic acid is $\Delta H=3695-13.56t+0.0736t^2$ ($t=^\circ\text{C.}$), or 3100 g.-cal. at the m. p., 71.4°, corresponding with a molal entropy of fusion of 0.9 g.-cal./1° at the m. p. S. K. TWEEDY.

Velocity of hydration of dehydrated gypsum. P. P. BUDNIKOV (Kolloid-Z., 1928, 46, 95—97).—Hydration of natural and synthetic gypsum which has been dehydrated at 140° proceeds rapidly at first with formation of the hemihydrate, and then slowly with formation of a gel on the surface of gypsum nuclei; finally, the velocity increases once more as the dihydrate is formed. The first process lasts for 1 to 2 sec., the velocity of absorption of water depending on the time taken to dehydrate the original gypsum. E. S. HEDGES.

Velocity of dehydration of gypsum at various temperatures. P. P. BUDNIKOV (Kolloid-Z., 1928, 46, 97—99).—At the beginning of the process, the velocity of dehydration of synthetic gypsum is less than that of natural gypsum, except at 160°, where they are equal. Subsequently, the curve for the synthetic form meets that of the natural form at some point depending on the temperature, and thereafter lies above it. At the point corresponding with the formation of the hemihydrate a retardation in the velocity of dehydration was observed at 100° and at 140°. E. S. HEDGES.

Pharmaceutical combinations and the formation of molecular compounds. P. PFEIFFER and R. SEYDEL (Z. physikal. Chem., 1928, 137, 107—125).—Phase diagrams have been obtained for a number of binary mixtures of organic compounds which are often used medicinally. Orthoform (new) and antipyrine yield a molecular compound (1:1), m. p. 92°, sarcosine anhydride and orthoform (new) a (1:1) compound, m. p. 146°, sarcosine anhydride and methyl *p*-hydroxybenzoate a (1:2) compound, m. p. 99°, sarcosine anhydride and *o*-aminophenol a (1:1) compound, m. p. 101°, and sarcosine anhydride and methyl *m*-aminobenzoate a (1:2) compound, m. p. 64°. No evidence has been obtained of compound formation between orthoform (new) and pyramidone or acetamidoantipyrine; antipyrine and luminal, *o*-aminophenol, methyl *m*- or *p*-aminobenzoate, or methyl *p*-hydroxybenzoate; pyramidone and *o*-aminophenol, methyl *p*-hydroxybenzoate, or methyl *m*- or *p*-aminobenzoate. H. F. GILLBE.

System $\text{KNO}_3\text{-HNO}_3\text{-H}_2\text{O}$. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 844—846; cf. A., 1927,

628).—The earlier work at 25° has been extended to 40° and 60°. At neither temperature is there evidence of double salt formation. R. W. LUNT.

System $\text{KNO}_3\text{--Al}(\text{NO}_3)_3\text{--H}_2\text{O}$. G. MALQUORI (Atti R. Accad. Lincei, 1928, [vi], 7, 846–848).—Data for this system at 0°, 40°, and 60° show, in agreement with earlier work at 25° (A., 1927, 518), that the solid phase consists of KNO_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. R. W. LUNT.

Ternary system ammonium chloride, ammonium succinate, and water. (MISS) J. C. LANZING (Rec. trav. chim., 1928, 47, 901–903).—No compound is formed between the components of this system at 25.2°. O. J. WALKER.

Ternary systems. VII. Periodates of the alkali metals. A. E. HILL (J. Amer. Chem. Soc., 1928, 50, 2678–2692; cf. A., 1927, 1142).—The influence of potassium hydroxide on aqueous potassium metaperiodate solution at 25° indicates that KIO_4 and $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ (dimesoperiodate) are the only salts which can be obtained from the solution at this, or higher, temperature. There is no indication of the salts $\text{K}_3\text{HI}_2\text{O}_9$ and $\text{K}_3\text{IO}_5 \cdot 4\text{H}_2\text{O}$. The solubility of potassium metaperiodate is recorded; it is 0.0238 mol./litre at 25°. The dimesoperiodate is very soluble and the temperature coefficient is large; it undergoes transition to the anhydrous form at about 78°. Similar experiments with sodium metaperiodate show that this is readily soluble (12.62% at 25°) and is converted into the slightly soluble (0.23% at 25°) paraperiodate (not hydrated dimesoperiodate), $\text{Na}_2\text{H}_3\text{IO}_6$, in presence of the smallest quantity of sodium hydroxide. The only other salt precipitated from the aqueous solution is $\text{Na}_3\text{H}_2\text{IO}_6$, and then only when excess of sodium hydroxide is present; this salt, which is a true salt of the para-series, cannot be crystallised from water without hydrolysis, which explains discrepancies previously observed in the preparation of sodium metaperiodate by oxidation of the iodate by chlorine. The transition $\text{NaIO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{NaIO}_4 + 3\text{H}_2\text{O}$ occurs at 34.5°. The solid salt, Na_5IO_6 , appears not to exist. The solubilities at 25° of the metaperiodates in periodic acid solutions do not disclose the formation of any acid periodates. The possible application of the results in the analytical separation of potassium and sodium is discussed. Lithium periodate could not be prepared pure and ammonium periodate could not be prepared at all by the oxidation by chlorine of the iodates in presence of the appropriate base. The solubility of the crystals $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$, d 2.3, is about 53% at the ordinary temperature. S. K. TWEEDY.

System $\text{AlCl}_3\text{--KCl--HCl--H}_2\text{O}$ between 0° and 80°. G. MALQUORI (Gazzetta, 1928, 58, 562–568; cf. this vol., 956).—The only solids which can exist in contact with the saturated solutions are potassium chloride and the hydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Tetrahedral diagrams are given showing the composition of the aqueous phase at the various temperatures. From these a model is constructed which gives the proportions of potassium chloride, aluminium chloride, and hydrochloric acid in solutions saturated with respect to the two salts. O. J. WALKER.

Formation and decomposition of sodium salicylate. I. A. DAVIES (Z. physikal. Chem., 1928, 134, 57–86).—The formation of sodium salicylate from sodium phenoxide and carbon dioxide and the thermal decomposition of sodium salicylate have been investigated by means of measurements of the p -time curves at various temperatures and of the p -temperature curves. Above 140°, sodium phenoxide and carbon dioxide result primarily from the thermal decomposition of sodium salicylate, and this is a case of “unilateral” equilibrium (cf. Baur and Orthner, A., 1916, ii, 232). Secondly, disodium salicylate and phenol are formed by double decomposition from the phenoxide and salicylate. This equilibrium over the range 160–220° is completely reversible. The p -temperature curve shows a break at 190° and 4.15 atm., corresponding with a quintuple point in the three-component system with the phases sodium salicylate, disodium salicylate, the phenoxide, solution, and gas. Below this point the system salicylate–disodium salt–phenoxide–gas is stable, and above, the system salicylate–disodium salt–solution–gas. In the formation of sodium salicylate from sodium phenoxide and carbon dioxide, two definite intermediate products, “ester salt I and II,” are formed. Both of these show a definite dissociation pressure, the first being metastable to the second, which in turn is metastable with regard to sodium salicylate. L. S. THEOBALD.

Sodium salicylate and salicylic acid and “unilateral” equilibrium. E. BAUR (Z. physikal. Chem., 1928, 134, 87–91).—The work of Davies (cf. preceding abstract) is discussed. Data on the thermal dissociation of salicylic acid show this to be another case of “unilateral” equilibrium. L. S. THEOBALD.

Establishment of equilibrium from one side or from both sides, as described in the literature. E. BAUR (Z. physikal. Chem., 1928, 137, 63–71).—Discursive. H. F. GILLBE.

Heat of dilution of potassium chloride up to infinite dilution. E. LANGE and P. A. LEIGHTON (Z. Elektrochem., 1928, 34, 566–571).—The integral heats of dilution of $N/100$, $N/200$, and $N/300$ (approx.) solutions of potassium chloride were measured at 12.5° and 25° in a slightly improved form of the apparatus previously described (Lange and Messner, this vol., 134). Below $N/100$ the heat of dilution is proportional to the square root of the salt concentration, as required by the Debye–Hückel theory. As far as can be inferred from the unsatisfactory and meagre results available the heats of dilution of uni-univalent salts are equally great in very dilute solution. S. K. TWEEDY.

Effect of certain corrections on the heat of combustion of organic compounds. W. SWIENTOSLAWSKI and H. STARCZEWSKA (Bull. Acad. Polonaise, 1928, A, 87–97).—See this vol., 845.

Accuracy of Stohmann's thermochemical data. W. SWIENTOSLAWSKI (Rec. trav. chim., 1928, 47, 896–900).—Polemical. A reply to the criticism by Verkade and Coops (this vol., 712) of the author's correction of Stohmann's data. O. J. WALKER.

Electrical conductivity of hydrochloric, hydrobromic, and hydriodic acids, and the mobility of

the hydrogen ion. M. HLASKO and D. WAZEWSKI (Bull. Acad. Polonaise, 1928, A, 181—190).—The equivalent conductivities of hydrochloric, hydrobromic, and hydriodic acids were determined by Kohlrausch's method, with a view to discover whether the strength of the acid increased as the atomic weight of the atom attached to the hydrogen atom increased. This increase in strength has been found in similar series of acids. It was found that hydriodic acid was a stronger acid than hydrobromic, and hydrobromic than hydrochloric, although the differences are small. The values of the equivalent conductivity obtained are greater than those usually accepted. In very concentrated solutions, however, the equivalent conductivity and degree of dissociation of hydrochloric acid are larger than those of hydrobromic acid, and the latter than those of hydriodic acid. This can be explained by the rule of Nernst and Thomson if the difference in dielectric constants of solutions of equivalent concentrations are taken into account. The viscosities and densities of the concentrated acid solutions were also determined. The viscosities diminish in the order hydrochloric, hydrobromic, hydriodic acid. The differences are, however, small. The mobility of the hydrogen ion at 25° was found to be 355.1.

A. J. MEE.

Relaxation time of ionic layers in the irreversible passage of electricity in strong electrolytes. H. FALKENHAGEN and J. W. WILLIAMS (Z. physikal. Chem., 1928, 137, 399—420; cf. this vol., 596, 957).—In amplification of previous work the significance of the ionic relaxation time is considered, and it is shown that it affords explanations of the dispersion effect in conductivity and of the field strength effect of Wien. The possibility thereby arises of eliminating experimentally the effect of the mutual coupling of ions, and of determining the actual degree of ionisation existing in a strong electrolyte solution.

F. G. TRYHORN.

Electrical conductivity and diffusion in crystallised compounds. A. SMEKAL (Z. Elektrochem., 1928, 34, 472—480).—A general account of work on this subject which has mostly been abstracted previously (cf. A., 1926, 564; 1927, 192).

S. K. TWEEDY.

Calculation of theoretical [electrode] potentials from thermal data. P. DROSSBACH (Z. Elektrochem., 1928, 34, 715—716).—A reply to Devoto's criticism (this vol., 481) of the author's method of calculation of the theoretical potentials of sodium, potassium, and calcium (cf. this vol., 481). The method is shown to have a thermodynamic basis.

In a note added by DEVOTO, it is pointed out that his own values for the alkali metals agree with those calculated by Latimer by a different method (cf. A., 1927, 941).

L. L. BIRCUMSHAW.

Nature of gas-metal electrodes. S. J. FRENCH and L. KAHLENBERG (Trans. Amer. Electrochem. Soc., Sept. 1928. Advance copy, 28 pp.).—The separate effects of the gases oxygen, hydrogen, and nitrogen on the single potentials of various metals half immersed in a potassium chloride solution have been examined. The gases were introduced under a bell-tube suspended over the metal electrode and escaped from an outlet

at the top of this tube. With hydrogen and nitrogen the potentials of the metals became temporarily less negative but then notably more negative than the values in air and approached constant values which are specific for each metal and gas. On closing the gas outlet from the bell-tube and stopping the gas stream so that the metal remains half in the gas-saturated electrolyte and half in the gas atmosphere above, a sharp change of potential, usually towards more negative values, is generally observed, but on further keeping the potential tends to become less negative again, and eventually approaches the air potential. On passing oxygen the potential of a metal becomes somewhat more positive than the value in air, and, on stopping the gas stream when a constant value has been attained, a sharp change in potential is often observed, but the direction of the change depends on the metal employed. Most metals could readily be changed from hydrogen electrodes to oxygen electrodes, whereas the reverse change took a considerable time; with platinum and palladium the converse is true. If the solution was vigorously stirred when a metal base assumed its equilibrium potential in air, the potential immediately changed to a somewhat less negative value, but on passing hydrogen a more negative equilibrium value was attained than in an unstirred solution. Stopping the gas supply while stirring was continued caused no abrupt change of potential, but stopping stirring produced a sharp change of potential. It is suggested that the potentials of metals in the presence of gases arise, not only from absorption of the gas by the metal, but also from the formation of a condensed layer of the gas on the metal surface. Bubbling the gas through the electrolyte or stirring it vigorously prevents the formation of this condensed layer. Experiments with metals coated with collodion, gum mastic, or similar substances showed that the behaviour of a coated electrode in an unstirred solution was the same as that of an uncoated electrode in a stirred solution. Such coatings therefore prevent the formation of the condensed layer. Among other gases, carbon monoxide and methane alter the potentials of platinum and palladium materially, and helium has a very slight effect.

H. J. T. ELLINGHAM.

Oxidation-reduction potentials of the pentacyanoferroates. D. DAVIDSON (J. Amer. Chem. Soc., 1928, 50, 2621—2630).—The oxidation-reduction potentials of some complex iron cyanides were measured against the *N*-calomel electrode. Evidence was obtained for the existence of the compound $2\text{Na}_3\text{Fe}(\text{CN})_5 \cdot \text{H}_2\text{O} \cdot 3\text{Na}_2\text{Fe}(\text{CN})_5 \cdot \text{H}_2\text{O}$.

S. K. TWEEDY.

Oxidation-reduction systems of biological significance. I. Reduction potential of cysteine. L. MICHAELIS and L. B. FLEXNER (J. Biol. Chem., 1928, 79, 689—722).—A definite negative potential, which is a logarithmic function of the concentration of cysteine and of hydrogen ions, is slowly established at a platinum electrode in a solution of cysteine in the complete absence of oxygen. Bubbling hydrogen through the solution, after attainment of equilibrium, causes the potential to become more negative. The presence of small amounts of oxygen accelerates the establishment of a definite potential and makes this:

potential more positive. Gold-plated platinum electrodes behave similarly, save that the establishment of the final potential is slower, and its magnitude is less affected by hydrogen. With solid gold electrodes equilibrium is attained more rapidly, but the potential reached varies with each electrode. Mercury electrodes give the same final potential as platinum, but equilibrium is reached much more quickly and is less affected by oxygen. In accordance with the results of Dixon and Quastel (J.C.S., 1923, 123, 2943), cystine is without effect on the cysteine potential; ferrous sulphate and potassium cyanide were also without effect. The explanation of Dixon (A., 1927, 209) of the behaviour of cysteine is rejected on the ground that, on his hypothesis, saturation of a cysteine solution with hydrogen, by suppressing diffusion of the latter from the metal, should lead to establishment of the hydrogen potential, which is, experimentally, not the case; it is considered that no satisfactory explanation of the phenomenon can yet be offered. It is pointed out that the anaërobic potential of cysteine is sufficiently negative to account for the reduction of indicator dyes by tissues under anaërobic conditions.

C. R. HARRINGTON.

Pyrochemical Daniell cells. R. LORENZ and F. MICHAEL (Z. physikal. Chem., 1928, 137, 1—17).—The following *E.M.F.* (millivolts) have been determined: $\text{Sn}|\text{SnCl}_2|\text{Ti}_2\text{Cl}_2|\text{Ti}$, $403 + 0.45(T - 500)$ for $T > 427^\circ$, and $370 + 0.18(T - 427)$ for $T < 427^\circ$; $\text{Pb}|\text{PbCl}_2|\text{TiCl}|\text{Ti}$, $365 + 0.39(T - 500)$; $\text{Zn}|\text{ZnCl}_2|\text{SnCl}_2|\text{Sn}$, $306 - 0.1(T - 500)$; $\text{Zn}|\text{ZnCl}_2|\text{CdCl}_2|\text{Cd}$, $148 - 0.13(T - 575)$; $\text{Zn}|\text{ZnCl}_2|\text{PbCl}_2|\text{Pb}$, $276 - 0.095(T - 500)$; $\text{Zn}|\text{ZnCl}_2|\text{TiCl}|\text{Ti}$, $110 + 0.48(T - 500)$; $\text{Mg}|\text{MgCl}_2|\text{PbCl}_2|\text{Pb}$, $1078 + 1.075(T - 720)$; $\text{Mg}|\text{MgCl}_2|\text{CdCl}_2|\text{Cd}$, $974 + 1.07(T - 720)$; $\text{Mg}|\text{MgCl}_2|\text{TiCl}|\text{Ti}$, $530 - 0.43(T - 720)$; $\text{Mg}|\text{MgCl}_2|\text{ZnCl}_2|\text{Zn}$, $759 - 0.73 \times (T - 720)$.

H. F. GILLBE.

Characteristics of alkali cells and their significance for photo-electric methods of measurement. R. FLEISCHER and H. GOLDSCHMIDT (Physikal. Z., 1928, 29, 691—698).—The discharge method of measuring light intensity is discussed theoretically. Experimental work on alkali cells constructed in different ways shows that the inclination of the current-voltage characteristic to the abscissa depends largely on the frequency of the incident light. The angle, starting from the red end of the spectrum, at first increases with increasing frequency, reaches a maximum, and then decreases. The position of the maximum varies with different types of cells. Without a knowledge of the cell characteristic, comparable and trustworthy data cannot be secured especially when corrections due to insulation defects are necessary. The best results are obtained when the current-voltage curves run parallel to the voltage axis, a condition obtained only with highly evacuated cells.

R. A. MORTON.

Gaseous explosion rates at constant pressure. F. W. STEVENS (Ind. Eng. Chem., 1928, 20, 1018—1026).—Constant pressure conditions were adopted, as hydrodynamic disturbances are then less profound than at constant volume. Various mixtures of carbon monoxide and methane with oxygen were enclosed in a soap bubble and exploded from the centre, the

soap bubble acting as a constant-pressure bomb. The rate of propagation of the zone of explosive reaction, determined by photographing the explosion on a film moving at a known speed, was uniform for each individual mixture and proportional to the product of the concentrations of the reacting gases. The effect on the rate of propagation of adding various percentages of inert gases, viz., helium, argon, nitrogen, and carbon dioxide, was similar for small additions, but for large additions depended on the physical characteristics of the gas added. Mixtures of methane, carbon monoxide, and oxygen followed the same laws as the simpler mixtures of two gases, and it was found possible to predict the velocity of propagation in any such mixture if its composition and the coefficients governing the explosions between (a) carbon monoxide and oxygen and (b) methane and oxygen are known. The maximum velocities for methane-oxygen and carbon monoxide-oxygen mixtures were 625 cm. per sec. and 100 cm. per sec., respectively, those for the ternary mixtures lying between these limits.

F. J. DENT.

"Normal" propagation of flame in gaseous mixtures. W. PAYMAN (Ind. Eng. Chem., 1928, 20, 1026—1032).—A correlation of the available data on flame speeds in mixtures of air with hydrogen, carbon monoxide, methane (and other paraffin hydrocarbons), ethylene, and acetylene ignited under different conditions, e.g., in tubes of varying diameter, in closed cylinders, etc. A comparison of the speed-percentage curves reveals relationships which it is hoped to extend as a result of work now in progress, a preliminary description of which is given. The determination of absolute values of flame speed is discussed, and the utility of the law of flame speeds in calculating speed-percentage curves for complex inflammable gases is indicated.

A. WILSON.

Gaseous explosions. VI. Flame and pressure propagation. J. V. HUNN and G. G. BROWN (Ind. Eng. Chem., 1928, 20, 1032—1040; cf. B., 1925, 487; 1927, 243, 322).—Previous investigators of gaseous explosions have noted the rise in pressure at one point of the explosion chamber. Apparatus is now described whereby pressure records at several points are obtained. A cylindrical steel bomb, provided with a narrow longitudinal plate-glass window, was fitted with six equally-spaced pressure elements of the diaphragm type, placed above the flame window. Flame travel and time pressure charts were obtained photographically, the latter from the deflexion of a pencil of light from a concave mirror, mounted on the pressure elements and focussed on a revolving drum. Carbon disulphide and oxygen were used in the bomb. Examination of these charts showed that during the propagation of the flame through the explosive mixture a pressure wave behind, but travelling at a greater velocity than, the flame front was set up in the burning mixture. The maximum pressure of this wave was greater than that of the flame front or the unignited mixture. This pressure wave, overtaking the flame front, causes the latter to halt and recede. Maximum pressure in mixtures promoting after-burning was developed some time after total inflammation of the charge.

C. B. MARSON.

Influence of steam and of hydrogen on the burning of carbon monoxide. H. B. DIXON (*Nature*, 1928, 122, 805).—The effect of hydrogen and of steam on the ignition temperature of carbon monoxide in air depends on the atmospheric pressure and differs in the two cases. Carbon monoxide containing 1% of hydrogen may ignite in dry air either above or below the temperature at which carbon monoxide ignites in air containing 1% of steam. A. A. ELDRIDGE.

Flame speed of hydrogen sulphide. D. S. CHAMBERLIN and D. R. CLARKE (*Ind. Eng. Chem.*, 1928, 20, 1016—1018).—Apparatus and a method for determining the flame speed of hydrogen sulphide in air are described, the gas being burnt in a horizontal glass tube (1 m. \times 2.5 cm. diam.) and flame records made by the photographic method, using a moving film. The flame speed curve of hydrogen sulphide-air mixtures resembles those of other combustible gases except for deviations due to formation of sulphur and selective oxidation of hydrogen under certain conditions. A mixture containing 10.8% of hydrogen sulphide gave the maximum flame speed of 49.5 cm. per sec. The production of sulphur trioxide by burning hydrogen sulphide in an internal-combustion engine is suggested. C. B. MARSON.

Explosibility of anæsthetics. A. P. HORNER and C. B. GARDENIER (*Anæsth. and Analg.*, 1928, 7, 69—72).—The following percentage limits of explosibility were determined: ethylene 4—14.5, air 96—85.5; ethylene 5—70, oxygen 95—30; ethylene 5—35, nitrous oxide 95—65; ethylene 5—47, nitrous oxide 85—43 (oxygen 10); ethylene 5—20, nitrogen 85—70 (oxygen 10); ethylene 5—55, oxygen 95—40 (carbon dioxide 5); ether 5—14.5, air 95—85.5; ether 5—65, oxygen 95—35; ether 5—30, nitrous oxide 85—60 (oxygen 10); ether 5—60, oxygen 90—35 (carbon dioxide 5). CHEMICAL ABSTRACTS.

Chemical interactions corresponding with the constant of mass action being a function of the volume and masses of the constituents as well as of the temperature, and catalytic action. R. D. KLEEMAN (*Phil. Mag.*, 1928, [vii], 6, 648—659; cf. this vol., 937).—Further applications of the author's earlier thermodynamic deductions are made. It is deduced that a solid substance which condenses a gaseous substance on to its surface has a catalytic effect on the constant of mass action involving the gaseous substance. An extension of the principles to ionisation in solution indicates that when an electrolyte dissociates easily into ions the constant of mass action (dissociation constant) is a function of the volume of the solution as well as of the temperature. This is interpreted as signifying that either the chance of a molecule dissociating into ions depends on its previous encounters with other molecules, or that the chance of two ions of opposite sign combining on collision depends on previous encounters with other ions and molecules, or that both effects occur. Values of the dissociation constant of potassium chloride, in aqueous solution, calculated from the theory are in fair agreement with those usually accepted. A. E. MITCHELL.

Oxidation of sulphur vapour at low pressures. N. SEMENOV and G. RJABININ (*Z. physikal. Chem.*, 1928, B, 1, 192—204).—As in the case of phosphorus vapour (this vol., 483; cf. Chariton and Walta, A., 1927, 122), sulphur vapour can burn in oxygen only between definite limits of pressure. This pressure interval increases with rise of temperature which fixes the pressure of sulphur vapour. The velocity of ignition, which may be very great, is independent of the oxygen pressure, and probably depends on the velocity of volatilisation of sulphur. It is supposed that, outside these limits of pressure, the number of active centres which, from the conditions of the experiments, may be either ozone molecules or oxygen atoms, does not reach the necessary value for ignition. The values of the limiting partial pressures of oxygen are not altered, as in the case of phosphorus vapour, by the presence of foreign gases. Even in the region of effective pressures spontaneous ignition takes place only when a very small quantity of ozone is introduced by some means. These results are regarded as confirmation of the theory of chain reactions and might probably form a basis for the theoretical treatment of some of the phenomena of homogeneous catalysis, e.g., the part played by traces of moisture. M. S. BURR.

Action of iodine on phosphorous acid and sodium phosphite. A. BERTHOUD and W. E. BERGER (*J. Chim. phys.*, 1928, 25, 568—580).—Reaction velocity measurements have been made for the action of iodine on (a) phosphorous acid and (b) sodium phosphite in aqueous solution (cf. Steele, J.C.S., 1908, 93, 2203). In reaction (a) the velocity is proportional to the concentration of iodine and to the concentration of undissociated phosphorous acid, increases slightly with the hydrogen-ion concentration, and is independent of the iodide concentration. In all the experiments phosphorous acid or phosphite and potassium iodide were present in excess from the beginning of the reaction. In reaction (b) the velocity is also proportional to the iodine concentration, but increases slightly more rapidly than the phosphite concentration. Increase in concentration of hydrogen ion or of iodide decreases the velocity. The temperature coefficients of the unimolecular velocity coefficients are for (a) about 3.8 between 25° and 45° and for (b) 4.81—4.01 between 0° and 30°. The different mechanisms of the two reactions are discussed. In neither case is the reaction sensitive to light. O. J. WALKER.

Neutral salt action in ionic reactions. II. Concentrated salt solutions. A. VON KISS (*Z. physikal. Chem.*, 1928, 134, 26—32; cf. A., 1927, 632, 1150).—The reaction between persulphate and iodine ions in the presence of various salts has been investigated. With solutions of magnesium sulphate as solvent, the effect of the concentration of the reacting components on the velocity coefficient disappears almost completely in concentrated salt solutions. The reaction is accelerated markedly and to widely varying extents by the presence of the sulphates of magnesium and sodium, the nitrates of magnesium, potassium, and ammonium, and the chlorides of lithium, sodium, and potassium. The data show

that in concentrated salt solutions neutral salt action follows the law of Grube and Schmid (A., 1926, 474) that the value of $\log k$ is linearly proportional to the salt concentration.

L. S. THEOBALD.

Alkaline hydrolysis of edestin. I. S. JAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1928, 60, 929—932).—Sodium hydroxide solutions hydrolyse edestin three to four times as rapidly as acids of the same concentration.

R. TRUSZKOWSKI.

Velocity coefficients of hydrolysis of nitroacetanilide and of the secondary reaction of hydrolysis of *p*-nitroaniline with elimination of ammonia. A. A. KUROTSCHKIN (J. Russ. Phys. Chem. Soc., 1928, 60, 1147—1150).—The velocity coefficient for the hydrolysis with 4% sodium hydroxide solution of *p*-nitroacetanilide at 100° is 0.0025, and that of formation of *p*-nitrophenol from *p*-nitroaniline is 0.0005.

R. TRUSZKOWSKI.

Velocity of esterification of anisic and gallic acids in ethylene glycol and glycerol. A. KAILAN and A. BRABÉE (Monatsh., 1928, 50, 149—180; cf. this vol., 961, 962).—The velocity of esterification of anisic and gallic acids at 25° in anhydrous and moist ethylene glycol and glycerol in presence of hydrogen chloride as catalyst has been measured, and the unimolecular velocity coefficients have been expressed as a function of the concentration of water (w) and of hydrogen chloride (c) in intrapolation formulæ. The velocity coefficients, even at small water concentrations, increase more rapidly than the concentrations of hydrogen chloride. The ratios of the velocity coefficients in ethyl alcohol (k_a) (cf. Kailan, A., 1907, ii, 242), in glycerol (k_g), and in ethylene glycol (k_e), are, for anisic acid at $c=0.166$ mol./litre, $k_a/k_g=1.53$, $k_e/k_g=0.87$, and, at $c=1.35$, 0.34 and 1.64. The corresponding figures for gallic acid are 1.90, 1.06, 0.41, and 1.25. Thus gallic acid, like most of the acids already investigated, is more rapidly esterified in ethylene glycol than in glycerol, but this is the case with anisic acid only at high concentrations of water. In ethylene glycol and glycerol, as in alcohol, the effect of methylation of a *p*-hydroxyl group is small. In the case of gallic acid, as of all disubstituted benzoic acids so far investigated, the velocity coefficient of the esterification catalysed by hydrogen chloride is less than that calculated on the assumption that the effect of substituents is simply additive. At 183° the uncatalysed esterification of anisic acid in glycerol, similarly to previously investigated acids, follows the equation for a "sesquimolecular" reaction. The coefficients in glycerol when $w=1$ are about 20% less than in anhydrous glycerol. Increase of w to 2 causes no further decrease. In the uncatalysed esterification at 183° the back-reaction cannot be neglected as in the catalysed reactions at 25°.

R. K. CALLOW.

Rate of reaction of liquid and gaseous zinc with carbon monoxide. R. W. MILLAR (J. Amer. Chem. Soc., 1928, 50, 2707—2709).—The above reaction is extremely slow at 600—700° in the absence of a catalyst, such as iron. It is possibly slower than the reaction $2CO=CO_2+C$ under the same conditions. Zinc reduces carbon dioxide rapidly at these temperatures.

S. K. TWEEDY.

Action of aqueous sodium polysulphide solutions on metallic copper. K. FISCHBECK and E. ELBEN (Z. Elektrochem., 1928, 34, 642—645).—The times taken by sulphide solutions of various concentrations to form cuprous sulphide layers on metallic copper of a standard colour were measured. With solutions containing virtually sodium pentasulphide the velocity of thickening of the layer is proportional to the polysulphide content of the solution and inversely proportional to the thickness of the layer. An analogous result is obtained with sulphur vapour. The method of observation previously used (A., 1926, 692) cannot be applied to the interaction of sulphur and copper. Some observations are made on sulphide solutions; the pentasulphide ion is probably more highly coloured than the tetrasulphide ion.

S. K. TWEEDY.

Metallic corrosion in the light of quantitative measurements. II. G. D. BENGOUGH, J. M. STUART, and A. R. LEE (Proc. Roy. Soc., 1928, A, 121, 88—121; cf. this vol., 250).—Corrosion-time curves have been obtained for annealed zinc in conductivity water and in dilute potassium chloride solution ($N=0.00005N$) under 1 atm. of oxygen pressure at 25°. The curves usually have a short branch, concave upwards, extending from zero time to 2—3 days, during which period a negative electrode potential is probably being built up at certain isolated positions on the metal surface. As far as the oxygen type of corrosion is concerned, the initial branches pass into second branches which may be either exponential or linear in form. The exponential type is reached when there is an ample supply of oxygen and the main controlling factor is the rate of withdrawal of chlorine ions from the solution. These conditions are satisfied only in solutions weaker than 0.001*N*, even in large vessels. The straight-line type is realised in solution stronger than 0.001*N* in medium-sized vessels, when oxygen is the controlling factor. The final branches of the curves are approximately straight lines, slightly inclined to the horizontal. With conductivity water and potassium chloride solutions of 0.00005*N* or less, no evolution of hydrogen is observed, but with solutions from 0.00001*N* and upwards, hydrogen is always evolved, except when very highly purified zinc is used. The cause of the hydrogen evolution from neutral salt solutions is discussed. Gas evolution-time curves have been obtained under various conditions, and their form is explained on the assumption that overvoltage as affected by metallic impurities is the determining factor. The proportion of total corrosion due to hydrogen varies between about 5 and 14% for solutions between 0.00001*N* and 0.1*N*. Curves for total corrosion are not exponential in form, probably because part of the corrosion is being carried on by some secondary process independent of chlorine ions, especially as regards hydrogen evolution and during the later period of the experiments. It is suggested that the relative maintenance of hydrogen-evolution type of corrosion may be due to the accumulation of potassium hydroxide towards the end of the experiments. The total amount of corrosion obtained for standard specimens in water of about 0.055 mho

conductivity is only about 1 mg. of zinc after 50 days. This is probably partly due to traces of non-metallic impurity (e.g., dust particles). The total amount of corrosion that has occurred when the corrosion-time curves of potassium chloride have become nearly horizontal is independent of the oxygen supply, but dependent on the concentration of the solution, and the rate of withdrawal of chlorine ions from current-carrying capacity. The effect of precipitated corrosion products on the rate and amount of corrosion is found to be very small, even after 100 days from the start of the experiment. Extreme purification of the zinc has only a slight effect on the total corrosion in 0.0001*N*-potassium chloride, the effect being due to the suppression of the gas-evolution type of corrosion. In potassium chloride solution, the total corrosion is greatly affected by the nature of the metallic surface. Highly-worked surfaces give more variable, and usually lower, results than annealed surfaces. Annealing the specimens for a week at 250–260° gives fairly concordant results. The most satisfactory methods for determining relative corrosion are discussed. L. L. BIRCHSHAW.

Double carbonate of copper and sodium. F. DE CARLI and P. AGOSTINI (*Atti R. Accad. Lincei*, 1928, [vi], 7, 921–925).—The rate of dehydration of the double carbonate of sodium and copper, $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$, has been examined at 80° and 120°. At the lower temperature 1 mol. of water of crystallisation is lost and at the higher temperature the anhydrous salt is formed. The decomposition of the anhydrous salt is reversible according to the reaction $\text{Na}_2\text{CO}_3 \cdot \text{CuCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{CuO} + \text{CO}_2$; from the variation of the partial pressure with temperature the heat of formation of copper carbonate per mol. is found to be 138,300 g.-cal. R. W. LUNT.

Velocity of acid hydrolysis of cotton cellulose by hydrochloric acid, alone, and in the presence of alkali chloride. E. HUNTER (*J.C.S.*, 1928, 2643–2648).—An attempt has been made to determine whether the principles of activity can be extended to the consideration of the catalysis by hydrogen ions of a heterogeneous reaction such as the hydrolysis of cotton cellulose in solutions of hydrochloric acid both alone and in the presence of potassium, sodium, or lithium chlorides. With dilute acid solutions the ultimate product of hydrolysis is hydrocellulose, and under such conditions there exists a linear relationship between the rate of hydrolysis and the hydrogen-ion activity of the solution. For strongly acid solutions the results of the velocity measurements are untrustworthy owing to the tendency of the hydrocellulose to undergo further hydrolysis.

The linear relationship between hydrogen-ion activity and rate of hydrolysis does not hold for acid-salt solutions. Over the range of concentrations examined, of two solutions having the same hydrogen-ion activity, that with neutral salt present gives a higher reaction velocity than that with acid alone. It is suggested that these results may be explained by assuming that the added salt lowers the activity coefficient of the "critical complex" [(cellulose) H^+ , H_2O]. F. J. WILKINS.

Photographic study of detonation in solid explosives. I. Measurement of rate of detonation. E. JONES.—See B., 1928, 875.

Sixth report of committee on contact catalysis. R. E. BURK (*J. Physical Chem.*, 1928, 32, 1601–1645).

Thermodynamic theory of catalysis. R. DUBRISAY (*J. Chim. phys.*, 1928, 25, 581–586).—The various definitions of the term "catalyst" are reviewed. A catalyst is defined theoretically as a substance which modifies the velocity of a chemical reaction whilst obeying the following two conditions: (a) it can be introduced into or removed from the system without any accompanying energy change, and (b) it is itself unchanged at the end of the reaction. These conditions are not obeyed ideally, but are fulfilled sufficiently exactly by many catalysts, since the amount of catalyst is small compared with the amounts of the reactants and of the products. The thermodynamic treatment of catalysis starting from this definition is not opposed to the kinetic explanation of catalytic phenomena by means of the Arrhenius theory, which makes use of activated molecules. O. J. WALKER.

Problems in homogeneous catalysis. T. M. LOWRY (*Trans. Faraday Soc.*, 1928, 24, 545–551).—A paper introductory to a general discussion on homogeneous catalysis. F. G. TRYHORN.

Homogeneous catalysis. C. N. HINSHELWOOD (*Trans. Faraday Soc.*, 1928, 24, 552–559).—A review of studies of the mechanisms of homogeneous reactions and of the influence on them of traces of foreign substances and of solvents and inert gases, and of the theories of the energy transfer phenomena characteristic of such reactions. F. G. TRYHORN.

Influence of nitrogen peroxide on the union of hydrogen and oxygen. A problem of "trace catalysis." C. H. GIBSON and C. N. HINSHELWOOD (*Trans. Faraday Soc.*, 1928, 24, 559–562).—The union of hydrogen and oxygen is accelerated and the explosion temperature lowered by 200° by the presence of traces of nitrogen peroxide. There occurs, however, no transition region as the percentage of nitrogen peroxide in the mixture is increased. The catalysed reaction occurs abruptly when a certain lower limit in the amount of nitrogen peroxide is reached, and ceases as abruptly when the peroxide is present in amounts greater than a fixed upper limit. At 371° these limits are 0.22 mm. and 0.83 mm., respectively, for a mixture of hydrogen and oxygen in stoichiometric proportions and of a total pressure of 600 mm. The lower limit of effectiveness of the nitrogen peroxide was practically constant between 371° and 421°, but the upper limit increased from 0.83 to >3.3 mm. over the same temperature range. It is suggested that the explosion of the hydrogen and oxygen is initiated by ordinary ignition by the heat liberated in some independent reaction of the nitrogen peroxide. F. G. TRYHORN.

Catalytic phenomena in the tautomerism of certain α -diketones. H. MOUREU (*Trans. Faraday Soc.*, 1928, 24, 562–565).—A study has been made of the catalytic interconversion of the tautomeric forms of benzylmethylglyoxal and phenylbenzylglyoxal. If

the ketonic form (*B*) of lower m. p. is treated in the super-cooled state with a trace of an alkaline catalyst (benzylamine, diethylaniline, quinoline, pyridine, diethylamine, piperidine, or potassium hydroxide) there follows a change, more or less rapid (from a few seconds up to three days in duration) according to the nature and concentration of the catalysts, into the enolic (*A*) form of higher m. p. If the temperature is below that at which equilibrium exists between the two forms in a saturated solution of isomeride *A* in isomeride *B*, isomeride *A* crystallises out and the conversion into this form is complete. The change is also complete if the reaction occurs at the b. p. of the form *B* owing to the removal of this form by reason of its greater volatility. At intermediate temperatures an equilibrium mixture of *A* and *B* is formed of which the composition is dependent on temperature. Investigation of the effect of temperature on the composition of the equilibrium mixture showed that rise of temperature favoured the formation of the ketonic form, and that the conversion of the ketonic form into the enolic is exothermal. Evidence is adduced indicating that an intermediate compound is formed with the catalyst during the conversion. Glass acts as a catalyst for this change, but the *B* isomeride may be preserved unchanged in quartz vessels.

F. G. TRYHORN.

Ionisation in chemical change. N. R. DHAR (Trans. Faraday Soc., 1928, 24, 565—567).—A summary of the types of reaction of which the mechanism can be explained by assuming the generation of ions in exothermal chemical changes, followed by the adsorption by the reactants of the ions and electrons thus generated.

F. G. TRYHORN.

Negative catalysis in slow and induced oxidations. N. R. DHAR (Trans. Faraday Soc., 1928, 24, 567—570).—A discussion of negative catalytic effects in slow and induced reactions from the point of view of the author's theory of the generation of ions in exothermal chemical changes, in which it is shown that the conception of the occurrence of chain reactions in thermal oxidations is unnecessary.

F. G. TRYHORN.

Inhibition in chemical reactions. E. K. RIDEAL (Trans. Faraday Soc., 1928, 24, 571—574).—A summary of the theories suggested to explain inhibition effects in chemical reactions.

F. G. TRYHORN.

Phosphorescence and autocatalysis during slow combustion. F. GILL, E. W. J. MARDLES, and H. C. TETTER (Trans. Faraday Soc., 1928, 24, 574—587).—Measurements have been made of the temperatures at which fog, phosphorescence, and slow combustion occur when air charged with the vapours of carbon disulphide, ethyl ether, acetaldehyde, amylene, or *n*-hexane is passed through a heated glass tube. The action of a number of inhibitory substances on the phosphorescence of these vapours was studied. With an air-carbon disulphide vapour mixture containing 19% by weight of carbon disulphide fog occurred at 100°, phosphorescence at 150°, and rapid combustion at 195°. Carbon disulphide-air mixtures are anomalous inasmuch as the richer mixtures appear to be the more stable towards oxidation. The phosphorescence of these mixtures was inhibited by

benzene, bromine, amyl nitrite, ethyl nitrate, iodine, pentane, acetaldehyde, ethyl acetate, ethylene dibromide, pyridine, acetone, chloroform, methyl alcohol, ethyl alcohol, lead tetraethyl, iron carbonyl, and by the gases acetylene, ethylene, hydrogen sulphide, and coal gas. The initial temperature of slow combustion was reduced in the presence of a number of metals. Carbon monoxide was alone found to promote phosphorescence. It is suggested that an unstable peroxide CS_2O_2 is formed and acts as a catalyst of combustion. This catalyst is reduced by inhibiting agents and is destroyed also by an excess of carbon disulphide, $\text{CS}_2 + \text{CS}_2\text{O}_2 = \text{CS}_2 + \text{SO}_2 + \text{CS}$. Results of a similar type were found for the mixtures of air with the other vapours used. The results suggest that peroxidation, occurring at the interfaces of nuclear particles, is directly responsible for phosphorescence, autocatalysis, and detonation in the internal-combustion engine. Inhibitory agents, by reacting with the primarily formed peroxides, remove from them their active oxygen and energy, thus destroying the positive catalyst of combustion and the cause of phosphorescence, and detonation. Evidence is adduced that the glow of hexane is due, not to the intermediate formation of aldehydes, but specifically to the formation of primary peroxides of hexane. In experiments carried out by inserting various metals in the combustion tube the glow seemed usually to be confined to the metal surface, which remained unaltered during the process, and the intermediate combustion products were diminished in amount and self-ignition was delayed. This inhibitory action of metals is in accord with the view that organometallic compounds, such as lead tetraethyl, owe their efficacy to the colloidal metal formed by thermal decomposition at the surface of nuclear particles.

F. G. TRYHORN.

Theory of chain reactions. J. A. CHRISTIANSEN (Trans. Faraday Soc., 1928, 24, 596—601).—A review.

Mechanism of inhibition in autoxidation reactions. H. L. J. BACKSTRÖM (Trans. Faraday Soc., 1928, 24, 601—605).—To investigate the relation between inhibition and induced reactions the velocity of oxidation of sodium sulphite solutions has been measured in the presence of *isobutyl*, *sec.*-butyl, and benzyl alcohols. The results are in agreement with the chain theory of the above reaction (A., 1927, 737, 1151), the inhibitory action of the alcohols arising from the breaking of the reaction chains through the preferential oxidation of the alcohol molecules to acetone, methyl ethyl ketone, and benzaldehyde, respectively. When two alcohols are present in the solution at the same time, the theory requires that they should be oxidised in proportion to their concentrations and relative inhibitory powers, but that the total number of molecules oxidised in a given time should remain constant. This was verified for an equimolecular mixture of benzyl and *isopropyl* alcohols. Photochemical experiments with *isopropyl* alcohol as an inhibitor showed that in a solution of a given composition the chain-length is the same whether the chains are started thermally or photochemically. The chain-length (58 mols.) deduced from data for the thermal reaction with benzyl alcohol

as an inhibitor agrees well with that obtained (64 mols.) from previous quantum efficiency measurements. Values obtained from the copper-catalysed sulphite oxidation reaction show that copper salts accelerate the total reaction without changing the ratio of sulphite oxidised to alcohol oxidised, and therefore without altering the chain-length.

F. G. TRYHORN.

Inhibition of chain reactions by bromine. M. PÓLÁNYI (Trans. Faraday Soc., 1928, 24, 606—611).—An account of investigations by the author and co-workers (cf. this vol., 373).

F. G. TRYHORN.

Theory of acid and basic catalysis. J. N. BRÖNSTED (Trans. Faraday Soc., 1928, 24, 630—640).—A summary.

Catalytic effects of acids and bases and the influence of inert salts. H. M. DAWSON (Trans. Faraday Soc., 1928, 24, 640—651).—A derivation and summary of the dual theory of catalysis.

F. G. TRYHORN.

Compounds between catalysts and substrates. H. VON EULER (Trans. Faraday Soc., 1928, 24, 651—662).—A review of the author's theory so far as it applies to catalytic hydrolysis by acids and bases.

F. G. TRYHORN.

Salt action in homogeneous catalysis. H. S. HARNED and G. ÅKERLÖF (Trans. Faraday Soc., 1928, 24, 666—678).—A summary.

Kinetics of acid and basic catalysis. A. SKRABAL (Trans. Faraday Soc., 1928, 24, 687—696).—A theoretical discussion of earlier work in which an explanation of acid and basic catalysis has been sought in the theories which have been advanced from the point of view of chemical kinetics. In these theories two types of intermediate compounds are postulated, the Arrhenius type, which is in equilibrium with the initial materials, and the van 't Hoff type, which is independent of this equilibrium and is less stable than the former. Lowry's electrolytic theory of catalysis accords best with experimental facts, and the intermediate compounds postulated by this theory are of the van 't Hoff type.

F. G. TRYHORN.

Kinetics of the reaction between iodine and potassium nitrite in light and darkness. A. BERTHOUD and W. E. BERGER (J. Chim. phys., 1928, 25, 542—561).—See this vol., 484.

Oxidation of potassium nitrite by iodine induced by sodium thiosulphate. A. BERTHOUD and W. E. BERGER (J. Chim. phys., 1928, 25, 562—567).—See this vol., 486.

Definition of "area" in contact catalysis. F. P. BOWDEN (Nature, 1928, 122, 647—648).—In studying the catalytic properties of a surface for a particular reaction the significant area is not the arbitrarily defined maximum area (Constable, this vol., 1101), but the area of the catalyst which can be reached by the reactants concerned. In a method for the measurement of the areas of metallic surfaces by the electrolytic deposition of hydrogen from solution, the quantity measured is the amount of hydrogen added to the surface in order to cause a given change in the electrode potential (Bowden and Rideal, this vol., 1088); it does not follow that the hydrogen is

sparsely distributed over the plate. The catalytic activity of a surface probably depends mainly on the first few atomic layers. The applicability of the electrolytic and interference methods in studying the "area" and properties of the surface atoms is considered; the former method is preferred.

A. A. ELDRIDGE.

Catalytic oxidation of carbon monoxide. IV. Pore volume of the catalysts manganese dioxide, copper oxide, and mixtures of these oxides. H. D. DRAPER (J. Amer. Chem. Soc., 1928, 50, 2637—2653; cf. Bray and Doss, A., 1926, 917).—Determinations of the densities of many samples of the porous, granular oxide catalysts previously used (copper oxide, manganese oxide, MnO_x , where $x < 2$, and mixtures of these) indicate that the granules contain few very small micro-capillaries, or else they offer small resistance to filling by the immersion liquid. The pure oxides are less porous than mixtures containing them, which is explained by colloidal phenomena; the oxides do not combine on mixing. A theoretical discussion of absorption curves (liquid-solid) is given; an expression is deduced relating the volume of sorbed liquid with the curvature of the liquid surface corresponding with the equilibrium pressure of the liquid vapour, the number, and the radii and average length of the capillaries in the solid. This criterion indicates that the poorest of the above catalysts have the finest grained structure and the best catalysts have high porosity with a few fine pores and many large cavities. No explanation can be given for the effect on the catalytic activity of mixing the oxides, beyond the consequent difference in accessibility of the surfaces of the oxides. In spite of the enormous difference in pore size, practically all the catalysts have approximately equal surface exposure per unit pore volume, an anomaly for which no explanation is forthcoming.

S. K. TWEEDY.

Poisoning effects of certain substances on the iron catalyst in the decomposition of carbon monoxide. T. WATANABE (Bull. Inst. Phys. Chem. Res. Japan, 1928, 7, 1078—1087).—Permanent poisoning of the catalyst occurred after the addition of thiophen or hydrogen sulphide. Poisoning caused by naphthalene persisted for only a short time after the addition of the latter had ceased. Nitrogen, methane, and benzene had no effect, whilst acetylene was partly decomposed into carbon and hydrogen; water vapour formed carbon dioxide, hydrogen, and methane, and hydrogen was partly converted into methane.

F. S. HAWKINS.

Fission of carbon monoxide by nickel. N. A. BAHR and T. BAHR (Ber., 1928, 61, [B], 2177—2183).—Metallic nickel and its oxide cannot continuously catalyse the reaction $2\text{CO} = \text{C} + \text{CO}_2 + 38.9 \text{ kg.-cal.}$ Fission of carbon monoxide is due to the carbide Ni_3C at temperatures from about 270° . Catalysis by metallic nickel is only apparent; below 270° decomposition of carbon monoxide is effected with decreasing rapidity only until the metal is completely converted into the carbide. Above 270° to about 380 — 420° the action is catalytic, but the free metal is not present. The amount of carbon corresponding with the composition Ni_3C is invariably united with the metal, whereas

any excess of carbon is uncombined. Above 380—420° free metal is again present in the catalyst, since the carbide decomposes at this temperature. Combined carbon is readily converted by molecular hydrogen into methane at 180—380° (preferably 250—270°), whereas free carbon remains unchanged under these conditions. The carbide Ni_3C is thermostable below about 380—420°. Since it accelerates the decomposition of carbon monoxide above 270°, a higher carbide, Ni_3C_x , must be formed as a labile, intermediate product which immediately decomposes into Ni_3C and free carbon; the higher carbide probably has the composition Ni_3C_2 . The carbide Ni_3C , formed from carbon and molten nickel, is considered identical with that derived from the metal and carbon monoxide at 270°.

H. WREN.

Influence of acids and bases on the inhibitory effect of gelatin on the catalytic decomposition of hydrogen peroxide by colloidal platinum. H. V. TARTAR and N. K. SCHAFER (J. Amer. Chem. Soc., 1928, 50, 2604—2610).—Acetic, sulphuric, and phosphoric acids, and potassium, sodium, and barium hydroxides were used over a very wide p_{H} range. In the case of the acids, for which the reproducibility of the results was only fair, the inhibition depends both on the nature of the acid and on the hydrogen-ion concentration, whereas in alkaline solutions the hydroxyl-ion concentration is the chief factor. The catalysis itself seems to be influenced by the acids and alkalis, and at any p_{H} value the inhibition depends on the concentration of the hydrogen peroxide and of the platinum.

S. K. TWEEDY.

Catalytic decomposition of gaseous acetaldehyde at surface of various metals. P. C. ALLEN and C. N. HINSHELWOOD (Proc. Roy. Soc., 1928, A, 121, 141—155).—The decomposition of acetaldehyde has been shown to be bimolecular as a homogeneous gas reaction, and the present work is a study of the catalytic decomposition of the vapour at the surface of heated wires of platinum, platinum-rhodium alloy, gold, and tungsten. The apparatus used has been previously described (Hinshelwood and Prichard, J.C.S., 1925, 127, 327). The decomposition products are primarily methane and carbon monoxide, but with prolonged heating the former is to some extent decomposed. The reaction has been studied between 685° and 975° and at a number of initial pressures. The times required for 25, 50, and 75% change (denoted by t_{25} , t_{50} , and t_{75} , respectively) are constant above 150 mm., but below this pressure they increase rapidly as the pressure falls. The products of the reaction exert a retarding influence. For small pressures of carbon monoxide, the first additions have less effect than subsequent amounts, and at a pressure greater than 100 mm. this gas has no further effect, but the reaction rate is not reduced to zero. The actual reaction rate is proportional to the surface area of the wire and inversely proportional to the volume of the vessel. The reduced rates (in mm. per min.) at 1000° and 300 mm. initial pressure for platinum, platinum-rhodium, tungsten, and gold (two samples) are 9.6, 5.5, 5.0, 10.5, and 9.6, respectively. From a consideration of the variation of t_{25} and t_{50} with the initial pressure it is concluded that

the reaction is bimolecular, but it is necessary to show why the apparent order approaches unity at high pressures. A number of possibilities are discussed, and it is suggested that the mechanism involves the reaction of a molecule in the gas phase with an activated molecule adsorbed on the wire. In support of this, it is found that the number of molecules striking the wire is always proportional to the pressure, whilst the number on the wire is at low pressures proportional to the pressure and at high pressures constant. A remarkable similarity is found between the different metals in respect of the relation between the reaction rate and pressure, the heat of activation, and the absolute rate of reaction. Examination of the molecular statistics of the reaction indicates that collisions between molecules from the gas and adsorbed molecules are inelastic, with a duration of 10^{-6} — 10^{-8} sec.

L. L. BIRCUMSHAW.

Ceria-thoria catalysts. A. B. GOGGS (J.C.S., 1928, 2667—2669; cf. Swan, A., 1924, ii, 400).—The influence of mixed ceria-thoria catalysts on the combustion of carbon monoxide has been studied. The rate of formation of carbon dioxide attains a maximum with mixtures containing 0.96% of ceria. The catalyst which Swan had found to be the most efficient for the oxidation of hydrogen is, therefore, also the most efficient for the oxidation of carbon monoxide.

F. J. WILKINS.

High-voltage arcing and alternating-current electrolysis. J. W. SHIPLEY and C. F. GOODEVE (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 87—102; cf. B., 1927, 633).—The rate of decomposition of boiling alkaline solutions by voltages of 110—2100 volts, applied to steel wire electrodes, depends chiefly on the rate of consumption of electrical energy and is independent of Faraday's law and the law of alternating-current electrolysis. It increases with the diameter of the electrodes. Arcing does not occur with low currents, and at high voltages commences at a definite current varying inversely as the potential between the electrodes. At constant voltage arcing commences at a current density which falls with increase in the electrode diameter. The principal factor is the potential gradient near the electrodes. Up to 220 volts, arcing which occurs at atmospheric pressure can be suppressed by raising the pressure. The high temperature reached in the arc is mainly responsible for the decomposition.

C. W. GIBBY.

Preparation of potassium ferricyanide without the use of a diaphragm; effect of superimposed alternating current. H. PAWECK and P. HIRSCH (Z. Elektrochem., 1928, 34, 684—696).—Attempts were made to prevent cathodic reduction in the electrolytic preparation of potassium ferricyanide by reducing the current density and using a cathodic diaphragm. A large number of substances were employed as diaphragms, but in no case was any permanent effect observed. The results indicate that ammonium tungstate could be used successfully in other oxidation processes. Cathodic reduction may be largely prevented by means of a diaphragm formed mechanically on the cathode—e.g., a layer of cement or gypsum—and similar results are obtained by the use of a superimposed alternating current. The

influence on the current efficiency of the cathode material, the cathodic current density, the ratio of direct to alternating current, and the frequency has been studied in detail, and the results are tabulated. Solid potassium ferri-cyanide may be obtained by the electrolysis, without a diaphragm, of saturated ferri-cyanide solution saturated with potassium ferrocyanide, using direct current and a high current density. The use of a superimposed alternating current or of a cathode envelope (e.g., a tile casing) results in a higher yield. L. L. BIRCUMSHAW.

Electrolytic oxidation of formaldehyde in alkaline solution. E. MÜLLER and S. TAKEGAMI (Z. Elektrochem., 1928, 34, 704—713).—A study has been made of the relations between anode potential and current density in the electrolysis of a 24% formaldehyde solution mixed with an equal volume of 2*N*- or 4*N*-sodium hydroxide solution, using as anode material smooth or spongy platinum, palladium, rhodium, gold, and silver. The current-potential curves are all similar in form. They exhibit first a current rise at a low potential, a few tenths of a volt above the hydrogen potential, terminating at a definite current strength. The polarising potential being kept constant, the anode rises more or less rapidly to a higher potential with simultaneous decrease of the current strength, and on increasing the polarising potential, a second current rise occurs in the high potential region. Quantitatively, three differences are shown: (1) the current density at which the jump takes place is different for different smooth metals; (2) the first rise is steeper and leads to higher current densities for spongy electrodes than for smooth; (3) on the first rise a marked evolution of hydrogen occurs with gold and silver, a slight evolution with rhodium and palladium, and no evolution with platinum. Experiment showed that, in the high potential region, the products of electrolysis were both formic and carbonic acids, but that in the low potential region, no carbon dioxide was formed with any of the metal anodes. The following reactions evidently occur in the low potential region: (i) $\text{H}\cdot\text{CHO} + \text{H}_2\text{O} + 2 \text{ faradays} = \text{H}\cdot\text{CO}_2\text{H} + 2\text{H}^+$; and (ii) $2\text{H}\cdot\text{CHO} + 2\text{H}_2\text{O} + 2 \text{ faradays} = \text{H}_2 + 2\text{H}\cdot\text{CO}_2\text{H} + 2\text{H}^+$. With gold and silver anodes, mainly (ii) takes place, with palladium and rhodium mainly (i), and with platinum (i) only. Process (i) is favoured by a rise in the current density, and at constant potential the ratio (ii)/(i) decreases with time. The significance of these results is discussed, with special consideration of the catalytic action of finely-divided metals on the decomposition of formaldehyde. A theory is developed to explain the observed phenomena, based on the supposed adsorption of glycol ions on the electrode surface (cf. Müller and Hindemith, this vol., 377). L. L. BIRCUMSHAW.

Co-deposition of copper and graphite. C. G. FINK and J. D. PRINCE.—See B., 1928, 822.

Electro-deposition of aluminium. D. B. KEYES, S. SWANN, jun., W. KLABUNDE, and S. T. SCHICKTANZ.—See B., 1928, 862.

Porosity of electro-deposited chromium. E. M. BAKER and A. M. RENTE.—See B., 1928, 819.

Steel anodes for chromium plating. E. M. BAKER and E. E. PETTIBONE.—See B., 1928, 823.

Causes and prevention of pitting in electro-deposited nickel. D. J. MACNAUGHTAN and A. W. HOTHERSALL.—See B., 1928, 823.

Velocity of photochemical reactions. J. PERRIN and (MLLE.) CHOUCROUN (Compt. rend., 1928, 187, 697—698).—The authors' method (A., 1926, 884, 885) is used to show that the law of mass action holds only for those photochemical reactions in which feebly or non-fluorescent reagents are involved (e.g., the atmospheric oxidation of indigo-carmin in ammonium oxalate by violet light, and the oxidation of helianthin in oxalic acid and ammonium oxalate). This is explained by the dependence on the concentration of the mean life in the activated state of a molecule of a fluorescent substance. J. GRANT.

Sensitised photolysis. E. BAUR (Z. Elektrochem., 1928, 34, 595—598).—A summary of the results previously obtained by the author and his co-workers in this field. S. K. TWEEDY.

Photochemical ozonisation and its relation to the polymerisation of oxygen. O. R. WULF (J. Amer. Chem. Soc., 1928, 50, 2596—2604; cf. this vol., 720).—Evidence is given that O_4 is the absorbing molecule in the photochemical ozonisation of oxygen at 2530 Å. and 2070 Å. From Warburg's absorption data (A., 1916, ii, 526), and assuming the absorption to be proportional to the number of O_4 molecules present, the equilibrium constant $p_{\text{O}_4}/p_{\text{O}_2}$ is calculated to be 1.2 g./c.c., in tolerable agreement with Lewis' computations from magnetic data (A., 1924, ii, 811). The molal absorption coefficient of O_4 for the above wave-length band is estimated to be $1.1 \times 10^4 \text{ cm}^2/\text{mol}$. S. K. TWEEDY.

Reaction between bromine and hydrogen in light of different wave-lengths. W. JOST (Z. physikal. Chem., 1928, 134, 92—96).—Preliminary experiments on the reaction between hydrogen and bromine illuminated by light of wave-length corresponding with the region of the bromine spectrum showing absorption bands and with that corresponding with the continuous spectrum show that the velocity coefficient is of the same order of magnitude in the two cases. L. S. THEOBALD.

Light reaction between ferric chloride and oxalic acid. (FRL.) G. KORNFELD [with E. MENCKE] (Z. Elektrochem., 1928, 34, 598—601).—The velocity is proportional to the square root of the intensity of the light in the blue, green, and violet and, within limits, is independent of the concentration of the reagents. The velocity varies with time and converges rapidly towards zero. Addition of ferrous sulphate retards the reaction at a rate proportional to the concentration of the added salt. The equation $x = k_1(1 - e^{-k_2 t})\sqrt{I}/k_2$ holds, where x is the concentration of ferrous ion formed and I the intensity of the light. Mechanisms are suggested for the reaction. S. K. TWEEDY.

Highly attenuated flames. I. H. BEUTLER and M. PÓLÁNYI (Z. physikal. Chem., 1928, B, 1, 3—20).—See this vol., 491.

Highly attenuated flames. II. Nozzle flames. Increase of light emission with increasing partial pressure of sodium vapour. S. VON BOGDANDY and M. PÓLÁNYI (*Z. physikal. Chem.*, 1928, B, 1, 21—29; cf. this vol., 491).—If the apparatus previously employed is altered in such a way that the halogen or halide vapour streams through a nozzle into the tube through which an excess of sodium vapour is passing, the amount of light emitted due to chemiluminescence is found to increase with increasing pressure of sodium vapour through the range 0.5×10^{-3} to 1×10^{-2} mm. For chlorine it increases from 0.5 to 30% of the theoretical, for bromine from 2 to 18%, and for mercuric chloride from 1 to 7%. The mercuric chloride curve showing increase of light emission with partial pressure of sodium appears to reach a maximum at a pressure of about 3×10^{-3} mm., but no such maximum is obtained with the halogens, although, at a certain point, the curve becomes less steep. The following reactions are supposed to take place: (1) In the alkali metal vapour and halogen the primary reaction is $\text{Na} + \text{Cl}_2 = \text{NaCl} + \text{Cl}$, followed by the reaction $\text{Na} + \text{Cl} = \text{NaCl}$, taking place on the walls of the tube, and the reaction $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$ which produces light, in the gaseous phase. (2) In the alkali metal vapour and volatile halogen salt, e.g., mercuric chloride, the primary reaction is $\text{Na} + \text{HgCl}_2 = \text{NaCl} + \text{HgCl}$ and the secondary one $\text{Na} + \text{HgCl} = \text{NaCl} + \text{Hg}$. On the assumption that light is excited when a sodium atom strikes a freshly-formed sodium chloride molecule rich in energy, the light thus emitted should increase proportionately to the pressure of sodium vapour, as long as the mean free path between sodium chloride molecules and sodium atoms is greater than the dimensions of the tube. When the reverse conditions are reached the light emission approaches a limiting value as in the case of mercuric chloride. The continued rise at a slower rate in the case of the halogen curve is due to the increase in the molecular concentration, Na_2 , of the sodium vapour with increasing pressure, since the light-exciting reaction in the gas, $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$, is increasingly favoured in contrast to the reaction taking place on the walls of the tube without light emission. M. S. BURR.

Highly attenuated flames. III. Sodium-chlorine flame. Evidence for and analysis of the reaction and luminosity mechanism. Both reaction types. Survey of the whole work. M. PÓLÁNYI and G. SCHAY. **IV. Sodium-iodine flame. V. Sodium-mercuric chloride flame.** H. OOTUKA and G. SCHAY (*Z. physikal. Chem.*, 1928, B, 1, 30—61, 62—67, 68—73; cf. preceding abstract).—III. The suggested difference in mechanism between the two types of reaction, sodium with halogen and sodium with halide (*loc. cit.*), is confirmed by certain experimental observations. In type I the curve of distribution of light emission along the tube, when the flame burns at the nozzle, is much broader than the precipitation curve of solid halide; superheating of the reaction zone reduces the light to a small fraction; the increase of light emission is relatively more rapid than the increase in partial pressure of sodium vapour; and in presence of hydrogen hydrogen chloride

is formed. In type 2, on the other hand, the light curve for the nozzle approximates more closely to the precipitation curve; superheating of the reaction zone has no effect; increase of light emission is relatively slower than increase in partial pressure of sodium vapour; and in presence of hydrogen no hydrogen chloride is formed. The presence of nitrogen has an extinguishing action on the excited light in the sodium-chlorine flame. The reduction of light by superheating follows an exponential law. The effect is due to the dissociation of the sodium molecule. From the data the heat of dissociation is calculated to be 18 ± 2 kg.-cal., and the dissociation constant at 600° Abs. approximately 3×10^3 at a pressure of 1 bar. The "true light emission," which gives the probability c that a sodium chloride molecule formed by the elementary process $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$ emits light by collision with a sodium atom, is 0.7—1, which indicates that a considerable portion of the chemical energy is transformed into vibrational energy. The velocity coefficient for the reaction $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$, when $c = 0.7$, is calculated to be 4×10^{-7} .

IV. When iodine is substituted for chlorine similar results are obtained. The "true light emission" of the elementary process $\text{Na}_2 + \text{I} = \text{NaI} + \text{Na}$ in sodium vapour is 0.3—0.5. The velocity coefficient of this reaction is 5×10^{-8} . The heat of dissociation of the sodium molecule, calculated from the suppression of light by superheating, is of the same order as calculated from the data of the sodium-chlorine flame.

V. For the sodium-mercuric chloride flame without nozzle the velocity coefficient of the primary reaction $\text{Na} + \text{HgCl}_2 = \text{NaCl} + \text{HgCl}$ is approximately 1.5×10^{-6} and for the secondary reaction $\text{Na} + \text{HgCl} = \text{NaCl} + \text{Hg}$, deduced from the nozzle flame, it is 1×10^{-7} . In the flame without nozzle the position of the light maximum relatively to the precipitate maximum can be calculated from the dependence of light emission on the pressure of sodium vapour. For mercuric chloride c is 0.11. M. S. BURR.

Photolysis of medium-free silver bromide. Determination of silver. H. KIESER (*Z. wiss. Phot.*, 1928, 26, 1—45).—Darkened silver halide consists of colloidal silver in a medium of silver halide. To determine the elementary silver, the photographic layer is washed into a flask and shaken with alkaline thiosulphate for 20 min. in the dark, when the halide dissolves. The precipitate is then collected and ignited wet. This method, however, may be in error up to 50% unless the proper conditions, which are here investigated, are observed.

The silver bromide used was prepared by slowly adding 13.25 c.c. (i.e., a very slight excess) of 2*N*-silver nitrate solution (cold) to 400 c.c. of 0.0667*N*-potassium bromide solution at 83°; 10 c.c. of water were added, the liquid was stirred until the supernatant layer cleared, and the whole heated at the b. p. for 15 min. with constant stirring. Finally it was filtered, the precipitate washed with 400 c.c. of cold water, and spread out into a thin layer. By this method the presence of excess of silver or bromine ions in the bromide was avoided. The analysis of the darkened bromide must be carried out immediately after exposure; otherwise the silver partly redissolves as silver halide under the

joint action of the halogen ions and the atmospheric oxygen present, this recombination being accelerated by the presence of potassium bromide. A positive error occurs owing to the formation of silver sulphide and a negative one owing to incomplete coagulation of the colloidal silver in the thiosulphate solution; the sulphide error is the larger, however, and by subtracting 10% from the weight of the total precipitate after ignition the correct silver value is obtained. The quantity of silver sulphide in the precipitate (before ignition) was determined by washing with dilute nitric acid (33 vol.-%) for 1 hr., when the silver was selectively dissolved. The proportion of sulphide decreases as the amount of photolytically-formed silver increases; it increases with the time of fixing and also with the amount of thiosulphate solution, which must therefore be kept at the minimum which will effect dissolution. For very small precipitates the method fails, as the proportion of sulphide is so large. The entrance of carbon dioxide (e.g., during shaking) into the thiosulphate solution accelerates the formation of sulphide only very slowly. The peptisation of the silver is increased by gelatin and decreased by electrolytes, e.g., ammonium acetate.

The formation of silver sulphide is due to the adsorption of the sodium silver thiosulphate on the silver sol, which accelerates the decomposition of the thiosulphate; where, however, the sol concentration is large (i.e., small volume of thiosulphate), the colloidal particles are so close that the adsorption forces bring about coagulation.

The quantum efficiency for blue light (500–400 $\mu\mu$) was determined for different times of exposure to light of 436 $\mu\mu$, the absorption being calculated from reflexion measurements owing to the thickness of the layer. For short exposures the quantum efficiency is approximately unity for silver bromide in sodium nitrite as acceptor, and $\frac{1}{10}$ – $\frac{1}{100}$ in water. For green and red light with unexposed silver bromide the absorption values are independent of the presence of sodium nitrite, which must therefore be a true acceptor. For longer exposures the fall of quantum efficiency and the yield of silver decrease to an extent depending on the form of the precipitate and thus on its preparation.

S. J. GREGG.

Photochemistry of silver halides. III. Relation between the gravimetrically determined silver and the lowering of sensitivity caused by dichromate-sulphuric acid reagent with subsequent chemical and primary and secondary physical development. H. H. SCHMIDT (Z. wiss. Phot., 1928, 26, 86–95).—According to Lüppe-Cramer (cf. "Grundl. d. Negativverfahren," 3rd ed., 9) highly sensitive emulsions contain more "silver nuclei" or sensitivity centres, which might be thought to be connected with the gravimetrically determined excess of silver ions which always exists in the emulsion layer after decomposition with nitric acid.

To test this, the sensitivity changes of a control plate washed in conductivity water and of a plate washed in a dilute solution of sulphuric acid and potassium dichromate, respectively (both plates unsensitised), were compared, the plates being dried, exposed, and developed under identical conditions.

The sensitivity of the dichromate plate was reduced with chemical and primary physical development to an extent independent of the gravimetrically determined silver values, but bearing a direct relationship to the sensitivity. This must be a development phenomenon, for with secondary physical development (i.e., development after fixing) the dichromate treatment produces no reduction of sensitivity, which disproves the view that the dichromate destroys the sensitivity centres.

No accurate method is yet available for the determination of the excess of silver in sensitised plates. Treatment with dichromate has the same effect on plates sensitised with acid dyes as on unsensitised plates of high sensitivity, but with plates sensitised with basic dyes, the dichromate causes great reduction in sensitivity for all three forms of development. This is due to the decomposition of the complex compounds of the silver halide with the basic dye which are much less stable towards dichromate than the silver compounds of the acid dye.

S. J. GREGG.

Formation of the photographic latent image. S. E. SHEPPARD.—See B., 1928, 837.

Photochemical studies. I. J. HOUBEN and W. FISCHER (Arb. biol. Reichsanst. Land- u. Forst-wirtsch., 1928, 15, 601–608; Chem. Zentr., 1928, i, 2486).—Photochemical decomposition of water into hydrogen and hydrogen peroxide, or synthesis of formaldehyde from carbon dioxide and water, could not be detected. Formaldehyde in ultra-violet light affords strongly reducing substances (pentoses); methyl alcohol and potassium nitrite produce form-hydroxamic acid, which is rapidly decomposed by formaldehyde in light. Neither purine substances nor α -amino-acids were detected. Instead of alkaloids, which Baly claims to have isolated, alkylamines giving the usual alkaloid reactions were obtained.

A. A. ELDRIDGE.

Action of light on acetylene. H. REINICKE (Z. angew. Chem., 1928, 41, 1144–1146).—An apparatus is described for the study of the action of light on acetylene. Hempel's apparatus cannot be used. Carefully dried and purified acetylene was unchanged in sunlight or in daylight either in glass or quartz vessels. Polymerisation occurs if the gas is exposed to the light from a mercury lamp, but only radiation of wave-length less than 300 $\mu\mu$ is active. Polymerisation occurs easily at atmospheric pressure as well as at higher pressures, and also at the ordinary temperature. Oxygen and moisture hinder the process, in the latter case aldehyde being formed. A. J. MEE.

Action of X-rays on chloroform and analogous compounds. P. GÜNTHER, H. D. VON DER HORST, and G. CRONHEIM (Z. Elektrochem., 1928, 34, 616–625).—Chloroform produces hydrogen chloride in yields proportional to the radiated energy; in the presence of moisture hypochlorous acid is also produced. From dry carbon tetrachloride small yields of chlorine are obtained, acids being produced also if water is present. Very small yields of acids are obtained from mixtures of carbon tetrachloride or chloroform with petroleum and hexahydrobenzene; a reaction appears to occur between petroleum and

carbon tetrachloride. Hard rays are the most active. Other liquids were also used and numerous experiments are described in which iodoform in various solvents was exposed to X-rays (cf. Baumeister and Glocker, A., 1921, ii, 367). S. K. TWEEDY.

Influence of light on coloured [cotton] fabric. (MISS) E. HIBBERT.—See B., 1928, 854.

Syntheses with radiant energy. II. Photo-synthesis of $\alpha\beta$ -triphenyl-lactic acid. R. DE FAZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1287—1292; Chem. Zentr., 1928, i, 2174).—Phenylacetic acid (26 g.), benzophenone (30 g.), and anhydrous benzene (30 g.) were irradiated for 112 days in a tube attached to a U-tube containing calcium oxide. Crystals (0.5—2.5 g.) of $\alpha\beta$ -triphenyl-lactic acid were deposited from the solution which had become orange-yellow, and also contained a small quantity of oil, b. p. 318—322°, and a viscous oil, phenylacetic acid (21.5, 24.5 g.) and benzophenone (26, 28 g.). Irradiation of the above mixture in a silica tube with a mercury lamp for 100 hrs. gave no triphenyl-lactic acid and only traces of carbon dioxide; irradiation with a 2000 c. p. Osram lamp, however, produced abundant quantities of these substances. Exposure of phenylacetic acid alone in anhydrous benzene to sunlight (6 months) gave little carbon dioxide (more in presence of uranium acetate) and a little yellow oil; exposure at 25 cm. distance to a 2000 c. p. Osram lamp resulted in the evolution in 24 hrs. of detectable quantities of carbon dioxide, in 280 hrs. of fairly large quantities, and crystals, m. p. 51—52°, probably *s*-diphenylethane. A. A. ELDRIDGE.

Action of light on celluloid stained with malachite-green. (LORD) RAYLEIGH (Nature, 1928, 127, 645—646).—The conversion of celluloid stained with malachite-green into a material transmitting only deep red and infra-red rays by exposure to sunlight can be effected also by heating. The change is due to a specific reaction of the cellulose nitrate constituent. A. A. ELDRIDGE.

Activation of hydrogen in silent discharge. I. G. M. SCHWAB and F. SEUFFERLING (Z. Elektrochem., 1928, 34, 654—657).—Experiments are described which indicate that in the silent discharge hydrogen at 50 mm. forms one form or other of active hydrogen. When sulphur is absent, the active hydrogen contains only one tenth of the amount of hydrogen sulphide which is formed when sulphur is present. An accurate micrometric method of determining the amount of hydrogen sulphide in the hydrogen, by collecting the gas in a capillary U-tube, is described. S. K. TWEEDY.

Purification of helium. J. W. COOK (Physical Rev., 1927, [ii], 29, 920).—Up to its saturation capacity, activated coconut charcoal completely removed air at -78° . A. A. ELDRIDGE.

Helium. II. Employment of sensitive helium tests in questions of the transformation of the elements. F. PANETH and K. PETERS [with H. GEHLEN and P. L. GÜNTHER] (Z. physikal. Chem., 1928, B, 1, 170—191).—A method previously described for the detection and measurement of

quantities of helium of the order of 10^{-10} c.c. (this vol., 858) has been used to test the possibility of the formation of helium artificially, from other elements, under various conditions such as bombardment of potassium salts by cathode rays, passage of an electric discharge, with or without electrodes, through hydrogen or compounds of hydrogen, and action of β - and γ -rays on water and mercury. When precautions are taken to exclude the possibility of the entry of air, or the diffusion of helium from the air through hot glass, or the escape of helium occluded in glass, no helium in quantity larger than 10^{-10} c.c. is obtained by these methods. Experiments on the spontaneous production of helium in potassium and beryllium salts have not definitely excluded the possibility that this may take place. M. S. BURR.

Complex lithium, iron, and nitrogen compound. W. FRANKENBURGER, L. ANDRUSSOV, and F. DÜRR (Z. Elektrochem., 1928, 34, 632—637).—Nitrogen is reversibly absorbed by a heated mixture of iron and lithium nitride with the formation of a greyish-black crystalline compound, $\text{Li}_3\text{N}, \text{FeN}$, or $\text{Li}_3[\text{Fe}^{\text{III}}\text{N}_2]$. An X-ray powder photograph of the compound is given. The compound, which decomposes in water to black micro-crystalline iron oxide and ammonia, has a heat of formation of $22,600 \pm 2300$ g.-cal./mol. Magnetic observations are also recorded. Absorption of nitrogen occurs when the iron is replaced by nickel or cobalt, but not when replaced by osmium. The contradictory results obtained in the previous investigations of the absorption of nitrogen by iron are explained on the basis of the varying surface structure of the latter. S. K. TWEEDY.

Composition of precipitate obtained by the action of potassium ferrocyanide on calcium salts in presence of acetic acid. I. TANANAEV (J. Russ. Phys. Chem. Soc., 1928, 60, 905—908).—See this vol., 852. R. TRUSZKOWSKI.

Reduction of barium carbonate by aluminium. E. F. LINHORST and H. SCHLUNDT.—See B., 1928, 813.

Basic carbonates of zinc and cadmium. T. NISHIMURA and T. YAMAMOTO (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 985—995).—Normal zinc carbonate when prepared at a low temperature and in presence of carbon dioxide is stable when exposed to the air, but if air be bubbled through its aqueous suspension a basic carbonate of composition $\text{ZnO}, 0.421\text{CO}_2, n\text{H}_2\text{O}$, believed to be different from $5\text{ZnO}, 2\text{CO}_2, 3\text{H}_2\text{O}$, is formed. If zinc hydroxide is allowed to absorb carbon dioxide from the air, another compound, $\text{ZnO}, 0.363\text{CO}_2, m\text{H}_2\text{O}$, is obtained.

Cadmium carbonate is stable when dry or wet, unless it is prepared at a low temperature, when a temporary decomposition is caused by bubbling air through its aqueous suspension. Cadmium hydroxide absorbs atmospheric carbon dioxide rapidly up to 0.78 mol. CO_2 to 1 mol. CdO , and then the absorption suddenly slackens. No basic cadmium carbonate can be isolated. F. S. HAWKINS.

Separation on iron of carbon from carbon monoxide and light petroleum. II. Crystalline carbon with high adsorptive power. U. HOFMANN

(Ber., 1928, 61, [B], 2183—2194; cf. this vol., 853).—The isolation of crystalline carbon capable of activation (*loc. cit.*) appears contrary to the observations of Ruff (A., 1925, ii, 192), who considers this property to be confined to amorphous carbon. The presence of amorphous particles in the author's specimens is regarded as impossible, since carbon, deposited on iron at 400° or 520°, does not show any discontinuity in rate of oxidation or adsorptive power when treated with carbon dioxide until two thirds of the material has disappeared, and its action towards boiling sulphuric acid and mercury sulphate is precisely similar to that of the undoubtedly homogeneous graphite, retort graphite, and lustre carbon. On the other hand, non-homogeneous carbons, such as sugar and ash charcoal, are very irregularly oxidised. The adsorptive power of crystalline carbon must be ascribed to its loose texture, as is shown by the observation of slight activity in lustre carbon deposited from a mixture unusually rich in light petroleum and in carbon obtained from iron pentacarbonyl and light petroleum at 900°. Activation does not depend on sundry amorphous and therefore unoriented carbon atoms, but on the surface of crystallites composing the regular, graphite lattice. With large crystallites the active surface becomes so small in relation to the mass of carbon that adsorptive power is not manifested measurably. This is the case with carbon deposited on iron at 900°, and particularly with graphite; the limiting length of the edge of crystallite is estimated to be 10^{-4} cm. Below this limit, the relative extent of the active surface is so considerable that an active product is obtained if the carbon can be so loosely deposited that the surfaces of the crystallites are free for the greater part; this is not usually the case with retort graphite and lustre carbon. Activation, for example, by carbon dioxide depends on the removal of foreign matter already adsorbed and on the roughening of the complete surface. The chemical resistance of carbon, also, depends solely on the surface which can be reached by the reagent and is therefore governed by the size of the crystallites and the closeness of packing. The hardness of the individual crystallites is not involved.

H. WREN.

Reduction of carbonic acid. H. KAUTSKY (Naturwiss., 1928, 16, 204; Chem. Zentr., 1928, i, 2236).—Carbamidosiloxen, from carbon dioxide and aminosiloxen, when in contact with small quantities of oxygen yields hydrogen cyanide, the oxygen being taken up by the silicon compound.

A. A. ELDRIDGE.

Reaction between nitrous acid and hydrogen sulphide. L. S. BAGSTER (J.C.S., 1928, 2631—2643; cf. Divers, *ibid.*, 1887, 51, 48).—The products of the reaction between nitrous acid solution and hydrogen sulphide are mainly nitric and nitrous oxides with the former in excess and ammonia and hydroxylamine with the latter in excess. Only when the hydrogen sulphide concentration is very small does the relative proportion of sulphur trioxide become comparable with the free sulphur. It is suggested that the primary reaction occurs between nitrous acid and a sulphide ion to form hyponitrous acid when there is little hydrogen sulphide present, and hydroxyl-

amine and ammonia when the concentration of nitrous acid is small.

Hydrogen sulphide reduces ammonium nitrite very slowly to ammonia. The reaction rate is diminished by addition of ammonium sulphide and increased by the addition of polysulphide. It is suggested that the former acts by decreasing the hydrogen-ion concentration and therefore the concentration of nitrous acid molecules, whilst the latter, owing to the greater acidity of the polysulphide ion, increases the concentration of free sulphide ions. F. J. WILKINS.

Allotropic modifications of phosphorus obtained at high temperatures and pressures. V. IPATIEV and V. NIKOLAIIEV (J. Russ. Phys. Chem. Soc., 1928, 60, 885—892).—Crystalline, white phosphorus, m. p. 44.5°, d 1.82, is obtained by heating yellow phosphorus with benzene at below 200° at 70—80 atm. in an inert atmosphere. Purple phosphorus, ignition point 210—240°, d 1.93—2.05, is obtained in crystalline aggregates by heating ordinary phosphorus with water in a silver tube at 260—290° under 30—60 atm. pressure. Crystalline, ruby-violet phosphorus, ignition point 346°, d_{16}^{20} 2.11, is obtained by heating phosphorus with lead in a glass tube filled with nitrogen at 335° and 165 atm. Crystalline, black phosphorus, ignition point 485—490°, d_{16}^{20} 2.61—2.70, is prepared by heating yellow phosphorus in nitrogen for 4—5 days at 300—350° and 90—250 atm. At higher temperatures all the above allotropes pass into the white modification.

R. TRUSZKOWSKI.

Allotropic modifications and solid solutions of phosphorus. V. J. NIKOLAIIEV (J. Russ. Phys. Chem. Soc., 1928, 60, 1045—1051).—Four allotropes of phosphorus exist, viz., white phosphorus, d_{16}^{20} 1.82, ignition point 55°; purple, d_{16}^{20} 1.90, i. p. 200°; ruby-red, d_{16}^{20} 2.11, i. p. 346°; and black, d_{16}^{20} 2.70, i. p. about 490°. At d intermediate to the above a continuous series of solid solutions exists, in which the colours are also intermediate. Red phosphorus is a solid solution of the ruby-red and the purple forms, whilst violet phosphorus consists of ruby-red and black phosphorus.

R. TRUSZKOWSKI.

Preparation of phosphorus thiochloride. R. DE FAZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1293—1294; Chem. Zentr., 1928, i, 2240).—Anhydrous carbon tetrachloride (220 g.) and phosphorus pentasulphide (250 g.), when heated for 2 hrs. in a sealed tube at 180—200°, yield the compound PSCl_3 (150 g.).

A. A. ELDRIDGE.

Action of an electric discharge on the gaseous mixture $\text{SO}_2 + \text{O}_2$. J. MAISON (Bull. Soc. chim. Belg., 1928, 37, 326—333).—Berthelot's experiments on the action of an electric discharge on a mixture of equivalent quantities of sulphur dioxide and oxygen have been repeated. The pressure in the apparatus rapidly falls and an oil, or more frequently an opaque solid, is formed on the walls of the discharge tube. The product is insoluble in sulphuric acid, contrary to the statement of Berthelot, but dissolves in water without any violent reaction, forming a strongly oxidising solution. The substance does not fume in moist air and is relatively stable. The residual gases in the tube give the reactions of

the sulphate ion. The product is not S_2O_7 , as suggested by Berthelot, nor is its behaviour in agreement with Meyer's view (A., 1922, ii, 843) that it is a mixture of the anhydrides of sulphuric acid and Caro's acid, SO_3 and SO_4 , but it appears to be a definite compound, S_3O_{11} , which might be regarded as a mixed anhydride of persulphuric acid, $H_2S_2O_8$, and Caro's acid, $H_2S_2O_5$. M. S. BURR.

Sulphur nitride. II. S. A. VOZNESENSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 1037—1044).—The colour reactions given by sulphur nitride, N_4S_4 , and by thiotriazyl chloride, N_3S_4Cl , in various solvents and in acid and alkaline solutions are contrasted. The latter substance reacts with hydrochloric acid according to the equation: $2N_3S_4Cl + 12H_2O + 4HCl = 2H_2S_3O_6 + 6NH_4Cl + 2S$; with water: $2N_3S_4Cl + H_2O \rightarrow 2(NH_4)_2S_3O_6 + 2NH_4Cl + 2S$, and with 2% sodium hydroxide solution: $3N_3S_4Cl + nNaOH + mH_2O \rightarrow 2H_2S_2O_3 + H_2SO_3$.

R. TRUSZKOWSKI.

Constitution of some polythionates. J. A. CHRISTIANSEN (Z. Elektrochem., 1928, 34, 638—640).—*p*-Toluoyl tri-, tetra-, penta-, and hexathionates were prepared (cf. Troeger and Hornung, A., 1899, i, 905), and their X-ray spectra (*K* radiation), electric moments, and mol. wts. (b.-p. method) investigated. Only the trithionate had the accepted m. p.; the pentathionate exists in two modifications, m. p. 183° and 160°, respectively. The m. p. of the latter form rises to 180° on keeping; the compound is precipitated, together with sulphur, by heating the hexathionate with acetic acid in presence of platinum. The m. p. of the hexathionate (90°) and the tetrathionate (114°) indicate that these compounds may be mixtures of different forms. This isomerism, and also the electric moment data, do not support the classic formulæ of Blomstrand and Mendeléev. The data do not suffice to determine whether the compounds contain polysulphide or thiosulphate linkings. The absence of colour does not support the former constitution. The compounds are associated in benzene solution (cf. Aoyama, Kimura, and Nishina, A., 1927, 999).

S. K. TWEEDY.

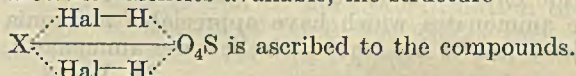
Co-ordination compounds of quinquevalent molybdenum: complex thiocyanates. R. G. JAMES and W. WARDLAW (J.C.S., 1928, 2726—2739; cf. A., 1927, 1044).—By the interaction of aqueous solutions of the compound $(NH_4)_2[MoOCl_5]$ and ammonium thiocyanate, dihydrogen molybdenum dioxytrithiocyanate has been prepared. Similarly by the interaction of the corresponding salts of the type $R_2[MoOCl_5]$ the thallous, quinolinium, and pyridinium salts have been isolated. Further, salts of the empirical formula $R_4[Mo_2O_3(CNS)_6]$ (where $R = NHMe_3$ or NMe_4) were prepared by treating $(NHMe_3)_2MoOCl_5$ and $(NMe_4)_2MoOCl_5$ with ammonium thiocyanate. They are given the configuration $R_4 \left[\begin{array}{c} (CNS)_3Mo \text{---} O \text{---} Mo(CNS)_3 \\ O \quad \quad \quad O \end{array} \right]$.

Both the tri- and octa-thiocyanates yield salts of the type $R_2[MoO(CNS)_5]$ ($R = C_5H_5N$, C_9H_7N , $NHMe_3$, NMe_4) with aqueous thiocyanic acid and a sulphato-compound, $(C_5H_5N)_4[Mo_2O_3(SO_4)(CNS)_6]$,

with 5*N*-sulphuric acid. The relationship between the complex chlorides and thiocyanates of quinquevalent molybdenum has been demonstrated. *Ditetramethylammonium molybdenyl pentachloride* has been isolated.

The co-ordination number of oxygen in these compounds is discussed and evidence is brought forward to show that it may occupy two positions in the co-ordination sphere. F. J. WILKINS.

Additive compounds of hydrogen halides and salts of heavy metals. III. F. EPHRAIM and A. SCHÄRER (Ber., 1928, 61, [B], 2161—2173; cf. A., 1926, 36, 587).—Addition of hydrogen chloride is not confined to the sulphates of copper, silver, zinc, cadmium, mercury, thallium, tin, lead, antimony, and bismuth, but extends to the dry phosphates, phosphites, and hypophosphites, which yield pulverulent adducts, but not to arsenates, selenates, and benzoates, which are immediately or rapidly decomposed. Hydrogen bromide and iodide give similar, but less stable, additive products. The following changes are possible: $XSO_4 + 2HBr \rightleftharpoons XSO_3 + 2HBr$; $XSO_4 + 2HBr \rightleftharpoons XBr_2 + H_2SO_4$; $XSO_4 + 2HBr \rightleftharpoons XSO_3 + H_2O + Br_2$. The additive products do not show any trace of free acid and their colour is identical with or similar to that of the metallic halide. Since the number of mols. of added halogen acid is invariably equal to the number of metallic valencies available, the structure



Hydrogen bromide is conveniently prepared by the gradual addition of bromine to a mixture of technical resorcinol and sand. With anhydrous cadmium sulphate it gives the compound $CdSO_4 \cdot 2HBr$, which slowly decomposes at the atmospheric temperature into cadmium bromide and sulphur dioxide. Copper sulphate immediately blackens, giving finally copper bromide, bromine, and sulphur dioxide. The substances $Ag_2SO_4 \cdot 2HBr$ and $PbSO_4 \cdot 2HBr$ are described. Zinc sulphate adds hydrogen bromide with difficulty. With thallous sulphate a thallosotthallic derivative is formed. Mercuric bromide gives the compound $HgSO_4 \cdot HBr$ at 100°; at 120°, mercuric bromide sublimes, and absorption of 2 mols. of the acid, which occurs slowly at 120—140°, is accompanied by double decomposition into mercuric bromide and sulphuric acid. Mercurous sulphate and hydrogen chloride when cold give the product $Hg_2SO_4 \cdot 2HCl$, quantitatively converted in a current of hydrogen chloride at 150° into mercuric chloride, sulphur dioxide, and water. Silver phosphate gives the compound $Ag_3PO_4 \cdot 3HCl$; the substance $Pb_3(PO_4)_2 \cdot 6HCl$ decomposes above 400° with separation of lead chloride. Mercuric phosphate absorbs hydrogen chloride, possibly with double decomposition; with zinc phosphate the results are ill-defined, whereas aluminium phosphate does not react. Ferric phosphate absorbs nearly 6 mols. of hydrogen chloride. Anhydrous nickel phosphate does not absorb hydrogen chloride, but the dihydrate unites with 7 mols. of the halide, giving a compound which loses water at 100° and passes at 200° into the substance

$\text{Ni}_3(\text{PO}_4)_2 \cdot 6\text{HCl}$. The compound $\text{Ag}_3\text{PO}_4 \cdot 3\text{HBr}$ is converted at 400° into silver bromide and phosphoric acid, whereas the analogous lead salt decomposes when strongly heated with evolution of phosphine. When cold, mercuric phosphate appears to yield the compound $\text{Hg}_3(\text{PO}_4)_2 \cdot 3\text{HBr}$, which undergoes double decomposition when heated; the latter change occurs exclusively when cooling is not adopted. Anhydrous nickel phosphate does not react, whereas the dihydrate gives the substance $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{HBr} \cdot 2\text{H}_2\text{O}$. Anhydrous cadmium phosphite, conveniently prepared from solid cadmium carbonate and phosphorous acid, absorbs rather more than 2 mols. of hydrogen chloride or bromide. Lead phosphite yields the compounds $\text{PbHPO}_3 \cdot 2\text{HCl}$ and (?) $\text{PbHPO}_3 \cdot 2\text{HBr}$, the preparation of the latter being accompanied by evolution of bromine. Calcium phosphite does not add either hydrogen halide. Cadmium hypophosphite appears to combine with 2 mols. of hydrogen chloride or bromide. Arsenates and selenates react with hydrogen halides with reduction of the acid radical, benzoates with double decomposition. Silver, cupric, and mercuric sulphates and ferric phosphate are immediately decomposed by hydrogen iodide, with separation of iodine and production of hydrogen sulphide from the sulphates. Additive compounds of lead phosphate or phosphite with hydrogen iodide possibly exist. Hydrogen cyanide and methyl chloride do not exhibit additive power. Hydrogen chloride effects the removal of ammonia only from those ammonates which have appreciable ammonia tension; it does not react with the lower ammonates.

H. WREN.

Formation of iodates from iodides. R. LYDÉN (Finska Kemistsamfundets Medd., 1927, 36, 126—141; Chem. Zentr., 1928, i, 2494).—Interaction of potassium chlorate and iodide (preferably 1:1.5 mol.) commences at $350\text{--}400^\circ$ and proceeds vigorously with marked evolution of oxygen: $\text{KClO}_3 + 6\text{KI} \rightarrow \text{KCl} + 3\text{K}_2\text{O} + 3\text{I}_2$; $5\text{KClO}_3 + 3\text{I}_2 \rightarrow 5\text{KCl} + 3\text{I}_2\text{O}_5$; $\text{K}_2\text{O} + \text{I}_2\text{O}_5 \rightarrow 2\text{KIO}_3$. With perchlorate (1.5:1 mol.), $3\text{KClO}_4 + 4\text{KI} \rightarrow 4\text{KIO}_3 + 3\text{KCl}$; with bromate (1.5:1 mol.), $\text{KBrO}_3 + \text{KI} \rightarrow \text{KBr} + \text{KIO}_3$.

A. A. ELDRIDGE.

Rhenium. W. NODDACK (Z. Elektrochem., 1928, 34, 627—629).—Rhenium obtained by reducing the sulphide in hydrogen is a heavy, grey powder, unaltered at 2000° in a vacuum; it inflames at 300° in oxygen with formation of a volatile white oxide, Re_2O_7 , m. p. $26\text{--}30^\circ$, sparingly soluble in water and acids. Yellow drops of the oxide ReO_3 also condense; they form hygroscopic crystals, m. p. 160° , b. p. 450° , which, on boiling, give the vapour of the white oxide. The latter becomes yellow at 150° . Reduction of these oxides by carbon monoxide or sulphur dioxide produces green, blue, and violet oxides, which, however, on prolonged heating are converted into the yellow or white oxide. The aqueous solution of the yellow oxide, which is acidic, is uninfluenced by hydrochloric, nitric, and sulphuric acids, by potassium and sodium hydroxides, by ammonia, and by oxidising agents. With barium hydroxide and silver nitrate it forms white precipitates, possibly BaReO_4 and Ag_2ReO_4 , soluble in dilute nitric acid. The silver precipitate darkens at 100° . Hydrogen

sulphide is oxidised by the yellow oxide solution to sulphur; in presence of acids a grey sulphide is quantitatively precipitated (together with sulphur), and this precipitation is not hindered by oxalic, tartaric, or phosphoric acids (distinction from tungsten). By heating the precipitate in carbon dioxide at $400\text{--}600^\circ$ unstable black sulphides, Re_2S_7 and ReS_3 , appear to be formed. Above 600° the stable black sulphide, ReS_2 , is produced. The acidified yellow oxide solution will not react with ammonium phosphate or potassium ferrocyanide, nor will it give a colour with potassium xanthate. This behaviour serves to distinguish the element from molybdenum, as also does the behaviour of the solution towards potassium thiocyanate and the greater volatility of rhenium oxide as compared with molybdenum oxide. Absence of reaction with potassium iodide distinguishes the element from osmium. By heating rhenium in chlorine two volatile chlorides are formed, viz., ReCl_6 , brown needles, subl. 150° , hydrolysed by water, and (?) ReCl_7 , green, more volatile than the lower chloride. With iodine and bromine vapour, respectively, dark volatile compounds are formed. The above properties place rhenium between tungsten and osmium.

S. K. TWEEDY.

Iron crystals. L. W. MCKEEHAN (Physical Rev., 1927, [ii], 29, 920).—Long crystals of iron are obtained by causing an electrically heated portion to move along a wire. The temperature of the hottest portion should be 1400° . Irregular tension and torsional stresses result in twinning.

A. A. ELDRIDGE.

Univalent iron, cobalt, and nickel. W. MANCHOT (Gazzetta, 1928, 58, 560—562; cf. this vol., 35).—A reply to Cambi's criticism (this vol., 258) of the author's previous work.

O. J. WALKER.

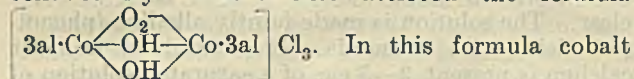
Action of mercury salts on iron pentacarbonyl. H. HOCK and H. STUHLMANN (Ber., 1928, 61, [B], 2097—2101).—Iron pentacarbonyl is converted by mercuric chloride (2 mols.) in aqueous solution into carbon dioxide, hydrogen chloride, and the compound $\text{Fe}(\text{CO})_4 \cdot \text{Hg}_2\text{Cl}_2$, which darkens at 100° , evolves carbon monoxide at 140° , and is completely decomposed at 300° , leaving iron and mercurous chloride. It is almost completely stable towards air and very sparingly soluble in the usual media. In well-cooled acetone the reactants give the unstable additive compound, $\text{Fe}(\text{CO})_5 \cdot \text{HgCl}_2$, which gradually passes into the tetracarbonyl derivative if mercuric chloride is in excess; if this is not the case, the tetracarbonyl compound is formed, but the excess of pentacarbonyl is decomposed with separation of ferrous chloride. In ethyl-alcoholic solution, the compound $\text{Fe}(\text{CO})_4 \cdot \text{Hg}_2\text{Cl}_2$ is produced. The reaction appears suitable for the determination of iron pentacarbonyl. Mercuric bromide and iodide do not appear to react similarly. The pentacarbonyl reacts immediately with mercuric acetate in water or acetone. With mercuric nitrate the primary reaction appears to be followed by the immediate oxidation of the carbonyl groups by nitrate. The action of mercurous nitrate causes brisk evolution of gas and precipitation of mercury. With aqueous mercuric sulphate a yellow precipitate is formed.

H. WREN.

Oxidation of cobalt in a solution of cobaltous nitrate by sodium bismuthate. S. KITASHIMA (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 1035—1040).—Cobaltous nitrate dissolved in concentrated nitric acid turns blue when shaken with sodium bismuthate owing to oxidation of the cobalt. The degree of oxidation depends on the time of shaking and the amount of sodium bismuthate present. If the salt is dissolved in very dilute nitric acid, it retains its red colour when shaken with sodium bismuthate, but a study of the absorption spectrum shows the presence of cobaltic salts. The degree of oxidation is almost independent of the time of shaking, and in each case the cobaltic salt is considerably reduced after 2 hrs.

F. S. HAWKINS.

Cobalt allylamines: a supposed co-ordination number of eight for cobalt. W. R. BUCKNALL and W. WARDLAW (J.C.S., 1928, 2648—2654).—The composition of the compound obtained by the atmospheric oxidation of an alcoholic solution of cobaltous chloride containing allylamine has been re-investigated, and from analysis, mol. wt., and conductivity measurements ascribed the formula



has a co-valency of six, in agreement with Sidgwick's rule. The formula of Pieroni (cf. A., 1921, i, 315), which ascribes a co-ordination number of eight for cobalt, is shown to be erroneous. F. J. WILKINS.

[Chlorides of ruthenium.] H. REMY (Ber., 1928, 61, [B], 2109—2110; cf. this vol., 722).—A reply to Gall and Lehmann (this vol., 975). Owing to an error in calculation, the results obtained by the manganate titration have been interpreted as establishing the exclusive tervalency of ruthenium in Gall and Lehmann's material, whereas they show the presence of 45% of the quadrivalent metal.

H. WREN.

[Chlorides of ruthenium.] E. ZINTL and P. ZAIMIS (Ber., 1928, 61, [B], 2110—2111; cf. A., 1927, 533).—A reply to Gall and Lehmann (this vol., 975) with regard to the potentiometric titration of ruthenium salts.

H. WREN.

Methods for the calculation of analyses. II. O. LIESCHE (Z. angew. Chem., 1928, 41, 1156—1159).—Indirect methods for the analysis of difficultly separable elements are discussed. Tables are prepared showing the essential calculations involved in the determination of mixed sodium and potassium salts, barium and strontium salts, halides, sulphides of antimony, and the constituents of fluorspar. Emphasis is laid on the importance of selecting analytical methods such that small differences in experimental figures do not lead to disproportionately large changes in the calculated results.

A. G. POLLARD.

Potentiometric quantitative analysis. B. KAMIENSKI (Bull. Acad. Polonaise, 1928, A, 33—60).—The method uses two electrodes, one placed directly in the solution, the other placed inside a tube of insulating material in the solution. The solution is rapidly stirred so that it passes first of all the first electrode, and then, immediately after-

wards, the electrode in the tube. The theory of the method is explained. If the liquid to be added to the solution is dropped in continuously from a burette, there will be a maximum *P.D.* between the electrodes when the end-point is reached, if the velocity of reaction is large enough. The method is successful only if the stirring is sufficiently rapid. Experiments were carried out with oxidation and reduction reactions, e.g., $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$, $\text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}^{3+} + \text{Cr}^{3+} \rightleftharpoons \text{Cr}^{6+} + \text{Fe}^{2+}$, $\text{Sn}^{2+} \rightleftharpoons \text{Sn}^{4+}$. In each case platinum electrodes were used, with potassium permanganate as oxidation agent and a chromous solution as reducing agent. Precipitation reactions were also investigated, but it was found that these could not be suitably treated. The sharpness of the titrations is satisfactory.

A. J. MEE.

Use of Emich filter-tubes for potentiometric analysis. T. HECZKO (Z. anal. Chem., 1928, 75, 183—190).—Continuing his attempts (this vol., 726, 980) to simplify the apparatus used for potentiometric titrations, the author describes a simple arrangement in which an Emich filter-tube carrying a wire of an appropriate metal and containing a solution of suitable electrolytes serves as a comparison electrode in actual contact with the titrated solution. A column of a dilute solution of copper sulphate in a capillary serves as a suitable resistance.

J. S. CARTER.

New iodoso- (iodoso-iodyl-)benzene electrode and its application to the determination of p_{OH} or p_{H} . F. GROSSMAN (Bull. Soc. chim., 1928, [iv], 43, 1063—1072).—See this vol., 607.

4-Methylumbelliferone as a fluorescent indicator. C. BÜLOW and W. DICK (Z. anal. Chem., 1928, 75, 81—86).—In acid solution 4-methylumbelliferone is colourless, whereas in alkaline solution it shows a blue fluorescence, the change-point occurring at p_{H} 6—7. It is a suitable indicator for the titration of strong acids and bases and its action is not masked by the presence of yellow, red, or blue compounds in the solution.

A. R. POWELL.

Use of methyl-orange for the detection of free chlorine and chloroamines. BESEMANN (Chem.-Ztg., 1928, 52, 826).—Methyl-orange is decolorized by chlorine in concentrations as low as 0.5 mg./litre, whereas chloroamines do not affect the indicator, but in acid solution they liberate iodine from potassium iodide. These tests therefore provide a means of distinguishing between free chlorine and chloroamines.

A. R. POWELL.

Preparation of o-tolidine reagent for free chlorine [in water]. C. S. BORUFF, S. J. VELLENGA, and R. H. PHELPS.—See B., 1928, 838.

[Use of dimethyl-*p*-phenylenediamine hydrochloride as] indicator for chlorine [in water]. K. ALFTHAN.—See B., 1928, 838.

Electrometric titration of hypochlorite and hypochlorite-carbonate mixtures. A. RIUS and V. ARNAL.—See B., 1928, 813.

Volumetric determination of sulphuric acid. G. TESTONI (Annali Chim. Appl., 1928, 18, 408—414).—When benzidine acetate is added gradually to a solution containing either free or combined sulphuric

acid, the separation of the benzidine sulphate is instantaneous and the end of the titration may be detected by placing a drop of the clear liquid on a strip of filter-paper previously soaked in a thin suspension of lead peroxide and dried, this giving a blue coloration with the benzidine. Greater accuracy may then be attained if, when the end of the titration is approached, a portion of the liquid is filtered off and treated with lead peroxide or potassium persulphate. When, of two volumes of the benzidine solution differing by 0.1 c.c., one does and the other does not give the blue colour in this way, the mean of the two volumes is taken as correct.

The reagent is prepared by dissolving 10 g. of benzidine in 100 c.c. of glacial acetic acid, making up to a litre, leaving for a day, and filtering; the exact titre is determined by means of 0.1N-sulphuric acid. In applying the method it is advisable to use always the same volume of liquid and concentrations not widely different. Test determinations on sulphates alone and on mixtures containing also chlorides and nitrates yield satisfactory results. T. H. POPE.

Determination of nitrogen by Dumas' method. I. MAREK [with M. KRAJČINOVIČ and G. ZALJESOV] (Arhiv Hemiju, 1928, 2, 169—174).—The combustion tube contains a small boat in which is placed the substance intimately mixed with copper oxide, a roll of oxidised copper gauze some 10 cm. in length, and, at the exit end, a similar roll of bright gauze. The usual packing of copper oxide is omitted. The portions of the tube occupied by the boat and the rolls of gauze are heated electrically. The rolls of gauze are surrounded by an asbestos coating so that the tube is tightly packed and gases pass through the interstices of the gauze. The position of the boat may be altered at will without interrupting the determination. The gauze may be oxidised or reduced by passing a stream of oxygen or hydrogen through the tube and heating the desired portion. Carbon dioxide is generated in a special apparatus and absorbed in a 50% solution of potassium hydroxide. J. S. CARTER.

Koch and McMeekin's method for the determination of nitrogen. H. A. DAVENPORT (J. Lab. Clin. Med., 1926, 12, 286—287).—Ordinary 3% hydrogen peroxide is added, a correction of 0.002 mg. N per drop being made for the acetanilide.

CHEMICAL ABSTRACTS.

Detection of nitrous acid. W. VAUBEL (Chem.-Ztg., 1928, 52, 842).—The solution to be tested for nitrous acid is added to a solution of an alkali naphthionate which has been acidified with hydrochloric acid. On adding sodium hydroxide or ammonia solution a red colour is obtained in the presence of nitric acid due to the coupling of a second molecule of naphthionic acid with the diazo-compound formed in acid solution. A. R. POWELL.

Acidimetric determination of phosphate. M. HEGEDŰS (Z. anal. Chem., 1928, 75, 111—120).—For the acidimetric determination of phosphate in alkali phosphates free from heavy metals or alkaline earths 0.1—0.2 g. of the salt is dissolved in dilute nitric acid and the solution boiled to expel carbon dioxide. After cooling, one drop of methyl-orange,

followed by carbonate-free, 0.1N-sodium hydroxide solution, is added until the colour matches that of a standard solution containing 0.1 g. of potassium dihydrogen phosphate and one drop of methyl-orange. The neutralised solution is then treated with a large excess of a saturated solution of silver acetate and the coagulated silver phosphate precipitate is separated after 10—15 min. The filtrate is treated with 2—3 g. of sodium chloride and titrated, without filtration, with 0.1N-sodium hydroxide solution, free from carbonate, using phenolphthalein as indicator. Chlorides, nitrates, and sulphates do not interfere, but ammonium salts must first be destroyed by boiling with sodium hydroxide. A. R. POWELL.

Determination of phosphate as magnesium pyrophosphate. N. KRILENKO (Arhiv Hemiju, 1928, 2, 197—205).—After the addition of 1 c.c. of concentrated sulphuric acid, 20 c.c. of solution containing not more than 0.2 g. of phosphorus pentoxide are evaporated to fuming; 2 c.c. of sulphuric acid and 4—5 c.c. of a cold, saturated solution of magnesium sulphate are added, and the whole is stirred with a glass rod until the solution becomes clear. The solution is made faintly alkaline (phenolphthalein) with ammonia. If aluminium, iron, or calcium is present, 3—5 c.c. of a saturated solution of ammonium citrate are added before precipitation with ammonia. After 30 min. 25 c.c. of a warm solution containing equal parts of 10% solutions of ammonia and ammonium chloride are added. The precipitate is washed by decantation with the ammonia-ammonium chloride solution until complete settling does not occur within 10 min., when the whole is transferred to the Gooch crucible and washed with a 2.5% solution of ammonia. The crucible is dried and heated at 900°. J. S. CARTER.

Sensitive reagent for the phosphate ion. Distinction between antimony and tin. T. GASPAR x ARNAL (Anal. Fis. Quím., 1928, 26, 181—183, and Chim. et Ind., 1928, 20, 631—632).—The solution obtained by adding a solution of antimony trichloride to one of sodium molybdate furnishes an exceedingly sensitive reagent for the phosphate ion.

H. F. GILLBE.

Sodium arsenite solution. W. MEYER (Süddeut. Apoth.-Ztg., 1928, 68, 226—227; Chem. Zentr., 1928, i, 2524).—The method for the analysis of the solution of sodium arsenite and hydroxide of the German pharmacopœia (6th ed.) is criticised.

A. A. ELDRIDGE.

Determination of small quantities of carbon monoxide and methane in mixtures of nitrogen and hydrogen. K. KELLER and W. KLEMPF.—See B., 1928, 813.

Determination of traces of carbonate. J. RAE.—See B., 1928, 856.

Determination of small quantities of carbonate in presence of excess of sulphide and chloride, with particular reference to the analysis of metallic corrosion products. W. H. J. VERNON and L. WHITBY.—See B., 1928, 856.

Thymolphthalein as indicator for titrimetric determination of carbon dioxide. C. J. SCHOLLEN-

BERGER (Ind. Eng. Chem., 1928, 20, 1101).—Thymolphthalein is preferable to phenolphthalein in the titration of excess of barium hydroxide in which carbon dioxide has been absorbed. Barium carbonate is sufficiently soluble to colour the latter. As the end-point with thymolphthalein is at p_H 10.0 a blank titration should be made. C. IRWIN.

Reagent for ammonium, rubidium, and caesium ions. Sensitive reagent for the potassium ion. T. GASPAR Y ARNAL (Anal. Fis. Quím., 1928, 26, 184—185).—A 5% uranium nitrate solution produces no precipitate with sodium or ammonium chromate solution, but with potassium chromate solution a yellow precipitate is formed which is soluble in concentrated solutions of sodium chloride and uranium nitrate and in acids. A solution of equimolecular quantities of sodium chromate and uranyl nitrate forms a sensitive reagent for potassium, rubidium, and chromium ions, the solubility of the precipitate decreasing in the order given; ammonium salts also yield a precipitate. H. F. GILLBE.

Use of gelatin-oleate mixtures for the demonstration of small amounts of calcium. S. AMBERG, J. LANDSBURY, and F. SAWYER (J. Amer. Chem. Soc., 1928, 50, 2630—2632).—Dilute gelatin solutions containing an oleate may be used to obtain ring reactions with solutions containing 0.0005 mg. of calcium in 1 c.c., but the reaction is not specific for this metal. S. K. TWEEDY.

Oxalate method for separating calcium and magnesium. W. T. HALL (J. Amer. Chem. Soc., 1928, 50, 2704—2707).—The precipitation of calcium oxalate in presence of magnesium ions requires excess of ammonium oxalate; if too much of the latter is added, however, the subsequent precipitation of magnesium ammonium phosphate or of the 8-hydroxyquinoline compound of magnesium (Hahn and Vieweg, A., 1927, 639) is incomplete. Seventy-five c.c. of 0.5*N*-ammonium oxalate solution suffice for the precipitation of 0.3 g. of calcium ions in 500 c.c., or of 0.02 g. of calcium ions in presence of five or six times this quantity of magnesium ions.

S. K. TWEEDY.

Determination of traces of lead. P. SCHMIDT (Deut. med. Woch., 1928, 54, 520; Chem. Zentr., 1928, i, 2190).—The material is ashed at a dull red heat in presence of sulphuric acid, the lead dissolved in nitric acid, recovered as sulphide, and precipitated electrolytically as dioxide from an acid solution; it is finally determined colorimetrically. Determination of 0.02 mg. is possible. A. A. ELDRIDGE.

Volumetric determination of copper and zinc. S. L. ROBERTON (J. Roy. Tech. Coll. Met. Club, Glasgow, 1927—1928, (6), 37—40).—An account of the separation of copper from iron by thiosulphate precipitation, the determination of copper by titration with cyanide, and the determination of zinc by titration with ferrocyanide using a ferrous salt as internal indicator. A. R. POWELL.

Detection of copper in presence of iron. L. SZEBELLÉDY (Z. anal. Chem., 1928, 75, 167—168).—To 5 c.c. of solution are added 1 g. of ammonium fluoride and 10 drops of a 1% solution of potassium

ferrocyanide. If the amount of iron, which should be present in the ferric state, does not exceed 0.1 g. there is no interference and quantities of copper of the order 0.02 mg. are readily detected. J. S. CARTER.

Macro- and micro-iodometric determination of copper in copper salts of organic acids and enols. M. I. USCHAKOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1151—1158, and Z. anal. Chem., 1928, 75, 228—235).—The presence in solution of enols, aliphatic acids or oxy-acids, aliphatic-aromatic acids, aromatic oxy-, amino- or amino-sulpho-acids, aliphatic or aromatic-aliphatic acids with one ethylenic linking, and of aromatic nitro-acids does not appear to interfere with the iodometric macro- or micro-determination of copper. This method cannot, however, be applied in the presence of sulphinic acids, which react with iodine. R. TRUSZKOWSKI.

Determination and separation of rare metals from other metals. XI. Quantitative analysis of gallium. I. L. MOSER and A. BRUKL (Monatsh., 1928, 50, 181—192).—Previous methods for the separation of gallium are critically reviewed. Precipitation of gallium hydroxide by ammonia solution is not a suitable method for determination, on account of its solubility in solutions containing ammonia and ammonium salts. The solubility of freshly-precipitated gallium hydroxide at 20° is 0.0010 g./litre in water, 0.0322 g./litre in 4.64% ammonia solution, and 0.574 g./litre in a solution containing *M*/109 ammonia and *M*/31 ammonium sulphate. Hydrolytic methods of precipitation are also unsatisfactory. Precipitation by the basic acetate method is incomplete, and although precipitation with chloride-bromate mixture in presence of sulphate is complete, the precipitate is too finely divided. A satisfactory method is precipitation with tannin in dilute acetic acid solution, and in this way gallium may be quantitatively separated from zinc, cadmium, cobalt, nickel, manganese, beryllium, and thallium. The solution, containing about 1% of acetic acid, is treated with 2% of ammonium nitrate, and 10% tannin solution (10 parts of tannin to 1 part of gallium hydroxide) are added to the boiling solution. The precipitate is washed with water containing ammonium nitrate and a trace of acetic acid, dissolved and reprecipitated, and finally ignited. A platinum crucible may not be used, as partial reduction of the gallium oxide occurs. Ignited gallium oxide is hygroscopic. If a large amount of gallium is present, it is convenient to remove the bulk of it by the basic acetate method before complete separation by the method described above. R. K. CALLOW.

Determination of iron in silicates. A. E. J. VICKERS.—See B., 1928, 816.

Determination of iron carbonyl. R. H. GRIFFITH and G. C. HOLLIDAY.—See B., 1928, 856.

Prussian-blue and Turnbull's-blue reactions [in presence of fluoride]. L. SZEBELLÉDY (Z. anal. Chem., 1928, 75, 165—167).—In presence of increasing amounts of ammonium fluoride the colour of the precipitate obtained on addition of 1 drop of a *N*-solution of potassium ferrocyanide to 5 c.c. of a 0.02*N*-solution of ferric salt changes in the direction

blue→violet→pink→white. The corresponding colour change with solutions of potassium ferricyanide and ferrous salt is blue→grey→yellow→white. When ammonium fluoride is added after the precipitation, the ferrous ferricyanide colour is discharged, but the ferric ferrocyanide colour remains unchanged. In presence of excess of potassium ferricyanide or of mineral acid the disturbing effect of fluoride is considerably repressed. J. S. CARTER.

Analysis of potassium ferrocyanide. P. P. BUDNIKOV (J. Russ. Phys. Chem. Soc., 1928, 60, 1159—1164).—Gravimetric methods for the analysis of potassium ferrocyanide are too slow to be of any practical value; precipitation methods using zinc or silver salts are rejected owing to their indefinite endpoint, iodometric methods give variable results, whilst good results are obtained by titration with 0.05N potassium permanganate. R. TRUSZKOWSKI.

Electrometric determination of chromic acid in the presence of vanadic acid by the use of induction and catalysis. E. ZINTL and P. ZAIMIS (Z. Elektrochem., 1928, 34, 714—715).—The criticisms of Lang and Zwerina (*ibid.*, 364) of the authors' method for the simultaneous determination of chromic and vanadic acids are refuted. The method may be used in the presence of large or small quantities of vanadium, an increase in the amount of catalyst (manganese salt) being necessary with larger quantities. The fact that Lang and Zwerina observed no potential change after the chromate reduction is probably due to their having used a hydrochloric acid solution. L. L. BIRCUMSHAW.

Determination of vanadium in steel. F. IBBOTSON.—See B., 1928, 861.

Determination of bismuth in substances used in the treatment of syphilis. BOUILLENNE and M. DUMONT (Compt. rend. Soc. Biol., 1928, 98, 879—880; Chem. Zentr., 1928, i, 2636).—A micro-method, depending on the colour reaction of bismuth salts in presence of potassium iodide, is described. A. A. ELDRIDGE.

Tungsten and zirconium oxide furnace. W. M. COHN (Z. tech. Physik, 1928, 9, 110—115; Chem. Zentr., 1928, i, 2521).—For furnaces employed below 1500° tungsten wire is used as resistance material. A furnace of tungsten and zirconium oxide employed for temperatures above 2000° is described. A. A. ELDRIDGE.

High-frequency induction furnace for chemical preparations above 1000°. C. N. SCHUETTE and C. G. MAIER.—See B., 1928, 822.

Thermostat. V. ČUPR (Z. Elektrochem., 1928, 34, 679—682).—Details are given of a thermostat which can be used over a wide range of temperatures with a constancy of $\pm 0.02^\circ$. The apparatus consists essentially of two vessels, one (A) the thermostat proper, the other (B) a glass tube surrounded either by a freezing mixture or a heating coil. In order to maintain a constant temperature, liquid is automatically drawn from A to B, as required, where it is either heated or cooled and returned to A. The whole arrangement is simple, and is specially advantageous for use from -40° to $+20^\circ$. L. L. BIRCUMSHAW.

Thermostat for polarimetric work. L. RAMBERG and J. F. HEUBERGER (Svensk Kem. Tidskr., 1928, 40, 227—229).—This thermostat is constant to within 0.01° and permits of rapid changing of the polarimeter tube. It consists of a brass trough with two small observation windows of plane glass let into opposite sides; heating is effected electrically by a wire resistance net mounted on the wooden stand which carries the bath, the regulator being a modification of Ramberg's earlier model (*ibid.*, 1926, 38, 94). The polarimeter tube is carried on supports in the bath, which can be levelled bodily by three set screws attached to the wooden stand. The stirrer bearing is carried by the cover of the bath, which is hung from a support in the ceiling, hence vibration due to motor and transmission is isolated from the polarimeter tube. The thermostat liquid is optically inactive petroleum. S. J. GREGG.

Ebullioscopic method of mol. wt. determination. H. SHIBA and T. IMASE (Bull. Inst. Phys. Chem. Res., Japan, 1928, 7, 996—998).—Cottrell's apparatus was improved by constructing the funnel-shaped part with a double wall which always contained the vapour phase, and so facilitated the boiling. Accurate determinations were made with 2.5 c.c. of solution. F. S. HAWKINS.

[Simple, automatic cryostat.] A. SIMON [with O. FISCHER, R. GLAUNER, and L. EHLING] (Ber., 1928, 61, [B], 2173—2174; cf. A., 1927, 335).—A simplified method of adjusting the pressure to the required value is described. H. WREN.

Measurement of low pressures. H. TEICHMANN (Z. tech. Phys., 1928, 9, 22—26; Chem. Zentr., 1928, i, 2273).

Hot centrifuge. C. HÜTTER.—See B., 1928, 801.

[Plate to prevent back-firing of] explosive gas mixtures. P. H. PRAUSNITZ.—See B., 1928, 803.

[Preparation of] nickel mirrors by the nickel carbonyl method. C. G. FINK and W. G. KING, jun.—See B., 1928, 819.

Voltaic hydrogen generator. W. C. GARDINER and G. A. HULETT.—See B., 1928, 822.

Oils, greases, and high vacua. C. R. BURCH (Nature, 1928, 122, 729).—Vapour-pressure experiments indicate the possibility and advantage of using oil instead of mercury as working fluid in condensation pumps. A. A. ELDRIDGE.

Laboratory agitator. C. B. CARPENTER and W. A. MANUEL (Ind. Eng. Chem., 1928, 20, 1072).—A pair of wooden wheels is mounted on a shaft with central bearing and driven from a motor connected to one wheel. On each wheel near its circumference are a number of coach screws which are the seats for universal clamps. In these the samples to be mixed are placed. Any type of motion can be given. C. IRWIN.

Apparatus for examining the solubility of gases or vapours in water and various body fluids. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1927, 97, 1561—1563; Chem. Zentr., 1928, i, 2231).

Ballistic galvanometer method of potentiometric measurement for high resistance cells. H. T. BEANS and G. H. WALDEN, jun. (J. Amer. Chem. Soc., 1928, 50, 2673—2678).—The method, which may be used with cell resistances as high as 50 megohms with an extreme deviation of ± 0.5 millivolt, is very similar to that of Jones and Kaplan (this vol., 954). S. K. TWEEDY.

Hydrogen electrode vessel useful for solutions of high resistance. R. J. BEST (Austral. J. Exp. Biol., 1928, 5, 233—236).—The vessel is described and figured. A saturated potassium chloride-3% agar bridge dips into the solution of low conductivity, the p_H of which is to be measured, and by means of it connexion is effected with a standard cell.

W. O. KERMACK.

Conductivity vessels. A. LOTTERMOSER and E. BUCHHOLZ (Z. angew. Chem., 1928, 41, 1181—1182).—A vessel for carrying out conductivity measurements over long periods comprises a tube with a cylindrical bulb at its lower end; the bulb has two side tubes sealed in the lower half at opposite ends of a diameter, and from these are suspended two platinum wires 20 mm. in length and 0.3 mm. in diam. The whole is made of Jena high-resistance glass and, after filling at the temperature of the experiment, is sealed up. A modified platinum wire dipping electrode for series measurements at 25° is also illustrated and briefly described.

A. R. POWELL.

Apparatus for electrolysis with high current densities. E. DUHME and H. GERDIEN.—See B., 1928, 863.

Geochemistry.

Natural gas. K. STOCKFISH (Z. angew. Chem., 1928, 41, 472—475).—Methods of classifying natural gases are considered. Analyses of such gases are given, and are collected in a table giving the locality of the source, and the quantity of gas evolved in a definite time.

A. J. MEE.

Composition of mineral springs in Berg-Cannstatt. I. F. EGGER and K. F. SCHMITT (Jahr. Ver. vaterl. Naturkunde Württemberg, 1927, 83, 8 pp.; Chem. Zentr., 1928, i, 2593).

Helium. V. Helium content and the age of meteorites. F. PANETH [with H. GEHLEN and P. L. GÜNTHER] (Z. Elektrochem., 1928, 34, 645—652; cf. this vol., 858, 1341).—The apparatus previously described for measuring minute quantities of helium is modified so that small portions of iron meteorites can be dissolved and small portions of stone meteorites can be fused with a suitable flux in complete absence of air. The ages of some meteorites are calculated from the helium and "radium" contents; a discussion of the results is given. Measurement of the helium content, which varies between very wide limits (e.g., 2×10^{-10} to 2×10^{-5} c.c./g.), reveals differences between meteorites which cannot be detected from the results of other analyses.

S. K. TWEEDY.

Florence meteorite of Williamson Co., Texas. J. T. LONSDALE (Amer. Min., 1927, 12, 398—404).—The meteorite (Jan. 21, 1922), 3640 g., is a breccia-like chondrite, and consists mainly of olivine, enstatite, iron, and ferrous sulphide; metal 17.62, troilite 5.01, rock 77.37%. The metallic portion contains Fe 91.277, Ni 8.270, Co 0.426, Cu 0.009, P 0.018%.

CHEMICAL ABSTRACTS.

Hydrothermal paragenesis of quartz and arsenic minerals in altered quartz porphyry from Saubach i. V.; properties of pharmakosiderite and symplectite. F. HEIDE (Z. Krist., 1928, 67, 33—90; Chem. Zentr., 1928, i, 2591).

Radioactive pyromorphite from Sardinia. P. MISCIATTELLI (Atti R. Accad. Lincei, 1928, [vi], 7, 929—932).—The feebly radioactive mineral con-

tained: PbO 80.243, P₂O₅ 14.640, Cl 2.4, SiO₂ 1.06%, As₂O₅ trace. Spectroscopic examination showed the presence of traces of neodymium. R. W. LUNT.

Marmatite and christophite. W. F. DE JONG (Z. Krist., 1928, 66, 515; Chem. Zentr., 1928, i, 2170).—X-Ray examination indicates that these substances are not individuals, but mixed crystals. Christophite, Zn_{0.66}Fe_{0.34}(+Mn)S, has a 5.420 ± 0.005 Å.; marmatite, Zn_{0.73}Fe_{0.27}(+Mn)S has a 5.414 ± 0.005 Å.; sphalerite, ZnS, has a 5.395 ± 0.005 Å.

A. A. ELDRIDGE.

Structure and constitution of feldspars. F. MACHATSCHKI (Zentr. Min. Geol., 1928, A, 97—104; Chem. Zentr., 1928, i, 2243—2244).—A discussion.

A. A. ELDRIDGE.

Composition of some alkali rocks from the Eastern Arabian desert. E. SCHÜRMANN (Zentr. Min. Geol., 1928, A, 121—124; Chem. Zentr., 1928, i, 2244).

Larsenite and calcium-larsenite, from Franklin, N.J. C. PALACHE, L. H. BAUER, and H. BERMAN (Amer. Min., 1928, 13, 142—144).—Larsenite, PbZnSiO₄, orthorhombic, white, has d 5.90, optically negative, $2V$ about 80°, $\rho > v$ perceptible; α 1.92, β 1.95, γ 1.96, and contains SiO₂ 16.87, PbO 56.66, ZnO 22.74, FeO 0.10, MnO 0.14, CaO 2.42, MgO 0.20, H₂O 0.76%. Calcium-larsenite, white, lemon-yellow fluorescence in ultra-violet light, has d 4.421, optically negative, $2V = 5^\circ$; α 1.760, β 1.770, γ 1.774, and contains SiO₂ 24.10, FeO 0.48, MnO 0.57, CaO 16.36, ZnO 30.61, PbO 27.63, MgO 0.23, H₂O 0.12%.

CHEMICAL ABSTRACTS.

Kernite. W. T. SCHALLER (Amer. Min., 1927, 12, 24—25).—Kernite, Na₂B₄O₇·4H₂O, from Kern Co., California, is orthorhombic, H 3, d 1.953, $2V$ nearly 90°, α 1.454, β 1.472, γ 1.488. Analyses of kernite and ulexite are recorded.

CHEMICAL ABSTRACTS.

Ammoniojarosite. E. V. SHANNON (Amer. Min., 1927, 12, 424—426).—Ammoniojarosite, probably uniaxial, negative, ω 1.800, ε 1.750, contained Al₂O₃ 0.02, Fe₂O₃ 49.30, CaO 0.05, MgO 0.13, Na₂O 0.22,

K₂O 1.56 (NH₄)₂O 4.23, SO₃ 34.49, H₂O 9.86, insol. 0.76%.
CHEMICAL ABSTRACTS.

Holdenite from Franklin, N.J. C. PALACHE and E. V. SHANNON (Amer. Min., 1927, 12, 144—148).—Holdenite, 8MnO₂·4ZnO·As₂O₅·5H₂O, orthorhombic, has $a : b : c = 0.3802 : 1 : 0.2755$, H 4, d 4.07, optically positive, $2V = 30^\circ 20'$, α 1.769, β 1.770, γ 1.785.
CHEMICAL ABSTRACTS.

Megovernite from Sterling Hill, N.J. C. PALACHE and L. H. BAUER (Amer. Min., 1927, 12, 373—374).—Megovernite, uniaxial positive, ω 1.754, d 3.719, contained SiO₂ 8.92, MnO 42.72, FeO 1.53, MgO 11.27, ZnO 10.22, As₂O₃ 4.45, As₂O₅ 12.48, H₂O 8.49%.
CHEMICAL ABSTRACTS.

Cahnite from Franklin, N. J. C. PALACHE and L. H. BAUER (Amer. Min., 1927, 12, 149—153).—Cahnite, 4CaO·B₂O₃·As₂O₅·4H₂O, has axial ratio 1:0.615, H 3, d 3.156, optically positive, ω 1.662, ϵ 1.663. The mineral exhibits abnormal interference colours.
CHEMICAL ABSTRACTS.

Lyndochite. H. V. ELLSWORTH (Amer. Min., 1927, 12, 212—218).—Lyndochite, a new mineral of the euxenite-polycrase group from Lyndoch Township, Renfrew Co., Ont., has d 4.909, H 6.5, and contains uranium, thorium, cerium, lanthanum, didymium, yttrium, erbium, zirconium, tantalum, and niobium. The age is computed to be 1100×10^6 years.
CHEMICAL ABSTRACTS.

Maberly (Ont.) euxenite. H. V. ELLSWORTH (Amer. Min., 1927, 12, 365—367).—The mineral contains PbO 1.01, UO₂ 7.25, UO₃ 1.51, ThO₂ 2.64, (Ce,La,Di)₂O₃ 0.87, (Yt,Er)₂O₃ 24.95, TiO₂ 25.04, Ta₂O₅ 5.32, Nb₂O₅ 22.28%, with smaller amounts of commoner elements. The age is computed to be 870×10^6 years.
CHEMICAL ABSTRACTS.

Sphalerite from Mantov, near Cholešov. F. ULRICH and V. VESELY (Vestn. stat. geol. úst. Českoslov., 1927, 3, 5 pp.; Chem. Zentr., 1928, i,

2798).—A new analysis does not include fluorine, but corresponds with the formula 9ZnS·FeS. The mineral has d^{18} 4.03.
A. A. ELDRIDGE.

Pelargosite from Tremonti, Adriatic Sea. E. ONORATO (Bull. Soc. Geol. Ital., 1926, 44, 17; Chem. Zentr., 1928, i, 2797—2798).—Pelargosite, d 2.834, H 4, n_D 1.529, contained CaCO₃ 79.47, MgCO₃ 3.13, SrCO₃ 2.27, CaSO₄ 3.94, Fe₂O₃ 0.23, Al₂O₃ 0.57, NaCl 3.66, KCl 1.63, SiO₂ 0.47, H₂O 2.44, organic material 2.10%.
A. A. ELDRIDGE.

Sarkinite from Långban. G. FLINK (Geol. För. Förh., 1924, 46, 661—670; Chem. Zentr., 1928, i, 2170).—Sarkinite, pink to blood-red, has d 4.173, H 4—5, n' 1.8085, n'' 1.8065, n''' 1.7930, and contains (analysis by ALMSTRÖM) As₂O₅ 42.55, MnO 50.60, FeO 0.15, CaO 1.09, MgO 0.29, Na₂O 1.30, H₂O 3.44, Al₂O₃ 0.10, insol. 0.14%.
A. A. ELDRIDGE.

Weslienite from Långban. G. FLINK (Geol. För. Förh., 1923, 45, 557—573; Chem. Zentr., 1928, i, 2170).—The mineral has d 4.967, H 6—7, and contains Sb₂O₅ 67.37, As₂O₅ trace, FeO 6.56, MnO trace, CaO 17.96, MgO 1.24, K₂O 0.62, Na₂O 5.40, loss on ignition 1.03%.
A. A. ELDRIDGE.

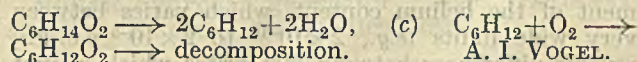
Lavas of the volcano Sumaco, Eastern Ecuador, S. America. R. J. COLONY and J. H. SINCLAIR (Amer. J. Sci., 1928, [v], 16, 299—312).—Analyses and petrographic descriptions are recorded of specimens of lavas of the volcano Sumaco.
C. W. GIBBY.

Ajkaite, a Hungarian fossil resin. L. ZECHMEISTER (Mat. term. Ertesitö, 1926, 43, 332—341; Chem. Zentr., 1928, i, 2799).—Ajkaite has d 1.05—1.06, H 2.5, n_D 1.5412. The light yellow and dark brown forms contain, respectively, C 80.38, 79.01; H 11.00, 9.89; O 7.20, 9.61; S 1.42, 1.99%. When heated, the material evolves hydrogen sulphide and then a pungent oil containing oxygen and a small amount of sulphur.
A. A. ELDRIDGE.

Organic Chemistry.

Preparation of pure methane and ethane. W. M. KEMULA (Przemysł Chem., 1928, 12, 411—412).—Methane prepared from aluminium carbide contains hydrogen, unsaturated hydrocarbons, oxygen, nitrogen, ammonia, and hydrogen sulphide, which may be removed by passing the gas through an ignition tube, packed with copper oxide and copper gauze, at the rate of 2 litres per hr. at 360°, and then through potassium hydroxide solution. Ethane produced by the electrolysis of potassium acetate is purified similarly.
R. TRUSZKOWSKI.

Oxidation of *n*-hexane. M. BRUNNER and E. K. RIDEAL (J.C.S., 1928, 2824—2825).—Investigation of the rate of oxygen consumption of *n*-hexane-air mixtures in a closed bulb maintained at 210° has shown that the rate of oxygen uptake during the initial period of no pressure change (this vol., 731) is quite rapid, and hence it is considered that the predominating reactions involved in the initial stages of the combustion at low temperatures are (a) C₆H₁₄ + O₂ → C₆H₁₄O₂ (active moloxide); (b) C₆H₁₄ +



Additive reactions of the ethylenic linking with formation of ethane compounds containing two asymmetric carbon atoms formed during the additive process and the influence of the velocity of reaction on its course. E. OTT [with R. SCHRÖTER and A. BEHR (Ber., 1928, 61, [B], 2124—2142).—The hydrogenation of the dimethylfumaric and dimethylmaleic acids as sodium salts in aqueous solution and of the stereoisomeric $\beta\gamma$ -diphenyl- Δ^2 -butenes in various solvents has been examined. The results, compared with those obtained by the addition of halogen or hydroxyl to the ethylenic linking, show an undoubted analogy in the course of all additive reactions, but the process is most obvious in the case of reduction owing to the absence of side reactions. A homogeneous addition is not the rule, but merely the exception which can be attained only by using a rate of reaction defined by the "reaction stage

rule" (cf. A., 1927, 441). In the cases of the acids and the dimethylstilbenes, the *cis*-forms, which are more reactive, have lower m. p., and hence are presumably richer in energy, are much more readily and therefore more speedily hydrogenated than the corresponding *trans*-varieties. Hydrogenation of the *cis*-forms in both cases therefore leads exclusively or predominately to the *meso*-forms, which, in each case, are richer in energy.

With the *trans*-compounds it is possible, by suitable choice of conditions of reaction under which addition occurs at a sufficiently slow rate, to convert dimethylfumaric acid exclusively into the racemic form of its additive product and to transform the butene almost entirely into *trans*-dimethylstilbene. With both compounds such an increase in the rate of reaction can be obtained by modifying the experimental conditions that the proportion of *meso*-form of the additive product far exceeds that of the racemic form. It has not been possible to make the *meso*-additive compound the sole product from the *trans*-derivative. The favoured *cis*-addition of hydrogen must doubtless be regarded as a stereochemical regularity, but its existence is merely a consequence of definite energy relationships. The course of the additive process in the case of the ethylenic linking is dependent on the differences in energy of the additive products and of those of the *cis*- and *trans*-initial materials and on the rate of reaction of the additive process. As in the case of the acetylenic linking, the processes are explained solely by considerations of energy, but the explanation is simpler with the triple linking, since a single initial material yields two products with differing energy content.

The preparation of dimethylmaleic anhydride is described in detail. It is isomerised to an equilibrium mixture of sodium dimethylmaleate and -fumarate in neutral aqueous solution; the change is readily effected in a steel flask at 180° and the established equilibrium is nearly maintained if the flask is cooled rapidly in water. Reduction of sodium dimethylmaleate in the presence of palladised charcoal or nickel, of sodium dimethylfumarate in presence of palladium under varied conditions or nickelised charcoal, and of dimethylfumaric acid by zinc dust and acetic acid is described. *s-l*-Dimethylsuccinic acid forms rhombic crystals, $a : b : c = 0.5332 : 1 : 0.4784$.

cis-βγ-Diphenyl-Δ^β-butene, m. p. 66°, is isolated from the products of the action of sulphuric and glacial acetic acids on *ββ*-diphenylbutan-*γ*-ol; its reduction in the presence of ether and palladised or nickelised charcoal is described. *trans-βγ-Diphenyl-Δ^β-butene* is reduced under very varied conditions. The racemic nature of the liquid variety of diphenylbutane is established by the preparation of the liquid hydrocarbon in its optically active form. For this purpose, phenylmethylcarbinol is resolved by the phthalic acid method and the active modification is transformed into the chloride by thionyl chloride (cf. McKenzie and Clough, J.C.S., 1913, 103, 687).

α-Chloroethylbenzene is converted by magnesium in absolutely anhydrous ether almost exclusively into the Grignard compound, whereas the action proceeds nearly completely in the direction of hydrocarbon synthesis if a little moist ether is added; the liquid diphenyl-

butane is mainly produced. If active *α*-chloroethylbenzene is used, complete racemisation occurs. Treatment of the active chloride with sodium in presence of ether gave an active *diphenylbutane* of opposite sign, the optical homogeneity of which is not established.

The following heats of combustion are recorded: *l*-dimethylsuccinic acid, 4599.2 and 4599.7 g.-cal./g., whereas the values for the corresponding *r*- and *meso*-acids are 4597.5 and 4607.7; *r-βγ*-diphenylbutane 10106 and 10098 g.-cal./g. and *meso-βγ*-diphenylbutane 10098 g.-cal./g. (as liquid). H. WREN.

Relative rates of bromination of the olefines. H. S. DAVIS (J. Amer. Chem. Soc., 1928, 50, 2769—2780).—The addition of bromine to olefines in carbon tetrachloride has been followed by colorimetric and titrimetric measurements. In solutions dried with phosphoric oxide, ethylene and bromine react very slowly in the dark. The bimolecular reaction coefficient, *K*, is not altered by the presence of oxygen or hydrogen bromide, but it may be increased 100—1000 times by adding traces of water or by exposure to sunlight. In the dark, *K* is increased 20—130 times by cooling the mixture from 25° to 0°. This probably indicates that bromination is effected mainly by a bromine hydrate, the formation of which is favoured by a fall in temperature. The rate of bromination of propylene is also increased by cooling from 25° to 0°, but those of trimethylethylene and *diisobutylene* are not appreciably changed. The following are comparative minimum values of *K* at 25° for bromination in the dark in carbon tetrachloride dried with phosphoric oxide: ethylene, 0.006; propylene, 0.2; *Δ^α*-butylene, 2.0; *Δ^β* and *iso*-butylenes, 60.0; trimethylethylene, 250.0; *diisobutylene*, 20.0. Exposure to light increases the rate of bromination in each case, but decreases the differences between the relative rates of bromination. H. E. F. NOTTON.

Relative rates of absorption of gaseous butylenes into sulphuric acid. H. S. DAVIS (J. Amer. Chem. Soc., 1928, 50, 2780—2782).—Calculations based on the work of Michael and Brunel (A., 1909, i, 197) show that the rate of dissolution of a butylene, whether pure or diluted with an inert gas, in sulphuric acid is proportional to the amount remaining undissolved. The following relative rates of dissolution at 28—30° are calculated from the absorption coefficients: *Δ^α*-butylene, 1; *Δ^β*-butylene, 2; *isobutylene*, 280—390. H. E. F. NOTTON.

Oxidation of hexadecylene. S. LANDA (Bull. Soc. chim., 1928, [iv], 43, 1086—1088).—Hexadecylene, b. p. 152—154°/13 mm., $d_{20}^{20} 0.7850$, $n_D^{20} 1.44327$, is readily oxidised to pentadecic acid, b. p. 193—195°/13 mm., m. p. 52—52.5° (ethyl ester, b. p. 172—174°/15 mm.), by agitation with 2 parts of potassium permanganate in warm 1% solution.

R. BRIGHTMAN.

Action of light on acetylene. H. REINICKE.—See this vol., 1340.

Semi-hydrogenation of the acetylenic linking and dependence of the geometrical configuration of the ethylenic compound so formed on the rate of reaction. E. OTT (Ber., 1928, 61, [B], 2119—2123; cf. Ott and Schroeter, A., 1927, 441; Salkind, *ibid.*, 643).—The occurrence of the irregular course of

reaction is regarded as a direct measure of the increase in velocity of reaction. In the hydrogenation of tetramethylbutinenediol, the catalysts may be arranged in the following order of efficiency. The irregular course is observed with palladised charcoal which has not come into contact with oxygen after precipitation of the metal on the carrier, but is not observed after contact with oxygen. Colloidal palladium and nickelised charcoal do not cause irregular hydrogenation even when shielded from oxygen. With spongy platinum the irregularity is particularly marked.

The following heats of combustion are recorded: diphenyldiacetylene, 9769 ± 2 g.-cal./g.; *trans-trans*-diphenylbutadiene, 9841 ± 3 ; *cis-cis*-diphenylbutadiene, m. p. 70° , 9864 ± 2 ; *cis-cis*-diphenylbutadiene (liquid), 9970 ± 4 . Determination of the heat of combustion of *isostilbene* prepared by various methods indicates a lack of homogeneity which is not disclosed by chemical analysis or examination of absorption spectrum or refractive index.

[With F. SCHÜRMANN.]— $\omega\omega'$ -*Tetramethyl-p-xylylene glycol*, m. p. 140° , from magnesium methyl bromide and *p*-diacetylbenzene, and $\omega\omega'$ -*tetramethyl-o-xylylene glycol*, m. p. 166° , from methyl phthalate and magnesium methyl bromide, are described. H. WREN.

Action of X-rays on chloroform and analogous substances. P. GÜNTHER, H. D. VON DER HORST, and G. CRONHEIM.—See this vol., 1340.

Production of isomerides in the formation of the double linking by dehydration of substituted alcohols. W. CHALMERS (Trans. Roy. Soc. Canada, 1928, [iii], 22, III, 69—78).—A study of the known cases of dehydration of the secondary alcohols, $\text{CH}_2\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{R}'$, shows that the unsaturated compound, $\text{CH}_2\text{R}\cdot\text{CH}:\text{CHR}'$ (I), is produced when $\text{R}=\text{Me}$, Et , Pr^β and $\text{R}'=\text{CH}_2\text{Ac}$, $\text{CH}_2\cdot\text{CHO}$, $\text{CH}_2\cdot\text{OEt}$, $\text{CHMe}\cdot\text{CO}_2\text{H}$, $\text{CHMe}\cdot\text{CHO}$. When $\text{R}=\text{Me}$ or CH_2Cl and $\text{R}'=\text{CH}_2\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\cdot\text{CN}$, the dehydration product is I, but if $\text{R}=\text{Et}$, Pr^β , Bu^β , a mixture of I and $\text{CHR}:\text{CH}\cdot\text{CH}_2\text{R}'$ is obtained. From these and other examples it is deduced that in a series of substituted alcohols a hydrogen atom will separate most easily from the following groups in the order given: $\text{CH}_2\cdot\text{CO}_2\text{H}$ ($\text{CH}_2\cdot\text{OEt}$, $\text{CH}_2\cdot\text{Ac}$, $\text{CH}_2\cdot\text{CHO}$, $\text{CH}_2\cdot\text{CO}_2\text{Me}$), $[\text{CH}_2\text{Cl}]$, Pr^β , Bu^β , Et , Me . The chloromethyl group appears to be anomalous: in the majority of examples of dehydration of chlorohydrins it occupies the position given. Saytzeff's rule (A., 1876, i, 541) is incapable of foretelling the isomeride produced.

Dehydration of α -chloro- β -methylbutan- β -ol by distillation over anhydrous oxalic acid gives a mixture of α -chloro- β -methyl- Δ^2 -butene (44%), b. p. $96\text{--}97^\circ$, d_4^{20} 0.9170, *trans*- β -chloromethyl- Δ^2 -butene (15%) (II), and 41% of *cis*- β -chloromethyl- Δ^2 -butene and β -chloromethyl- Δ^2 -butene. A similar mixture of chloro-amylenes and $\alpha\beta$ -dichloro- β -methylbutane, b. p. $133\text{--}135^\circ$, d_4^{20} 1.0785, is produced by the action of phosphorus pentachloride on *as*-methyl-ethylethylene oxide (cf. Seyer and Chalmers, A., 1927, 442). Dehydration of α -chloro- $\beta\gamma$ -dimethylbutan- β -ol, b. p. $162\text{--}164^\circ$, d_4^{20} 1.049, affords α -chloro- $\beta\gamma$ -dimethyl- Δ^2 -butene (48%), γ -methyl- β -chloromethyl- Δ^2 -butene

(20%), and γ -methyl- α -chloromethyl- Δ^2 -butene (32%) (III). The proportions of the isomerides in the above mixtures are found by determining the active (chloromethyl) halogen with alcoholic potassium hydroxide solution. When a 15% solution of sodium iodide in acetone is used (cf. Finkelstein, A., 1910, i, 453), II and III do not react, presumably because of some steric hindrance factor.

as-Methylisopropylethylene oxide has b. p. $100\text{--}101^\circ$, d_4^{20} 1.049. H. BURTON.

Preparation of nitro- and chloronitro-olefines.

E. SCHMIDT and G. RUTZ (Ber., 1928, 61, [B], 2142—2148).—The preparation of nitro- and chloronitro-olefines is effected by protracted heating of ethereal solutions of the acetyl derivatives of the corresponding chloro- or chloronitro-alcohols with potassium hydrogen carbonate: $\text{R}\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{NO}_2 = \text{R}\cdot\text{CH}:\text{CH}\cdot\text{NO}_2 + \text{AcOH}$ and $\text{R}\cdot\text{CH}(\text{OAc})\cdot\text{CHCl}\cdot\text{NO}_2 = \text{R}\cdot\text{CH}:\text{CCl}\cdot\text{NO}_2 + \text{AcOH}$. With increasing length of the hydrocarbon chain, the tendency of the nitro-olefines towards polymerisation diminishes rapidly and appears less pronounced when the chlorine atom is also present. The presence of the double linking in the $\alpha\beta$ -position follows from the difference in properties between nitropropylene and nitroallyl and from the physical properties of the compounds.

The following substances are described (cf. this vol., 504, and previous abstracts): α -nitro- β -propyl acetate, b. p. $94\text{--}95^\circ/8$ mm., d_4^{20} 1.1568, n_D^{20} 1.4242; α -chloro- α -nitro- β -propyl acetate, b. p. $90\text{--}91^\circ/9$ mm., d_4^{20} 1.2773, n_D^{20} 1.4391; α -nitro- β -butyl acetate, b. p. $105\text{--}106^\circ/11$ mm., d_4^{20} 1.1224, n_D^{20} 1.4285; α -chloro- α -nitrobutan- β -ol, b. p. $97\text{--}98^\circ/9$ mm., d_4^{20} 1.2827, n_D^{20} 1.4548, and its acetate, b. p. $98\text{--}99^\circ/12$ mm., d_4^{20} 1.2376, n_D^{20} 1.4429; α -nitro- β -amyl acetate, b. p. $111\text{--}113^\circ/10$ mm., d_4^{20} 1.0898, n_D^{20} 1.4339; α -nitro- β -octyl acetate; α -chloro- α -nitro-octan- β -ol, b. p. $140^\circ/9$ mm., d_4^{20} 1.1174, n_D^{20} 1.4570, and its acetate; α -nitro- Δ^2 -propene, b. p. $37^\circ/10$ mm., d_4^{20} 1.0661, n_D^{20} 1.4527, and its polymeride; $\alpha\beta$ -dibromo- α -nitropropane, b. p. $97\text{--}99^\circ/15$ mm., d_4^{20} 2.0303, n_D^{20} 1.5228; α -chloro- α -nitro- Δ^2 -propene, b. p. $51\text{--}52^\circ/13$ mm., d_4^{20} 1.2840, n_D^{20} 1.4759; α -nitro- Δ^2 -butene, b. p. $55^\circ/12$ mm., d_4^{20} 1.0251, n_D^{20} 1.4532; $\alpha\beta$ -dibromo- β -nitrobutane, b. p. $99\text{--}100^\circ/12$ mm., d_4^{20} 1.8857, n_D^{20} 1.5181; α -chloro- α -nitro- Δ^2 -butene, b. p. $57\text{--}58^\circ/10$ mm., d_4^{20} 1.2143, n_D^{20} 1.4728; α -nitro- Δ^2 -pentene, b. p. $69\text{--}70^\circ/12$ mm., d_4^{20} 0.9952, n_D^{20} 1.4550; α -nitro- Δ^2 -octene, b. p. $112^\circ/9$ mm., d_4^{20} 0.9476, n_D^{20} 1.4596; α -chloro- α -nitro- Δ^2 -octene, b. p. $110\text{--}111^\circ/9$ mm., d_4^{20} 1.0685, n_D^{20} 1.4700.

H. WREN.

Nitroso-compounds. J. C. EARL, F. C. ELLSWORTH, E. C. S. JONES, and J. KENNER (J.C.S., 1928, 2697—2703).—The marked tendency for a nitroso-group to undergo isomerisation to the oximino-form is demonstrated by a review of the literature. In appropriate cases the necessary hydrogen atom can be supplied by a hydroxymethyl group, with elimination of formaldehyde, as in the glycerol synthesis of Piloty and Ruff (A., 1897, i, 453). The authors have extended the work of Schmidt and Wilkendorf (A., 1919, i, 249) and of Wilkendorf and Trénel (A., 1923, i, 288) on α -nitrobutane- $\beta\gamma$ -triol by showing that the sodium salt of β -nitropropane- $\alpha\gamma$ -diol interacts with

nitrous acid, giving formaldehyde and β -hydroxy-ethylnitrolic acid, m. p. 76–77° (corr. decomp.), identical with the substance formed from β -nitroethyl alcohol. Similarly, ethylnitrolic acid has been prepared from the sodium salt of β -nitropropanol and nitrous acid.

Compounds containing one carbonyl group in place of the nitroso-group do not undergo loss of formaldehyde, although the authors consider that the oxidation of pentaerythritol by dilute nitric acid (Rave and Tollens, A., 1893, i, 617) proceeds by such a mechanism.

R. J. W. LE FÈVRE.

Electrolytic oxidation of alcohols. IV. Propyl alcohol in alkaline solution. S. KOIDZUMI (Mem. Coll. Sci. Kyōtō, 1928, [A], 11, 391–400).—Electrolytic oxidation of methyl alcohol in sodium hydroxide solution at 15–17° at a platinum anode gives a mixture of hydrogen (79–84.5%), oxygen (13.8–19.5%), and carbon monoxide (1.0–2.6%) (cf. Müller, A., 1921, i, 218). After about 27 hrs. the proportion of hydrogen decreases rapidly, carbon monoxide increases, and carbon dioxide is formed also, presumably by oxidation of the aldehyde and acid produced. *n*-Propyl alcohol in aqueous methyl-alcoholic sodium hydroxide solution gives, in addition to hydrogen, ethylene and ethane, an increased amount of the hydrocarbons being obtained at lower temperatures. The production of ethylene is explained $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{O} \rightarrow \text{CH}_2\text{O} + \text{CH}_2\text{Me} \rightarrow \text{CH}_2\cdot\text{CH}_2 + \text{H}^+$, and an analogous mechanism is suggested for the production of ethylene during the electrolysis of propionates.

H. BURTON.

Configurational relationships of hexan- β -ol and of α -hydroxy-*n*-hexoic acid to lactic acid; relationship of chemical structure to optical activity. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1928, 79, 475–488).—1- α -Hydroxy-*n*-hexoic acid, $[\alpha]_D^{20} -1.9^\circ$ (sodium salt, $[\alpha]_D^{20} +11.8^\circ$), gave ethyl *d*- α -hydroxy-*n*-hexoate, b. p. 91–93°/17 mm., $[\alpha]_D^{20} +11.0^\circ$, which was reduced to *n*-hexane- α - β -diol, $[\alpha]_D^{20} +10.8^\circ$ in alcohol (*di*- α -naphthylcarbamate, m. p. 155–160°, $[\alpha]_D^{20} -5.7^\circ$ in acetic acid). The same glycol, b. p. 110–113°/6 mm., $[\alpha]_D^{20} +15.2^\circ$, was obtained in larger amount by yeast fermentation of *n*-hexan- α -ol- β -one (prepared through α -chlorohexan- β -ol, b. p. 74–77°/12 mm., and α -chlorohexan- β -one, b. p. 70°/15 mm.), and was converted into *d*- α -bromo-*n*-hexan- β -ol, b. p. 93–95°/17 mm., $[\alpha]_D^{20} +2.85^\circ$, which was reduced to *d*-*n*-hexan- β -ol, b. p. 135–140°, $[\alpha]_D^{20} +15.0^\circ$ in ether (α -naphthylcarbamate, m. p. 61–65°, $[\alpha]_D^{20} +6.3^\circ$ in alcohol). Δ^c -Hexen- β -ol, b. p. 138–140°, was obtained by the reduction of allylacetone and was resolved through the hydrogen phthalate, thus yielding *d*- Δ^c -hexen- β -ol, $[\alpha]_D^{20} +18.2^\circ$ in ether (hydrogen phthalate, $[\alpha]_D^{20} +43.75^\circ$ in ether). *l*- Δ^c -Hexen- β -ol, $[\alpha]_D^{20} -14.1^\circ$ in ether, on reduction with hydrogen and palladium, gave *l*-*n*-hexan- β -ol, b. p. 138–139°, $[\alpha]_D^{20} -10.8^\circ$ in ether (α -naphthylcarbamate, m. p. 78–81°, $[\alpha]_D^{20} -10.4^\circ$ in alcohol); *d*- Δ^c -hexen- β -ol, $[\alpha]_D^{20} +18.2^\circ$ in ether, when treated with ozone, gave *d*- γ -hydroxyvaleric acid, $[\alpha]_D^{20} +10.5^\circ$ (barium salt, $[\alpha]_D^{20} +3.5^\circ$). It follows that *d*-*n*-hexan- β -ol and *l*- α -hydroxy-*n*-hexoic acid are configuratively related to *d*- γ -hydroxyvaleric acid and hence to

d-lactic acid (A., 1926, 1024). Up to the present this research indicates that in the carbinols the direction of rotation is determined by the distribution of masses around the asymmetric carbon atom (cf. Guye, A., 1890, 722), but that in the hydroxy-acids the effect of polarity outweighs that of mass as a determining factor.

C. R. HARRINGTON.

Catalytic hydrogenation under reduced pressure. I. Reduction of the methylheptenols. R. ESCOURROU (Bull. Soc. chim., 1928, [iv], 43, 1101–1115).—A recapitulation of earlier work (A., 1923, i, 740). Under diminished pressure, and preferably in presence of pumice impregnated with platinum oxide (A., 1922, ii, 558), the methylalkylheptenols afford the corresponding heptanols already described. Hydrogenation under ordinary pressure at 180–200° in presence of nickel affords the corresponding saturated hydrocarbons. The following are described: $\beta\zeta$ -dimethylheptane, b. p. 133–134°/740 mm., d^{20}_4 0.7209, n^{20}_D 1.40672; $\beta\zeta$ -dimethyloctane, b. p. 158–159°/750 mm., d^{20}_4 0.7410, n^{20}_D 1.41611; $\beta\zeta\eta$ -trimethyloctane, b. p. 173–176°/752 mm., d^{20}_4 0.7637, n^{20}_D 1.4270; $\beta\zeta$ -dimethylnonane, b. p. 173–176°/745 mm., n^{20}_D 1.4214, d^{20}_4 0.7506; $\beta\zeta$ -dimethyldecane, b. p. 193–196°/752 mm., d^{20}_4 0.7642, n^{20}_D 1.42821; $\beta\zeta\iota$ -trimethyldecane, b. p. 206–208°/745 mm., d^{20}_4 0.7756, n^{20}_D 1.43362, and the acetate of $\beta\zeta$ -dimethyloctan- ξ -ol, b. p. 98–100°/15 mm., d^{20}_4 0.861, n^{20}_D 1.42971. Poisoning of the catalyst may be occasioned by selective absorption of reaction products, particularly in the hydrogenation of nitriles. Reactivation may be effected by extraction with ether and combustion of the remaining impurities in a current of oxygen at 300°. Under diminished pressure the activity of catalyst is reduced and removal of the reaction products from the heated zone facilitated, thus favouring selective hydrogenation.

R. BRIGHTMAN.

Preparation of chaulmoogryl alcohol. M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 33–35).—Chaulmoogryl alcohol (40 g.), m. p. 36°, $[\alpha] +58.5^\circ$ in chloroform, iodine value 95.1, was obtained from ethyl chaulmoograte (100 g.) by Prins' method (A., 1923, i, 1172).

CHEMICAL ABSTRACTS.

Catalytic influence of hydrogen ions on the internal dehydration of a *cis*-ethylenic γ -glycol in the presence of water. BOURGUEL and RAMBAUD (Compt. rend., 1928, 187, 663–666).—The velocity of the dehydration of $\beta\epsilon$ -dimethyl- Δ^c -hexene- $\beta\epsilon$ -diol in acidic media at the ordinary temperature is shown to be a unimolecular reaction approximately proportional to the concentration of hydrogen ions. The reaction is slightly retarded on increasing the concentration of the glycol owing possibly to a weak basic action of the hydroxyl groups. The glycol is stable to alkaline media even at 100°.

G. A. C. GOUGH.

[Synthesis of the diastereoisometric trisubstituted α -glycols.] J. PASCAL (Anal. Fis. Quím., 1928, 26, 219–221).—Polemic against Tiffeneau and Lévy (A., 1924, i, 825).

H. F. GILLBE.

History of ethyl ether. E. DARMSTÄDTER (J. pr. Chem., 1928, [ii], 120, 74–88).

isoPropyl β -dibromopropyl ether. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1928, **16**, 53—55).—Propyl and isopropyl allyl ethers were prepared by boiling the sodium derivatives of the alcohols with allyl iodide. Bromination of isopropyl allyl ether in carbon disulphide yielded isopropyl β -dibromopropyl ether, b. p. 205—207°. R. K. CALLOW.

***n*-Butyl ether as solvent for the Grignard reagent.** C. S. MARVEL, A. T. BLOMQUIST, and L. E. VAUGHN (J. Amer. Chem. Soc., 1928, **50**, 2810—2812).—Under standard conditions of preparation (cf. Gilman, A., 1923, i, 193; ii, 272; 1927, 865) the yields of Grignard reagents in *n*-butyl ether are nearly equal to those obtained in ethyl ether. The resulting solutions are especially useful for reactions which require an elevated temperature for their completion. Thus, cyclohexylcarbinol (60% of the theoretical) is prepared from magnesium cyclohexyl bromide and paraformaldehyde in *n*-butyl ether at 100—110°.

H. E. F. NORTON.

Preparation of neutral sulphuric esters. R. LEVAILLANT (Compt. rend., 1928, **187**, 730—732; cf. this vol., 990).—The action of *n*-propyl alcohol on sulphuryl chloride cooled in a freezing mixture produces a 70% yield of *n*-propyl chlorosulphonate, b. p. 71—72°/22 mm., 44°/4 mm., n_D^{20} 1.4214, d_4^{19} 1.2855, which is stable at 0°, but slowly decomposes at the ordinary temperature, and is converted by the slow addition of a slight excess of *n*-propyl nitrite at 70—80° into *n*-propyl sulphate (yield 30—40%). Similarly from glycol monochlorohydrin is obtained β -chloroethyl chlorosulphonate, b. p. 101°/23 mm., n_D^{20} 1.4587, d_4^{23} 1.555 (yield 70%), which with β -chloroethyl nitrite, b. p. 89.5—90°, n_D^{20} 1.4125, d_4^{20} 1.212 (with a freshly-prepared sample), yields β -chloroethyl sulphate, b. p. 130°/3.5 mm., n_D^{20} 1.4620, d_4^{20} 1.481 (yield 40%).

J. W. BAKER.

Stereochemical studies. XVII. Optical separation and configuration. B. HOLMBERG (Z. physikal. Chem., 1928, **137**, 18—28).—Winther's hypothesis, that two acids derived from the same base must possess analogous configuration, has been investigated by separation of 22 racemic acids by active phenylethylamine. Although certain related groups of acids exhibit definite regularities, the anomalies render the hypothesis a doubtful method of determining configurations. The pairs *d*(-)-lactic acid, (-)- α -iodopropionic acid, *l*(-)-malic acid, (+)-monochlorosuccinic acid, and *d*(+)-tartaric acid, (-) dichlorosuccinic acid afford evidence for the inclusion, previously suggested by the authors on purely chemical grounds, of the (-)-halogeno-propionic and -succinic acids in the α series of the hydroxy-acids.

H. F. GILLBE.

Formation of allyl alcohol. Preparation of glycerol formins. R. DELABY and P. DUBOIS (Compt. rend., 1928, **187**, 767—769).—From the product of reaction of glycerol and formic acid under the conditions described by Koehler (A., 1914, i, 133) there were isolated by fractional distillation a glycerol monoformin, b. p. 154—157°/10 mm., d_4^{20} 1.3052, n_D^{20} 1.4614, and a diformin, b. p. 148—149°/15 mm., d_4^{20} 1.3209, n_D^{20} 1.4492 (cf. Wahl, A., 1925, i, 880). No

triformin was separated. By the reaction of sodium formate with glycerol α -chlorohydrin, $\alpha\gamma$ -dichlorohydrin, and $\alpha\beta$ -dibromohydrin, respectively, were prepared the α -monoformin, decomp. 150° in a vacuum (cf. van Romburgh, A., 1882, 378), the $\alpha\gamma$ -diformin, b. p. 144—146°/11 mm., d_4^{20} 1.3218, n_D^{20} 1.4486, and the $\alpha\beta$ -diformin, b. p. 151—153°/17 mm., d_4^{20} 1.3252, n_D^{20} 1.4503. R. K. CALLOW.

Interaction of bromine with acetic anhydride. IV. Bromination and chlorination compared. H. B. WATSON and E. H. ROBERTS (J.C.S., 1928, 2779—2786; cf. A., 1927, 1168; this vol., 153).—Measurements of the velocity of chlorination of acetic anhydride, acetyl chloride, and acetic acid have been made. The chlorination of acetic anhydride proceeds by two routes involving (a) the halogenation of the acid chloride and (b) the preliminary enolisation of the anhydride, but the velocity is slower than for bromination. Quinoline, pyridine, and sodium acetate, which inhibit the bromination of acetic anhydride, have little effect on chlorination and a theoretical interpretation of the difference is given. Chlorination of acetyl chloride proceeds more slowly than bromination, but is complicated by side reactions which are rendered imperceptible by the addition of a small quantity of iodine. Chlorination of acetic acid at 100° proceeds similarly to bromination but is slower; the reaction is accelerated by acetyl chloride or hydrogen chloride, but is almost unaffected by sulphuric acid or ferric chloride. A. I. VOGEL.

Polymerisation and condensation. IV. Glycidol acetate. P. A. LEVENE and A. WALTJ (J. Biol. Chem., 1928, **79**, 363—376).—Glycidol acetate was heated for 5 days at 132—145° and the product distilled. The fraction 101—125°/0.05 mm. was a mixture of crystals of bimolecular glycidol acetate with a liquid which was chiefly a mixture of acetins, with possibly a higher polymerisation product of glycidol acetate. The fraction 120—130°/0.05 mm. was a viscous liquid again consisting chiefly of a mixture of acetins. The vapours escaping from the main (water-cooled) receiver were condensed in a chilled tube, and yielded a partly crystalline product; it comprised for the most part a polymericide of glycidol acetate together with a small amount of a condensation product. Acetol acetate, after similar treatment, was recovered almost entirely unchanged.

C. R. HARRINGTON.

Esters of $\alpha\beta$ -dibromopropionic acid. V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1928, **16**, 49—52).—Methyl, propyl, and isopropyl $\alpha\beta$ -dibromopropionates were prepared by heating the acid with the appropriate alcohol and sulphuric acid. The isopropyl ester has b. p. 212—215°. R. K. CALLOW.

Glycerides of aliphatic acids. A. HEIDUSCHKA and H. SCHUSTER (J. pr. Chem., 1928, [ii], **120**, 145—159).—Triglycerides containing 1, 2, or 3 different aliphatic acid residues have been synthesised by methods which define their constitutions. Mono- and di-glycerides are prepared from the appropriate sodium salts and halogenohydrins (Guth, Z. Biol., 1902, **44**, 83), and the diglycerides converted into triglycerides by interaction with the requisite acid chloride in dry chloroform-pyridine solution, or with

the anhydride; when using unsaturated acid chlorides or anhydrides, the reaction should be carried out in dry carbon dioxide.

Thionyl chloride reacts only with primary alcoholic groups present in the glyceride, and thus serves to differentiate between $\alpha\beta$ - and $\alpha\alpha'$ -diglycerides. The wandering of an acyl group (cf. Fischer, A., 1920, i, 808) has been investigated by this means, and under the conditions of reaction $\alpha\beta$ -distearin is converted into the $\alpha\alpha'$ -isomeride to the extent of 20%. Thionyl chloride, followed by the appropriate sodium salt, may be used to introduce an acid residue into the α -position in the glyceride molecule, and by suitable combination of this with the above method any triglyceride may be obtained. The m. p. of glycerides are subject to alteration on keeping.

$\alpha\alpha'$ -Dipalmitin, m. p. 72°, prepared from $\alpha\alpha'$ -dichlorohydrin and sodium palmitate, when treated with lauryl chloride in chloroform-pyridine solution for 8–10 hrs. at 45–50° yields *glyceryl β -laurate $\alpha\alpha'$ -dipalmitate*, m. p. 54.6°. From $\alpha\beta$ -dipalmitin, m. p. 66.5°, by the action of thionyl chloride *$\alpha\beta$ -dipalmitin- α' -chlorohydrin*, m. p. 48.6°, is prepared, which, when heated for 8 hrs. at 150° with sodium palmitate, gives a 65% yield of *glyceryl $\alpha\beta$ -dipalmitate α' -laurate*, m. p. 53.5°. $\alpha\alpha'$ -Dimyristin, m. p. 60.5°, heated with excess of palmitic anhydride for 8–10 hrs. at 75–80°/20–25 mm., in an atmosphere of carbon dioxide, yields *glyceryl β -palmitate $\alpha\alpha'$ -dimyristate*, m. p. 49.5°. From $\alpha\beta$ -dimyristin, m. p. 58.1°, by treatment with palmityl chloride at 50° for 8 hrs. in chloroform-pyridine solution, *glyceryl α' -palmitate $\alpha\beta$ -dimyristate*, m. p. 47.8°, is prepared in 60% yield.

α -Myristin is converted by octoyle chloride, in chloroform-pyridine solution at 50–60° for several hours, into *glyceryl α -octoate α' -myristate* (an oil), which with lauric anhydride (1½ mols.) at 70–80° for 9 hrs. in carbon dioxide yields *glyceryl α' -octoate β -laurate α -myristate*, m. p. 17.7°, f. p. 3°. α -Chloro- α' -myristin is converted by octoyle chloride under the same conditions into *α -chloro- β -octoyle- α' -myristin*, which when heated for 8 hrs. at 150° with sodium laurate yields *glyceryl β -octoate α -laurate α -myristate*, m. p. 18.8°, f. p. 4.55°. α -Laurin, by successive treatment with octoyle chloride and myristyl chloride in chloroform-pyridine solution, gives a 54% yield of *glyceryl α -octoate α' -laurate β -myristate*, m. p. 14.1°, which closely resembles the product isolated from coconut oil (Bömer, B., 1914, 756). Similarly, α -octoin, by treatment with oleyl chloride in a carbon dioxide atmosphere, followed by myristic anhydride, gives a 60% yield of *glyceryl α -octoate β -myristate α' -oleate*, m. p. 10.5°, f. p. -1°; the isomeric *glyceryl α -octoate α' -myristate β -oleate*, m. p. 15.8°, f. p. 3.5°, is obtained in 35% yield from α -myristin by successive treatment with octoyle chloride and oleyl chloride. α -Chloro- α' -myristin, by treatment with sodium oleate for 8 hrs. at 150° in carbon dioxide, yields 80% of *glyceryl α' -myristate α -oleate*, m. p. 20–23°, which is converted by octoyle chloride in chloroform-pyridine solution into *glyceryl β -octoate α' -myristate α -oleate*, m. p. 14.8°, f. p. 6.7°, in 67% yield; the glyceride appears to be identical with that isolated from palm-kernel oil (Bömer, B., 1923, 1232). Improved methods for the preparation of α -stearin and

$\alpha\alpha'$ -distearin, m. p. 83.5° and 78.5°, respectively, are given. C. W. SHOPPEE.

Synthesis of behenolic acid. R. BHATTACHARYA, S. R. SALETORÉ, and J. L. SIMONSEN (J.C.S., 1928, 2678–2681; -cf. A., 1927, 339).—Methyl decanec- α -dicarboxylate, b. p. 170°/10 mm., was converted in poor yield into the *hydrogen ester*, m. p. 51°, by partial hydrolysis with cold alkali or by Grün and Wirth's method (A., 1922, i, 805), the potassium salt reduced with sodium and alcohol, and the resulting *hydroxy-acid*, m. p. 78–79° (*magnesium salt*), converted into *methyl λ -bromododecoate*, m. p. about 50°, with hydrogen bromide and methyl alcohol. Decinene, prepared from octyl iodide and sodium acetylide at 180° (cf. Picon, A., 1919, i, 429), b. p. 175–180°/685 mm., d_{20}^{20} 0.799, n_D^{20} 1.44, when condensed in the form of its sodio-derivative with methyl γ -bromododecoate in xylene solution at 160°, resulted in the formation of an oily ester which, when hydrolysed with methyl-alcoholic potassium hydroxide, gave an acid, m. p. 57°, identical in all respects with behenolic acid prepared from erucic acid. A. I. VOGEL.

Synthesis of iododihydrochaulmoogric acid and its ethyl ester. A. L. DEAN, R. WRENSHALL, and G. FUJIMOTO (U.S. Pub. Health Service Bull., 1927, No. 168, 28–30).—*Iododihydrochaulmoogric acid*, m. p. 68–69°, $[\alpha]_D^{25} +6.24^\circ$ in chloroform, acid value 139.8, saponif. value 274.8 (*ethyl ester*, m. p. 35–36°), obtained from chaulmoogric and hydriodic acids, is probably μ -(2- or 3-iodocyclopentyl)tridecoic acid. CHEMICAL ABSTRACTS.

Condensation of hydroxy-acids by catalysts in the presence of hydrogen at high pressures. V. IPATIEV and G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1928, 60, 909–912).— α -Hydroxybutyric and α -hydroxyisovaleric acids were treated with hydrogen at about 70 atm., in the presence of nickel oxide and alumina as catalysts. With α -hydroxybutyric acid, heating for 7 days at 280–290° gave a 10% yield of methylethylsuccinic, 25% of *n*-butyric, and small amounts of the higher fatty acids. The residual gas contained 35% of methane. α -Hydroxyisovaleric acid did not condense under the above conditions. The carboxyl group was eliminated to a great extent since formic acid and carbon dioxide were freely formed as well as considerable quantities of propyl alcohol. M. ZVEGINTZOV.

Condensation of hydroxy- and ketonic acids: β -, γ -, and *tert.*-hydroxy-acids. G. RAZUBAIEV (J. Russ. Phys. Chem. Soc., 1928, 60, 913–916).— β -Hydroxybutyric, lævulic, and α -hydroxyisobutyric acids were treated with hydrogen by Ipatiev's method (cf. preceding abstract). No dibasic condensation products were obtained. β -Hydroxybutyric acid gives a 33% yield of *n*-butyric acid, together with a number of degradation products—formic and acetic acids and carbon dioxide and a pleasant-smelling oil with a wide boiling range. Lævulic acid is reduced with greater difficulty, owing to the lower temperature (230°) which must be employed. The keto-group is first reduced to the hydroxyl, and the resulting γ -hydroxyvaleric acid is then further reduced to *n*-valeric acid (20% yield). Decomposition

products are also formed. Above 250° the acid is decomposed with evolution of carbon dioxide and methane and the formation of a tarry residue. α -Hydroxyisobutyric acid is easily reduced, giving a 60% yield of isobutyric acid, together with formic acid, carbon dioxide, and methane.

M. ZVEGINTZOV.

Complex oxalates of quinquevalent molybdenum. H. M. SPITTLE and W. WARDLAW (J.C.S., 1928, 2742—2756).—The three crystalline complex oxalates of quinquevalent molybdenum,

$\text{Mo}_2\text{O}_3(\text{OH})_4(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{Ba}\cdot\text{H}_2\text{O}$,
 $\text{Mo}_2\text{O}_3(\text{OH})_4\cdot\text{C}_2\text{O}_4\cdot\text{H}_2\text{R}_2\cdot 2\text{H}_2\text{O}$ ($\text{R}=\text{K}$ or NH_4),
 described by Bailhache (A., 1903, i, 66), are members of a series, $\text{R}[\text{MoO}_2(\text{C}_2\text{O}_4)_x\cdot\text{H}_2\text{O}]$, where $\text{R}=\text{K}$, NH_4 , 0.5Ba, etc., and $x=1$, 1.5, 2.5, or 3.5. When concentrated solutions of the pyridinium and quinolinium derivatives of the series $\text{R}_2[\text{MoOCl}_5]$ (A., 1927, 1044) are treated with oxalic acid, complex oxalates are obtained. Thus $(\text{C}_5\text{H}_5\text{N})_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$ gave *quinolinium molybdenum dioxoxalate*, $(\text{C}_9\text{H}_7\text{N})_2[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]$ (yellowish-brown); $(\text{C}_5\text{H}_5\text{N})_2[\text{MoOCl}_5]$ gave a complex *pyridinium molybdenum oxyoxalate*,

$(\text{C}_5\text{H}_5\text{N})_3\text{H}[\text{Mo}_4\text{O}_8(\text{C}_2\text{O}_4)_4\cdot 6\text{H}_2\text{O}]$ (orange-yellow) which with pyridine passed into $(\text{C}_5\text{H}_5\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{C}_5\text{H}_5\text{N}]$; barium chloride and $(\text{NH}_4)_2[\text{MoOCl}_5]$ gave *barium molybdenum dioxoxalate*, $\text{Ba}[\text{MoO}_2(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ (red), which with (a) potassium sulphate yielded the following *potassium molybdenum dioxoxalates*, $\text{K}[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot 3.5\text{H}_2\text{O}]$ (yellow crystals), $\text{K}[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot 2.5\text{H}_2\text{O}]$ (red), $\text{K}[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot 1.5\text{H}_2\text{O}]$ (yellow powder) and $\text{K}[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]$ (red), or (b) ammonium sulphate yielded *ammonium molybdenum dioxoxalates*, $(\text{NH}_4)[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot 2.5\text{H}_2\text{O}]$ (orange), $\text{NH}_4[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot 1.5\text{H}_2\text{O}]$ (yellow powder), $\text{NH}_4[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]$ (red crust), or (c) quinolinium sulphate gave *quinolinium molybdenum dioxoxalate* $(\text{C}_9\text{H}_7\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]$ (yellowish-brown), or (d) pyridinium sulphate gave a normal *pyridinium molybdenum oxyoxalate*, $(\text{C}_5\text{H}_5\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]$ (chrome-yellow), which on steam distillation in an atmosphere of nitrogen was transformed into the acid salt, $(\text{C}_5\text{H}_5\text{N})_3\text{H}[\text{Mo}_4\text{O}_8(\text{C}_2\text{O}_4)_4\cdot 6\text{H}_2\text{O}]$ (orange-yellow), or (e) with dilute sulphuric acid in an atmosphere of nitrogen a pale yellow *oxyoxalate* of quinquevalent molybdenum $[\text{HMoO}_2(\text{C}_2\text{O}_4)_2\cdot 1.5\text{H}_2\text{O}]$ was produced, regarded as the parent acid of the series. Determinations of mol. wts. and molecular conductivities are described and these are in accord with the coordination formulæ in dilute solutions, but polymerisation is indicated in concentrated solutions.

A. I. VOGEL.

Oxidation of $\alpha\beta\gamma\delta$ -tetrahydroxyhexoic acids by nitrous acid, and the reduction products of δ -ketorhamnolactone. E. VOTOČEK and L. BENEŠ (Chem. Listy, 1928, 22, 362—364, 385—391).— δ -Ketorhamnolactone (*p*-nitrophenylhydrazone, m. p. 176°), δ -ketorhodeolactone, and δ -ketofucolactone are prepared by adding a cold aqueous solution of nitrous acid (1 mol.) to the corresponding lactone. δ -Ketorhamnolactone yields on reduction with sodium amalgam a mixture of tetrahydroxyhexoic acids, chiefly *l*-rhamnonic, isolated as lactones. A highly laevorotatory rhamnolactone, $[\alpha]_D -99^\circ$, previously

described by Kiliani (A., 1922, i, 1111) as a lactone of guleonic acid, a supposed stereoisomeride of rhamnonic acid, is found in this mixture, and shown to be a different lactone of the same acid. The phenylhydrazones of the above reaction mixture are separated into rhamnonic phenylhydrazone, m. p. 195—196°, and *gulomethylonic phenylhydrazone*, m. p. 153°, yielding on warming with barium hydroxide *gulomethylolactone*, distinguished from rhamnolactone by its initial and final $[\alpha]_D$, -58.3° and -38.3° , respectively, its indefinite m. p., 103—153°, and by the solubility of its phenylhydrazone in 96% alcohol. This new lactone on reduction yields *d-gulomethyllose* (annexed formula), $[\alpha]_D -17.1^\circ$ (*phenyl-osazone*, m. p. 140—142°).

R. TRUSZKOWSKI.

Water of crystallisation of calcium citrate. F. PERCIABOSCO (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1368; Chem. Zentr., 1928, i, 2171).—Calcium citrate tetrahydrate loses 5.5% of its water at 100° and becomes anhydrous at 138—140°.

A. A. ELDRIDGE.

Nitrile esters of dicarboxyglutaconic acid. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 219—226; cf. this vol., 49).—Condensation of ethyl ethoxymethylenecyanoacetate with methyl sodiocyanoacetate in ethyl alcohol yields diethyl $\alpha\alpha'$ -dicyanoglutaconate hemihydrate, but in methyl alcohol the product is *methyl ethyl $\alpha\alpha'$ -dicyanoglutaconate hemihydrate*, m. p. 197° (corr.). This product is also obtained by the condensation of methyl ethoxymethylenecyanoacetate with ethyl sodiocyanoacetate in ethyl alcohol, but when this condensation is carried out in methyl alcohol the product is dimethyl $\alpha\alpha'$ -dicyanoglutaconate hemihydrate. Interchange of alkyl groups must occur when the cyanoacetic ester reacts with the sodium alkoxide, since no such interchange takes place when dimethyl sodiocyanoglutaconate is boiled with ethyl alcohol for 1 hr. By similar replacement condensation, methyl malonate with ethyl ethoxymethylenemalonate in ethyl alcohol yields *methyl triethyl dicarboxyglutaconate*, whilst in methyl alcohol the product is the *dimethyl diethyl ester*. By examination of various free nitrile esters of dicarboxyglutaconic acid and their sodium derivatives of known constitution it is shown that these give a colour with ferric chloride only when the sodium is attached to carbon bearing two carbethoxyl groups, and hence the constitution of the sodium derivative obtained by the action of ethyl ethoxymethylenemalonate on sodium malononitrile, or of ethoxymethylenemalononitrile on ethyl sodiomalonate, is $\text{C}(\text{CN})_2\cdot\text{CH}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$, from which the oily, unstable *ethyl $\gamma\gamma$ -dicyano- Δ^8 -propylene- $\alpha\alpha$ -dicarboxylate* is liberated by dilute acids. The alcoholic solution of this ester on keeping yields crystals of ethyl γ -cyano- γ -carbamyloxy- Δ^8 -propylene- $\alpha\alpha$ -dicarboxylate. Similar arguments lead to the structure $\text{C}(\text{CN})(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ for ethyl sodiocyano-carbethoxyglutaconate. Since previous work (this vol., 1216) has shown that the α and γ positions in glutaconic esters are not identical, the formation of the same sodio-derivative by the condensation of methyl (or ethyl) ethoxyethylidenecyanoacetate with ethyl (or methyl) sodiocyanoacetate, respectively, is

explained by the following scheme: $CXY:CH \cdot OEt + CH_2X'Y' \text{ (or } CX'Y':CH \cdot OEt + CH_2XY) \longrightarrow$

$CXHY:CH(OEt) \cdot CHX'Y' \xrightarrow{NaOEt} CXY:CH \cdot CNaX'Y' \text{ or } CX'Y':CH \cdot CNaXY$, the hydrogen on the carbon with the smallest number of attached cyano-groups being substituted by sodium, and that on the carbon atom with the larger number of cyano-groups being eliminated with the ethoxy-group as alcohol.

J. W. BAKER.

Photochemical studies. I. J. HOUBEN and W. FISCHER.—See this vol., 1340.

Oxidation reactions of aldehydes. J. B. CONANT and J. G. ASTON (J. Amer. Chem. Soc., 1928, 50, 2783—2798; cf. A., 1927, 116).—When 0.14M-aqueous isobutaldehyde is oxidised with potassium ferricyanide in slightly alkaline solution at 80° 2:2:5:5-tetramethyldihydropyrazine (27.5% of the theoretical), m. p. 83—84°, b. p. 160° (dinitroso-derivative, m. p. 208—210°), is formed. In 0.28M-solution, the aldehyde yields, in addition, 3:6-dicyano-2:2:5:5-tetramethyldihydropyrazine, m. p. 193—194.5° (dinitroso-derivative, decomp. 178°), which is also formed from the above dihydropyrazine and aqueous hydrogen cyanide. Quantitative experiments in borate or phosphate buffer solutions show that the nitrogen in these products is derived from part of the ferricyanide, 65% of which is recovered as ferrocyanide and the remainder as ferric hydroxide and formic acid. No isobutyric acid is obtained. Methyl isopropyl ketone is similarly oxidised to hexamethyl-2:5-dihydropyrazine (33% yield) (Gabriel, A., 1911, i, 212), but acetaldehyde yields only indefinite products. Similar reactions, involving oxidation of the β -carbon atom, occur with acid oxidising agents and are favoured by increasing dilution. Thus, isobutaldehyde gives with potassium dichromate in 2N-sulphuric acid at 80° isobutyric acid and 20—40% of acetone. *n*-Butaldehyde undergoes β -oxidation under these conditions to a similar extent, liberating carbon dioxide. With ceric sulphate in 2N-sulphuric acid at 80°, isobutaldehyde yields acetone, β -hydroxyisobutaldehyde, carbon dioxide, a trace of a substance, m. p. 166—169°, and 20% of the theoretical of isobutyric acid. The same products are obtained in acid solution with permanganate or cobaltic sulphate. Chloranil and palladium-black yield β -hydroxyisobutaldehyde but no acetone. Acetaldehyde, when kept in excess, is oxidised by very dilute permanganate at 80° to carbon dioxide (20%) as well as acetic acid. These reactions probably do not involve oxidation of the enolic forms of the aldehydes (cf. Evans and Adkins, A., 1919, i, 572).

H. E. F. NOTTON

Determination of trioxymethylene. M. E. ALESSANDRINI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1356—1367; Chem. Zentr., 1928, i, 2191).—The decomposition of the liberated formaldehyde by sodium hydroxide in Orlov's method is avoided by adding exactly the required amount of alkali to the Nessler reagent. Romijn's method can be carried out in a 2% alcoholic potassium hydroxide solution or in a 0.1N-potassium cyanide solution. Romeo's method gives too high results. A. A. ELDRIDGE.

Polymerides of aliphatic chloroaldehydes. F. D. CHATTAWAY and E. G. KELLET (J.C.S., 1928,

2709—2714).—The interaction of chloral and a large excess of concentrated sulphuric acid at 15—20° gives metachloral as the main product together with about 2% of chloralide (trichloroethylidene trichlorolactate) and about 1% of α -parachloral, m. p. 116°, b. p. 223°/760 mm. (capillary tube), and β -parachloral, m. p. 152°, b. p. 250° (capillary tube), which are separated by fractional crystallisation from alcohol. The polymerides are trimeric in benzene, not interconvertible, odourless, stable to boiling aqueous alkalis, do not react with phenylhydrazine or potassium cyanide, and dissociate into chloral on distillation under ordinary pressures, but distil unchanged at 15 mm. The isomerism is probably of the *cis-trans* type corresponding with the two possibilities in the paraldehyde ring, one having all the three trichloromethyl residues on the same side of the plane of the ring and the other having two on one side and one on the other (cf. Hantzsch and Oechslein, A., 1907, i, 1009). Paradichloroacetaldehyde does not appear to exist in isomeric forms. Butylchloral hydrate on treatment with not less than 6 parts by weight of concentrated sulphuric acid gave an 80% yield of the two α - and β -parabutylchlorals, which were separated by crystallisation from acetic acid. α -Parabutylchloral has m. p. 180°, b. p. 235°/760 mm. (capillary tube), and β -parabutylchloral has m. p. 157°, b. p. 233°/760 mm. (capillary tube); they are trimeric in benzene and resemble the parachlorals in properties. Butylchloral appears not to form a polymeride of the meta-type; it is unaffected by hydrogen chloride and is converted into a mixture of the two parabutylchlorals by pyridine. Anhydrous butylchloral is best prepared by distillation of the hydrate with about half its weight of acetic anhydride in the absence of moisture or by distillation of the dry polymeride under ordinary pressure (quantitative yield).

A. I. VOGEL.

Action of ketones on mercuric iodide in presence of alkali. E. MONTIGNIE (Bull. Soc. chim., 1928, [iv], 43, 1115—1117).—When boiled with mercuric iodide and aqueous potassium hydroxide acetone gives a yellow precipitate of a compound, $COMe \cdot CHMg_3I_2$, decomp. at 180°, insoluble in all solvents and very slowly attacked by warm 30% potassium hydroxide. It is readily decomposed by cold dilute acids, but not by dry hydrogen chloride. Potassium iodide removes mercuric iodide. The following ketones give a similar reaction: methyl ethyl ketone, methylheptenone, acetophenone, benzylacetone, methyl benzyl ketone, cyclohexanone, essence of rue (mixture of methyl heptyl ketone and methyl nonyl ketone), antipyrine, and, in alcoholic solution, benzophenone and benzylideneacetone and in aqueous alcohol, camphor. The reaction is not given by quinones, and it can be utilised for the determination of acetone in urine by adding 0.5 c.c. of phosphoric acid to 100 c.c. of the urine, distilling, and using 25 c.c. of the distillate for the test.

R. BRIGHTMAN.

Determination of constitution by means of ozone. R. ESCOURROU (Bull. Soc. chim., 1928, [iv], 43, 1088—1100).—Methylheptenone, obtained by hydrolysis of citral, yields a colourless ozonide which, on decomposition with ice-water, affords acetone and

lævulaldehyde (cf. Harries, 1903, i, 605) with a little lævulic acid and probably a polymeride of high b. p. This methylheptenone accordingly has the β -structure, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{COMe}$, only traces of the α -isomeride being present. When similarly treated the methylheptenone obtained as a by-product in the preparation of ψ -ionone gives much formaldehyde, which may be due to the presence of dipentene in the methylheptenone. Proof of the presence of the α -isomeride in this product is afforded by the formation of formaldehyde from the ozonide of the benzylmethylheptenol, b. p. 146—147°/7 mm., obtained from it by means of magnesium benzyl chloride. The presence of impurities containing a terminal CH_2 group vitiates the direct ozonisation of methylheptenone, b. p. 60—61°/10 mm., d^{20}_D 0.8531, n^{20}_D 1.46195, α_D -45.33°, obtained by fractionation of essence of lemon-grass, but decomposition of the ozonide of inactive methylisoamylheptenone, b. p. 120—122°/13 mm., d^{20}_D 0.8565, n^{20}_D 1.45947, prepared from it affords formaldehyde and a considerable amount of acetone, indicating that the original methylheptenone consists of both α - and β -forms with the latter predominating. The dimethyldecadiene obtained by dehydration of methylbutylheptenol is similarly shown to consist almost entirely of $\beta\beta$ -dimethyl- $\Delta^{8,9}$ -decadiene, since its ozonide affords on decomposition acetone, butaldehyde, and lævulaldehyde with only traces of formaldehyde, possibly from $\beta\beta$ -dimethyl- $\Delta^{8,9}$ -decadiene. Quantitative experiments in aqueous acetic acid as solvent confirm the results obtained previously with Java geraniol and citronellol (A., 1925, i, 772). Similarly, limonene, b. p. 175—176°, d^{14}_D 0.847, n^{20}_D 1.4717, $[\alpha]^{20}_D$ +116.1, is shown to contain about 80% of the limonenic and 12% of the terpinolenic form, the remaining 8% being probably α -terpene. Decomposition of the ozonide gives a small quantity of an insoluble waxy substance, m. p. 88—90°. Analysis of methylisoamylheptenol shows that this product contains 10—11% of the α -form. R. BRIGHTMAN.

Action of alkali and carbon disulphide on xylan. E. HEUSER and G. SCHORSCH (Cellulosechem., 1928, 9, 109—119; cf. this vol., 1219).—The trustworthiness of two methods for the determination of carbon, (1) oxidation with chromic and phosphoric acids and direct measurement of the volume of carbon dioxide evolved (Berl and Innes, A., 1909, ii, 520), (2) oxidation with an excess of potassium dichromate and sulphuric acid and determination of excess of dichromate by titration, was tested on pure sodium oxalate. In this case the former method gave the better results, but with xylan the results obtained by this method varied by as much as 10% from the theoretical value. Better results (2% error) are obtained, in the case of xylan, by the titration method when the following conditions are fulfilled. The xylan is oxidised with 33.3—66.6% excess of potassium dichromate solution (90 g./litre) in a solution containing 20—25 vol.-% of concentrated sulphuric acid with addition of several drops of mercury, by heating for 3—5 min. After cooling, an excess of ferrous ammonium sulphate solution is added and the excess titrated with 0.1N-potassium permanganate solution.

J. W. BAKER.

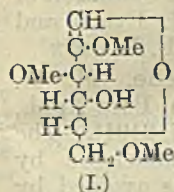
Gasometric determination of reducing sugars. D. D. VAN SLYKE and J. A. HAWKINS (J. Biol. Chem., 1928, 79, 739—767).—The solution containing sugar is heated with a known amount of potassium ferricyanide in presence of alkali; the excess of ferricyanide remaining is determined by measurement of the nitrogen evolved when it is caused to react with excess of hydrazine in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to blood (0.2 c.c. and upwards), after removal of proteins with tungstic acid, and may be applied directly to diluted urine. In the case of blood from anaesthetised patients, care must be taken to remove all ether by boiling before carrying out the gasometric analysis.

C. R. HARRINGTON.

Determination of reducing sugars, especially dextrose, in presence of hydrocyanic acid, with alkaline copper solutions. M. HÉRISSEY and A. CHALMETA (J. Pharm. Chim., 1928, [viii], 8, 393—406).—The presence of hydrocyanic acid in the sugar solution causes a diminution in the weight of copper oxide formed. The losses of copper oxide have been found to be due to (a) reaction of the hydrocyanic acid with dextrose according to the Kiliani reaction, (b) the formation of small quantities of copper cyanide, (c) the formation of soluble sodium copper cyanide. Satisfactory results can be obtained by preliminary removal of the hydrocyanic acid by heat, by a current of air, or by precipitation and removal as silver cyanide, the small excess of silver nitrate necessary for the precipitation being removed with sodium chloride. The end-point in the titration of a sugar solution in presence of hydrocyanic acid with an alkaline copper solution is very indistinct. E. H. SHARPLES.

Oxygen bridges in sugars. IV. Anhydrides of 2:3:6-trimethylglucose. K. HESS and F. MICHEEL (Annalen, 1928, 466, 100—114; cf. A., 1927, 1056).—Repetition of the preparation of 2:3:6-trimethylanhydroglucose previously described (*loc. cit.*) yielded the same product, b. p. 111—113°/0.2 mm., $[\alpha]^{18}_D$ +70.6° in chloroform, contrary to the statement of Freudenberg and Braun (this vol., 399), but the behaviour of the product with pyridine and acetic anhydride and the action of bromine indicate that instead of being a mixture of the strained and unstrained forms of trimethylanhydroglucose in the proportions 75% and 25%, respectively (not 25% and 75% as previously misprinted), it contains the unstrained form and an unsaturated compound, probably (I), which gives an oily acetyl derivative, $[\alpha]^{18}_D$ +45.5° in chloroform.

An attempt was made to complete an analogous series of reactions with derivatives of 2:3:6-trimethylglucose containing a butylene oxide ring. 2:3:6-Trimethylglucose, conveniently prepared in quantity by hydrolysis of trimethylcellulose with methyl-alcoholic sulphuric acid, was converted into a mixture of the α - and β -forms of butylene-oxidic 2:3:6-trimethylmethylglucoside (cf. Schlubach and Bomhard, A., 1926, 600). The action of benzoyl chloride in pyridine yielded the 5-benzoyl derivative, $[\alpha]^{20}_D$ -35° to -43° in methyl alcohol,



which was converted by hydrogen chloride into butylene-oxidic 1-chloro-5-benzoyl-2:3:6-trimethylglucose, m. p. 122—123°, $[\alpha]_D^{20}$ -114.5° in chloroform. Reaction with trimethylamine yielded butylene-oxidic 5-benzoyl-2:3:6-trimethylglucosidotrimethylammonium chloride, m. p. 146—149° (decomp.), $[\alpha]_D^{20}$ -60.2° in water (additive compound with pyridine hydrochloride, m. p. 102—194°, $[\alpha]_D^{20}$ -48.4° in water). Attempts to prepare an anhydride by the action of alkali yielded only butylene-oxidic 2:3:6-trimethylglucosidotrimethylammonium hydroxide, m. p. 187—188°, $[\alpha]_D^{20}$ -68.3° in water (chloride, m. p. 165° $[\alpha]_D^{20}$ -68.4° in water), and decomposition occurred on more vigorous treatment. The unbenzoylated base began to decompose at 180° when heated in a vacuum, without any sign of anhydride formation. Butylene-oxidic 5-acetyl-2:3:6-trimethylglucosidotrimethylammonium chloride, $[\alpha]_D^{20}$ -33.9° in water, prepared from the base, could not be converted into an anhydride. Following the conclusion that only one anhydride was formed in the reaction previously described (*loc. cit.*), and assuming that the configuration of the ammonium salt must be favourable to anhydride formation, it follows that the α -configuration must be assigned to both the present compounds and those previously described, but this is in conflict with the evidence of relative rotatory powers.

R. K. CALLOW.

Oxygen bridges in sugars. V. Method of determining α - or β -configuration of disaccharides. K. HESS, F. MICHEL, and O. LITTMANN (Annalen, 1928, 466, 115—130).—If a disaccharide is hydrolysed by methyl-alcoholic hydrogen chloride, the proportions of α - and β -methylhexosides derived from the hexose present as hexoside may be expected to vary according to the nature of the linking in the original disaccharide, and an excess of one form as compared with the proportion present in the equilibrium mixture may be taken as evidence that the hexoside linking in the disaccharide is of that configuration, assuming that no inversion takes place. In the application of this method to the determination of the configurations of lactose and cellobiose, the fully methylated sugars were used, in order to avoid shifting of the oxygen bridge, and the hydrolysis was performed at 0°, with the addition of sufficient methyl chloride to keep the concentration of acid sensibly constant. The tetramethylmethylhexoside mixture was separated from the mixed sugars after benzylation by extraction with water and distillation. The equilibrium mixtures were obtained by keeping the tetramethylmethylhexosides under the conditions used in the hydrolysis and working up in a similar way. Both lactose and cellobiose yielded tetramethylmethylhexoside mixtures containing the β -form in larger proportion than the equilibrium mixture, as determined by observations of the rotatory powers of the mixtures and the pure components, and the β -configuration deduced by fermentation methods was thus confirmed.

α -Methylgalactoside, $[\alpha]_D^{20}$ +175.6° in water (as hydrate) (cf. Fischer, A., 1895, i, 437), prepared by passing hydrogen chloride into a solution of galactose in methyl alcohol and keeping, was converted by acetic anhydride in pyridine into 2:3:4:6-tetraacetyl- α -methylgalactoside, m. p. 86—87°, $[\alpha]_D^{20}$ +132.5°

in chloroform, which yielded the unchanged α -methylgalactoside on hydrolysis. Methylation of the acetate by methyl sulphate and alkali yielded 2:3:4:6-tetramethyl- α -methylgalactoside, b. p. 80—84°/0.05 mm., $[\alpha]_D^{20}$ +188.5° in water (Irvine and Cameron, J.C.S., 1904, 85, 1078, give +143.4°), and +148.0° in alcohol. Octamethylcellobiose, m. p. 86°, $[\alpha]_D^{20}$ -15.70° in water, -14.63° in chloroform, was prepared by repeated treatment of hepta-acetylmethylcellobioside with methyl sulphate and sodium hydroxide. The other substances were prepared by known methods.

R. K. CALLOW.

Reactivity of methylated sugars. III. Action of dilute alkali on tetramethyl- d -mannose. R. D. GREENE and W. L. LEWIS (J. Amer. Chem. Soc., 1928, 50, 2813—2825).—Mainly a more accurate repetition of previous work (cf. A., 1927, 751; this vol., 509). The equilibrium solution obtained from mannose in presence of dilute alkali contains mannose (71.7%), dextrose (8.9%), and α -lactulose (16.9%). At the same alkali concentration, pure tetramethylmannose, m. p. 50.5—51.5°, $[\alpha]_D^{20}$ +23.0° in chloroform (crystallographic data), undergoes 50% conversion into tetramethylglucose. The sugars have been isolated almost quantitatively from the product by fractional crystallisation of their anilides from aniline. Tetramethylmannoseanilide has a variable initial rotation changing to $[\alpha]_D^{20}$ -8.5° in ethyl alcohol containing a trace of hydrochloric acid, and tetramethylglucoseanilide has $[\alpha]_D^{20}$ +230° changing to +59°.

H. E. F. NOTTON.

Acetylmonosaccharides. V. Rates of hydrolysis of tetra-acetylmethylmannosides and of triacetylmethyl-lyxosides. P. A. LEVENE and M. L. WOLFROM (J. Biol. Chem., 1928, 79, 471—474).—The α - and β -forms of methylmannoside tetraacetate and the α -form of methyl-lyxoside triacetate hydrolyse at the same (slow) rate, whilst the γ -forms in both cases hydrolyse rapidly, these three forms corresponding with those described by Fischer and others (A., 1921, i, 96) in the case of the methylrhamnoside triacetates.

C. H. HARRINGTON.

Periplocymarin and periplogenin. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1928, 79, 519—530).—Periplocin (cf. Lehmann, A., 1897, i, 626), or extracts of the stems and branches of *Periploca græca*, on treatment with strophanthobiase (cf. A., 1926, 982) yielded a chloroform-soluble glucoside periplocymarin, $C_{30}H_{46}O_8$ (also +MeOH), m. p. 148°, $[\alpha]_D^{20}$ +29° in 95% alcohol; when hydrolysed with dilute hydrochloric acid this gave periplogenin, $C_{23}H_{34}O_5$, m. p. variable, $[\alpha]_D^{20}$ +31.5° in alcohol (benzoate, m. p. 235°); periplogenin is an unsaturated lactone, since on boiling with alkali it neutralises one equivalent, and with hydrogen and palladium it gives the dihydro-derivative, m. p. 204°. When treated with methyl-alcoholic sodium hydroxide, periplogenin gave isoperiplogenin, m. p. 258°, which, with sodium hypobromite, yielded isoperiplogenic acid, m. p. 215° (with water of crystallisation; methyl ester, m. p. 252°), which still contained a lactone group. The chemical behaviour of periplogenin is therefore closely analogous to that of strophanthidin and digitoxigenin.

C. R. HARRINGTON.

Polysaccharides. II. Acetylation and methylation of starch. W. N. HAWORTH, E. L. HIRST, and J. I. WEBB (J.C.S., 1928, 2681—2690).—Potato starch, precipitated from its aqueous solution by alcohol, when acetylated in presence of traces of sulphur dioxide and chlorine as catalysts gives triacetyl starch, $[\alpha]_D^{20} +170^\circ$ in chloroform, in 96% yield, which is similar to Bergmann and Knehe's triacetyl amylose (A., 1927, 342). The regenerated starch produced by deacetylation appears to be identical with amylose. The relationship between amylose and amylopectin is discussed and the views of Samec and Meyer (A., 1921, i, 707) are supported. Methylation of triacetyl starch in acetone solution with methyl sulphate and dilute alkali gave after six methylations an 89% yield of trimethyl starch (44% OMe), m. p. 148° , $[\alpha]_D^{20} +208^\circ$ in chloroform, probably identical with Irvine and Macdonald's material (A., 1926, 823) derived from rice and potato starch. Hydrolysis with methyl-alcoholic hydrogen chloride gave an 80% yield of trimethyl-methylglucoside, which on further hydrolysis with 5% aqueous hydrochloric acid gave only β -D-trimethylglucose (yield 85%). Methylation of triacetyl starch in aqueous solution gave an 80% yield of "dimethyl starch" (OMe 31.8%), $[\alpha]_D^{20} +143^\circ$ in chloroform, which is not homogeneous (cf. Irvine and Macdonald), since when hydrolysed it gave a mixture of trimethyl-, dimethyl-, and monomethyl-glucose.

A. I. VOGEL.

Polysaccharides. III. Molecular complexity of inulin. H. D. K. DREW and W. N. HAWORTH (J.C.S., 1928, 2690—2697).—Determinations of the mol. wt. of inulin in water by the b. p. method show a continuous diminution over a period of time, the initial value being about 4000, which fell to about 900. It is considered that the initial mol. wt. of inulin in boiling water is not less than 3200 or 3600 and hence that the polysaccharide is composed of fructofuranose units linked together in chains containing 20—24 such units. The results of Pringsheim, Aronowsky, and Lassmann (A., 1921, i, 545; 1922, i, 634) by the cryoscopic and ebullioscopic methods are criticised. Inulin when treated in aqueous solution by carbon dioxide or when the solid is exposed to ethyl chloroformate vapour, is transformed into a product, termed "inulin laevulin," which is readily soluble in cold water to a clear solution and has a greater specific rotation and greater reducing action towards hot Fehling's solution than inulin itself. This represents the intermediate stage in the hydrolysis of inulin to laevulose.

A. I. VOGEL.

Cellulose. XXXII. Characterisation of cellulose preparations by the rotation method. K. HESS and N. LJUBITSCH (Annalen, 1928, 466, 1—18).—The identity of the rotatory power of cuprammonium solutions of cellulose from different sources and of the course of variation of rotatory power with concentration (cf. A., 1925, i, 1246) is reaffirmed, contrary to the observations of Hägglund and Klingstedt (B., 1928, 119). The exact experimental procedure is now described in greater detail. Repetition of the measurements recorded by Hägglund and Klingstedt, using samples of the same material, showed that when appropriate precautions were

taken, including preparation of solutions in absence of air and complete removal of foreign materials from the crude cellulose material, the figures for cotton and pine-wood cellulose agreed closely with those for "standard cellulose" (*loc. cit.*).

In view of the suggestion that foreign materials might influence the values of the rotatory power, the behaviour of mannan and xylan from pine wood (cf. this vol., 1361) was examined. The mannan is completely precipitated as a copper-alkali complex under the standard conditions of the determinations and therefore has only an indirect influence on the figures obtained if it is not removed. In absence of alkali the rotatory power is much less than that of cellulose, but the rotatory power-concentration curve is of the same type. The xylan has a slightly greater rotatory power than cellulose, and the curve is again of the same type. Rotatory powers, but not the course of the curve, may, therefore, be affected by these impurities, and an estimate of their amount may be obtained by measurement of the rotatory power of the crude material.

R. K. CALLOW.

Cellulose. XXXIII. Detection of a foreign substance in cellulose fibres. II. K. HESS, F. MICHEEL, and W. REICH (Annalen, 1928, 466, 73—79; cf. A., 1927, 44).—Further investigation of the nitrogenous, ash-containing, foreign substance in cotton fibres showed that it was destroyed completely by hydrolysis with concentrated hydrochloric acid, partly destroyed by acetolysis with acetic acid and hydrogen bromide, or, to a smaller degree, with acetic anhydride and sulphuric acid. The last process yields an ash-free substance. A similar foreign substance can be isolated from ramie fibres. The substance can be obtained practically free from ash by precipitation of the calcium in aqueous solution by oxalic acid. Treatment of the ash-free substance with calcium hydroxide yields a substance containing 33% of ash.

R. K. CALLOW.

Cellulose. XXXIV. Trimethylcellulose. K. HESS, C. TROGUS, and H. FRIESE (Annalen, 1928, 466, 80—94).—There is no real discrepancy between the results of methylation of cellulose by Hess and Pichlmayr (A., 1927, 44) and by Urban (B., 1926, 531) and Freudenberg and Braun (this vol., 399). A sample of the product obtained by the last-named could be partly dissolved in water with suitable mechanical treatment (shaking with glass beads in water, or keeping in water for several weeks), or after swelling and dissolving in indifferent solvents. The water-soluble fractions in each case had the same rotatory power and X-ray diagrams. Such difference as appears to exist at first sight is caused by preservation of the non-cellulosic coating of the fibre due to incomplete purification in the case of the cotton from which "insoluble" trimethylcellulose is prepared. There are, therefore, no grounds for assuming either that an insoluble trimethylcellulose exists or that soluble trimethylcellulose is a disintegration product. [With H. PICHLMAYR.]—Further details are given of the preparation of crystalline trimethylcellulose.

R. K. CALLOW.

Cellulose. XXXV. Crystalline triethylcellulose. II. K. HESS and A. MÜLLER (Annalen, 1928,

466, 94—99; cf. A., 1927, 861).—Triethylcellulose was prepared in 70% yield by repeated treatment of purified cotton with ethyl sulphate and sodium hydroxide, and had the same properties as the material from other sources (*loc. cit.*). Hydrolysis by ethyl-alcoholic hydrogen chloride furnished *triethyl-ethyl-glucoside*, b. p. 120—123°/0.2 mm., $[\alpha]_D^{18} + 63.37^\circ$ in water, in 94% yield. Further hydrolysis of the latter yielded triethylglucose. R. K. CALLOW.

Substances accompanying cellulose. III. Isolation of mannan and xylan from pine sulphite pulp. K. HESS and M. LÜDTKE (*Annalen*, 1928, 466, 18—26; cf. this vol., 1360).—Extraction of pine sulphite pulp with 2*N*-sodium hydroxide and addition of acetic acid to the extract yielded a precipitate containing mannan, cellulose, and xylan. The mannan was isolated by precipitating the copper-alkali complex from cuprammonium solution by the addition of sodium hydroxide to a concentration of 0.2*N*. From the solution of the complex in water, made faintly acid with acetic acid, methyl alcohol precipitated crude mannan. After redissolving in cuprammonium solution and two repetitions of the above process, pure mannan was separated, the rotatory power of which was unchanged by further purification, and showed identical properties with mannan *A* from ivory nut (A., 1927, 960). The alkaline cuprammonium solution from which the mannan had been precipitated yielded on neutralisation a precipitate of cellulose. Crude xylan was precipitated from the filtrate by methyl alcohol and purified by precipitation from cuprammonium and aqueous solution. The *xylan* thus obtained differed from that from bamboo (cf. following abstract); it gave no reaction with zinc chloride-iodine, was soluble in water only when freshly precipitated, and had $[\alpha]_D^{20} - 87.44^\circ$ in 2*N*-sodium hydroxide, and $\alpha_{D}^{20} - 4.55^\circ$ in cuprammonium solution under standard conditions. Xylose, characterised by the osazone and the cadmium bromide compound of xylonic acid, was the only product of hydrolysis. R. K. CALLOW.

Substances accompanying cellulose. IV. Cell membrane of plants. K. HESS and M. LÜDTKE (*Annalen*, 1928, 466, 27—58; cf. this vol., 559).—Bamboo stalks, after disintegration by treatment with chlorine dioxide and sodium sulphite, yielded a fibre containing 70% of cellulose. By extraction of the fibres with sodium hydroxide, precipitation of the extract by methyl alcohol, and purification by precipitation from cuprammonium solution with acetic acid, a *xylan* was isolated, $\alpha_{D}^{20} - 4.85^\circ$ in cuprammonium solution under standard conditions, coloured violet by zinc chloride-iodine, and yielding only xylose on hydrolysis. Further fractionation from cuprammonium solution gave no evidence of separation. The pentosan content of the fibre was 22.5%, but after removal of long fibres by sieving this rose to 39%, and it is concluded that the *xylan* is essentially a constituent of the parenchyma. This is confirmed by microscopical observation of corrosion of the fibres by sodium hydroxide and by 12% hydrochloric acid. Cutin was detected in residual epidermal cells after treatment of the fibre with cold 75% sulphuric acid.

A further account is given of the detection of a substance of "furfuroid" nature, not a carbohydrate, present in the primary layer of the bamboo fibre (cf. *loc. cit.*), characterised by a reddish-violet coloration with phloroglucinol and alcoholic hydrochloric acid which appears after 1—2 days. Bamboo fibres swollen in cuprammonium solution assume the appearance of a string of beads. This phenomenon appears to be due to an outer skin on the fibre and crosswise subdivision of the fibre at intervals of 10—30 μ by layers of the above substance. Microscopical observation of the swelling also indicates that the fibre is constructed of concentric layers, probably separated by a substance similar to that which forms the skin, and a lengthwise striation is also visible. It is suggested that the sections of fibre formed in this way yield the "cell-wall units" isolated by Hess and Schultze from the bast-fibres of ramie (A., 1927, 861). Further subdivisions of the cell-wall may exist in the form of actual or potential fibrillae. The investigations of bamboo fibres confirm the previous conclusion (*loc. cit.*) that lignin is not chemically combined with the cellulose. R. K. CALLOW.

Substances accompanying cellulose. V. Cellulose from young shoots and old heart wood. K. HESS, M. LÜDTKE, and H. REIN (*Annalen*, 1928, 466, 58—72).—The fibre obtained from 14-day-old beech shoots by treatment with chlorine dioxide and sodium sulphite was repeatedly extracted with sodium hydroxide of increasing concentrations. The residue was pure cellulose. The extracts contained no cellulose, but only a xylan and a small amount of a new glucosan. Similar treatment of 385-year-old wood of *Sequoia gigantea* yielded cellulose indistinguishable from the first in rotatory power or viscosity in cuprammonium solution.

[With C. TROCUS.]—The separation of the cellulose from each of the raw materials was followed by observation of the X-ray diagrams. In each case the characteristic cellulose interference rings, at first faint, are intensified as the interference by foreign substances decreases. The crystallites appear to be less uniformly oriented in the young shoot. R. K. CALLOW.

True lignin. II. Action of bromine on acetylated pine wood. W. FUCHS and O. HORN (*Ber.*, 1928, 61, [B], 2197—2202; cf. this vol., 743).—Dry, acetylated wood is uniformly converted by bromine in carbon tetrachloride in presence of iodine as catalyst with small loss of acetyl groups and slight evolution of hydrogen bromide into *perbromoacetylated wood I*, containing about 6% Br. This somewhat unstable material loses two thirds of its bromine as hydrogen bromide when treated with a solution of alkali acetate, giving *bromoacetylated wood I*, which retains the structure of wood and, after restoration of the removed acetyl, contains 2% Br, 38—39% OAc, and 17% of lignin. Hydrolysis of *perbromo-* and *bromo-*acetylated wood I with acid gives a lignin preparation having about 11% Br, so that the firmly-bound portion of the halogen, at any rate, must be contained almost exclusively in the lignin component. *Bromo-*acetylated wood I is transformed by bromine into *perbromoacetylated wood II*, which loses three fifths of its bromine as hydrogen bromide under the influence

of alkali acetate, giving *bromoacetylated wood* II containing, after restoration of any removed acetyl, 3.5% Br, 18% of lignin, and 37% OAc. Hydrolysis transforms these products into *bromolignin* II, containing about 18% Br. Bromoacetylated wood II does not absorb bromine. On the basis of the bromine content of the various preparations, the minimum mol. wt. of the lignin present in acetylated wood is calculated to be 690 ± 40 .

The simplest explanation of the bromination phenomena is found in the assumption of the presence of a double linking in a tetrahydrobenzene ring which, by a process of exhaustive bromination, passed into a derivative of bromobenzene.

H. WREN.

Methoxyl content in the degradation of the lignin and cellulose of wood. R. FALCK and W. COORDT (Ber., 1928, 61, [B], 2101—2106; cf. B., 1927, 213).—Great variations are observed in the methoxyl content of wood, before and after extraction with a mixture of alcohol and benzene and after "corrosion and destruction" in varying degree. The methoxyl content of lignin isolated by Urban's process is about 6% lower than in extracted wood. As "destruction" proceeds the difference sinks to about 3%, so that, according to methoxyl content, three types of lignin may be distinguished: (1) that in sound, corroded, and feebly destroyed wood, (2) that in greatly destroyed wood, and (3) Urban's lignin. The isolated lignin preparations have suffered change during chemical treatment leading to a minimal loss of about 6% OMe. On the other hand, the lignin obtained by biological degradation of wood by corrosion or the early stages of destruction is primarily unchanged in methoxyl content. When, however, the cellulose is mostly consumed by destruction, the lignin content is lowered but not so strongly as in the isolation of the pure material by chemical means. As far as the methoxyl content is concerned, lignin obtained by the bacterial destruction process is less changed than that prepared by chemical methods.

H. WREN.

Nitrogen trichloride and unsaturated hydrocarbons. II. G. H. COLEMAN, G. M. MULLINS, and E. PICKERING (J. Amer. Chem. Soc., 1928, 50, 2739—2741; cf. A., 1924, i, 131).—Ethylene and nitrogen trichloride in carbon tetrachloride at 20—25° for 2 weeks yield β -chloroethyldichloroamine, which is converted by concentrated hydrochloric acid into β -chloroethylamine (*hydrochloride*, m. p. 104—105°; *benzoyl* derivative). Propylene at -10° gives α -chloro- β -dichloroaminopropane, isolated as α -chloro- β -propylamine (*hydrochloride*, m. p. 74—75°; *benzoyl* derivative), which is reduced by sodium amalgam and acid to isopropylamine. *iso*Butylene reacts readily, even at -50°, giving α -chloro- β -amino- β -methylpropane (*hydrochloride*, m. p. 83—84°; *benzoyl* derivative); Δ^2 -pentene at 0—10° gives β -(or γ)-chloro- γ -(or β)-amylamine (*hydrochloride*, m. p. 106—107°; *p*-nitrobenzoyl derivative); and cyclohexene at -19° gives 1-chloro-2-cyclohexylamine (*hydrochloride*, m. p. 162—163°; *benzoyl* derivative). The yields of chloroamine are 10—23% of the theoretical.

H. E. F. NOTTON.

Nitrogen trichloride and unsaturated hydrocarbons. III. Nitrogen chloride and diphenyl-

keten. G. H. COLEMAN and A. W. CAMPBELL (J. Amer. Chem. Soc., 1928, 50, 2754—2757).—Styrene and nitrogen trichloride in carbon tetrachloride at -10° yield nitrogen, ammonium chloride, and a solution which, when treated with hydrogen chloride, gives β -chloro- α -phenylethylamine hydrochloride (benzoyl derivative, m. p. 133—134°; cf. Gabriel and Colman, A., 1914, i, 828). Stilbene is similarly converted into β -chloro- α - β -diphenylethylamine. $\alpha\alpha$ -Diphenyl-, triphenyl-, and tetraphenyl-ethylenes and $\alpha\alpha$ -diphenyl- Δ^2 -propylene do not give amines under these conditions, nearly all the nitrogen being evolved as such. Diphenylketen reacts rapidly at -10°, probably forming diphenylchloroacetdichloroamide, which is converted by hydrogen chloride into benzophenoneimide hydrochloride.

H. E. F. NOTTON.

Cobalt allylamines. W. R. BUCKNALL and W. WARDLAW.—See this vol., 1345.

Attempted resolution of triethylenediamine-nickel chloride. W. R. BUCKNALL and W. WARDLAW (J.C.S., 1928, 2739—2742).—X-Ray evidence indicates that in salts such as $[\text{Ni}(\text{en})_3]\text{Cl}_2$, the units are octahedrally distributed round the nickel atom (Wyckoff, A., 1922, ii, 573), but attempts to confirm this by resolution of *triethylenediaminenickel chloride*, $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, prepared from crystallised nickel chloride and ethylenediamine hydrate, by means of tartaric acid and *d*-camphorsulphonic acid (*triethylenediaminenickel tartrate*, $[\text{Ni}(\text{en})_3](\text{C}_4\text{H}_4\text{O}_6) \cdot 3\text{H}_2\text{O}$; *triethylenediaminenickel d-camphorsulphonate*, $[\text{Ni}(\text{en})_3](\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_2 \cdot \text{H}_2\text{O}$) were unsuccessful.

A. I. VOGEL.

$\alpha\beta\beta$ -Trialkylhydroxylamines. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1928, 50, 2742—2747).— $\alpha\beta$ -Dimethylhydroxylamine (this vol., 744) is converted by methyl iodide in ether into its *hydriodide*, m. p. 134°, and $\alpha\beta\beta$ -trimethylhydroxylamine, b. p. 30° [*hydrochloride*, m. p. 123°; *chloroplatinate*, m. p. 159° (decomp.)], which shows no tendency to isomerise to trimethylamine oxide, and is hydrolysed by hydrochloric acid at 190° to methyl chloride and the decomposition products of $\beta\beta$ -dimethylhydroxylamine, formaldehyde and methylamine. Formaldehyde and dimethylamine cannot be the primary reaction products, since the latter remains unchanged under these conditions. $\alpha\beta$ -Diethylhydroxylamine does not react with ethyl iodide, but with methyl iodide it gives β -methyl- $\alpha\beta$ -diethylhydroxylamine, b. p. 79° (oily *hydrochloride*; *chloroplatinate*, m. p. 158°). Attempts to prepare $\alpha\beta\beta$ -triethylhydroxylamine from $\alpha\beta$ -diethylhydroxylamine hydrochloride, acetaldehyde, and isopropyl alcohol yielded only acetone and ethylamine hydrochloride.

Trimethylhydroxylamine and methyl iodide yield methoxytrimethylammonium iodide, identical with that prepared from trimethylamine oxide (Meisenheimer, A., 1913, i, 595).

H. E. F. NOTTON.

Neutral salt additive compounds of N-methylated glycines: their formulation and that of their hydrates. W. K. ANSLOW and H. KING (Biochem. J., 1928, 22, 1253—1263).—The following compounds have been prepared. *Trisarcosine calcium bromide* (anhyd.), *disarcosine calcium iodide trihydrate*, *disarcosine barium iodide dihydrate*, *sarcosine strontium*

chloride tetrahydrate, sarcosine strontium bromide tetrahydrate, sarcosine strontium iodide tetrahydrate, tri-sarcosine potassium chloride pentahydrate, *N*-dimethylaminoacetic acid hydrochloride and its chloroaurate, m. p. 96—98°, the hydrobromide, m. p. 158—160°, the monohydriodide, m. p. 149°, and the hemihydriodide ($C_4H_9O_2N$)₂·HI·H₂O, m. p. 157°, the calcium chloride tetrahydrate, di-(*N*-dimethylaminoacetic acid) calcium bromide hexahydrate, ($C_4H_9O_2N$)₂·CaBr₂·6H₂O, *N*-dimethylaminoacetic acid calcium iodide, the barium chloride tetrahydrate, the barium bromide tetrahydrate, di-(*N*-dimethylaminoacetic acid) barium iodide tetrahydrate, *N*-dimethylaminoacetic acid strontium chloride tetrahydrate, the strontium bromide tetrahydrate, di-(*N*-dimethylaminoacetic acid) strontium iodide trihydrate, *N*-dimethylaminoacetic acid lithium chloride dihydrate, the lithium bromide monohydrate and di-(*N*-dimethylaminoacetic acid) lithium bromide, the lithium iodide hexahydrate, di-(*N*-dimethylaminoacetic acid) sodium chloride dihydrate, *N*-dimethylaminoacetic acid sodium bromide monohydrate and di-(*N*-dimethylaminoacetic acid) sodium bromide sesquihydrate, *N*-dimethylaminoacetic acid sodium iodide trihydrate, the potassium iodide sesquihydrate, pentabetaïne di(calcium iodide) undecahydrate, ($C_5H_{11}O_2N$)₅(CaI₂)₂·11H₂O, betaine barium iodide tetrahydrate, the strontium chloride tetrahydrate the strontium bromide pentahydrate, the lithium bromide hydrate, dibetaine strontium iodide tetrahydrate, ($C_5H_{11}O_2N$)₂·SrI₂·4H₂O, the lithium iodide monohydrate, the lithium chloride, betaine sodium chloride sesquihydrate, dibetaine sodium bromide sesquihydrate, betaine sodium iodide trihydrate and the ammonium iodide dihydrate. The constitution of the above compounds is discussed from the point of view of electron sharing. S. S. ZILVA.

Hydroxyamino-compounds which show the biuret reaction. IV. Anhydride formation of γ -amino- β -hydroxybutyric acid. M. TOMITA and T. FUKAGAWA (Z. physiol. Chem., 1928, 178, 302—305).—In an attempt to prepare the free ester of γ -amino- β -hydroxybutyric acid from the ester hydrochloride by the action of the theoretical amount of sodium in methyl alcohol, γ -hydroxy- α -pyrrolidone was obtained. The original acid was regenerated on heating with barium hydroxide.

J. H. BIRKINSHAW.

Solubility of cystine under various conditions. Preparation of cystine. L. OKABE (J. Biochem. Japan, 1928, 8, 441—457).—The solubility of cystine in salt solutions varies with the concentration and nature of the salt and the hydrogen-ion concentration. The solubility is increased by ammonium sulphate, or sodium chloride or sulphate, decreased by ethyl alcohol, and unaffected by ammonium chloride or acetate.

Dry, washed hair, or fat-free wool (100 g.), is boiled with 20% hydrochloric acid (300—500 c.c.) under reflux for 7—10 hrs., then for 0.5 hr. after stirring with animal charcoal (10—20 g.). The decolorised solution is filtered, evaporated in a vacuum to a thick syrup, dissolved in water (100 c.c.), 90% alcohol (50 c.c.) is added, and sufficient 10% ammonia solution to produce a bluish colour (p_H 4.8). The hydrolysate is cooled for 2 hrs. at 0° and the crystals obtained are

filtered by suction. The cystine is purified by decolorising a solution in 10% ammonia with charcoal and adjusting the reaction to p_H 4.8 with 36% acetic acid.

CHEMICAL ABSTRACTS.

Zinc chloride-nitroprusside reaction of cysteine. Y. OKUDA and Y. NISHIJIMA (Bul. Sci. Fak. Terkult. Kjusu, 1928, 2, 209—212).—The addition of zinc chloride in the nitroprusside test for cysteine renders the colour more stable and the reaction more sensitive, the colouring matter being adsorbed on the white precipitate of zinc hydroxide.

CHEMICAL ABSTRACTS.

Aminofibroin. A. MOREL and P. SISLEY (Bull. Soc. chim., 1928, [iv], 43, 1132—1133).—Diazotised fibroin when reduced with sodium hyposulphite in the dark gives a product containing the same percentage of nitrogen as the original fibroin. This "aminofibroin" (cf. A., 1927, 1212) can also be obtained from Vignon and Sisley's nitrated silk (A., 1891, 1111), and when diazotised gives the same colorations on coupling with phenols and amines as are obtained by the direct diazotisation of fibroin. The affinity of aminofibroin is greater for basic dyes but towards acid and substantive dyes its affinity is unchanged.

R. BRIGHTMAN.

$\alpha\beta$ -Unsaturated dinitriles. B. B. CORSON and R. W. STROUGHTON (J. Amer. Chem. Soc., 1928, 50, 2825—2837).—These have been prepared from aldehydes and malononitrile in presence of piperidine or dilute aqueous alkali (cf. Heuck, A., 1895, i, 651). Some, e.g., $\beta\beta$ -dicyanostyrene and its *m*-nitro- and *o*-chloro-derivatives, have an irritant physiological action. They resemble $\alpha\beta$ -unsaturated aldehydes and ketones in that (a) with equimolecular proportions of sodium hydrogen sulphite they form sulphonc acids from which they are not regenerated by acids or bases; (b) they are readily oxidised to acids by permanganate in acetone; thus, $\beta\beta$ -dicyanostyrene yields benzoic acid; (c) they are reconverted into aldehyde and nitrile by acids or alkalis, and (d) they combine with hydrogen cyanide to derivatives of $\alpha\beta\beta$ -tricyanoethane. These act as weak acids, forming potassium, sodium, and silver salts which are mixtures containing between 1 and 2 equivalents of base. The trinitriles are hydrolysed by boiling acids to succinic acids. The following derivatives of $\beta\beta$ -dicyanostyrene are described: *o*-methoxy-, m. p. 84—84.5°; *p*-hydroxy-, m. p. 188.5—189.5°; *m*-nitro-, m. p. 104.5—105°; 3:4-methylenedioxy-, m. p. 199—200°; *o*-chloro-, m. p. 95—96°, and 4-hydroxy-3-methoxy-, m. p. 133.5—134.5°; also cyclohexyldienemalononitrile, m. p. 173.5—174.5°, and the following derivatives of $\alpha\beta\beta$ -tricyanoethane: α -phenyl-, m. p. 124.5—125°; α -*p*-methoxyphenyl-, m. p. 122—122.5° (potassium and silver salts); α -*o*-methoxyphenyl-, m. p. 140.5—141°, and 3:4-methylenedioxyphenyl-, m. p. 153—153.5°. The potassium-derivative of $\alpha\beta\beta$ -tricyano- α -phenylethane, which may be obtained directly from $\beta\beta$ -dicyanostyrene and potassium cyanide, is converted by methyl iodide into $\alpha\beta\beta$ -tricyano- α -phenylpropane, m. p. 83—84°, identified by its hydrolysis to α -phenyl- β -methylsuccinic acid (I), m. p. 182—183°. Methyl α -cyanocinnamate is converted by potassium cyanide and acid into methyl $\alpha\beta$ -dicyano- β -phenyl-

propionate, m. p. 100—101°, the sodio-derivative of which yields with methyl iodide *methyl αβ-dicyano-β-phenylisobutyrate*, m. p. 87—88°. This is hydrolysed by hydrochloric acid to an acid identical with I. *Methyl p-methoxyphenylsuccinate*, m. p. 93—94°, is obtained from αββ-tricyano-α-p-methoxyphenylethane and alcoholic sulphuric acid. *o-Methoxyphenylsuccinic acid* has m. p. 184—185° (rapid heating).

H. E. F. NOTTON.

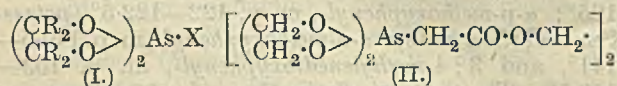
Preparation of aliphatic compounds of selenium, tellurium, and arsenic. G. NATTA (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1326—1331; Chem. Zentr., 1928, i, 2245).—Interaction between aluminium or magnesium selenide etc. with alcohols or ethers is employed: $\text{Al}_2\text{M}_3 + 3\text{R}\cdot\text{OH}$ (or $3\text{R}_2\text{O}$) = $\text{Al}_2\text{O}_3 + 3\text{MHR}$ (or 3MR_2); $2\text{AlM} + 3\text{R}\cdot\text{OH} = \text{Al}_2\text{O}_3 + \text{MHR}_2 + \text{MH}_2\text{R}$; $2\text{AlM} + 3\text{R}_2\text{O} = \text{Al}_2\text{O}_3 + 2\text{MR}_2$; further: $2\text{MHR} = \text{MR}_2 + \text{MH}_2$; $\text{MHR}_2 + 2\text{MH}_2\text{R} = \text{MR}_3 + \text{MH}_3$. Aluminium selenide and telluride react preferably at 250—300° with alcohols, and at 300—350° with ethers; aluminium arsenide reacts with difficulty above 300°, magnesium arsenide more readily. The presence of water in the alcohols and ethers only slightly affects the purity of the products. The following compounds were prepared: diethyl selenide, b. p. about 110°; diethyl diselenide, orange-yellow, b. p. 137°, m. p. —90° to —98°; ethyl hydrogen selenide; diisopropyl selenide; isopropyl hydrogen selenide, b. p. 70—75°; diisopropyl diselenide; dimethyl telluride; ethyl hydrogen telluride; trimethylarsine, b. p. 68—73°; dimethylarsine; black substances, $(\text{CH}_3\text{As})_x$ and $(\text{C}_2\text{H}_5\text{As})_3$; mono-, di-, and tri-ethylarsine. Amines and phosphines were also prepared.

A. A. ELDRIDGE.

Organic arsenic derivatives. Action of alkalis on diethylchloroarsine. E. GRYSZKIEWICZ-TROCHIMOWSKI, M. BUCZWIŃSKI, and J. KWAPISZEWSKI (Rocz. Chem., 1928, 8, 423—431).—Sodium carbonate, hydrogen carbonate, and hydroxide react with diethylchloroarsine to yield a mixture of *diethylarsine oxide*, b. p. 225—230°, *d* 1.2986, triethylarsine (*mercurichloride*, m. p. 163—164°), and ethylarsine oxide.

R. TRUSZKOWSKI.

Compounds from α-glycols with arsenic acid and arsenoacetic acid. B. ENGLUND (J. pr. Chem., 1928, [ii], 120, 179—184; cf. A., 1927, i, 121).—Arsenic acid and arsenoacetic acid combine with aliphatic dihydroxy-compounds to yield products which are regarded as esters of type I. They are hydrolysed with extreme ease by water, and can be titrated with sodium hydroxide as arsenic acid or arsenoacetic acid, respectively.



By dissolving arsenic acid (1 mol.) in warm ethylene glycol (2 mols.) is obtained *di-ethylene glycol arsenic acid*, [(I); R=H, X=OH], m. p. 120°, bimolecular in bromoform solution; the *pyridine* and *brucine* salts are described. A mixture of di- and tri-ethylene glycol arsenic acids is obtained when 3 mols. of glycol are

used, but the triethylene glycol arsenic acid could be isolated only as the *aniline*, *pyridine*, and *brucine* salts. *Di-ethylene glycol arsenoacetic acid* [(I); R=H, X=CH₂·CO₂H], m. p. 142° (*brucine* salt), is obtained in 60% yield by dissolving arsenoacetic acid in warm ethylene glycol; it is bimolecular in bromoform solution. If the solution of arsenoacetic acid in ethylene glycol be heated for a short time at 100°, only small quantities of *ethylene glycol bis(di-ethylene glycolarseno)acetate* (II), m. p. 130° (decomp.), are obtained, which is not hydrolysed to free arsenoacetic acid by water. The same solution heated at 130° evolves carbon dioxide, and yields *di-ethylene glycol methylarsinic acid* [(I); R=H, X=Me], b. p. 135—136°/15 mm.; at 140° the same product, isolated as the monohydrated *lead* salt of methylarsinic acid by hydrolysis with water and precipitation with lead acetate solution, is produced in 70% yield.

Dipinacolarsenic acid [(I); R=Me, X=OH], m. p. 131° (*pyridine* salt), and *dipinacolarsenoacetic acid* [(I); R=Me, X=CH₂·CO₂H], m. p. 188° (decomp.), are similarly obtained from pinacol and the appropriate acid in acetone and ethyl-alcoholic solution, respectively. *d*-Tartaric acid, but not *meso*-tartaric acid, heated with arsenoacetic acid for a few minutes in boiling glacial acetic acid solution yields the substance $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{O} > \text{AsO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, decomp. above 250°.

C. W. SHOPPEE.

Action of fuming sulphuric acid on cyclohexane. V. MENSCHUTKIN and M. WOLF (Neft. Choz., 1927, 13, 340—342).—By the action of fuming sulphuric acid (25% SO₃; 27 parts) on cyclohexane (1 part), sulphur dioxide and benzenesulphonic acids (up to 70%) are formed, together with some pitch.

CHEMICAL ABSTRACTS.

Conversion of hydroaromatic into aromatic compounds. III. 3:5-Dichloro-1-phenyl-Δ^{2:4}-cyclohexadiene and its behaviour with chlorine. L. E. HINKEL and D. H. HEY (J.C.S., 1928, 2786—2791; cf. this vol., 760).—Phenyldihydroresorcinol is converted by phosphorus pentachloride in the presence of dry chloroform into 3:5-dichloro-1-phenyl-Δ^{2:4}-cyclohexadiene, b. p. 156°/10 mm. (main product) (I), and a small quantity of 3:5-dichlorodiphenyl, b. p. 166°/10 mm., m. p. 36°. Chlorination of I at the ordinary temperature affords 3:5-dichlorodiphenyl, m. p. 36°, whilst at a higher temperature 2:3:5-trichlorodiphenyl, m. p. 41°, is also formed (the constitution of the latter was confirmed by its synthesis from 3:5-dichloro-2-aminodiphenyl), the two chlorodiphenyls being separated by regulated oxidation with chromic acid or through their nitro-derivatives. Nitration of 3:5-dichlorodiphenyl gave chiefly 3:5-dichloro-4'-nitrodiphenyl, m. p. 146° (corresponding amino-compound, m. p. 124°, and its acetyl derivative, m. p. 188°); 3:5:4'-trichlorodiphenyl, m. p. 88°, together with a small quantity of 3:5-dichloro-2'-nitrodiphenyl, m. p. 75° (corresponding amino-compound, m. p. 74°, and its acetyl derivative, m. p. 163°); 3:5:2'-trichlorodiphenyl, m. p. 58°. Nitration of 2:3:5-trichlorodiphenyl gave a mono-nitro-compound, regarded as 2:3:5-trichloro-4'-nitrodiphenyl.

A. I. VOGEL.

Action of silver on diphenyltert.-butylethynylmethylbromide. P. L. SALZBERG and C. S. MARVEL (J. Amer. Chem. Soc., 1928, 50, 2840—2844; cf. this vol., 988).—*Diphenyltert.-butylethynylcarbinol*, $\text{CMe}_3\text{C}\equiv\text{C}\cdot\text{CPh}_2\cdot\text{OH}$, m. p. 66.5—67.5°, obtained by the successive addition of magnesium ethyl bromide and benzophenone to *tert.*-butylacetylene, is converted by phosphorus tribromide in light petroleum into the corresponding *bromide*, m. p. 58.5—60.5° (corr.). This is debrominated in an inert atmosphere by “molecular” silver in ether, giving a solution which absorbs only a trace of oxygen and contains a *hydrocarbon*, $\text{C}_{28}\text{H}_{28}$, m. p. 153.5—155° (corr.), which is stable in alcoholic solution at 100°. In an atmosphere of oxygen, however, the reaction proceeds with vigorous oxidation and a large excess over the amount necessary for the formation of a peroxide is absorbed. Only indefinite products are obtained. The hydrocarbon does not react with 1% sodium amalgam, but with 40% amalgam or with sodium-potassium alloy it gives a coloured metallic derivative, which does not yield the expected acid on treatment with carbon dioxide. It is probably not tetraphenyldi*tert.*-butylethynylethane, but an isomeride formed by its dissociation to diphenyl*tert.*-butylethynylmethyl, and subsequent rearrangement. H. E. F. NOTTON.

Structure of benzene and the alicyclic hydrocarbons. F. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1928, 60, 871—883).—The structure of benzene, cyclohexane, cyclohexadiene, heptamethylene, cyclooctane, and cyclooctatetraene is discussed from the point of view of the various structural formulæ proposed. The factors which are supposed to determine the configurations are taken to be (1) equal distances between the atoms constituting the ring, (2) equal angles between all the valency linkings, (3) the tendency of the angles to approach the “normal” angle, 109.5°. The conclusions reached are, that in systems of 5 carbon atoms or less Baeyer’s theory holds; with more carbon atoms, several configurations are possible, which form a consecutive series. For C_6H_6 , C_6H_8 , C_6N_{10} , and C_6H_{12} there exist analogous series of configurations, of which, for benzene, V. Henri’s formula is the most stable. C_6H_{12} has the octahedral structure, to which the structures of C_7H_{14} and C_8H_{16} are analogous. C_8H_{12} and C_8H_8 are both hexahedral. The properties of the various compounds are explained from the point of view of the structural formulæ assigned to them.

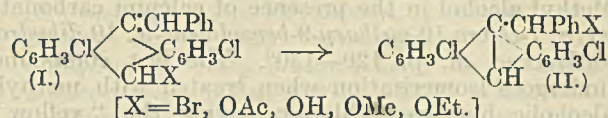
M. ZVEGINTZOV.

Chlorination of naphthalene in benzene solution. J. TRAUBENBERG and E. WASSERMAN (J. pr. Chem., 1928, [ii], 120, 177—178; cf. this vol., 627).— α -Chloronaphthalene is obtained in 85% yield by chlorination of naphthalene in cold benzene suspension in the presence of iron. Some naphthalene can be recovered, and if allowance for this be made, the yield is 90%. The benzene is almost entirely unaffected under the above conditions.

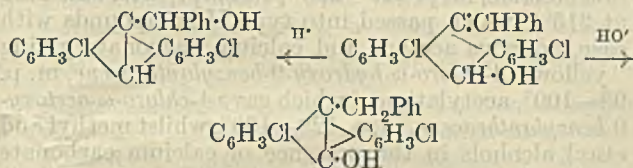
C. W. SHOPPEE.

Transannular anionotropic migrations. J. W. COOK (J.C.S., 1928, 2798—2810).—Experimental evidence is described which favours structures of

type I rather than a bridged formula for the colourless forms of derivatives of 1:5-dichloro-9-benzylanthracene, the coloured forms being of type II.



The change I \longrightarrow II is evidently a case of mobile anion tautomerism, since (a) the order of mobility of anions ($\text{Br} > \text{OAc} > \text{OH}$ or OR) is identical with that found by Burton and Ingold (this vol., 904) for another system and (b) prototropic and anionotropic changes can be effected by the action of hydroxyl and hydrogen ions, respectively:



Thus 1:5-dichloro-10-hydroxy-9-benzylidene-9:10-dihydroanthracene is converted by boiling with alcoholic sodium hydroxide into 1:5-dichloro-9-benzylanthrone. The conversion of a new geometrical (?) isomeride of 1:5-dichloro-10-ethoxy-9-benzylidene-9:10-dihydroanthracene (cf. Barnett and others, this vol., 52) (from 1:5-dichloroethoxyanthrone and magnesium benzyl chloride followed by dehydration of the resulting dihydroanthranol) into the ω -ethoxy-compound by alcoholic hydrogen chloride was slow and incomplete (cf. stereoisomeric hexatrienes, Farmer and others, this vol., 151). Replacement of ethoxyl by bromine gave a monobromo-derivative identical with the monobromination product of 1:5-dichloro-9-benzylanthracene. This inversion of geometrical configuration is considered to pass through a form of type II.

Attempts to oxidise compounds of type I to the corresponding anthrones are described. The mobile hydrogen was fixed by replacement by phenyl; thus 1:5-dichloro-9-benzyl-10-phenylanthracene gave a reactive monobromo-derivative, m. p. 179—180°, but the *hydroxy*-, m. p. 189—191°, and *ethoxy*-, m. p. 173—174°, derivatives (obtained respectively by treatment with aqueous acetone and ethyl alcohol in the presence of calcium carbonate) were of the “yellow” type, which is therefore probably II. 1-Chloro-9-benzylanthracene, m. p. 119—120° (the corresponding 1-chloro-9-hydroxy-9-benzyl-9:10-dihydroanthracene has m. p. 126—127°), and 4-chloro-9-benzylanthracene, m. p. 120°, were prepared from the appropriate chloro-9-anthrone (obtained by reduction of chloro-anthraquinones with aluminium and sulphuric acid). The former when brominated gave an unstable dibromide, which decomposed into a mixture of 30% of 1-chloro-10-bromo-9-benzylanthracene (type II), m. p. 160°, and 70% of benzylidene compound (IV, type I), m. p. 151—153°.

From IV compounds of types I and II were obtained (X=OH, OAc, or OR). Thus the action of aqueous acetone and calcium carbonate gave 1-chloro-10-

hydroxy-9-benzylidene-9:10-dihydroanthracene, m. p. 185°, acetylation of which gave 1-chloro-10-acetoxy-9-benzylidene-9:10-dihydroanthracene, m. p. 151—153°. Methyl alcohol in the presence of calcium carbonate gave 1-chloro-10-methoxy-9-benzylidene-9:10-dihydroanthracene, m. p. 129—130°. The last compound undergoes isomerisation when treated with methyl-alcoholic hydrogen chloride, giving the "yellow" (type II) form, m. p. 135—135°. Similarly, the "yellow" form of the above acetoxy-derivative (prepared also by acetylation of the "colourless" hydroxy-compound) has m. p. 157—158°.

4-Chloro-9-benzylanthracene gives an unstable dibromo-derivative leading to (reactive) 4-chloro- ω -bromo-9-benzylanthracene, m. p. 165—166° (ω -pyridinium bromide, m. p. 220—225° [decomp.] after sintering at 215°), which passed into type II compounds with ease, aqueous acetone and calcium carbonate giving "yellow" 4-chloro- ω -hydroxy-9-benzylanthracene, m. p. 98—100°, acetylation of which gave 4-chloro- ω -acetoxy-9-benzylanthracene, m. p. 129—130°, whilst methyl and ethyl alcohols in the presence of calcium carbonate gave 4-chloro- ω -methoxy-9-benzylanthracene, m. p. 144° (also formed by methylation of the ω -hydroxy-compound with methyl-alcoholic hydrogen chloride), and 4-chloro- ω -ethoxy-9-benzylanthracene, m. p. 135—137°, respectively. The differences between the 1- and the 4-chloro-derivatives of 9-benzylanthracene are ascribed to steric effects of the α -chlorine atom. The ω -methoxy-compound gave an unstable dibromide which spontaneously decomposed into benzaldehyde and 4-chloro-9-bromoanthracene [identical with the substance, which is incidentally oriented by the present work, obtained by Barnett and Matthews (A., 1924, i, 752) from α -chloroanthracene dibromide]. 4-Chloro-9-bromoanthracene is stable in presence of excess of bromine. 1-Chloro-9-bromoanthracene was not isolated from the product of thermal decomposition of the dibromide of 1-chloro- ω -methoxy-9-benzylanthracene, only 1-chloro-9:10-dibromoanthracene being obtained. These results are attributed to the steric effect of the α -chlorine atom on the assumption that bromination is preceded by 9:10 addition of bromine.

Only 4-chloro-9-bromoanthracene was isolated from the action of excess of bromine on 1-chloro-10-bromo-9-benzylanthracene. R. J. W. LE FÈVRE.

Reactions of stable azides. A. BERTHÓ (J. pr. Chem., 1928, [ii], 120, 89—118).—A summary of work already published (this vol., 1028, and previous papers), discussed in relation to results obtained by other workers. Organic azides fall into two groups on the ground of purely chemical behaviour: (a) containing all azides in which the carbazido-group, $\cdot\text{CO}\cdot\text{N}_2$, is directly attached to carbon; these are accessible by the Curtius reaction, and (b) containing the so-called stable azides, which include all alkyl and aryl azido-compounds, sulphonazides, and those carbazides of which the carbazido-group is attached to nitrogen or oxygen; with a few exceptions, the members of this group are not accessible by the Curtius reaction. The reactions of the stable azides towards aromatic hydrocarbons and bases, towards doubly and triply unsaturated aliphatic compounds

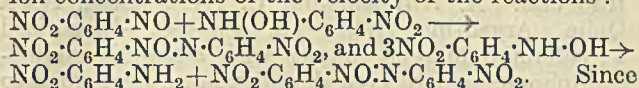
(including reactive CH and CH_2 groups), and towards azo-compounds are considered. C. W. SHOPPEE.

Reduction of aromatic nitro-compounds with sodium alkoxides. C. M. SUTER and F. B. DAINS (J. Amer. Chem. Soc., 1928, 50, 2733—2739).—The yields of amines and azoxy-derivatives from benzene suspensions of sodium alkoxides and aromatic nitro- and halogenonitro-derivatives in some 50 experiments are tabulated. The proportion of amine formed is increased by the presence of benzene and by using the higher aliphatic alcohols, which are oxidised mainly to formic acid with traces of acetic acid and acetone. With propyl, butyl, and isoamyl alcohols, the yields of amine and azoxy-derivative together total 50—90% of the theoretical. Sodium benzyloxide gives practically no amine, but high yields of azoxy-derivative, being oxidised to benzaldehyde and benzoic acid. Whilst the *m*- and *p*-halogenonitrobenzenes react normally, the *o*-derivatives give with alkoxides of the type $\text{R}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{ONa}$ anilino-acids instead of azoxy-derivatives. Thus, sodium *n*-propoxide and *o*-chloronitrobenzene afford *o*-chloroaniline (40%) and α -*o*-chloroanilinopropionic acid (60%), m. p. 150°, which is also formed from *o*-chloroaniline and α -bromopropionic acid. α -*o*-Chloroanilinobutyric acid, m. p. 95°; α -*o*-chloroanilinoisovaleric acid, m. p. 75°; α -*o*-bromoanilinopropionic acid, m. p. 162—164°; α -*o*-bromoanilinobutyric acid, m. p. 83°; α -2:5-dichloroanilinopropionic acid, m. p. 163°; and α -*o*-chloroanilinophenylacetic acid, m. p. 160°, together with varying proportions of *o*-halogenoanilines, are obtained similarly. *o*-Iodonitrobenzene and sodium propoxide give a trace of α -*o*-iodoanilinopropionic acid, m. p. 157°, but *o*-nitroanisole gives only *o*-aminoanisole and tarry products. *o*-Chloroaniline and ethyl sulphate yield *o*-chloro-*N*-ethylaniline, b. p. 219°/726 mm., d_4^{25} 1.104 (hydrochloride, m. p. 138—139°; phenylurethane, m. p. 144°). H. E. F. NOTTON.

Reduction of aromatic mono- and poly-nitro-compounds. K. BRAND and A. MODERSOHN (J. pr. Chem., 1928, [ii], 120, 160—176).—The reduction of aromatic mono- and poly-nitro-compounds to β -arylhydroxylamines in so-called neutral solution has been investigated, and it is shown that, using aqueous-alcoholic calcium chloride solution and zinc dust, the solution becomes alkaline slowly at the ordinary temperature and more rapidly on heating. The rôle played by the calcium chloride is obscure, and a scheme is given for the reaction which does not include this substance, but zinc and water only. Zinc dust and ammonium chloride solution react in the absence of a nitro-compound to produce hydroxyl ions, but the concentration of the latter is much lower than that produced by zinc dust, calcium chloride, and a nitro-compound.

On the basis of the above facts it is possible to explain the results of Brand (A., 1906, i, 80), who showed that reduction of *m*-dinitrobenzene with zinc dust and calcium chloride gives, not *m*-nitro- β -phenylhydroxylamine, but *mm'*-dinitroazoxybenzene. Brand and Kowallek (unpublished observation) find that the velocity of combination of *m*-nitronitrosobenzene with *m*-nitro- β -phenylhydroxylamine to yield *mm'*-dinitroazoxybenzene in "neutral" solution is greater than

that of nitrosobenzene with β -phenylhydroxylamine to azoxybenzene, under the same conditions. This difference is due to the acceleration by small hydroxyl-ion concentrations of the velocity of the reactions :



Since these small hydroxyl-ion concentrations prevail the velocity of formation of *mm'*-dinitroazoxybenzene increases and becomes greater than the reduction velocity of *m*-nitronitrosobenzene to *m*-nitro- β -phenylhydroxylamine and the formation of the azoxy-compound proceeds at the expense of the hydroxylamine. The velocity of formation of azoxybenzene is smaller than that of *mm'*-dinitroazoxybenzene, and although accelerated by increased hydroxyl-ion concentrations, does not overtake the velocity of reduction of nitrosobenzene to β -phenylhydroxylamine; consequently the latter is the main product. By adding traces of acids or acid salts (e.g., potassium hydrogen sulphate) at the commencement of the reaction, the hydroxylamines may be intercepted and preserved, and the formation of azoxy-compounds checked.

Owing to the lower concentration of hydroxyl ions produced, the use of zinc dust and ammonium chloride is preferable to that of zinc and calcium chloride for the general preparation of β -arylhydroxylamines; by adding traces of acids (acetic acid is recommended) hydroxylamines sensitive to very small hydroxyl-ion concentrations are readily obtained. The preparation of the following is described : *m*-nitro- β -phenylhydroxylamine, m. p. 118° (yield 58%); 2-nitro-6-hydroxylaminotoluene, m. p. 120–121° (yield 68%); 2-nitro-4-hydroxylaminotoluene, m. p. 108–109° (cf. lit.) (yield 50%); 2-nitro-4-hydroxylaminoanisole, m. p. 129°; 2:6-dinitro-4-hydroxylaminotoluene, m. p. 143–144°.

C. W. SHOPPEE.

Diphenyl series. VIII. Derivatives of 2- and 4-aminodiphenyl. F. BELL (J.C.S., 1928, 2770–2779).—2-*p*-Toluenesulphonamidodiphenyl, m. p. 99°, gives when nitrated successively 5-nitro-, m. p. 169°, and 3:5-dinitro-2-*p*-toluenesulphonamidodiphenyl, m. p. 186° (3:5-dinitro-2-aminodiphenyl has m. p. 182°), and on methylation 2-*p*-toluenesulphonmethylamidodiphenyl, m. p. 136°. Similarly, 4'-nitro-2-*p*-toluenesulphonamidodiphenyl, m. p. 163°, when gently nitrated gives 3:5:4'-trinitro-2-*p*-toluenesulphonamidodiphenyl, m. p. 190° (3:5:4'-trinitro-2-aminodiphenyl has m. p. 229°). 2-Acetamidodiphenyl with nitric and acetic acids gives mainly 5-nitro-2-acetamidodiphenyl, m. p. 133° (5-nitro-2-aminodiphenyl, m. p. 125°), which when further nitrated gives only 5:4'-dinitro-2-acetamidodiphenyl. 4-*p*-Toluenesulphonamidodiphenyl easily gives 3:5-dinitro-4-*p*-toluenesulphonamidodiphenyl, m. p. 189°, hydrolysed to 3:5-dinitro-4-aminodiphenyl, m. p. 177° (acetyl derivative, m. p. 146°; N-methyl derivative, m. p. 144°; 3:5-dinitro-4-acetmethylamidodiphenyl, m. p. 149°), different from the dinitro-base of Fichter and Sulzberger (A., 1904, i, 325). 2-*p*-Toluenesulphonmethylamidodiphenyl gives 5-nitro-2-*p*-toluenesulphonmethylamidodiphenyl, m. p. 152° (also formed by direct methylation of 5-nitro-2-*p*-toluenesulphonamidodiphenyl). Experimental details for the pre-

paration of *p*-nitrobenzenesulphonyl chloride from *p*-chloronitrobenzene are given. The following *p*-nitrobenzenesulphonates are described : *ethyl*, m. p. 91°, *menthyl*, m. p. 72°, *phenyl*, m. p. 114°, *m*-nitrophenyl, m. p. 133°, *p*-nitrophenyl, m. p. 156°, *p*-tolyl, m. p. 106°, 3-nitro-*p*-tolyl, m. p. 136°, and 2-nitro-*p*-tolyl, m. p. 116°. *p*-Tolyl *p*-nitrobenzenesulphonate and *p*-nitrobenzenesulphon-*p*-toluidide, m. p. 179–180°, give when nitrated 2-nitro-*p*-tolyl *p*-nitrobenzenesulphonate and *p*-nitrobenzenesulphon-3:5-dinitro-*p*-toluidide, m. p. 185°, respectively. Phenyl *p*-nitrobenzenesulphonate gives *p*-nitrophenyl *p*-nitrobenzenesulphonate (above).

2-Aminodiphenyl readily gives 5-acetoxymercuri-2-acetamidodiphenyl, m. p. 200°, which yields 5-bromo-2-acetamidodiphenyl with bromine in acetic acid. 4-Aminodiphenyl gives a *monomercuri*-derivative, $\text{C}_6\text{H}_5\text{Ph} \begin{smallmatrix} \text{NH} \\ \text{Hg} \end{smallmatrix}$ (?), m. p. 167°, which by warming with acetic acid forms 3-acetoxymercuri-4-acetamidodiphenyl, m. p. 205°. Treatment with bromine in acetic acid gives 3:4'-dibromo-4-acetamidodiphenyl. 3-Bromo-4-hydroxydiphenyl gives a *monomercuri*-derivative, m. p. 235°, which similarly yields 3:5:4'-tribromo-4-hydroxydiphenyl. The preparation of 3-acetoxymercuriaceto-*p*-toluidide, m. p. 178°, by direct mercuriation and by acetylation of acetoxymercuri-*p*-toluidine is described (cf. Schrauth and Schoeller, A., 1910, i, 459).

Bromination of 4-*p*-toluenesulphonamidodiphenyl gives only poor yields of 3-bromo-4-*p*-toluenesulphonamidodiphenyl, m. p. 119°.

2-Aminodiphenyl when diazotised and treated with copper powder gives no diphenylene, only 2-chlorodiphenyl and 2-azodiphenyl being formed.

R. J. W. LE FÈVRE.

Absorption spectra and constitution of azoxy-compounds. L. SZEGÖ (Ber., 1928, 61, [B], 2087–2091).—The absorption spectra of the α - and β -forms of *p*-bromo-, *p*-nitro-, and *p'*-bromo-*p*-nitroazoxybenzene, *p*-hydroxyazoxybenzene and its methyl and ethyl ethers, and of 5-hydroxy-2-methylazoxybenzene have been investigated. All the compounds exhibit a fairly well-defined band with an absorption maximum between 3600 and 3250 Å. A similar band is shown by azoxybenzene. The absorption spectra of all the isomeric hydroxy-substituted compounds and of *p'*-bromo-*p*-nitroazoxybenzene are markedly different, whilst those of *p*-bromo- and *p*-nitroazoxybenzene are almost identical, probably because the entry of a halogen as substituent into the benzene nucleus is generally without influence on the optical character of compounds. The relationships for the nitro-group are obviously similar. In general, the results are in harmony with the behaviour expected for the isomerides on the basis of Angeli's formulation. In addition to the band characteristic of all azoxy-derivatives, all the α -forms exhibit a second band in the neighbourhood of 2600–2500 Å., which is not shown by the β -varieties. α -5-Hydroxy-2-methylazoxybenzene has a third maximum which does not occur with the corresponding β -compound. In explanation, it is assumed that the oxygen atom of the azoxy-group is attached by residual valencies to the neighbouring nucleus.

H. WREN.

Azopicric acid [2:4:6:2':4':6'-Hexanitro-5:5'-dihydroxyazobenzene]. K. ELBS and O. H. SCHAAF (J. pr. Chem., 1928, [ii], 120, 1—35; cf. A., 1924, i, 255).—The methyl and ethyl ethers of azopicric acid could not be obtained from it directly, but only by nitration of the corresponding ethers of *m*-azophenol. When recrystallised they become deep red, possibly owing to a change into the *aci*-nitro-form. Reduction of azopicric acid to an analogue of picramic acid does not occur, a phenylbenztriazole derivative being formed. Azopicric acid is decomposed by alkalis, sodium and potassium carbonates yielding nitrohydroxylaminophloroglucinol derivatives. The absorption of light by azopicric acid and related compounds was investigated.

Azopicric acid and its ethers are most readily prepared from *m*-nitroaniline, which is diazotised and converted into *m*-nitrophenol. This could not be directly reduced to azophenol, but reduction of the methyl ether by zinc dust and aqueous-alcoholic sodium hydroxide in two stages yielded successively 3:3'-dimethoxyazoxybenzene, m. p. 49°, and 3:3'-dimethoxyazobenzene, m. p. 76—77°, and from the ethyl ether were obtained 3:3'-diethoxyazoxybenzene, m. p. 75—76°, and 3:3'-diethoxyazobenzene, m. p. 90° (hydrazo-compound, m. p. 78—80°). Nitration of the azo-compounds in sulphuric acid containing potassium nitrate, to which fuming sulphuric acid was added, yielded, on pouring into water, yellow products, which gave on recrystallisation 2:4:6:2':4':6'-hexanitro-5:5'-dimethoxy-, red, m. p. 127°, and -5:5'-diethoxyazobenzene, m. p. 138—139°, respectively. These compounds gave no evidence of formation of additive compounds with aromatic hydrocarbons. They were hydrolysed to azopicric acid by boiling with water or 25% aqueous alcohol containing a trace of hydrochloric acid.

Reduction of azopicric acid by sodium hydrogen sulphide in amount corresponding with 4 mols. of hydrogen yielded 5:7:2':4':6'-pentanitro-4:3'-dihydroxy-2-phenylbenztriazole, m. p. 176—180° (decomp.). Excess of reducing agent yielded amorphous materials which appeared to contain amino-derivatives of the benztriazole.

The action of aqueous alkali hydroxides on azopicric acid yielded tarry products. Neutralisation of the warm aqueous solution by potassium carbonate solution yielded the potassium salt, and from the filtrate on further addition of potassium carbonate and acidification a substance, m. p. 110°, and trinitrophloroglucinol, m. p. 157—158°, were obtained. The action of more concentrated potassium carbonate solution at a higher temperature yielded, with evolution of nitrogen, a product, red in acid and yellow in alkaline solution, from which was separated (?)mononitrodihydroxylaminophloroglucinol, m. p. 166°, and (?)dinitrohydroxylaminophloroglucinol, m. p. 146—148°. The formation of these products is supposed to take place analogously to the formation of trinitrophloroglucinol from *s*-tribromotrinitrobenzene and sodium carbonate.

The absorption spectra and extinction curves of azopicric acid, *m*-azophenol, and picric acid are similar, apart from the considerable displacement of absorption towards the red shown by azopicric

acid, and demonstrate their constitutional relationship. R. K. CALLOW.

Substantive dyes derived from 2:7-diaminofluorene. A. NOVELLI and C. RUIZ (Anal. Asoc. Quím. Argentina, 1928, 16, 56—64).—Diazotised 2:7-diaminofluorene couples with α -naphthylamine-4-sulphonic acid to give the *disazo-dye*, analogous to Congo-red. The free acid is blue, and the sodium salt, m. p. above 300°, red, dyeing wool, cotton, and silk in red shades not fast to alkali. The constitution was confirmed by reduction. The analogous *disazo-dye* obtained by coupling with α -naphthol-4-sulphonic acid, violet, dyeing cotton violet, was not obtained pure. The existence of these dyes supports the analogy between fluorene and 2:2'-substituted diphenyl derivatives. R. K. CALLOW.

Manufacture of azo dyes [and new dichloro-*p*-xylydines]. I. G. FARBENIND. A.-G.—See B., 1928, 549.

Interaction of chloral and 2:4:6-trihalogen-substituted phenylhydrazines. F. D. CHATTAWAY and F. G. DALDY (J.C.S., 1928, 2756—2762).—Chloral condenses smoothly in glacial acetic acid with 2:4:6-trichlorophenylhydrazine, giving an unstable hydrazone which rapidly passes into $\alpha\alpha$ -dichloro- β -2:4:6-trichlorobenzeneazoethylene (I), m. p. 54°, evidently by reversible loss of hydrogen chloride, since treatment of this product with hydrogen chloride and hot acetic anhydride gives chloral- α -acetyl-2:4:6-trichlorophenylhydrazone, m. p. 144°. The compound I in acetic acid gives with chlorine in the cold chloral- ω -chloro-2:4:6-trichlorophenylhydrazone, m. p. 104°, which when heated at the b. p. of the solvent gives $\alpha\alpha\beta$ -trichloro- β -2:4:6-trichlorobenzeneazoethylene, m. p. 75°. The analogous $\alpha\alpha$ -dichloro- α -bromo- β -2:4:6-trichlorobenzeneazoethylene has m. p. 108.5°.

The compound I is converted by hot hydrogen chloride and acetic acid into glyoxylic acid 2:4:6-trichlorophenylhydrazone, m. p. 167° (decomp.) (or by hot hydrogen chloride and ethyl alcohol into ethyl glyoxylate 2:4:6-trichlorophenylhydrazone [II], m. p. 97.5°), also prepared directly from glyoxylic acid and trichlorophenylhydrazine. The ester II gives (a) with hot acetic anhydride ethyl glyoxylate α -acetyl-2:4:6-trichlorophenylhydrazone, m. p. 112.5°; (b) with chlorine in acetic acid ethyl glyoxylate ω -chloro-2:4:6-trichlorophenylhydrazone, m. p. 73.5° (also formed by long boiling of $\alpha\alpha\beta$ -trichloro- β -2:4:6-trichlorobenzeneazoethylene in alcohol); (c) with bromine in acetic acid, ethyl glyoxylate ω -bromo-2:4:6-trichlorophenylhydrazone, m. p. 75°. Chlorination of glyoxylic acid 2:4:6-trichlorophenylhydrazone in acetic acid gives glyoxylic acid ω -chloro-2:4:6-trichlorophenylhydrazone, m. p. 151.5° (decomp.).

Diazotised 2:4:6-trichloroaniline and ethyl acetate give ethyl 2:4:6-trichlorobenzeneazoacetate, m. p. 94.5°, which by chlorination (bromination) in acetic acid gives ethyl glyoxylate ω -chloro-(bromo)-2:4:6-trichlorophenylhydrazone.

A similar series of reactions with 2:4:6-tribromophenylhydrazine gave rise to the following new compounds: $\alpha\alpha$ -dichloro- β -2:4:6-tribromobenzeneazoethylene, m. p. 92°; $\alpha\alpha\beta$ -trichloro- β -2:4:6-tri-

bromobenzeneazoethylene, m. p. 105°; $\alpha\alpha$ -dichloro- β -bromo- β -2:4:6-tribromobenzeneazoethylene, m. p. 115°; glyoxylic acid 2:4:6-tribromophenylhydrazone, m. p. 170.5° (decomp.); ethyl glyoxylate 2:4:6-tribromophenylhydrazone, m. p. 126°; ethyl glyoxylate α -acetyl-2:4:6-tribromophenylhydrazone, m. p. 133.5°; ethyl glyoxylate ω -chloro-2:4:6-tribromophenylhydrazone, m. p. 108.5°; ethyl glyoxylate ω -bromo-2:4:6-tribromophenylhydrazone, m. p. 102.5°; and ethyl 2:4:6-tribromobenzeneazoacetate, m. p. 96.5°.

R. J. W. LE FÈVRE.

Absorption spectra and constitution of diazotates. L. CAMBI and L. SZEGÖ (Ber., 1928, 61, [B], 2081—2086; cf. A., 1927, 1063).—Observation of the absorption spectra of the compounds $[\text{PhN}(\text{O})\text{N}]\text{K}$, $[\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{O})\text{N}]\text{K}$, $[\text{C}_6\text{H}_4\text{Br}\cdot\text{N}(\text{O})\text{N}]\text{K}$, $[\text{PhN}\cdot\text{N}\cdot\text{O}]\text{K}$, $[\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{O}]\text{K}$, and $[\text{C}_6\text{H}_4\text{Br}\cdot\text{N}\cdot\text{N}\cdot\text{O}]\text{K}$ shows the absence of an ultra-violet absorption band in the spectrum of all normal salts (and in the normal diazotate of sulphanilic acid), whereas all the *iso*-compounds exhibit a distinct band. It follows therefore that the normal and *isodiazotates* cannot possibly be stereoisomerides. Examination of the curves of the compounds $[\text{PhN}(\text{O})\text{NO}]\text{Na}$, $[\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{O})\text{NO}]\text{Na}$, $[\text{C}_6\text{H}_4\text{Br}\cdot\text{N}(\text{O})\text{NO}]\text{Na}$, $[\text{PhN}\cdot\text{N}(\text{O})\cdot\text{O}]\text{Na}$, $[\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}(\text{O})\cdot\text{O}]\text{Na}$, and $[\text{C}_6\text{H}_4\text{Br}\cdot\text{N}\cdot\text{N}(\text{O})\cdot\text{O}]\text{Na}$ proves that the nitrosoarylhydroxylamines and nitroamines have a maximal absorption in the ultra-violet between 2900 and 2800 Å., whilst the latter compounds have small extinction coefficients. The compounds are distinct optically from the normal diazohydrates. From purely formal considerations, a similarity would be expected between the *isodiazotates* and the nitroamines which is actually observed, but a correspondence between the normal diazotates and nitrosohydroxylamines does not exist, probably because the anion of the normal diazotates has nothing in common with the nitrosoarylhydroxylamines. The *isodiazohydrates*, nitrosoarylhydroxylamines, and nitroamines have the chain $-\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{O}-$, which may be regarded as responsible for the band. On the other hand, the structure of the normal diazohydrates, $-\text{C}_6\text{H}_4\cdot\text{N}(\text{N})\cdot\text{O}-$ or $-\text{C}_6\text{H}_4\cdot\text{N}(\text{O})\cdot\text{N}-$, in which the central nitrogen atom has the nitro-character is totally different. The optical behaviour of the normal diazohydrates is quite distinct from that of the diazonium compounds, all of which show a characteristic band in the ultra-violet. This is explained by the hypothesis that the central nitrogen atom has ammonium character in the diazonium compounds and nitro-properties in the normal diazotates.

H. WREN.

Nitration of phenol. K. BEAUCOURT and E. HAMMERLE (J. pr. Chem., 1928, [ii], 120, 185—192).—Nitration of phenol in water, ethyl alcohol, or glacial acetic acid (cf. Arnall, A., 1924, i, 636) with nitric acid of *d* 1.35 at 7—12° yields 77—82% of nitro-compounds, which consist of 40% of *o*-nitrophenol, 35—40% of *p*-nitrophenol, and 2.5% of 2:4-dinitrophenol (for details the original should be consulted). With nitric acid of *d* 1.42, a yield of 75% of mono-nitro-compounds is obtained, but the *o*:*p*-ratio is shifted in favour of the *p*-isomeride. Variation of temperature has only a small effect on the *o*:*p*-ratio, rise of temperature favouring the production of the

o-isomeride and *vice versa*. The yield of *o*-nitrophenol is but little affected by employing excess of nitric acid, but the yield of the *p*-isomeride is largely depressed, whilst the production of 2:4-dinitrophenol is correspondingly increased; this is probably due to the greater solubility of *p*-nitrophenol in the residual nitric acid. This residual acid, containing dissolved *p*-nitrophenol, after restoration to the original nitric acid concentration by addition of nitric acid, may be used again.

C. W. SHOPPEE.

Directive action of the carbethoxyl group in phenols. E. GEBAUER-FÜLNEGG and J. SMITH-REESE (Monatsh., 1928, 50, 231—234).—The specific *p*-directive action of the carbethoxyl group in phenols noticed in the reaction with chlorosulphonic acid (Gebauer-Fülneegg and Schlesinger, this vol., 631) is also evident in nitration. This has been shown by parallel observations of the nitration of phenol, anisole, and carbethoxyphenol by acetyl nitrate (cf. Pictet, Ber., 1907, 40, 1163) and by benzoyl nitrate (cf. Francis, J.C.S., 1906, 89, 1; A., 1907, i, 53). The results of these authors were confirmed, and rough quantitative observations made of the preponderant formation of *p*-nitro-derivative in the case of carbethoxyphenol. Nitration of carbethoxyphenol by potassium nitrate and sulphuric acid was incomplete, but the *p*-derivative was again formed in largest amount.

R. K. CALLOW.

Derivatives of *p*-dichlorobenzene containing sulphur. E. GEBAUER-FÜLNEGG and E. NEUMANN (Monatsh., 1928, 50, 235—236).—The 2:5-dichloro-nitrobenzenesulphonyl chloride obtained by Gebauer-Fülneegg and Figdor (this vol., 280) has m. p. 59—60°. When boiled with potassium hydroxide solution the dipotassium salt of 4-chloro-2-nitrophenol-6-sulphonic acid (+H₂O) is formed, and separates on cooling. It is a derivative of the *aci*-form. The monopotassium salt (acetyl derivative) is also described. The mother-liquors of the dipotassium salt yield potassium 2:5-dichloro-4-nitrobenzenesulphonate.

The substance described as *p*-dichlorobenzene-2:5-disulphonyl chloride, m. p. 100°, by Quilico (this vol., 169) appears to be a mixture of the 2:5- and 2:6-disulphonyl chlorides, m. p. 182° and 114°, respectively, previously described (*loc. cit.*).

R. K. CALLOW.

Halogenoaminophenols. H. H. HODGSON and A. KERSHAW (J.C.S., 1928, 2703—2705).—The preparation of the following 3-halogenoaminophenols from the corresponding nitro-compounds by reduction with alkaline sodium hyposulphite is described: 3-chloro-2-aminophenol, m. p. 122° (hydrochloride); 3-bromo-2-aminophenol, m. p. 138° (hydrochloride); 3-iodo-2-aminophenol, m. p. 137° (decomp.) (hydrochloride); 3-chloro-4-aminophenol hydrochloride; 3-bromo-4-aminophenol, m. p. 151° (hydrochloride); 3-iodo-4-aminophenol, m. p. 145.5° (hydrochloride); 3-chloro-6-aminophenol, m. p. 154° (hydrochloride); 3-bromo-6-aminophenol, m. p. 150° (hydrochloride); 3-iodo-6-aminophenol, m. p. 141° (hydrochloride). These compounds are more stable than the unsubstituted aminophenols. The orders of rate of reduction of ammoniacal silver nitrate are: for the 3-halogeno-6-aminophenols, Cl > Br > I; the 3-halo-

geno-2-aminophenols, $I > Br > Cl$; the 3-halogeno-4-aminophenols, $Cl > Br > I$. The water-solubility of the 3-halogenoaminophenols decreases in the order $Cl > Br > I$. R. J. W. LE FÈVRE.

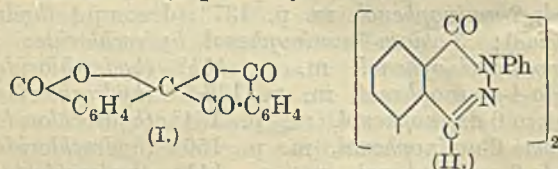
Mobility of some halogen atoms. A. ANGELI and R. POGGI (Atti R. Accad. Lincei, 1928, [vi], 7, 966—969).—*p*-Anisylmethyl chloride changes gradually on keeping from a mobile liquid to a red, glassy mass, with the evolution of hydrogen chloride and methyl chloride. The product has the empirical formula $C_{15}H_{14}O_2$ and exhibits the properties of an artificial resin. F. G. TRYHORN.

Condensation of chloroindane with phenols. C. COURTOT (Compt. rend., 1928, 187, 661—663).—1-Chloroindane condenses with phenol in benzene or ethereal solution or in the homogeneous state (cf. Courtot and Dondelinger, A., 1923, i, 1090) to give *p*-indanylphenol, b. p. 190—193°/8 mm., m. p. 92—93° (benzoyl derivative, m. p. 108°; *m*-nitrobenzoyl derivative, m. p. 96—97°). The constitution of this substance is indicated by the fact that the same *p*-indanylanisole, b. p. 201—202°/19 mm., m. p. 40°, is obtained by the direct methylation of indanylphenol or by the interaction of magnesium *p*-methoxyphenyl bromide and 1-chloroindane. In the first-named reaction small amounts of *indanoxybenzene*, b. p. 185—190°/9 mm., and a viscous liquid, b. p. 293°/8 mm. (probably containing two indane residues), are also formed. Chloroindane reacts with sodium phenoxide or with magnesium phenyl bromide to give the expected products. G. A. C. GOUGH.

New compounds from indene and phenols [3-hydroxyphenylhydrindenes]. I. G. FARBEN-IND. A.-G.—See B., 1928, 845.

Acid from oxidation of α -naphthol. O. DISCHENDORFER (Monatsh., 1928, 50, 97—104).—The acid obtained by Henriques (A., 1888, 843) in small quantity by the oxidation of α -naphthol with alkaline permanganate solution, to which he assigned the formula $C_{20}H_{14}O_8$, is identified as benzil-2:2'-dicarboxylic acid (Graebe and Juillard, A., 1888, 154) (silver and barium salts; diethyl ester, m. p. 154—155°). It is suggested that its formation from α -naphthol proceeds through the stages di- α -naphthol, di- β -naphthaquinone (cf. Korn, A., 1885, 392), a compound of *o*-carboxycinnamic acid type being a possible intermediate compound in the last stage.

Observations made by Henriques of the reactions of the acid were repeated and corrected. When heated for a few minutes above its m. p. the acid yields the anhydride, m. p. 164° (cf. Graebe and Juillard, *loc. cit.*), probably of the constitution I,



which decomposes on further heating with the formation of diphtalyl and phthalic anhydride. Heated with phenylhydrazine in alcohol, the acid yields the *bisphenylhydrazone*, decomp. 175°, and,

when the heating is prolonged, the *bisphenyl-lactam* (II), m. p. 305—306°. R. K. CALLOW.

Catalytic production of polynuclear compounds. I. G. R. CLEMO and R. SPENCE (J.C.S., 1928, 2811—2819).—The dinaphthol obtained by ferric chloride oxidation of β -naphthol (Dianin, A., 1874, 262; Julius, A., 1887, 56) has been synthesised and its identity thereby definitely established. 1-Bromo-2-naphthol gave, when heated in presence of copper, β -dinaphthol, 1:1'-dinaphthylene-2:5':2':8-dioxide and 1:1'-dinaphthylene-2:2'-oxide, the last being also formed by prolonged heating of β -dinaphthol with 4% of vanadium pentoxide.

β -Naphthol, when heated at 300° in contact with air with either tungsten or molybdenum trioxides, gave 2:2'-dinaphthylether. Similar treatment using vanadium pentoxide gave β -dinaphthol; at 340° 1:1'-dinaphthylene-2:2'-oxide was formed, but in the absence of air only 2:2'-dinaphthylether was obtained. Titanium dioxide gave mostly 2:2'-dinaphthyl ether and some 1:1'-dinaphthylene-2:2'-oxide.

Similar treatment of β -naphthol with alkaline-earth oxides gave an isooxide, m. p. 158—159° (either 2:2'-dinaphthylene-3:3'-oxide or 1:2'-dinaphthylene-2:3'-oxide) (*dibromo*-derivative, m. p. 193°), identical with the compound of Merz and Weith (A., 1881, 605), accompanied by a second compound, m. p. 300° (cf. Niederhausen, A., 1882, 1211).

Both 1:1'-dinaphthylene-2:2'-oxide and the isooxide are stable to red-hot zinc dust or fused potassium hydroxide; with hydriodic acid they give hydrogenated naphthalenes, and by oxidation with sulphuric acid, phthalic acid is formed in both cases. Chromic acid destroys the first compound, but converts the isooxide into an isodinaphthaquinone oxide (I), m. p. 268°, which does not condense with *o*-phenylenediamine and is therefore probably 1:2'-dinaphthylene-1':4'-quinone-2:3'-oxide. Distillation of I over zinc dust regenerates the isooxide; by reduction with zinc and acetic anhydride *diacetoxisodinaphthylene oxide*, m. p. 245—246°, is formed. With alcoholic sodium hydroxide I undergoes ring scission, giving *dihydroxydinaphthaquinone*, m. p. 222° (*diacetyl* derivative, m. p. 167°), which loses water on heating, forming an isomeric (red) *o*-dinaphthaquinone oxide, m. p. 255—256°, which condenses with *o*-phenylenediamine to give a substituted *phenazine*, m. p. 240°.

Attempts are described to synthesise 2:2'-dinaphthylene-3:3'-oxide. The Ullmann reaction applied to 2-chloro-3-naphthoic acid gives only β -naphthoic acid. The chlorine atom in ethyl 2-chloro-3-naphthoate is stable to copper-bronze under the conditions employed.

2-Methoxy-3-naphthylamine, m. p. 109.5° (*acetyl* derivative, m. p. 124—125°), by the Hofmann reaction from 2-methoxy-3-naphthoamide, was converted into 3-bromo-2-methoxynaphthalene, m. p. 76°, b. p. 178—190°/16 mm., and 3-iodo-2-methoxynaphthalene, m. p. 65°. The former gives 3-bromo- β -naphthol, m. p. 80—81°, by heating with hydrobromic acid; when hydriodic acid was used only β -naphthol was isolated. Under the conditions of Ullmann's reaction the last three halogen compounds give β -methoxynaphthalene or β -naphthol.

Only dinaphthaxanthone (Strohbach, A., 1902, i, 171) was isolated from the action of tungsten trioxide or vanadium pentoxide on 2-hydroxy-3-naphthoic acid or its ethyl ester.

α -Naphthol is converted by vanadium pentoxide or calcium oxide into α -dinaphthylene oxide (Merz and Weith, *loc. cit.*), also formed by the dehydration of α -dinaphthol. R. J. W. LE FEVRE.

Compounds of 2:3-dihydroxynaphthalene with tervalent iron and aluminium and with arsenic acid. R. WEINLAND and H. SEUFFERT (Arch. Pharm., 1928, 266, 455—464).—Dihydroxynaphthalene, like pyrocatechol, forms co-ordination compounds with tervalent iron and aluminium and with arsenic acid. Two series of compounds, one red and the other violet, are formed with ferric iron. The red compounds, which are stable towards alkalis but not towards acids, are obtained as dark brownish-red powders from ferric acetate, dihydroxynaphthalene, and the corresponding alkali hydroxide in aqueous or dilute alcoholic solution. The iron has the co-ordination number 6, the compounds being formulated as $[\text{Fe}(\text{O} \cdot \text{C}_{10}\text{H}_6 \cdot \text{O})_3]_3\text{M}_3$. The following are described: *potassium* (+2H₂O), *ammonium* (+2H₂O), and *sodium* (+H₂O) *tri*-(2:3-dihydroxynaphthalene)*ferrates*. The corresponding *potassium*, *ammonium*, and *sodium tri*(dihydroxynaphthalene)*aluminates* are colourless and less well-defined.

The violet compounds in which iron has the co-ordination number 4, $[\text{C}_{10}\text{H}_6 \text{---} \text{O} \text{---} \text{Fe} \cdot \text{O} \cdot \text{C}_{10}\text{H}_6 \cdot \text{O}]_4\text{M}$, are obtained from dihydroxynaphthalene, ferric acetate, and the corresponding alkali acetates in concentrated alcoholic solution. They are more stable towards acids than the red compounds. *Di*-(2:3-dihydroxynaphthalene)*ferric acid* (2H₂O), the *potassium* (4H₂O), *ammonium* (4H₂O), and *sodium* (1H₂O) salts are described.

Tri(dihydroxynaphthalene)*arsenic acid* (5H₂O) is obtained from dihydroxynaphthalene and arsenic acid in absolute-alcoholic solution. S. COFFEY.

Bathochromic action of the methylthiol group in azo-dyes. I. E. BLUMENSTOCK-HALWARD and E. JUSA. II. E. BLUMENSTOCK-HALWARD and E. RIESZ [with P. G. BUM] (Monatsh., 1928, 50, 123—138, 139—143).—I. Advantage was taken of the bathochromic action of the methylthiol group observed by Brand (cf. A., 1925, i, 397) to prepare from 3:6:8-trimethylthiol- β -naphthol and diazotised *p*-nitroaniline a reddish-violet azo-dye, markedly deeper in shade than the other dyes of this class ("ice colours"). The shade deepens successively in the dyes derived from the trisulphonic acid, trithiol, and trimethylthiol derivatives, corresponding with the change from sexavalent to bivalent sulphur, and methylation, respectively. The poor yield of the trithiol derivative obtained makes technical application impossible in this case.

Potassium O-carbethoxy- β -naphthol-3:6:8-trisulphonate, when heated with phosphorus pentachloride, yielded the *trisulphonyl chloride*, m. p. 195°. The action of aniline caused partial hydrolysis of the carbethoxyl group, completed on recrystallisation, and yielded β -naphthol-3:6:8-trisulphonanilide (cf.

Pollak, Gebauer-Fülneegg, and Blumenstock-Halward, this vol., 751). *O-Carbethoxy-3:6:8-trithiol- β -naphthol*, m. p. 80—86° (decomp.), which could not be obtained pure, was formed in 15—20% yield by the reduction of the trisulphonyl chloride by adding hydrochloric acid to the alcoholic solution containing zinc dust in suspension. It was readily oxidised to polysulphides, and yielded, with simultaneous hydrolysis of the carbethoxyl group, a dark red azo-dye with diazotised *p*-nitroaniline, slowly formed in neutral solution, rapidly in alkaline solution. The orange-red lead salt of the trithiol was obtained with alcoholic lead acetate. The action of ethyl chloroformate yielded *O-carbethoxy-6:8-dithiol-3-carbethoxythiol- β -naphthol*, m. p. 115—120° (decomp.). Hydrolysis with potassium hydroxide yielded 2:2'-dihydroxy-6:6':8:8'-tetraethioldinaphthalene 3:3'-disulphide (lead salt), which yielded 3:6:8-trithiol- β -naphthol (isolated as the lead salt) on reduction. *O-Carbethoxy-3:6:8-trimethylthiol- β -naphthol*, resinous, no characteristic m. p., accompanied in certain circumstances by 2:2'-di(carbethoxyoxy)tetramethylthioldinaphthalene disulphide, was obtained by treatment of the trithiol derivative with methyl sulphate and sodium carbonate, and yielded 3:6:8-trimethylthiol- β -naphthol, m. p. 140°, on hydrolysis with alcoholic potassium hydroxide.

II. The azo-dye derived from 3:6-dimethylthiol- β -naphthol and diazotised *p*-nitroaniline had a similar dull reddish-violet colour to the 3:6:8-trimethylthiol derivative; the 8-methylthiol group thus appears to have no influence on the colour of the dye.

The following compounds were prepared, chiefly by the methods described above: *O-carbethoxy-3:6-dithiol- β -naphthol*, m. p. 117° [from the disulphonyl chloride (cf. Pollak and others, *loc. cit.*)], which yielded 3:6-dithiol- β -naphthol, m. p. 152°, when hydrolysed with dilute alkali; 3:6-dimethylthiol- β -naphthol, m. p. 125° (methyl ether, m. p. 93°); 1-*p*-nitrobenzeneazo-3:6-dimethylthiol- β -naphthol, m. p. 258°. Combined reduction and acetylation of *O-carbethoxy- β -naphthol-3:6-disulphonyl chloride* by treatment with acetic anhydride, acetic acid, zinc dust, and sodium acetate yielded *O-carbethoxy-3:6-diacylthiol- β -naphthol*, m. p. 120°. R. K. CALLOW.

Action of phosphoric oxide on benzyl alcohol in benzene solution. S. S. NAMETKIN and D. A. KURSANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 917—920).—The less volatile products of the action of phosphoric oxide on benzyl alcohol in benzene solution were investigated, to determine whether other compounds besides diphenylmethane are formed. The fraction of b. p. 218—220°/11 mm. gave on recrystallisation *p*-dibenzylbenzene, m. p. 87°, which must have been formed by the further action of benzyl alcohol on diphenylmethane, since it was obtained by heating these compounds with phosphoric oxide.

M. ZVEGINZOV.

Electrolytic oxidation of alcohols. III. **Benzyl alcohol.** S. KOIDZUMI (Mem. Coll. Sci. Kyōto, 1928, [4], 11, 383—390).—Electrolytic oxidation of benzyl alcohol in acid or alkaline media gave, in most experiments made, a mixture of benzaldehyde and benzoic acid. The experiments were carried out

in a divided cell with a rotating cathode of iron plate, lead, or nickel gauze, and a cathode solution of either sulphuric acid, sodium hydroxide, or sodium carbonate solutions enclosed in a porous cylinder. In acid solution with lead peroxide as anode material and iron as cathode, the current density has no effect on the products formed, but the amount of aldehyde diminishes with current quantity. With platinum or gold anodes and a lead cathode, oxidation efficiency is low, but the product is almost free from benzoic acid. In sodium carbonate solution the maximum yield of benzaldehyde, free from benzoic acid, is about 71%.

H. BURTON.

Electrolytic reduction of aldehydes. III. *o*- and *p*-Hydroxybenzaldehydes. IV. Vanillin and piperonal. G. SHIMA (Mem. Coll. Sci. Kyōtō, 1928, [A], 11, 407—418, 419—427).—III. Electrolytic reduction of salicylaldehyde to salicyl alcohol is best carried out at 16—18°, using a mercury cathode, an almost neutral catholyte, and a current density of 4 amp./100 cm.² The yield of alcohol is 85%. With an alkaline catholyte there are formed dihydroxyhydrobenzoin (cf. Law, J.C.S., 1906, 89, 1512) and 9:10-dihydroxy-9:10-dihydrophenanthrene. *p*-Hydroxybenzaldehyde gives a 92% yield of *p*-hydroxybenzyl alcohol under the above conditions.

IV. Reduction of vanillin suspended in a slightly acid catholyte at 8—10° gives hydrovanilloin (10%) and 4-hydroxy-3-methoxybenzyl alcohol (82%; *di-benzoyl* derivative, m. p. 120°). At higher temperatures there is an increase in the amount of hydrovanilloin and other condensation products. In slightly alkaline suspension the yield of alcohol is 92%. Under similar conditions piperonal gives a 90% yield of 3:4-methylenedioxybenzyl alcohol, m. p. 56° (lit. 51°; *benzoate*, m. p. 66°).

H. BURTON.

Attempt to dehydrate benzhydryl by Tschugaev's xanthate method. D. N. KURSANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 921—924; cf. A., 1926, 399).—When methyl benzhydryl xanthate was decomposed by heating at 190—260°, among the products tetraphenylethylene was obtained in a manner analogous to stilbene in the experiments of Nametkin and Kursanov (*loc. cit.*). These products indicate a new mechanism for Tschugaev's reaction.

M. ZVEGINTZOV.

Urethanes of nuclear-substituted benzyl alcohols. I. G. FARBENIND. A.-G.—See B., 1928, 873.

Amines of the hydroaromatic-aliphatic series [*cyclohexyl-β*-aminoethyl alcohol etc.]. I. G. FARBENIND. A.-G.—See B., 1928, 846.

Oxidation of cholesterol by molecular oxygen. G. BLIX and G. LÖWENHIJLM (Biochem. J., 1928, 22, 1313—1322).—Oxycholesterol is formed by the action of atmospheric oxygen when cholesterol is heated in the air at temperatures slightly above the m. p. or by aëration of cholesterol suspensions. Aqueous suspensions of pure cholesterol are very stable against atmospheric oxygen even at boiling temperature. The impurities which catalyse the formation of oxycholesterol adhere, however, very stubbornly to the cholesterol. Alkali soaps catalyse the oxidation,

whilst other hydrophilic colloids, higher fatty acids, triglycerides, or heavy metal salts have no catalytic influence. The degree of dispersion is of great importance in the oxidation of cholesterol by molecular oxygen.

S. S. ZILVA.

Metacholesterol bromide. I. LIFSCHÜTZ (Arch. Pharm., 1928, 266, 518; cf. A., 1922, i, 251, 541).—Metacholesterol bromide melts at 104—105° and shows the same behaviour on melting as cholesterol dibromide, m. p. 93—94°.

S. COFFEY.

Preparation of cholestenone. W. A. SEXTON (J.C.S., 1928, 2825—2826).—An 80% yield of cholestenone is obtained by the distillation of a mixture of cholesterol and copper-bronze under 2—3 mm. pressure.

A. I. VOGEL.

Ultra-violet irradiation of dehydroergosterol. A. WINDAUS and O. LINSERT (Annalen, 1928, 465, 148—166).—During ultra-violet irradiation ergosterol loses its levorotatory power and eventually becomes slightly dextrorotatory; there is at the same time a change in the ultra-violet absorption spectrum, and the activated ergosterol has greater solubility and is no longer precipitated by digitonin. Since the change occurs in absence or presence of air or solvents and the mol. wt. remains the same, it is probably due to isomerisation. The hydroxyl content, determined by Zerewitinov's method, is unchanged, and a ketonisation of the type $\cdot\text{CH}(\text{OH})\cdot\dot{\text{C}}\text{H}\cdot\text{CH}:\text{CH}\cdot\rightarrow$

$\cdot\text{CO}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ (cf. A., 1927, 557) is thus excluded. Cyclisation, with consequent loss of a double linking (cf. Sernagiotto, A., 1918, i, 444), is also improbable, since titration with perbenzoic acid gives similar figures before and after irradiation and the same amount of hydrogen (3 mols.) is absorbed in presence of platinum sponge. The remaining possibilities are migration of double linkings or stereoisomerisation or both. Esters and other derivatives of ergosterol, and also dehydroergosterol, show the same isomerisation and activation by irradiation as ergosterol itself; dehydroergosterol compounds have the advantage of forming crystallisable products.

Dehydroergosterol, $\text{C}_{27}\text{H}_{40}\text{O}$, m. p. 146°, b. p. 230°/0.5 mm. almost without decomposition, $[\alpha]_D^{25} + 149^\circ$ (digitonin additive product; *acetate*, m. p. 146°, $[\alpha]_D^{25} + 193^\circ$; *phenylurethane*, m. p. 161—162°, $[\alpha]_D^{25} + 202^\circ$; *peroxide*, m. p. 158°), is prepared by distilling in high vacuum the trihydric *alcohol*, $\text{C}_{27}\text{H}_{44}\text{O}_2$, m. p. 227°, $[\alpha]_D^{25} - 121.6^\circ$, obtained by reduction of ergosterol peroxide with zinc and alcoholic potassium hydroxide; it is more conveniently prepared by boiling ergosterol in alcohol with mercuric acetate. Air-dried dehydroergosterol contains $1\text{H}_2\text{O}$, removable with difficulty. Insolation of dehydroergosterol after boiling with eosin in alcohol yields *dehydroergopinacone*, $\text{C}_{24}\text{H}_{38}\text{O}_2$, m. p. 196° (decomp.). Hydrogenation of the acetate leads, as with ergosterol, to γ -ergosterol (*allo-α*-ergosterol), with intermediate production of α -ergosterol (tetrahydroergosterol). By the action of ultra-violet light dehydroergosteryl acetate (0.1% solution in alcohol) is converted into two products, separable as acetates by fractional crystallisation and as alcohols after hydrolysis by precipitation with digitonin. The more soluble acetate gives on hydrolysis an *alcohol*,

$C_{27}H_{40}O$, m. p. 134° , $[\alpha]_D^{20} +119.5^\circ$, without antirachitic properties, which by acetylation yields an *acetate*, m. p. 126 — 127° , $[\alpha]_D^{20} +87.0^\circ$ (hydrogenated to an *octahydro-acetate*). The less soluble *acetate*, m. p. 178° , is hydrolysed to an *alcohol*, m. p. 175° , precipitable with digitonin, which also has no antirachitic value.

C. HOLLINS.

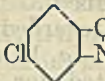
Reaction between the binary system, magnesium-magnesium iodide, and aromatic acids and acid derivatives. M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1928, 50, 2762—2769; cf. A., 1927, 245, 1190).—Although the aromatic acids in 5% ethereal solution react very slowly with magnesium, they are readily and quantitatively converted by the above binary system into iodomagnesium salts. The acid and magnesium iodide probably react reversibly, forming hydrogen iodide, which then attacks the magnesium or the ether. Hydrogen bromide also dissolves magnesium in ether, but hydrogen chloride acts only in presence of magnesium bromide, giving apparently homogeneous magnesium chlorobromide. The additive products of magnesium bromide with organic acids, $2R \cdot CO_2H, MgBr_2, 2Et_2O$, are less soluble than those of magnesium iodide. The iodomagnesium salts separate as oily or crystalline etherates, mixed with normal magnesium salts formed by their decomposition. They are slowly reduced by the binary reagent in boiling ether to the bimolecular derivatives, $[CR(OMgI)_2]_2$ and $[CR(OMgI)]_2$, which are hydrolysed by water to benzils and benzoin, respectively. The combined yields of the latter products are: from benzoic acid 43%; *p*-toluic acid, 30%; α -naphthoic acid, 30—35%; β -naphthoic acid, 75%, and from *p*-phenylbenzoic acid, 46% of the theoretical. Alkyl esters of aromatic acids are decomposed by magnesium iodide to alkyl iodides and iodomagnesium salts, both of which react with the binary system; thus benzyl benzoate yields dibenzyl and benzoin, and methyl benzoate yields a little benzoin. Phenyl benzoate is decomposed to iodomagnesium phenoxide and benzoyl iodide which gives resinous products. Benzoyl peroxide and magnesium iodide quantitatively yield iodine and iodomagnesium benzoate.

H. E. F. NOTTON.

4-Chloroanthranilic acid. G. HELLER and L. HESSEL (J. pr. Chem., 1928, [ii], 120, 64—73).—The tendency of 4-chloroanthranilic acid to yield condensation products containing four-, five-, and six-membered heterocyclic systems has been investigated and examples of each type have been obtained. The methyl ester of the acid, m. p. 68.5° (ethyl ester, m. p. 41°), with hydrazine hydrate yields 4-chloro-2-amino-benzhydrazide, m. p. 151° , which with acetic anhydride in ethyl acetate solution is converted into 4-chloro-2-aminobenzdiacetylhydrazide, m. p. 214° , which is easily soluble in dilute acids and therefore considered to bear both acetyl groups on the hydrazine residue (cf. Heller, A., 1925, i, 1322). When the hydrazide, m. p. 151° , is heated at 200° for 5 hrs., bis-(4-chloro-2-aminobenz)hydrazide, m. p. 272° , is obtained, which when treated with nitrous acid yields bis-4-chlorobenzazamide, m. p. 245° .

With benzoyl chloride in pyridine solution, 4-chloro-

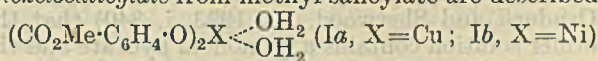
anthranilic acid yields 4-chloro-N-benzoylanthranil, m. p. 198° [I: R=Bz], together with

(I.)  4-chloro-2-benzamidobenzoic acid, m. p. 219°, which with concentrated sulphuric acid gives the preceding compound. This compound is converted by alcoholic hydrazine into 6-chloro-3-hydrazino-3-phenyl-3:4-dihydro-2:4-benzoxazole, m. p. 214° , which when heated in glacial acetic acid solution at 100° undergoes rearrangement with loss of 1 mol. of water to give 7-chloro-3-amino-2-phenyl-4-quinazalone, m. p. 198° . The acid when treated with hot acetic anhydride yields 4-chloro-N-acetylanthranil, m. p. 145° [(I): R=Ac], slowly converted by water and more rapidly by alkali into 4-chloro-2-acetamidobenzoic acid, m. p. 213° , and giving with alcoholic hydrazine 7-chloro-3-amino-2-methyl-4-quinazalone.

4-Chlorophenyl-2-glycine-1-carboxylic acid, m. p. 228° , could not be obtained by condensation of 4-chloroanthranilic acid with chloroacetic acid, but was prepared by alkaline hydrolysis of 4-chloro-2-cyanomethylaminobenzoic acid, m. p. 215° , obtained by the action of formaldehyde and potassium cyanide on 4-chloroanthranilic acid in the presence of acetic acid. The dimethyl ester of 4-chlorophenyl-2-glycine-1-carboxylic acid has m. p. 189° , and could not be converted into chloroindoxyl ester by heating with sodium methoxide solution. By heating 4-chlorophenyl-2-glycine-1-carboxylic acid with acetic anhydride and sodium acetate, followed by treatment with sodium hydroxide, is obtained 2:2'-dichloroindigotin, identical with the synthetic product.

C. W. SHOPPEE.

Metallic derivatives of hydroxy-esters. I. Copper and nickel derivatives of methyl salicylate. B. W. DOAK and J. PACKER (J.C.S., 1928, 2763—2769).—The preparations of methyl cuprisalicylate dihydrate (Ia), decomp. 115° , methyl nickelosalicylate dihydrate (Ib), and anhydrous methyl nickelosalicylate from methyl salicylate are described.



When boiled with water, methyl cuprisalicylate is hydrolysed to methyl salicylate and copper hydroxide, whereas methyl nickelosalicylate yields methyl salicylate and methyl hydroxynickelosalicylate, $CO_2Me \cdot C_6H_4 \cdot O \cdot Ni \cdot OH$. Passage of wet air over Ia at 100° gives methyl hydroxycuprisalicylate, which when heated at 100° in dry air gives a basic compound (II), $CO_2Me \cdot C_6H_4 \cdot O \cdot Cu \cdot O \cdot Cu \cdot O \cdot C_6H_4 \cdot CO_2Me$. The reaction $(CO_2Me \cdot C_6H_4 \cdot O)_2Cu + H_2O \rightleftharpoons CO_2Me \cdot C_6H_4 \cdot OH + CO_2Me \cdot C_6H_4 \cdot O \cdot Cu \cdot OH$ is reversible and proceeds slowly (left to right) at the ordinary temperature.

Ia and Ib undergo reversible alcoholysis with methyl alcohol, yielding the respective methoxymetallosalicylates, $CO_2Me \cdot C_6H_4 \cdot O \cdot X \cdot OMe$. With ethyl alcohol the alcoholysis occurs less readily, but with the copper compound is more complete, methyl salicylate and cupric ethoxide being formed. Ib gives methyl ethoxynickelosalicylate. Methylation of sodium cuprisalicylate by methyl sulphate gave II in good yield. By the action of ammonia on alcoholic solutions of Ia and Ib, ammine complexes are formed, only methyl diamminenickelosalicylate (III),

($\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{O}$) $_2\text{Ni}(\text{NH}_3)_2$, being isolated (two meta-stable and a stable octahedral form described).

The copper and nickel atoms are regarded as possessing the co-ordination number 4 in Ia, Ib, and III; a similar constitution is suggested for the aluminosilicates of Burrows and Wark (this vol., 288).

R. J. W. LE FÈVRE.

Derivatives of *p*-methoxycinnamic acid. P. A. FOOTE (J. Amer. Pharm. Assoc., 1928, 17, 958—962).—The following esters of *p*-methoxycinnamic acid have been prepared: *phenyl*, m. p. 76—77°; *β-naphthyl*, m. p. 130—131°; *thymyl*, m. p. 58—59°; *carvacryl*, m. p. 78—79°; *eugenyl*, m. p. 112—113°; *phenacyl*, m. p. 136° (*monoxime*, m. p. 116—117°); also the *gold*, *mercuric*, *zinc*, and *ammonium* salts. *Carvacryl cinnamate*, m. p. 65—66°, and *eugenyl cinnamate*, m. p. 90—91°, are described. The above esters have no toxic action on *B. typhosus* or *B. staphisaurius*.

E. H. SHARPLES.

4-Bromophthalic acid. L. C. BAKER (J.C.S., 1928, 2829).—Details are given of the preparation of ethyl 4-bromophthalate (yield 66%) and 4-bromophthalic acid (yield 88%) from ethyl 4-aminophthalate by Sandmeyer's reaction and acid hydrolysis of the product, respectively.

R. J. W. LE FÈVRE.

Absorption spectra of phthaleins and sulphonphthaleins of phenol and *o*-cresol. R. C. GIBBS and C. V. SHAPIRO (J. Amer. Chem. Soc., 1928, 50, 2798—2810; cf. A., 1922, ii, 806; 1924, ii, 346; this vol., 526, 1019).—The presence of a pair of bands between the frequency numbers 3500 and 3700 mm^{-1} in the absorption spectra of phenol-phthalein (I) and -tetrachlorophthalein and *o*-cresol-phthalein (II) and -tetrachlorophthalein in neutral absolute alcoholic solutions indicates that these substances have a benzenoid structure (cf. this vol., 570). The absorption spectra of phenolsulphonphthalein (III) in (a) water or 95% alcohol and (b) absolute alcohol are of different types, which confirms the suggestion (Orndorff and Sherwood, A., 1923, i, 340) that the former solution contains a quinonoid hydrate and the latter an internal complex salt. After long keeping in the dark, the latter solution acquires an absorption closely similar to that of the lactonoid phenol-sulphonphthalein diethyl ether, which is probably present in equilibrium with a small quantity of a quinonoid form. The corresponding solutions of *o*-cresolsulphonphthalein (IV) have closely similar absorption curves to those of III, but the slow fading of the alcoholic solution is not, in this case, due simply to the formation of the diethyl ether. The absorption spectra of I, II, III, and IV in sulphuric acid or in a large excess of hydrochloric acid (cf. A., 1926, 884) are all very similar, but IV is slowly sulphonated by sulphuric acid. The absorption curves of the dibasic salts of III and IV are obtained in solutions containing 100 mol. proportions of alkali. With 2 mols. of alkali considerable hydrolysis to the free phthalein occurs in dilute solutions and the use of these derivatives for p_H comparisons is, therefore, possible only under closely similar conditions of concentration. Potassium hydroxide, 33%, converts III in a few days and IV in several months into the colourless tripotassium salts of the carbinolcarboxylic

acids. The absorption spectra of the solutions mentioned are shown graphically and the frequency numbers of the heads of the bands are tabulated.

H. E. F. NOTTON.

Enolisation of homophthalic anhydrides. T. S. STEVENS and J. L. WILSON (J.C.S., 1928, 2827—2828).—4:5-Methylenedioxyhomophthalic anhydride, m. p. 178—180° (obtained by boiling the parent acid with acetic anhydride), forms yellow alkali salts (cf. Davies and Poole, this vol., 885), the oxidation of which by alkaline permanganate give methylenedioxyphthalidecarboxylic acid, m. p. 213—215° (decomp.) (lit. 216° decomp.), and methylenedioxyphthalide.

R. J. W. LE FÈVRE.

Constitution of " β -resodicarboxylic acid." K. BRUNNER [with, in part, N. MADERSBACHER and E. GORITSCHAN] (Monatsh., 1928, 50, 216—224).—" β -Resodicarboxylic acid," first prepared from 3:5-dihydroxybenzoic acid by Senhofer and Brunner (A., 1881, 265), has now been prepared by an improved method and its constitution determined. From its method of formation, the non-formation of an anhydride or imide, and comparison of the *dimethyl ether* of the acid with 3:5-dimethoxyphthalic acid (Fritsch, A., 1897, i, 569), it is concluded that it is 3:5-dihydroxyterephthalic acid.

3:5-Disulphobenzoic acid was prepared from benzoic acid by treatment with fuming sulphuric acid containing 50% of anhydride and hydrogen chloride, or by heating with pure chlorosulphonic acid, and separated as the dipotassium salt (+3H₂O and +2H₂O), which yielded 3:5-dihydroxybenzoic acid, subliming at 190—195°/14 mm., when fused with potassium hydroxide. 3:5-Dihydroxybenzoic acid, when heated with potassium hydrogen carbonate and glycerol in a stream of carbon dioxide, yielded 3:5-dihydroxyterephthalic acid, separated as the *ammonium hydrogen salt* (+H₂O). The *dimethyl ester*, m. p. 151.5—152°, by treatment with methyl iodide and potassium hydroxide gave *methyl 3:5-dimethoxyterephthalate*, m. p. 121.5—122°, which was hydrolysed to 3:5-dimethoxyterephthalic acid, m. p. 285°.

R. K. CALLOW.

Ethyl 1:2:3:6-tetracarbethoxy-5-methoxy- $\Delta^{2:5}$ -cyclohexadiene-1-acetate, a derivative of triethyl aconitate. G. URUSHIBARA (Bull. Chem. Soc. Japan, 1928, 3, 217—219).—When a mixture of ethyl aconitate (1 mol.), sodium ethoxide (1 mol.), and an excess of methyl iodide in alcohol solution is heated in a sealed tube at 115—120°, the product is *ethyl 1:2:3:6-tetracarbethoxy-5-methoxy- $\Delta^{2:5}$ -cyclohexadiene-1-acetate*, b. p. 225—230°/1 mm. The mechanism of its formation is probably similar to that involved in the condensation and methylation of ethyl glutaconate (Curtis and Kenner, J.C.S., 1914, 105, 282), the sodium derivative of ethyl 1:2:3:6-tetracarbethoxy-5-keto- Δ^2 -cyclohexene-1-acetate being first produced and then converted into the above *O*-methyl derivative.

J. W. BAKER.

Condensation of heptaldehyde with aromatic aldehydes. I. B. N. RUTOVSKI and A. Y. KOROLEV (J. Russ. Phys. Chem. Soc., 1928, 60, 925—927).—Benzaldehyde and heptaldehyde in the presence of alkali hydroxides in aqueous alcohol give β -*phenyl*-

α -*n*-amylacraldehyde, a yellow liquid with an odour of jasmine, b. p. 174—175°/20 mm., d_{20}^{25} 0.97108, n_D^{25} 1.5381. The *oxime*, m. p. 72.5—73°, and *semicarbazone*, m. p. 117.5—118°, were prepared. By condensing the β -phenyl- α -*n*-amylacraldehyde with benzoylglycine, 2-phenyl-4- α -benzylideneheptylidene-5-oxazolone, m. p. 97—98°, was obtained. M. ZVEGINTZOV.

Vinylene homologues of *p*-dimethylaminobenzaldehyde. W. KÖNIG, W. SCHRAMMEK, and G. RÖSCH (Ber., 1928, 61, [B], 2074—2080).—*p*-Dimethylaminobenzaldehyde condenses readily with paracetaldehyde in the presence of concentrated sulphuric acid, giving compounds, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}:\text{CH}]_n \cdot \text{CHO}$, in which *n* depends greatly on the duration of the change. Thus, after 3 hrs. the product when treated with 60% of the sodium hydroxide required for neutralisation of the sulphuric acid affords the trivinylene aldehyde (see later), the filtrate from which, after further neutralisation with sodium hydroxide, gives *p*-dimethylaminocinnamaldehyde, m. p. 141°, maximum absorption, 399 μ (phenylhydrazone, m. p. 169°; *oxime*, m. p. 151°). If reaction is extended to 5—6 hrs., the main product is streptotrivinylene-*p*-dimethylaminobenzaldehyde (η -*p*-dimethylaminophenyl- $\Delta^{8\frac{1}{2}}$ -heptatrienal), m. p. 184° or 176° from light petroleum or ethyl acetate, absorption maximum, 440 μ (phenylhydrazone, m. p. 217°). On one occasion, the attempted purification of the trivinylene aldehyde by means of 60% sulphuric acid led to the isolation of streptopentavinylene-*p*-dimethylaminobenzaldehyde (λ -*p*-dimethylaminophenyl- $\Delta^{8\frac{1}{2}}$ -undecapentaenal), m. p. 209°, in which the number of vinylene groups is confirmed by spectroscopic analysis (absorption maximum, 470 μ). Aldehydes containing an even number of vinylene groups do not appear to be produced from paracetaldehyde or crotonaldehyde. streptodivinylene-*p*-dimethylaminobenzaldehyde (ϵ -*p*-dimethylaminophenyl- $\Delta^{8\frac{1}{2}}$ -pentadienal), m. p. about 155°, is identified spectroscopically as by-product of the condensation of *p*-dimethylaminocinnamaldehyde and pyruvic acid in presence of sulphuric acid; its absorption maximum is at 420 μ . H. WREN.

Nitration of piperonal. J. B. EKELEY and M. S. KLEMM (J. Amer. Chem. Soc., 1928, 50, 2711—2715).—Attempts to obtain the *isomeride*, m. p. 143°, present in commercial *o*-nitropiperonal (cf. A., 1922, i, 934) from piperonal and nitric acid alone or in presence of sulphuric acid, acetic acid, or catalysts, yielded only *o*-nitropiperonal, nitro- (m. p. 144°) and dinitro-methylenepyrrocatechol, nitropiperonylic acid, and a new *nitromethylenepyrrocatechol*, m. p. 70°, probably formed from the desired *isomeride*. Nitric acid (*d* 1.38) at 45° gives the best yield of *o*-nitropiperonal. H. E. F. NOTTON.

Derivatives of phenacyl sulphide. A. CHRZASZCZEWSKA and S. CHWALIŃSKI (Rocz. Chem., 1928, 8, 432—444).—*p*-Methylphenacyl sulphide, $(\text{C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CH}_2)_2\text{S}$, m. p. 88.8—89.3° (*dioxime*, m. p. 158—159°), is obtained by adding aqueous sodium sulphide solution to a boiling alcoholic solution of *p*-tolyl chloromethyl ketone. *p*-Bromophenacyl sulphide, m. p. 142.2—143.1° (*dioxime*, m. p. 180—180.5°), and *p*-chlorophenacyl sulphide *dioxime*, m. p. 150—

150.5°, and *diphenylhydrazone*, m. p. 127—128°, are prepared similarly. R. TRUSZKOWSKI.

Hydroxy- ω -aminoacetophenone derivatives [hydroxyphenacylamines and their ethers]. H. LEGERLOTZ.—Sec B., 1928, 837.

Organic compounds of sulphur. X. Action of air on thiobenzophenone. A. SCHÖNBERG, O. SCHÜTZ, and S. NICKEL (Ber., 1928, 61, [B], 2175—2177; cf. this vol., 897).—Thiobenzophenone is converted by exposure to air into a trisulphide, $\text{C}_{26}\text{H}_{20}\text{S}_3$ (cf. Staudinger and Freudenberger, this vol., 1246), regarded as $\text{CPh}_2 \cdot \text{S} \cdot \text{S} \cdot \text{S} \cdot \text{CPh}_2$, which is decomposed by heat into thiobenzophenone and sulphur.

[With J. PETER.]—*Dibenzhydryl sulphide*, m. p. 66.5°, prepared from benzhydryl mercaptan and diphenylbromomethane in dry benzene, yields thiobenzophenone at 275°. H. WREN.

Action of nitric acid on derivatives of ethylene.

II. Nitration of styrene derivatives. J. VAN DER LEE (Rec. trav. chim., 1928, 47, 920—933; cf. A., 1926, 1245).—Nitration of 4:4'- and 3:3'-dinitro-distyryl ketone, obtained by the action of potassium hydroxide solution on 3-nitrostyryl methyl ketone, with absolute nitric acid affords ω :4- and ω :3-dinitrostyrenes, respectively. The same dinitro-compounds are formed during the nitration of 4- and 3-nitrostyryl methyl ketones. 3-Nitrophenyl 3-nitrostyryl ketone is nitrated under various conditions, yielding 3-nitrophenyl α :3-dinitrostyryl ketone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{C}(\text{NO}_2) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 152.5—154°, which is converted by methyl-alcoholic potassium hydroxide and bromine water into $\beta\beta$ -dibromo- β :3-dinitro- α -methoxyethylbenzene. The trinitroketone is converted by methyl and ethyl alcohols into *m*-nitrophenyl β -(α :3-dinitro- β -methoxy)phenylethyl ketone, m. p. 128.5°, and the corresponding ethoxy-derivative, m. p. 120.5—121°, respectively. These ketones are converted by aqueous potassium hydroxide and bromine water into $\beta\beta$ -dibromo- β :3-dinitro- α -alkoxyethylbenzenes.

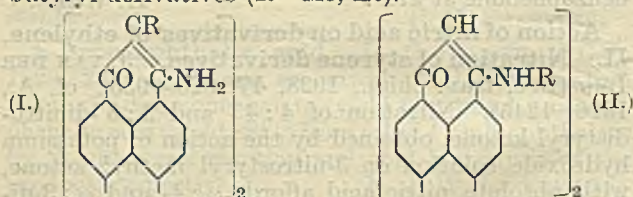
p-Nitrobenzaldehyde condensed with 3-nitroacetophenone in presence of alcohol and a small amount of sodium hydroxide solution yields 3-nitrophenyl 4-nitrostyryl ketone, m. p. 205.5°. Nitration of this gives 3-nitrophenyl α :4-dinitrostyryl ketone, m. p. 135°, converted by methyl alcohol into *m*-nitrophenyl β -(α :4-dinitro- β -methoxy)phenylethyl ketone, m. p. 122.5° (decomp.).

The action of potassium hydroxide solution on methyl β -hydroxy- β -*p*-nitrophenylethyl ketone is to form 4:4'-dinitrodistyryl ketone (cf. Baeyer and Becker, A., 1883, 1120). H. BURTON.

Pungent principles of ginger. V. Distillation of methylzingerol. H. NOMURA and K. IWAMOTO (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 973—984).—Distillation of methylzingerol (*oxime*, m. p. 85.5—86.5°) under ordinary pressure yields hexaldehyde (isolated as its *oxime*, and *semicarbazone*, m. p. 113.5—114°; lit. 106°) in the distillate, whilst the residue consists of methylzingerone and an unsaturated ketone which on reduction yields β :3:4-dimethoxyphenylethyl *n*-heptyl ketone and is therefore methylshogol (cf. A., 1918, i, 446),

$C_6H_3(OMe)_2[CH_2]_2 \cdot CO \cdot CH \cdot CH \cdot [CH_2]_4 \cdot Me$. No trace of *n*-heptaldehyde (semicarbazone, m. p. 111–112°; lit. 109°) was detected. Methylzingerol itself is probably $C_6H_3(OMe)_2[CH_2]_2 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot [CH_2]_4 \cdot Me$ (cf. Lapworth and others, J.C.S., 1917, 111, 779). Methylzingerol distils at 194–200°/0.1–0.4 mm. with very little decomposition into methylzingerone, but at 3 mm. the distillate contains a much larger proportion of the latter. J. W. BAKER.

Perylene and its derivatives. XVIII. A. PONGRATZ (Monatsh., 1928, 50, 87–96).—3:9-Dichloro-4:10-diacylperylene containing aliphatic acyl groups yield, when boiled with cuprous cyanide in quinoline, vat-dyes having the constitutions I or II, of which I is supported by the absence of detectable alkylimino-groups, and II by the non-reactivity of benzaldehyde with the dyes from the propionyl and butyryl derivatives ($R=Me, Et$).



3:9-Dichloro-4:10-dibutyrylperylene, m. p. 258–259°, was prepared by a Friedel-Crafts reaction from 3:9-dichloroperylene and butyryl chloride. The dyes from 3:9-dichloro-4:10-diacetyl-, -dipropionyl-, and -dibutyryl-perylenes were coloured dark violet. They were purified by reduction to the vats (red), and reoxidation. The dye from the diacetyl derivative was also formed in pyridine at 200° under pressure. Oxidation of the dyes by potassium permanganate or chromic acid yielded perylene-3:4:9:10-tetracarboxylic acid. The dye from the diacetyl derivative yielded a tetrabenzoyl derivative, which did not form a vat, and reacted with benzaldehyde to yield a benzylidene derivative, which was reduced to the vat with difficulty. R. K. CALLOW.

Plumbagin. A. MADINAVEITIA and M. GALLEGO (Anal. Fis. Quím., 1928, 26, 263–270).—The therapeutic action of plumbagin (cf. Greshoff, A., 1891, 334), the active principle of *Plumbago europea*, appears to be due to its antiseptic properties. It is best obtained by extraction of the plant with ether, the yield being 3% of the dry rhizomes. The substance thus obtained, recrystallised from alcohol, had the composition $C_{11}H_8O_3$, m. p. 76°. Its properties are typical of a hydroxyquinone, and it yields an acetyl derivative, m. p. 115°, and a monoxime, m. p. 210°. It resembles juglone in forming a copper derivative, $Cu(C_{11}H_7O_3)_2$, and a nickel derivative appears to be formed in solution. Distillation with zinc dust yielded an oily hydrocarbon. Oxidation with hydrogen peroxide gives an acid, probably a hydroxymethylphthalic acid, separated as the monopotassium salt, $C_9H_8O_4K$. Plumbagin is considered to be a methyljuglone (methyl-5-hydroxy- α -naphthaquinone).

R. K. CALLOW.

7-Acylamino- α -naphthaquinones. I. G. FARBENIND. A.-G.—See B., 1928, 846.

Dihydroanthraquinone derivatives. I. G. FARBENIND. A.-G.—See B., 1928, 847.

Condensation products of the benzanthrone series. I. G. FARBENIND. A.-G.—See B., 1928, 847.

New derivatives of anthanthrone. I. G. FARBENIND. A.-G.—See B., 1928, 848.

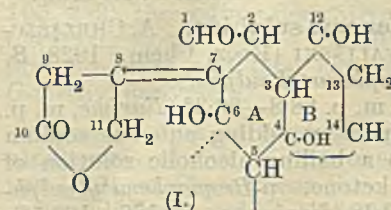
Digitalis glucosides. II. Gitoxigenin and isogitoxigenin. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, 79, 553–562).—*Gitoxigenin*, m. p. 231–232°, has the formula $C_{23}H_{34}O_5$ (cf. Windaus, Chem. Zentr., 1928, ii, 669), and is therefore isomeric with periplogenin (this vol., 1359); with chromic acid, it yielded *gitoxigenone*, $C_{23}H_{32}O_5 \cdot H_2O$, m. p. 206–207°, and, on hydrogenation, *dihydrogitoxigenin*, m. p. 249–250°. Difficulty was experienced with the isomerisation; on treatment of gitoxigenin in pyridine at 0° with methyl-alcoholic potassium hydroxide, there was, however, obtained, in 25% yield, *isogitoxigenin*, m. p. 249–250°, which failed to give the nitroprusside reaction and could not be hydrogenated; with sodium hydroxide this gave *isogitoxigeninic acid*, $C_{23}H_{36}O_6 \cdot 1.5H_2O$, m. p. 152–153°, methyl ester, m. p. 145°; the latter failed to react with semicarbazide, and, with chromic acid, yielded *methyl isogitoxigenonate*, a neutral substance, $C_{24}H_{34}O_6$, m. p. 170–172°. Treatment of *isogitoxigeninic acid* with hypobromite gave an acid, $C_{21}H_{30}O_6$, m. p. 252–253° (methyl ester, m. p. 105° and 180°), possessing no lactone group, so that the oxidation probably involved the original lactone group of gitoxigenin. The difference in the behaviour of *isogitoxigenin* from that of *isostrophanthidin* and of *isodigitoxigenin* may be due to the absence, in the former, of a carbinol group γ - or δ - to the γ -carbon atom of the lactone. C. R. HARRINGTON.

Strophanthin. XV. Hispidus strophanthin. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1928, 79, 531–537).—The aqueous extract of the seeds of *Strophanthus hispidus* when extracted with chloroform yielded a small amount of cymar. The chloroform-insoluble glucoside was hydrolysed by hydrochloric acid to strophanthidin; the action of strophanthobiase from *S. courmonti* gave a trace of dextrose, but no cymar; prolonged treatment with a similar enzyme preparation from *S. hispidus* gave dextrose with a little cymar. *Hispidus strophanthin*, like *Kombe strophanthin*, is therefore a mixture of glucosides, but the structure of the latter is different in the two cases (cf. A., 1926, 982).

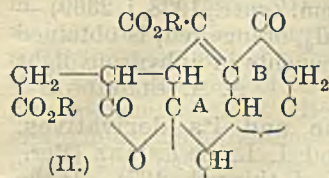
C. R. HARRINGTON.

Strophanthin. XVI. Degradation in the isostrophanthidin series. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, 79, 539–552).—As the result of previous work (A., 1927, 1194) strophanthidin is now partly formulated (I), although in view of the recent work (this

vol., 1120) on digitoxigenin the attachment of the lactone group remains uncertain as between positions 7 and 5. Careful oxidation with permanganate of anhydro- α -isostrophanthonic dimethyl



ester (A., 1927, 1194), for which formula II is preferred,



yields principally *undephanthonic acid dimethyl ester*, $C_{24}H_{32}O_9$, m. p. 179—180°, which, with diazomethane, gave the *trimethyl ester*, m. p. 154.5—155.5°; the latter gave an *oxime*, m. p. 188—189° and 226—227°, and a *phenylhydrazone*, m. p. 196.5—197.5°, which when heated yielded a *phenyl-γ-lactazam*, m. p. 155—157° and 240—242°; it was therefore a β-ketonic ester. Partial hydrolysis gave the *monomethyl ester*, m. p. 237—238°, which could also be obtained by oxidation of anhydro-α-isostrophanthonic monomethyl ester. The trimethyl ester, on boiling with *N*-sodium hydroxide, neutralised 5 equivalents, corresponding with three ester groups, one lactone group, and ring cleavage at the ketonic group; the monomethyl ester, however, with 0.1*N*-sodium hydroxide, underwent ketonic decomposition, with the production of *duodephanthondiacid*, $C_{21}H_{28}O_7$, m. p. 266—268° (from acetone); this was a dibasic lactone acid and gave a *dimethyl ester*, m. p. 166—167°, and a *trimethyl ester oxime*, m. p. 187—189°. The formation of undephanthondiacid is therefore regarded as resulting from cleavage of ring B (formula II), with loss of carbon atom 12, carbon atoms 3 and 13 becoming carbonyl and carboxyl, respectively; duodephanthondiacid would thus be derived by loss of carbon atom 1.

In the oxidation of anhydro-α-isostrophanthonic acid dimethyl ester, there was further obtained a small amount of a *lactonetric acid dimethyl ester*, $C_{25}H_{32}O_{10}$, m. p. 188—190° (*trimethyl ester*, m. p. 236—237°; *free acid*, m. p. 187—189°); the trimethyl ester gave no ketonic reactions, and it could not be acylated, although the Grignard reagent indicated two active hydrogen atoms; it failed to give the Legal reaction; with methyl alcohol it formed a *compound*, $C_{26}H_{34}O_{10} \cdot MeOH$, m. p. 193—195°.

C. R. HARRINGTON.

Constitution of bixin. I. J. RINKES (Rec. trav. chim., 1928, 47, 934).—The compounds isolated from the oxidation of methylbixin (Rinkes and van Hasselt, A., 1917, i, 660) do not support the constitution assigned to bixin by Kuhn and others (this vol., 644, 869).

H. BURTON.

Occurrence of *d*-β-pinene [*d*-nopinene]. B. N. RUTOVSKI and I. V. VINOGRADOVA (J. pr. Chem., 1928, [ii], 120, 41—48).—The fruit of *Ferula Badrakema* (*F. galbaniflua*) yielded on steam-distillation 2.35% of essential oil, $d_{20}^{25} 0.8736$, $\alpha_D +16.16^\circ$, $n_D^{20} 1.4765$, acid value 1.2, ester value 6.65, ester value after acetylation 31.78, and 10.3% of wax and resin on extraction with light petroleum and alcohol. Fractionation of the essential oil showed the presence of 30% of *d*-nopinene, together with *dl*-α- and *d*-α-pinene (40%), *d*-limonene (1.5%), an unidentified alcohol (3%), a ketone (1%), and traces of acids. The *d*-nopinene was separated in a pure state after repeated fractionation, and had b. p. 162—163°, $d_{20}^{25} 0.8662$, $\alpha_D +20.75^\circ$, $n_D^{20} 1.4745$, $[R]_D 44.17$. These properties, with the exception of α_D , correspond with

those found by Halse and Dedichen (A., 1917, i, 398) and by Aschan (A., 1919, i, 336) for *d*-nopinene from other sources. The identification was confirmed by oxidation to *d*-nopinic acid, m. p. 126.5—127°, $[\alpha]_D +17.00^\circ$ in alcohol, and further oxidation to *l*-nopinone, m. p. 0—1°, $[\alpha]_D -18.35^\circ$ in ether (*semicarbazone*, m. p. 187—188°), and comparison with the optically isomeric derivatives from *l*-nopinene.

R. K. CALLOW.

Action of substituted aromatic amines on camphoric anhydride. Bromo- and iodo-camphoranilic acids and camphoro-bromo- and -iodo-phenylimides. M. SINGH, R. S. AHUJA, and K. LAL (J.C.S., 1928, 2410—2414).—When a substituted aniline is condensed with camphoric anhydride a camphoranilic acid and the corresponding imide are formed. The ratio of the acid to the imide decreases when the aniline is substituted by CO_2H , Me, Cl, I in that order, no imide being formed by the aminobenzoic acids. The position of the substituent in the aniline ring also affects the relative yields, the yield of imide decreasing in the order $p < m < o$. The relative effect of the substituents in diminishing the molecular rotatory power of these compounds when dissolved in acetone or in methyl ethyl ketone is in the same order as their effect in diminishing the optical activity of menthyl and *sec*-β-octyl esters of mono-substituted acetic and benzoic acids (cf. Rule, this vol., 221). When methyl or ethyl alcohol is the solvent the order of the substituents is displaced. The following are described: camphoro-*o*-bromophenylimide, m. p. 142°; *m*-bromo-derivative, m. p. 190° (lit. 139—140° and 184—185°, respectively); 2'-bromocamphoranilic acid, m. p. 168°, $[M]_D -61.1^\circ$ in acetone (lit. m. p. 78°, $[M]_D -41.1^\circ$); 3'-bromocamphoranilic acid, m. p. 224° (lit. 215—217°); 4'-bromocamphoranilic acid, m. p. 206—207°; camphoro-*p*-bromophenylimide, m. p. 182.5°; 2'-iodo-camphoranilic acid, m. p. 147—148°, and the corresponding 3'- and 4'-iodo-acids, m. p. 226—227° and 221°, respectively; camphoro-*m*- and -*p*-iodophenylimides, m. p. 172° and 197°, respectively; 2-methoxycamphoranilic acid has $[M]_D -90.75^\circ$ in methyl ethyl ketone. The rotations of these compounds in methyl and ethyl alcohols, acetone, and in methyl ethyl ketone are given.

M. CLARK.

Mono- and sesqui-terpene series. I. West Indian sandalwood oil. II. Nomenclature of the caryophyllene series. E. DEUSSEN (J. pr. Chem., 1928, [ii], 120, 119—144).—I. Previous work by von Soden and Rojahn (A., 1900, i, 401, 677) and the author (A., 1900, ii, 579; 1902, i, 552) indicates that the oil contains a mixture of sesquiterpene hydrocarbons and alcohols. The hydrocarbon fraction consists of at least two isomerides, one being β-caryophyllene (A., 1912, i, 368); the other is now shown to be *d*-cadinene. By repeated fractionation in a vacuum over potassium, two fractions, b. p. 131—133.5°/10.5 mm. and 138—140°/13 mm., of almost pure *d*-cadinene were obtained, which when dehydrogenated with sulphur yielded cadalene, b. p. 159—163°/15 mm., identified as the picrate, m. p. 114.5°, and the styphnate, m. p. 138°; catalytic hydrogenation with platinum-black in 96% alcohol gives tetra-

hydrocadinene, b. p. 135—137°/14 mm., d_{40}^{20} 0.8874, n_D^{20} 1.48157 (cf. Semmler and Jonas, A., 1915, i, 63).

The sesquiterpene alcohol fraction appears to consist of two alcohols, $C_{15}H_{25}\cdot OH$ (termed amyrol by von Soden and Rojahn) and $C_{15}H_{23}\cdot OH$, the former predominating, which can be only imperfectly separated by fractionation owing to the proximity of their b. p. After removal of the latter alcohol by oxidation, the resulting amyrol has been shown to consist of a mixture of two isomeric alcohols, $C_{15}H_{25}\cdot OH$, called α - and β -amyrol. A fraction consisting mainly of amyrol, b. p. 160°/15 mm., d_{40}^{20} 0.972, on dehydrogenation with sulphur, yielded cadalene. Sodium did not react with amyrol in xylene solution, but potassium gave a *potassium* derivative which reacted with methyl iodide, yielding potassium iodide; no other product was isolated. On treatment with phenylcarbimide, 1 mol. of water was eliminated, yielding diphenylcarbamide and a sesquiterpene hydrocarbon, $C_{15}H_{24}$. Attempted benzylation of amyrol using Einhorn's method led to the production of a sesquiterpene hydrocarbon, $C_{15}H_{24}$, b. p. 130—132°/12 mm.; by the Ruzicka-Stoll method a small quantity of an impure *benzoyl* derivative was obtained. Zinc dust at 100—160° under pressure had no effect, but at 220° loss of 1 mol. of water occurred, yielding cadinene. Similarly 85% formic acid with amyrol yields a sesquiterpene hydrocarbon, $C_{15}H_{24}$, b. p. 157—160°/31 mm., d_{40}^{20} 0.9192. By treatment of amyrol with powdered potassium permanganate in aqueous acetone at 0° and fractionation of the product were obtained α -amyrol, b. p. 137—138°/5 mm., d_{40}^{20} 0.9814, n_D^{20} 1.51147, hydrogenated in alcoholic solution in the presence of palladised calcium carbonate to α -dihydroamyrol, b. p. 134—136°/6 mm., d_{40}^{20} 0.9659, n_D^{20} 1.50068, and β -amyrol (contaminated with a little of the α -isomeride), b. p. 149.5—150.5°/10 mm., d_{40}^{20} 0.9463, n_D^{20} 1.50158 (cf. Ruzicka and Huyser, this vol., 425).

II. In reply to Chapman (this vol., 646), the author admits the identity of humulene and α - or inactive caryophyllene, but suggests that the latter name be retained for the hydrocarbon to avoid confusion.

The work of Henderson and his collaborators (A., 1926, 298, 841) in the caryophyllene series is criticised on the ground of nomenclature and the apparent non-acquaintance of these authors with the work of Deussen and Ober (A., 1923, i, 813) and of Asahina and Tsukamoto (A., 1922, i, 845). C. W. SHOPPEE.

Colouring matters of flowers. P. KARRER (Bull. Soc. chim., 1928, [iv], 43, 1041—1058).—A lecture.

Nitro- and dinitro-thiophens. V. S. BABASINIAN (J. Amer. Chem. Soc., 1928, 50, 2748—2753).—Cautious addition of thiophen in acetic anhydride to nitric acid in glacial acetic acid at 10° affords more than 80% of the theoretical yield of 2-nitrothiophen (cf. Steinkopf, A., 1914, i, 426). This with sulphuric and nitric acids readily yields a mixture, m. p. 52° (>80% yield), of isomeric dinitrothiophens, m. p. 54° and 78°, respectively. Contrary to the statement of Meyer and Stadler (A., 1885, 141), these are not interconvertible by distillation in steam, by heating at 140°, or by ultra-violet irradiation.

H. E. F. NOTTON.

Dipyridine iodostannate. A. G. DIMITRIOU (Praktika, 1927, 2, 496; Chem. Zentr., 1928, i, 2369).—The compound $(C_5H_5N)_2SnI_4$, orange-red, is obtained by interaction of the components in anhydrous light petroleum. A. A. ELDRIDGE.

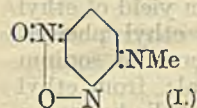
2-Methylaminopyridine and its derivatives. A. E. TSCHITSCHIBABIN and I. L. KNUNIANZ (Ber., 1928, 61, [B], 2215—2217; cf. this vol., 427).—If the methylation of 2-aminopyridine by methyl sulphate is effected under conditions such that considerable proportions of the monomethyl compound are produced, its isolation is readily effected by exhaustive benzylation of the mixture. Unchanged 2-aminopyridine is transformed thereby into the dibenzoyl derivative, which is insoluble in dilute acid, in which dimethylaminopyridine and methylbenzamidopyridine dissolve readily. The last two compounds are separated from one another by distillation under diminished pressure. 2-Methylbenzamidopyridine, b. p. 200°/11 mm., m. p. 61—62°, is hydrolysed by 20% hydrochloric acid to 2-methylaminopyridine, b. p. 90°/9 mm., m. p. 15°. It is readily converted into the corresponding *nitrosoamine*, b. p. 123—124°/30 mm. (*picrate*, m. p. 186—187°), which is not isomerised by warm sulphuric acid, but is reduced by zinc dust and 80% acetic acid to *as-methyl-2-pyridylhydrazine*, b. p. 105°/10 mm. (*benzylidene* compound, m. p. 67—68°). H. WREN.

Nitro-derivatives of the methylated α -aminopyridines. II. A. E. TSCHITSCHIBABIN and A. W. KIRSANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 915—982).—The conclusions of Tschitschibabin and Konvalova (A., 1925, i, 1328) concerning the isomerisation mechanism in the nitro-derivatives of the methylated aminopyridines are found to be incorrect. Methyl iodide and 5-nitro-2-aminopyridine reacted at 120° to give a 90% yield of 5-nitro-2-methylaminopyridine, m. p. 181°. With 3-nitro-2-aminopyridine, 3-nitro-2-methylaminopyridine, m. p. 63—64°, b. p. 262—262.5°/740 mm., was obtained as golden-yellow crystals. By the action of sulphuric acid on methyl-2-pyridonenitroimine considerable quantities of the 5-nitro-2-methylaminopyridine, m. p. 181°, were formed, together with traces of the 3-compound. The nitration of 2-methylaminopyridine gave 2-methyl-nitroaminopyridine, m. p. 30—31°, which isomerised by sulphuric acid to a mixture of 3- and 5-nitro-2-methylaminopyridines, m. p. 181° and 63—64°.

When boiled with concentrated alkali hydroxide solutions the nitroaminopyridines are decomposed, whilst with dilute alkalis good yields of nitrohydroxy-pyridines are obtained. The 3- and 5-nitro-2-methylaminopyridines gave the corresponding 3- and 5-nitro-2-hydroxypyridines, m. p. 190—191° and 221—222°, whilst with nitrous acid the products were 3- and 5-nitro-2-nitrosomethylaminopyridine, both melting at 112—113°. Bromine in potassium bromide solution gave 5-bromo-3-nitro-2-aminopyridine, m. p. 163—164°, with the 3-nitro-compound, and 3-bromo-5-nitro-2-aminopyridine, m. p. 149—150°, with the 5-nitro-compound. The 5-nitro-compound had been nitrated by Tschitschibabin and Konvalova (*loc. cit.*), and the compound obtained, m. p. 59—60°, must now be assigned the structure of 5-nitro-2-methylnitroaminopyridine. The 3-nitro-compound, under the same

conditions, gave 3-nitro-2-methylnitrosoaminopyridine, m. p. 89°. On methylation of 3- and 5-nitro-2-nitroaminopyridine, the corresponding 3- and 5-nitro-2-methylnitrosoamino-compounds are obtained, together with small amounts of the 3- and 5-nitro-*N*-methyl-2-pyridonenitroimines. Both the 3- and 5-nitro-2-methylnitrosoaminopyridines when treated with sulphuric acid gave 3:5-dinitro-2-methylaminopyridine, m. p. 147—148°, whilst the 3-nitro-2-methylpyridine-nitroimine under the same conditions yielded at high temperatures the dinitro-, and at low temperatures the mononitro-derivative. With 3-nitro-2-nitroaminopyridine, dinitroaminopyridine, m. p. 190—191°, was obtained.

The action of methyl iodide at 125° on 5-nitro-2-methylaminopyridine gave a bright yellow solid, m. p. 149.5—150.5°, identical with that obtained by nitrating methylpyridonemethylimine, for which formula I is suggested. The mother-liquor contained small quantities of 5-nitro-2-dimethylaminopyridine. On boiling the solid with water, 5-nitro-*N*-methyl-2-pyridone, m. p. 171—172°, was obtained. M. ZVEGINTZOV.



Reactions of the bromo-substituted derivatives of 2-aminopyridine. A. E. TSCHITSCHIBABIN and A. V. KIRSANOV (J. Russ. Phys. Chem. Soc., 1928, 60, 983—994; cf. preceding abstract).—The behaviour of methylated halogen derivatives of 2-aminopyridines and their nitration products was investigated, to discover whether reactions similar to those of the nitro-derivatives of the α -aminopyridines took place. 3:5-Dibromo-2-aminopyridine, m. p. 105°, gives with methyl iodide 3:5-dibromo-*N*-methyl-2-pyridoneimine, m. p. 99—100°. If the sodium derivative of the 3:5-dibromo-2-aminopyridine is methylated with methyl sulphate, 3:5-dibromo-2-methylaminopyridine, m. p. 56.5—57°, b. p. 137—138°/8 mm., and the corresponding dimethyl compound are obtained. Bromination of 2-methylaminopyridine gives both the dibromo-compound and 5-bromo-2-methylaminopyridine, m. p. 70—71°.

With nitrous acid, the dibromo-compound yields a colourless nitroso-derivative, m. p. 56—57°. 3:5-Dibromo-2-methylnitrosoaminopyridine, m. p. 100—101°, can be obtained by nitrating the dibromo-compound. If 3:5-dibromoaminopyridine is nitrated, some bromine is lost, and together with the 3:5-dibromo-2-nitroaminopyridine, m. p. 123°, some 3-bromo-5-nitro-2-aminopyridine, m. p. 216—217°, is formed. On methylating 3:5-dibromo-2-nitroaminopyridine, 3:5-dibromo-2-methylaminopyridine results, together with 3:5-dibromo-*N*-methyl-2-pyridonenitroimine, m. p. 186—187°, and 3:5-dibromo-*N*-methyl-2-pyridone, m. p. 182°. Of the last two, the former is also obtained by nitrating 3:5-dibromo-*N*-methyl-2-pyridoneimine, whilst the latter is obtained by the action of alkali hydroxides on the nitroimine, or of nitrous acid on the pyridoneimine. Sulphuric acid converts 3:5-dibromo-2-nitroaminopyridone into 3:5-dibromo-2-hydroxypyridine, m. p. 208°, together with dibromoaminopyridine, 3:5-dibromo-2-methylnitrosoaminopyridine, into the same product, together with 3:5-dibromo-2-

methylnitrosoaminopyridine, m. p. 56—57°, and 3:5-dibromo-*N*-methyl-2-pyridonenitroimine into 3:5-dibromo-*N*-methyl-2-pyridoneimine. In the last case, if air is blown through the reaction mixture, some 3:5-dibromo-*N*-methyl-2-pyridone, m. p. 182°, is obtained, i.e., there is no ejection of bromine by the nitro-group, or migration of the methyl radical.

M. ZVEGINTZOV.

Action of thionyl chloride on pyridinemono-carboxylic acids. H. MEYER and R. GRAF (Ber., 1928, 61, [B], 2202—2215; cf. A., 1901, i, 407).—The action of thionyl chloride on pyridinemono-carboxylic acids gives primarily the corresponding acid chlorides of low m. p. More extended or drastic treatment leads to chlorination in the nucleus. If the crude acid chlorides are preserved in a vacuum over potassium hydroxide, a product of high m. p. is obtained, identified as the acid chloride hydrochloride [instead of a polymeric acid chloride as assumed previously (*loc. cit.*)], which ultimately passes into the acid hydrochloride if a trace of moisture is present.

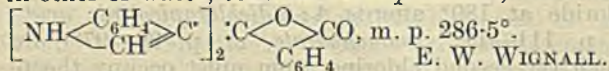
Picolinyl chloride, m. p. 46° (cf. Späth and Spitzer, A., 1926, 958), is converted by hydrogen chloride in benzene into picolinyl chloride hydrochloride, m. p. 118—122° (decomp.), the production of which does not occur in the complete absence of moisture. Nicotinyl acid hydrochloride is more stable than the corresponding picolinyl derivative, but is transformed into nicotinyl chloride, b. p. 85°/12 mm., m. p. 15—16°, by prolonged ebullition with thionyl chloride. It is also prepared from sodium nicotinate and thionyl chloride. Similar methods are employed in the preparation of isonicotinyl chloride, m. p. 15—16°. Protracted treatment of picolinyl chloride with technical or homogeneous thionyl chloride yields 4-chloropicolinyl chloride hydrochloride, converted by water into 4-chloropicolinic acid, m. p. 182° (decomp.). The constitution of the acid is deduced by converting its ammonium salt by ammonia at 180° into 4-aminopicolinic acid, m. p. 260° (decomp.), which yields 4-aminopyridine, m. p. 157—158°, when heated above its m. p. 4-Aminopicolinic acid hydrochloride, $C_6H_6O_2N_2 \cdot HCl$, m. p. 240° (decomp.), and methyl 4-aminopicolinate, m. p. 129°, are described. 4-Aminopicolinic acid is converted in the usual manner into 4-hydroxypicolinic acid, m. p. 254—255° (decomp.), converted above its m. p. into 4-hydroxypyridine, m. p. 65—66°. 4-Chloropicolinyl chloride, m. p. 46°, methyl 4-chloropicolinate, m. p. 57—58°, phenyl 4-chloropicolinate, m. p. 68°, and 4-chloropicolinamide, m. p. 158°, are described. 4-Chloropicolinic acid is converted by boiling hydriodic acid and red phosphorus through the basic iodohydrate of 4-iodopicolinic acid, m. p. 185—190° (decomp.), into 4-iodopicolinic acid, m. p. 169° (decomp.) (methyl ester, m. p. 75—76°), in which the iodine atom is replaced by chlorine under the influence of thionyl chloride. Protracted treatment of 4-chloropicolinic acid with thionyl chloride at 180° affords 4:6-dichloropicolinic acid, m. p. 111—112° (monohydrate, m. p. 96—97°), in which the second chlorine atom must occupy the 6 position since the acid is converted by boiling hydriodic acid (*d* 1.7) and red phosphorus into the basic iodohydrate of 4-iodopicolinic acid (see above).

Methyl 4:6-dichloropicolinate, m. p. 73—74°, *phenyl 4:6-dichloropicolinate*, m. p. 90—91°, and *4:6-dichloropicolinamide*, m. p. 172—174°, are described. *3(5):4:6-Trichloropicolinic acid (methyl ester)*, m. p. 122—123° is obtained as by-product of the preparation of dichloropicolinic acid.

5-Chloronicotinic acid, m. p. 171°, is obtained in modest yield from nicotinic acid hydrochloride and thionyl chloride at 130°. *5-Chloronicotinyl chloride*, b. p. 120°/12 mm., m. p. 53°, *methyl 5-chloronicotinate*, m. p. 88—89°, *phenyl 5-chloronicotinate*, m. p. 79°, and *5-chloronicotinamide*, m. p. 205—206°, have been prepared. *5-Chloronicotinic acid* is transformed by ammonia in presence of copper oxide at 180° into *5-aminonicotinic acid (copper salt)*, the *methyl ester*, m. p. 137°, of which is converted by diazotisation in concentrated hydrochloric acid into *methyl 5-chloronicotinate*. The acid passes above its m. p. into *3-aminopyridine*. *5:6-Dichloronicotinic acid*, m. p. 161—162° (monohydrate), is obtained from nicotinic acid hydrochloride and thionyl chloride at 150°. The corresponding *chloride* has m. p. 48—49°. *Methyl 5:6-dichloronicotinate*, m. p. 67—68°, *phenyl 5:6-dichloronicotinate*, m. p. 133°, and *5:6-dichloronicotinamide*, m. p. 218—220°, are described. Cautious heating of *5:6-dichloronicotinic acid* under diminished pressure at 150° affords *2:3-dichloropyridine*, m. p. 46—47°; less cautious treatment leads to loss of hydrogen chloride and production of *5-chloro-6-hydroxynicotinic acid*, m. p. 305° (incipient decomp.), more conveniently prepared by boiling *5:6-dichloronicotinic acid* with excess of potassium hydroxide.

isoNicotinic acid is converted by treatment with thionyl chloride at 180—220° into a mixture of *3-chloroisonicotinic acid*, m. p. (indef.) 235° (*methyl ester*, m. p. 32°; *3-hydroxyisonicotinic acid*, m. p. 312°), and *3:5-dichloroisonicotinic acid*, m. p. 217°. The last-named acid passes at 230° in a sealed tube into *3:5-dichloropyridine*, m. p. 64—65°, also prepared by transforming *5-chloronicotinic acid* into its *hydrazide*, m. p. 178°, and thence into the urethane and *5-chloro-3-aminopyridine*, from which the dichloro-compound is derived in the usual manner. *Methyl isocinchomeronate* is transformed into *2:5-diaminopyridine* and thence by diazotisation in presence of cuprous chloride into *2:5-dichloropyridine*, m. p. 60°. H. WREN.

Syntheses by means of magnesylpyrroles. Series II. XII. Indolephthalein. B. ONDO (Gazzetta, 1928, 58, 569—573).—The action of phthalyl chloride on magnesium 2-methylindyl bromide yields a phthalein (cf. A., 1925, i, 588; 1926, 1157); its action on magnesium indyl bromide is now found to give two products. One, soluble in water, is regarded as ω -[indolidene-indolyl]-*o*-toluic acid, m. p. 145°, of which some metallic salts and a monohydrochloride are described. The other, insoluble in ether or water, contains *indolephthalein*,



E. W. WIGNALL.

Manufacture of chloroiodo-compounds of the quinoline series. CHEM. FABR. AUF ACTIEN.—See B., 1928, 874.

Production of quinoline-4-carboxylic acids. A. HÄUSSLER ETC.—See B., 1928, 837.

Condensation of rhodanic acids with 5-nitroisatin. 5'-Nitro-3-rhodanylidene- $\Delta^{5:3}$ -oxindoles. H. A. JONES and R. M. HANN (J. Amer. Chem. Soc., 1928, 50, 2491—2493; cf. A., 1925, i, 987).—The following red *5'-nitro-3-aryl-rhodanylidene- $\Delta^{5:3}$ -oxindoles* have been prepared by condensing 5-nitroisatin with arylrhodanic acids in boiling glacial acetic acid in presence of sodium acetate: *-phenyl-*, m. p. 260—267°; *-o-anisyl-*, m. p. 247°; *-p-anisyl-*, m. p. 370°; *- ψ -cumyl-*, m. p. 245°, and *- β -naphthyl-*, m. p. 330°. H. E. F. NOTTON.

Preparation of ethyl phenylmalonate and of 5-phenyl-5- β -hydroxyethylbarbituric acid. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1928, 50, 2758—2762).—The maximum yield of ethyl phenylmalonate (I), d_4^{20} 1.095, from ethyl phenylacetate and ethyl carbonate in presence of sodium or sodamide is 20% of the theoretical; from ethyl phenylcyanoacetate and saturated alcoholic hydrogen chloride it is 78%. The latter is best obtained (70% yield) from phenylacetonitrile and ethyl carbonate in presence of sodamide in ether. Attempts to condense α -substituted phenylacetonitriles [e.g., *phenylvinyl-ethoxyethylacetonitrile*, b. p. 147°/8 mm., d_4^{20} 1.029, prepared from phenylacetonitrile and β -chloroethyl vinyl ether by the method of Bodroux and Taboury (A., 1910, i, 557)] with ethyl carbonate were unsuccessful. The ester (I) was converted into ethyl phenyl-ethylmalonate (61% yield), and this into 5-phenyl-5-ethylbarbituric acid (35% yield). Ethyl sodiophenylmalonate and β -chloroethyl vinyl ether in absence of solvent at 140—145° yield *ethyl phenylvinyl-ethoxyethylmalonate*, b. p. 196—197°/17 mm., d_4^{20} 1.098, which when condensed with carbamide and hydrolysed (cf. A., 1926, 180) yields *5-phenyl-5- β -hydroxyethylbarbituric acid* ("hydroxyluminal"), m. p. 200°. *2-Thio-5-phenyl-5- β -hydroxyethylbarbituric acid* has m. p. 167°. H. E. F. NOTTON.

Oxidation reactions of aldehydes. J. B. CONANT and J. G. ASTON.—See this vol., 1357.

Effect of substituents on the colour and absorption spectrum of indigotin, thioindigotin, and indirubin. J. FORMANEK (Z. angew. Chem., 1928, 41, 1133—1141).—By introducing chlorine or bromine into the benzene nucleus in indigotin the colour is changed from violet-blue to greenish-blue, the absorption spectrum showing a movement of the bands towards the red. Introduction of bromine causes displacement of the absorption bands proportionately more than introduction of chlorine; the position of the bands is dependent on the position of the halogen atom. If an alkyl group is introduced into one of the benzene nuclei, there is a negligible change in colour and absorption spectrum; if, however, it is substituted in the imino-group, the colour changes from violet-blue to green, and there is a marked displacement of the absorption bands. The indigotin derivatives dissolve in sulphuric acid with a green or bluish-green colour, and the solution gives no absorption bands. An essentially different effect on the colour and absorption spectrum of indigotin

is obtained by substituting halogen in the 6:6'-position. The colour changes to red and the absorption spectrum appears to be split up into bands. The same effect is obtained by introducing the amino-group into the 6:6'-position. By introducing halogen or alkyl groups into the benzene nucleus of thioindigotin, the absorption bands are moved in the same direction as for indigotin. Halogen, alkyl, and amino-groups substituted in the 6:6'-position give a change in colour from red to orange-yellow. The derivatives of thioindigotin dissolve in sulphuric acid with a green colour, the solutions giving either no absorption bands or only very weak ones. Similar derivatives are obtained with indirubin.

A. J. MEE.

Opening of the glyoxaline ring. II. B. ODDO and Q. MINGOIA (Gazzetta, 1928, 58, 573—584; cf. A., 1927, 260).—Benzoylglyoxaline (*loc. cit.*) forms a *di*bromo-derivative, m. p. 255°. E. W. WIGNALL.

Glyoxaline compounds. B. ODDO and Q. MINGOIA (Gazzetta, 1928, 58, 584—597).—The effect of reagents on magnesium glyoxalyl bromide is as follows. Water yields glyoxaline; methyl iodide, 1:2-dimethylglyoxaline (*picrate*, m. p. 179°); ethyl iodide, 1:2-diethylglyoxaline, m. p. 218—220°. Carbon dioxide, acetyl chloride, acetic anhydride, and ethyl acetate give negative results. Ethyl chloroformate furnishes *ethyl glyoxalinecarboxylate*, b. p. 135—138°/60 mm. (*picrate*, m. p. 182°); carbonyl chloride, *diglyoxalyl ketone (picrate)*, m. p. 204°. Ethoxalyl chloride and carbethoxyacetyl chloride cause opening of the ring, furnishing respectively *diethylglyoxalaldiaminoethylene*, b. p. 115—117°/52 mm., and *di(carbethoxyacetyl)diaminoethylene*, b. p. 270°/101 mm., together with formic acid in each case.

E. W. WIGNALL.

Conversion of oximes of *o*-diketones into pyrazines. O. WALLACH (Nachr. Ges. Wiss. Göttingen, 1927, 238—244; Chem. Zentr., 1928, i, 2177—2178).—The dioximes of *o*-diketones, on reduction, pass by way of the monoxime to the *o*-aminoketone, which by enolisation and condensation of two molecules affords a dihydropyrazine, readily oxidised in air to the pyrazine. Diacetyl-di- or -mon-oxime affords tetramethylpyrazine, $\begin{smallmatrix} \text{CMe}\cdot\text{N}\cdot\text{CMe} \\ | \\ \text{CMe}\cdot\text{N}\cdot\text{CMe} \end{smallmatrix}$, m. p. 75—78°, after drying over calcium chloride, m. p. 86—87°, b. p. 189—190° (*picrate*, m. p. 192—195°; chloroplatinate; mercuric chloride and cyanide compounds). Reduction of *cyclohexane-1:2-dione* dioxime affords dihydropyrazine, oxidised to pyrazine, m. p. 108° (hydrochloride; chloroplatinate; *picrate*; mercuric chloride compound).

A. A. ELDRIDGE.

Formation of 2-substituted benziminazoles. M. A. PHILLIPS (J.C.S., 1928, 2393—2399).—The reaction between boiling hydrochloric acid and mono- or di-acetyl-*o*-diamines or between acetic anhydride, hydrochloric acid, and *o*-phenylenediamine, whereby 2-methylbenziminazole is formed (this vol., 305), has been extended to the formation of 2-ethyl-, 2-hydroxy-methyl-, 2- α -hydroxyethyl-, and 2- α -hydroxybenzylbenziminazoles by substitution of the appropriate organic acid for acetic anhydride. Benziminazole is produced by reduction of *o*-nitroformanilide or by

the action of boiling hydrochloric acid on *o*-phenylenediamine monoformate, whilst 3-amino-4-formamidophenylacetonitrile, 3-amino-4-acetamidophenylacetonitrile, 3-amino-4-lactamidophenetole, and 3:4-di-formamidophenylacetonitrile, m. p. 92—95°, also pass smoothly into the corresponding benziminazole on boiling with hydrochloric acid. Since traces of 4-nitro-*o*-phenylenediamine, which increase with diminution in the length of heating with hydrochloric acid, accompany 5-nitro-2-methylbenziminazole in the formation of the latter compound from 4-nitrodiacetyl-*o*-phenylenediamine, it is now considered that the diacetyl-*o*-diamines are completely hydrolysed to the diamines with subsequent formation of the iminazole ring (cf. *loc. cit.*). Oxalic acid and *o*-phenylenediamine condense in the presence of boiling hydrochloric acid to give 2:3-dihydroxyquinoxaline, m. p. above 350° (*sodium salt*). With malonic acid, the same reagents yield *o*-phenylenemalonamide (*mono-sodium salt*) and 2-aminomalonanilic acid, m. p. 175—176°. Succinic acid and *o*-phenylenediamine (I) in equimolecular proportions with hydrochloric acid yield 2:2'-diaminosuccinanilide (II) and benziminazole-2-propionic acid (III). When 2 mols. of the base are used, II and $\alpha\beta$ -dibenziminazolyethane (IV) are formed. IV is also produced when a mixture of I and III or II alone is boiled with hydrochloric acid. Diacetylenediamine yields 2-methyl-4:5-dihydroglyoxaline when it is boiled with hydrochloric acid.

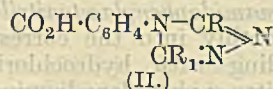
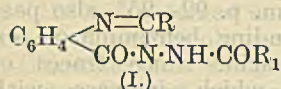
M. CLARK.

Relationship between ring closure and "specific affinity." Complex compounds of bivalent silver. W. HIEBER and F. MÜHLBAUER (Ber., 1928, 61, [B], 2149—2153; cf. this vol., 510, 511).—Addition of 2 mols. of *o*-phenanthroline (prepared from *o*-phenylenediamine, glycerol, arsenic and sulphuric acids) dissolved in water to a solution of silver nitrate gives a colourless, gelatinous precipitate which is quantitatively transformed by ammonium persulphate into the chocolate-brown, stable *di-o-phenanthroline silver persulphate*, $[\text{Ag}(\text{C}_{12}\text{H}_8\text{N}_2)]_2\text{S}_2\text{O}_8$. The salt is readily soluble without decomposition in 64% nitric acid, and addition of the requisite sodium salt to this solution leads to the formation of the corresponding *perchlorate*, $\text{Ag}(\text{ClO}_4)_2 \cdot 2\text{C}_{12}\text{H}_8\text{N}_2$, *chlorate*, and *hydrogen sulphate*; with sodium phosphate, ammonium fluoride, and sodium dichromate mixed salts appear to be formed. The bivalency of silver in the salts is established by determination of the carbon dioxide evolved when the perchlorate reacts with oxalic acid in presence of sulphuric acid and of iodine liberated when it is mixed with potassium iodide. Similar examination of the persulphate appears to indicate the presence of the hydrogen sulphate. Further confirmation of the bivalency of silver is found in the existence of isomorphism between its salts and analogous cupric and cadmium compounds with which mixed crystals are produced.

H. WREN.

Transformation of quinazolones into triazole derivatives. G. HELLER [with W. KÖHLER, S. GOTTFRIED, H. ARNOLD, and H. HERRMANN] (J. pr. Chem., 1928, [ii], 120, 49—63).—Quinazolones of type I, obtained from diacyl-*o*-aminobenzhydrazides

(A., 1925, i, 1322), are transformed by dilute alkali into triazolecarboxylic acids of type II. The latter are extremely stable, being unaffected by hydrochloric acid at 200° and by chromic and acetic acids



at 100°; they are also directly obtained under the same conditions, but less smoothly, from the diacyl-o-aminobenzhydrazides. 3-Benzamido-2-phenyl-4-quinazolone (*loc. cit.*) thus yields 2:5-diphenyl-1-o-carboxyphenyl-1:3:4-triazole, m. p. 310°, also obtained from dibenzoyl-o-aminobenzhydrazide (*loc. cit.*) Similarly, 3-acetamido-2-phenyl-4-quinazolone (*loc. cit.*) or 3-diacetamido-2-phenyl-4-quinazolone, m. p. 153°, prepared from 3-amino-2-phenyl-4-quinazolone by treatment with excess of acetic anhydride, yields 2-phenyl-1-o-carboxyphenyl-5-methyl-1:3:4-triazole, m. p. 241° (*hydrated form*, m. p. 140—145°; *anilide*, m. p. 253°; *methyl ester*, m. p. 156°; *ethyl ester*, m. p. 165°), nitrated in sulphuric acid to give a *dinitro-compound*, m. p. 273°, together with a yellow substance, and oxidised by potassium permanganate in concentrated nitric acid at 40° to an acid, $\text{C}_{10}\text{H}_9\text{O}_9\text{N}_3$, m. p. 259° (see below). o-Benzamido-benz-p-chlorobenzoylhydrazide, m. p. 175°, prepared from o-benzamidobenzhydrazide and p-chlorobenzoyl chloride in pyridine solution, is converted by dilute alkali into 2-phenyl-5-p-chlorophenyl-1-o-carboxyphenyl-1:3:4-triazole, m. p. 204°. Treatment of o-aminobenzhydrazide with p-chlorobenzoyl chloride in ethyl acetate solution yields o-4-chlorobenzamidobenzhydrazide, m. p. 225°, together with o-4-chlorobenzamidobenz-p-chlorobenzoylhydrazide, m. p. 227°; the former when benzoylated in pyridine solution yields o-4-chlorobenzamidobenzbenzoylhydrazide, m. p. 213°, converted by dilute alkali into 5-phenyl-2-p-chlorophenyl-1-o-carboxyphenyl-1:3:4-triazole, m. p. 212°, and the last with dilute alkali yields 2:5-di-p-chlorophenyl-1-o-carboxyphenyl-1:3:4-triazole, m. p. 345°.

To distinguish between the three formulæ proposed for the acid $\text{C}_{10}\text{H}_9\text{O}_9\text{N}_3$, m. p. 259°, attempts have been made to synthesise triazolecarboxylic acids, but without success. NN-Diacetylbenzhydrazide, m. p. 152°, is obtained in 90% yield by the action of boiling acetic anhydride on benzhydrazide (cf. A., 1895, i, 34); the corresponding monoacetyl compound heated with aniline and aniline hydrochloride at 100° yields benzoylbenzhydrazide (cf. A., 1912, i, 225) and at 140° benzanilide is also formed, but triazole formation does not occur; similarly with p-toluidine and its hydrochloride benzoylbenzhydrazide and benz-p-toluidide are obtained. Negative results were obtained by heating acetylbenzhydrazide with boiling aniline, but in the presence of phosphorus pentoxide triazole formation takes place to the extent of 10%; from acetylbenzhydrazide and aniline, o-toluidine, and p-toluidine, respectively, are produced 1:5-diphenyl-2-methyl-1:3:4-triazole, m. p. 161° (*picrate*, m. p. 182°), 5-phenyl-1-o-tolyl-2-methyl-1:3:4-triazole, m. p. 177.5° (*picrate*, m. p. 186°; *hydrochloride*, m. p. 210°), and 5-phenyl-1-p-tolyl-2-methyl-1:3:4-triazole, m. p. 162.5° (*picrate*, m. p.

160—162°; *hydrochloride*, m. p. 205—210°). Similarly, formylacethydrazide, m. p. 96°, obtained in 70% yield by treating formylhydrazide (cf. Schöfer and Schwan, A., 1895, i, 263) with acetic anhydride at 0°, is converted by aniline and phosphorus pentoxide at 190—200° into a triazole, which is, however, 1-phenyl-2:5-dimethyl-1:3:4-triazole, m. p. 236° (cf. Pellizzari, A., 1901, i, 488), and not the expected 1-phenyl-2-methyl-1:3:4-triazole; if in the preparation of formylacethydrazide cooling is not efficient, diformylhydrazide, m. p. 158°, is produced. By heating benzhydrazide and acetamide at 230—260°, 2-phenyl-5-methyl-1:3:4-triazole, m. p. 164.5° (*picrate*, m. p. 158°; *hydrochloride*, m. p. 230°), is obtained in poor yield, together with some benzoylbenzhydrazide. Similarly, acethydrazide and formanilide heated together at 150—230° yield 1-phenyl-1:3:4-triazole, m. p. 122° (*picrate*, m. p. 172°), and not the expected 1-phenyl-2-methyl-1:3:4-triazole prepared by Pellizzari (*loc. cit.*). The author concludes that the conditions necessary to produce triazole derivatives by the above methods render direct condensation of hydrazides with carboxylic acids to triazolecarboxylic acids impossible. Attempts to use compounds containing an amino-group, which could be converted into a carboxyl group after triazole formation, failed; thus with o-aminobenzhydrazide and acetamide at 200°, the latter acted as an acetylating agent, yielding 3-amino-2-methyl-4-quinazolone. An attempt to prepare dichlorohydrazides also failed, a tetrachloro-compound, probably di(chloroacetyl)benzhydrazide dihydrochloride, m. p. 143°, being produced.

C. W. SHOPPEE.

Condensation of pyrrole with aliphatic ketones. T. SABALITSCHKA and H. HAASE (*Arch. Pharm.*, 1928, 266, 484—492).—A well-defined compound is obtained by the condensation of 4 mols. of pyrrole with 4 mols. of acetone in presence of acids. This reaction is quite general and has been applied to other aliphatic ketones. It takes place less readily and with diminished yield, however, as the series is ascended. Compounds derived from the following ketones are described: acetone (m. p. 296° decomp.), methyl ethyl ketone (m. p. 149°), diethyl ketone (m. p. 208°), methyl propyl ketone (m. p. 226°), ethyl propyl ketone (m. p. 219°), methyl butyl ketone (m. p. 193—194°), ethyl isobutyl ketone (m. p. 199°), ethyl butyl ketone (m. p. 205—206°), methyl hexyl ketone (m. p. 178°). The compound from methyl ethyl ketone affords maleimide on oxidation with chromic acid, whilst the acetone compound furnishes α -isopropylpyrrole, b. p. 175°, when distilled with zinc dust. The compounds give a blood-red coloration when treated with warm nitric acid or ferric chloride solution and a deep bluish-red coloration with glacial acetic acid. The structure of these compounds and their possible connexion with the porphyrins are discussed. S. COFFEY.

Chlorophyll. I. Ætioporphyrins from plant- and blood-pigment porphyrins. H. FISCHER and A. TREIBS (*Annalen*, 1928, 466, 188—242).—Comparisons are made, mainly by spectrum analysis, of the ætioporphyrins obtained from various plant- and blood-pigment porphyrins by thermal decom-

position at 300–350° in a high vacuum. Thus, mesoporphyrin gives *mesoætioporphyrin*, $C_{32}H_{38}N_4$, m. p. 369° (Pregl block), which does not appear to be identical with any of the known ætioporphyrins (crystallisation tests, A., 1926, 1256). Mesophyllin affords ætiophyllin, from which after removal of magnesium with hydrochloric acid meso- and ætioporphyrins are obtained. Rhodoporphyrin, most probably $C_{32}H_{34}O_4N_4$ (ester, m. p. 269°), yields *rhodoætioporphyrin* (I), $C_{30}H_{34}N_4$ (or $C_{31}H_{36}N_4$), m. p. 294° (corr.), together with the probably intermediate pyrroporphyrin (II) [ester, m. p. 243° (corr.)]. When *rhodohæmin*, $C_{32}H_{32}O_4N_4ClFe$, and rhodoporphyrin are decarboxylated by heating with 5 parts of resorcinol at 200° (cf. Schumm, this vol., 1148), II is produced. Bromination of I in chloroform-acetic acid solution gives a perbromide, which on treatment with acetone passes into *bromorhodoætioporphyrin* (III), $C_{30}H_{33}N_4Br$ (?), m. p. 340° (Pregl block). When mesoætioporphyrin and ætioporphyrin I are brominated similarly, the resulting products contain only a small amount of bromine. Treatment of III with zinc dust and acetic acid does not effect elimination of bromine, but affords a zinc complex easily decomposed by acid. Oxidation with chromic anhydride and sulphuric acid gives methylethylmaleinimide and bromocitraconimide (?), whilst reduction with hydrazine in presence of a palladium-calcium carbonate catalyst regenerates I. Deuteroporphyrin and bromoporphyrin I (dibromodeuteroporphyrin) yield *deuteroætioporphyrin*, $C_{28}H_{30}N_4$, m. p. 285° [corr.; m. p. 335° (block), from deuterohæmin], identical spectroscopically with deuterio-, pyrro-, and rhodo-ætioporphyrins, and brominated to a *dibromo-derivative*, m. p. 371° (block). 1:4:6:7-Tetramethyl-2:3:8-triethyl-5-β-carboxyethylporphin affords an *ætioporphyrin*, $C_{32}H_{38}N_4$, m. p. 344° (block), identical with ætioporphyrin IV. Decarboxylation of II gives pyrroætioporphyrin (IV), m. p. 278° (corr.), identical with I. Phylloporphyrin affords, in addition to *phylloætioporphyrin* (V), $C_{30}H_{34}N_4$, m. p. 267° [corr.; iron complex; *monobromo-derivative*, m. p. 274° (block)], the three new colouring matters, *phyllorhodin*, $C_{31}H_{32}ON_4$, red, *phyllochlorin*, green, and *phylloverdin*, $C_{31}H_{32}ON_4$, green, probably formed by elimination of water. When V is heated with methyl-alcoholic potassium hydroxide, isomerisation into IV occurs. Synthetic isopyrroporphyrin (1:4:5:8-tetramethyl-3:6-diethyl-7-β-carboxyethylporphin) gives *isopyrroætioporphyrin* (bromo-derivative), identical with IV. *isoUroætio-*, m. p. 356°, and *uroætio-porphyrins*, m. p. 393–394° (cf. A., 1925, i, 307), are described. The ætioporphyrin, m. p. 341° (block), from hæmoporphyrin is identical (spectrum) with ætioporphyrin I.

When bromoporphyrin I is reduced with hydriodic acid and acetic acids and subsequently oxidised with lead dioxide and sulphuric acid, citraconimide and hæmopyrrolecarboxylic acid are obtained. Similar treatment of II furnishes methylethylmaleimide and the above acid. Oxidation of bromopyrroporphyrin (Treibs and Wiedemann, this vol., 1384) with chromic oxide and sulphuric acid affords, in addition to the maleimide, bromocitraconimide, showing that II, a porphinmonocarboxylic acid, contains a free methene

group in which bromination takes place without loss of carbon. Magnesium methyl iodide converts II or its ester into a *porphyrin alcohol*, $C_{33}H_{40}ON_4$, m. p. 260°. Similarly, mesoporphyrin dimethyl ester yields a *carbinol*, $C_{37}H_{46}O_3N_4$ or $C_{38}H_{50}O_2N_4$, m. p. 295° (corr.) from methyl alcohol, 308° from acetic acid.

The *xanthoporphinogen* (cf. A., 1927, 1206) from mesoætioporphyrin crystallises with 1 mol. of benzene easily replaced by 1 mol. of water. *Ætio-xanthoporphinogen* I (*mono-* and *di-potassium* and *disodium* salts) crystallises with 3COMe₂. *Mesoxanthoporphinogen* (ethyl ester) is intensely yellow and very hygroscopic.

Nitration of ætioporphyrin I with cold nitric acid (*d* 1.48) gives a *trinitro-derivative*, m. p. 305° [Pregl block; *nitrate*; *hydrochloride*; *copper*, m. p. 313° (block), and *iron* salts]. *Trinitroætioporphyrin* II [*hydrochloride*; *copper* salt, m. p. 285° (block)] has m. p. 246° (block) and is spectroscopically identical with its isomeride.

Crystallographic data [by STEINMETZ] for several ætioporphyrins and the absorption spectra of a large number of the above compounds and those of the *copper* salts and *hæmochromogen* derivatives of meso-, rhodo-, deuterio-, and phyllo-ætioporphyrins are given.

H. BURTON.

Chlorophyll. II. Rhodins and verdins. H. FISCHER, A. TREIBS, and H. HELBERGER (Annalen, 1928, 466, 243–264).—In an attempt to introduce an acetyl group into the porphin molecule pyrroporphyrin was treated with an excess of acetyl chloride in presence of carbon disulphide and aluminium chloride. The product isolated was *pyrrorhodin*, $C_{31}H_{32}ON_4$, m. p. 280° (block), probably identical with phyllorhodin (cf. following abstract). Similar treatment of mesoporphyrin gives *mesorhodin* (I), $C_{31}H_{36}O_3N_4$, m. p. 297° [block; *methyl ester*, m. p. 268° (corr.), from the *potassium* salt and methyl sulphate; *copper* salt; *iron* complex, $C_{34}H_{34}O_3N_4ClFe$; *magnesium* complex (*phyllin*), by the action of magnesium methyl iodide], together with *mesoverdin*, $C_{34}H_{36}O_3N_4$, m. p. 298° (*hydrochloride*; *copper* salt). Fuming sulphuric acid converts mesoporphyrin into I. The action of concentrated methyl-alcoholic potassium hydroxide on I in pyridine solution yields a mesoverdin, m. p. 308° (block).

Fuming sulphuric acid at 50° converts 1:4:6:7-tetramethyl-2:3:8-triethyl-5-β-carboxyethylporphin into a *rhodin*, $C_{33}H_{36}ON_4$ (*copper*, *magnesium*, and *iron* complexes), which on oxidation with chromic oxide and sulphuric acid yields methylethylmaleimide. The absorption spectra of the majority of the above compounds are tabulated.

The production of these rhodins from porphin-carboxylic acids is due to elimination of water between the β-carboxyethyl group and either the imino- or methene hydrogen in the porphin ring. Thus, mono-acidic porphins yield chemically indifferent rhodins (i.e., pyrro-), whilst diacidic porphins give acidic rhodins (meso-).

H. BURTON.

Chlorophyll. III. A. TREIBS and E. WIEDEMANN (Annalen, 1928, 466, 264–291).—Alkaline fission of phæophytin gives a mixture of phytochlorin e (I), $C_{35}H_{38}$ or $40O_7N_4$, and phytorhodin g (II),

$C_{35}H_{36}$ (or 38) O_8N_4 (cf. Willstätter and Stoll, A., 1911, i, 659). Degradation of a mixture of I and II with methyl-alcoholic potassium hydroxide at 155° in presence of pyridine gives a mixture of pyrro- and phyllo-porphyrins; at 145 – 150° only phyllo-; at 220° only pyrro-. Similarly, I at 155° affords pyrro- (10%) and phyllo- (40%), whilst II at 165° yields a small amount of pyrro-porphyrin (cf. Willstätter, *loc. cit.*).

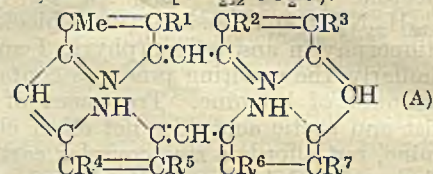
Pyrroporphyrin (III) [methyl ester, m. p. 241° (corr.; iron salt); copper and magnesium salts], when treated with bromine in acetic acid solution, furnishes a perbromide, which on treatment with acetone passes into bromopyrroporphyrin [methyl ester, m. p. 261° (corr.)]. Willstätter's phylloporphyrin contains pyrroporphyrin. Pure phylloporphyrin (IV), $C_{31}H_{34}O_8N_4$ [methyl ester, m. p. 235° (corr.; iron salt); copper salt], is brominated to bromophylloporphyrin (V) (methyl ester), which on oxidation with chromic oxide and sulphuric acid yields methylethylmaleimide, bromocitraconimide, and hæmatic anhydride. When IV or V is heated with methyl-alcoholic potassium hydroxide at 190 – 200° in a sealed tube, III is obtained. Absorption spectra of most of the above compounds are tabulated. Phyllo- and pyrro-rhodins (cf. preceding abstract) are shown to be identical.

H. BURTON.

Porphyrin syntheses. XVIII. Syntheses of coproporphyrins I and II, and mesoporphyrins II, V, and XII. H. FISCHER, H. FRIEDRICH, W. LAMATSCH, and K. MORGENROTH (Annalen, 1928, 466, 147–178).—When the brominated methene from cryptopyrrolecarboxylic acid (I) (Fischer and Andersag, A., 1926, 1261) is heated with succinic acid at 180 – 190° , hydrogen bromide is eliminated, and esterification of the resulting product with methyl alcohol gives coproporphyrin tetramethyl ester (II), m. p. 252° [corr.; manganese complex, m. p. 267° (corr.); zinc compound, m. p. 299° (corr.); tetrahydrazide not melted at 320°]. Methyl-alcoholic hydrogen bromide converts I into the compound $C_{20}H_{26}O_4N_2Br$, which when treated with succinic or tartaric acids at 180 – 200° gives 3 or 6% of coproporphyrin. Treatment of coproporphyrin iron salt, m. p. 240° (corr.; *loc. cit.*), with hot 10% sodium hydroxide solution and subsequent treatment of the product obtained after acidification with a mixture of pyridine and acetic acid gives coproporphyrin iron salt acetate. Similar treatment of coprohæmin tetramethyl ester in presence of hydrochloric acid affords coprohæmin, which when crystallised from acetic anhydride loses a part of its halogen. Oxidation of II with lead dioxide in chloroform-acetic acid solution yields coproxanthoporphinogen tetramethyl ester, m. p. 315° (uncorr.; decomp.; free acid), reduced by sodium amalgam and acetic acid to II. When (4-methyl-3-ethyl-5-carbethoxypyrryl)-(2:4-dimethyl-3- β -carboxyethylpyrrolenyl)methene is heated progressively with sodium methoxide solution at 130 – 210° a mixture of ammonia-soluble (probably ætio-) and -insoluble, m. p. 204° (corr.), porphyrins is obtained.

When heated with formic and hydrobromic acids ethyl 2:4-dimethyl-3- β -carboxyethylpyrrole-5-carboxylate and cryptopyrrolecarboxylic acid are con-

verted into (3:5-dimethyl-4- β -carboxyethylpyrryl)-(3:5-dimethyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. 214 – 215° (hydrochloride; picrate, m. p. 214°). When this is heated with (3-methyl-5-bromomethyl-4- β -carboxyethylpyrryl)-(3-methyl-5-bromomethyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, obtained by bromination of bis-(2:4-dimethyl-3- β -carboxyethylpyrryl)methene hydrobromide, in presence of succinic acid at 140 – 150° , mesoporphyrin XII [methyl ester, m. p. 190 – 191° (copper compound, m. p. 215° ; hæmin derivative, obtained by the action of ferrous acetate on the ester in presence of acetic acid and sodium chloride); ethyl ester, m. p. 195 – 196° (corr.; copper complex, m. p. 203°); hydrochloride; copper compound; hæmin derivative], is obtained. Mesoporphyrin XII has, therefore, the structure A ($R^1=R^2=Et$; $R^3=R^5=R^6=Me$; $R^4=R^7=[CH_2]_2\cdot CO_2H$).



Opsopyrrolecarboxylic acid aldehyde and hæmopyrrolecarboxylic acid react in presence of hydrobromic acid, forming (3-methyl-4- β -carboxyethylpyrryl)-(4:5-dimethyl-3- β -carboxyethylpyrrolenyl)-methene hydrobromide, m. p. 175° (decomp.) after darkening at 120° , brominated to (5-bromo-3-methyl-4- β -carboxyethylpyrryl)-(4:5-dimethyl-3- β -carboxyethylpyrrolenyl)methene hydrobromide. When this is heated with succinic acid at 220° , coproporphyrin I (tetramethyl ester) is produced. This porphyrin is, therefore, A with $R^1=R^3=R^4=R^6=[CH_2]_2\cdot CO_2H$; $R^2=R^5=R^7=Me$.

Opsopyrrolecarboxylic acid and cryptopyrrolecarboxylic acid aldehyde condense in presence of hydrobromic acid, yielding (3:5-dimethyl-4- β -carboxyethylpyrryl)-(3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. 200° (decomp.) after darkening at 150 – 180° . This is brominated to (3:5-dimethyl-4- β -carboxyethylpyrryl)-(5-bromo-3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, which when heated with succinic acid at 220° affords 6% of coproporphyrin II [in A, $R^1=R^2=R^5=R^6=[CH_2]_2\cdot CO_2H$ and $R^3=R^4=R^7=Me$; tetramethyl ester, m. p. 288°] (cf. this vol., 902).

(5-Bromo-3-methyl-4- β -carboxyethylpyrryl)-(3:5-dimethyl-4-ethylpyrrolenyl)methene hydrobromide, m. p. 251° (decomp.) after darkening at 215° , is converted by heating with succinic acid at 180° into mesoporphyrin V [in A, $R^1=R^6=[CH_2]_2\cdot CO_2H$; $R^2=R^5=Et$; $R^3=R^4=R^7=Me$; dimethyl ester, m. p. 274° ; copper salt, m. p. 285 – 286° ; hæmin derivative]. (3:5-Dimethyl-4-ethylpyrryl)-(3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide, m. p. 180 – 190° (decomp.) after darkening at 140° , prepared from cryptopyrrolealdehyde and opsopyrrolecarboxylic acid, is brominated to (3:5-dimethyl-4-ethylpyrryl)-(5-bromo-3-methyl-4- β -carboxyethylpyrrolenyl)-methene hydrobromide, which also affords mesoporphyrin V.

Hæmopyrrole and opsopyrrolecarboxylic acid alde-

hyde afford (3-methyl-4- β -carboxyethylpyrrol)-(4:5-dimethyl-3-ethylpyrrolenyl)methene hydrobromide, brominated to (5-bromo-3-methyl-4- β -carboxyethylpyrrol)-(4:5-dimethyl-3-ethylpyrrolenyl)methene hydrobromide, which in turn yields, after fusion with succinic acid at 200°, mesoporphyrin II [in A, $R^1=R^6=[CH_2]_2\cdot CO_2H$; $R^2=R^5=R^7=Me$; $R^3=R^4=Et$; methyl ester, m. p. 233°; copper salt, m. p. 261°; hæmin derivative], also obtained from (4:5-dimethyl-3-ethylpyrrol)-(5-bromo-3-methyl-4- β -carboxyethylpyrrolenyl)methene hydrobromide [unbrominated methene hydrobromide, m. p. 209° (decomp.) after darkening at 180°].

Ethyl 4-methyl-3- β -carboxyethylpyrrole-5-carboxylate, m. p. 106°, is prepared by decarboxylation of the corresponding -2-carboxylic acid at 250°. 5-Carboethoxyopopyrrole is converted by hydrocyanic and hydrochloric acids into its 2-formyl derivative, m. p. 230°. 4-Methyl-3- β -carboxyethyl-2:5-dicarbethoxy-pyrrole has m. p. 147—148°.

The absorption spectra of a large number of the above compounds are tabulated. H. BURTON.

Porphyrin syntheses. XIX. Synthesis of deuterohæmin and deuteroporphyrin. H. FISCHER and A. KIRSTAHLER (Annalen, 1928, 466, 178—188).—2:3-Dimethylpyrrole and 2:4-dimethylpyrrole-5-aldehyde condense in presence of alcoholic hydrobromic acid to give (4:5-dimethylpyrrol)-(2:4-dimethylpyrrolenyl)methene hydrobromide (I), m. p. 217° (decomp.) after darkening at 185° [free base, m. p. 115° (corr.; hydrochloride)], which is brominated in acetic acid solution to a compound (II), $C_{13}H_{15}N_2Br_3$, darkens at 220°, not melted at 300°. When a mixture of I and bis-(2-bromo-3-methyl-4- β -carboxyethylpyrrol)methene hydrobromide (III) is heated with succinic acid at 180—190°, deuteroporphyrin [methyl ester (IV), m. p. 219—220° (complex iron salt, m. p. 250°)], is obtained, and has, therefore, the formula A (preceding abstract) with $R^1=R^3=H$; $R^2=R^4=R^7=Me$; $R^5=R^6=[CH_2]_2\cdot CO_2H$. Similar treatment of a mixture of II and III gives deuteroporphyrin together with another porphyrin (methyl ester, m. p. 232°). Treatment of deuteroporphyrin with ferrous acetate, acetic acid, sodium chloride, and hydrochloric acid gives deuteroporphyrin iron salt (deuterohæmin), $C_{30}H_{28}O_4N_4ClFe$. Bromination of IV in acetic acid gives a perbromide, m. p. 138°, which on treatment with acetone passes into dibromodeuteroporphyrin dimethyl ester, m. p. 274°, not depressing the m. p. (267°) of the natural product. The copper salt, m. p. 288°, of this ester does not depress the m. p. of the copper salt of bromoporphyrin I ester. The absorption spectra of the synthetic deuteroporphyrin and the above salts are tabulated.

"Pyroporphyrin" (Schumm, this vol., 1263) and deuteroporphyrin are identical. H. BURTON.

So-called bithiohydantoin of Frerichs, Förster, and Höller. H. W. STEPHEN and F. J. WILSON (J.C.S., 1928, 2826—2827).—The 3:3-bis- ψ -thiohydantoin of Frerichs and Förster (A., 1910, i, 190) and of Frerichs and Höller (A., 1913, i, 909) are to be regarded as 2:4-diketo-5-alkyltetrahydrothiazole-2-ketazines, $CHR\begin{smallmatrix} CO\cdot NH \\ S-C\cdot N\cdot N\cdot C-S \end{smallmatrix}CH_2$, since on hydrolysis with hydrochloric acid hydrazine hydro-

chloride together with the corresponding 5-alkyl derivatives of 2:4-diketotetrahydrothiazole,

$CHR\begin{smallmatrix} CO\cdot NH \\ CO\cdot CO \end{smallmatrix}$, are formed (cf. this vol., 904).

Thus 2:4-diketo-5-methyltetrahydrothiazole-2-ketazine, m. p. 289° (lit. above 280°), yields hydrazine hydrochloride and 2:4-diketo-5-methyltetrahydrothiazole, m. p. 46—47°, whilst 2:4-diketo-5-ethyltetrahydrothiazole-2-ketazine, m. p. 233° (lit. 225—226°), gives hydrazine hydrochloride and 2:4-diketo-5-ethyltetrahydrothiazole, m. p. 64—65°.

A. I. VOGEL.

Oximes of N-methyl-2-benzthiazolone and N-methyl-2-quinolone. K. FUCHS and E. GRAU-
AUG (Ber., 1928, 61, [B], 2194—2197; cf. this vol., 430).—1-Chlorobenzthiazole is converted by methyl iodide below 80° into 1-iodobenzthiazole methiodide, transformed by an excess of hydroxylamine in anhydrous methyl alcohol into 2-methylbenzthiazolone-1-oxime, $C_6H_4\begin{smallmatrix} S \\ NMe \end{smallmatrix}C\cdot N\cdot OH$, m. p. 202—203°

(decomp.). Similarly, 2-iodoquinoline methiodide gives the oxime of 2-keto-1-methyl-1:2-dihydroquinoline, m. p. 180.5—181.5° (decomp.), which is remarkably stable towards hot acids and alkalis; the hydrochloride, m. p. 230—232° (decomp.), perchlorate, and sodium salt are described. Reduction of the oxime by stannous chloride and hydrochloric acid affords 2-aminoquinoline methochloride. Oxidation by bromine in pyridine, ferric chloride, or hydrogen peroxide does not appear to yield the nitroso-compound.

H. WREN.

Preparation of substituted μ -methylbenzthiazoles and their transformation into new heterocyclic polymethine dyes. W. KÖNIG [with P. SEIDEL and G. STÜHMER] (Ber., 1928, 61, [B], 2065—2074; cf. A., 1912, i, 495).—4:4'-Dichloro-2:2-dinitrodiphenyl disulphide is converted by zinc dust and boiling acetic anhydride into 4-chloro-1-methylbenzthiazole, m. p. 62° (methiodide, m. p. 212°, and corresponding perchlorate, m. p. 192°), from which the methylene base, $C_6H_3Cl\begin{smallmatrix} S \\ NMe \end{smallmatrix}C\cdot CH_2$, m. p. 138°

is derived by the action of sodium hydroxide on the methiodide suspended in acetone. 5-Chloro-1-methylbenzthiazole, m. p. 81°, is obtained by the action of potassium ferri cyanide on a solution of *p*-chlorothioacetanilide in sodium hydroxide or by the successive action of sodium hydroxide and acetic anhydride on an alcoholic solution of the product derived from sulphur chloride and aniline hydrochloride. The corresponding methiodide, m. p. 212°, methoperchlorate, m. p. 198°, methobromide, m. p. 270° (decomp.), and methylene base, m. p. 145°, are described. The last substance gives an additive compound, $C_6H_3NS_3$, decomp. above 275°, with carbon disulphide. 5-Bromo-1-methylbenzthiazole, from *p*-bromothioacetanilide, m. p. 153°, gives a methiodide, m. p. 208°, methoperchlorate, m. p. 216°, and methylene base, C_6H_3NSBr , m. p. 148°. 5-Methoxy-1-methylbenzthiazole, b. p. 170°/20 mm., 284°/760 mm., obtained from thioacet-*p*-anisidine or from the product of the action of sulphur chloride on anisidine hydrochloride, gives a methiodide, m. p. 228°, and methobromide, m. p. 248° (decomp.); 5-methoxy-1-

methylene-1:2-dihydrobenzthiazole, m. p. 135°, and its additive compound with carbon disulphide, $C_{11}H_{16}ONS_3$, m. p. 239° (decomp.), are described. 4(?) -Chloro-5-methoxy-1-methylbenzthiazole, m. p. 64° (methiodide, m. p. 215°), is obtained as by-product of the preparation of 5-methoxy-1-methylbenzthiazole. o-Toluidine hydrochloride and sulphur chloride in water give a product, $(?)Cl \cdot C_6H_4Me \langle \begin{smallmatrix} NH \\ S \end{smallmatrix} \rangle S:O$ or

$Cl \cdot C_6H_4Me \langle \begin{smallmatrix} N \\ S \end{smallmatrix} \rangle S \cdot OH$, converted by successive addition of sodium hydroxide and acetic anhydride into 5-chloro-1:3-dimethylbenzthiazole, m. p. 79° (methiodide, m. p. 244°).

Chlorodimethylbenzthiazole methobromide is transformed by p-dimethylaminobenzaldehyde in presence of boiling acetic anhydride into 5-chloro-2-methyl-1-p-dimethylaminobenzylidenemethylbenzthiazolium bromide,

$C_6H_4 \langle \begin{smallmatrix} S \\ \text{Alk-N-X} \end{smallmatrix} \rangle C \cdot [CH:CH]_n \cdot C_6H_4 \cdot NAlk_2$, m. p. 249°.

5-Methoxy-2-methyl-1-p-dimethylaminobenzylidenemethylbenzthiazolium bromide, m. p. 255°, 4(?) -chloro-5-methoxy-2-methyl-1-p-dimethylaminobenzylidenemethylbenzthiazolium iodide, m. p. 214°, and 5-chloro-2:3-dimethyl-2-p-dimethylaminobenzylidenemethylbenzthiazolium iodide, m. p. 234°, are prepared similarly.

4-Chloro-1-methylbenzthiazole methiodide is converted by orthoformic ester in boiling acetic anhydride into 6:6'-dichloro-1:1'-dimethyl-2:2'-streptomono-vinylenethiocyanine iodide,

$C_6H_4 \langle \begin{smallmatrix} S \\ \text{Alk-N-X} \end{smallmatrix} \rangle C \cdot \begin{smallmatrix} CH \\ CH \\ CH \\ CH \end{smallmatrix} \cdot C \langle \begin{smallmatrix} S \\ \text{Alk-N} \end{smallmatrix} \rangle C_6H_4$, decomp. above

270°. 5:5'-Dichloro-1:1'-dimethyl-2:2'-streptomono-vinylenethiocyanine iodide, decomp. 286°; 6:6'-dimethoxy-1:1'-dimethyl-2:2'-streptomono-vinylenethiocyanine perchlorate, decomp. about 290°; 5:5'-dibromo-1:1'-dimethyl-2:2'-streptomono-vinylenethiocyanine iodide, decomp. 280°, and 5:5'-dichloro-1:1':7:7'-tetramethyl-2:2'-streptomono-vinylenethiocyanine iodide, m. p. 243°, are similarly prepared. The absorption curves of the new thiocyanines resemble closely that of thiazole-purple; in the visible spectrum they give a pronounced band which exhibits two sharp maxima for thin layers, the most persistent of which lies towards greater wave-length. The influence of substituents is in the same sense with thiocyanines and the simplest streptomono-vinylenethioflavines, although not so marked with the latter substances, which give a single, relatively broad, non-resolvable band in the visible spectrum.

H. WREN.

1:3:4-Oxiazines. II. J. VAN ALPHEN (Rec. trav. chim., 1928, 47, 909—919; cf. this vol., 780).—5-Keto-1:3:4-oxiazines are obtained by the action of chloroacetyl chloride on β -acylphenylhydrazines and subsequent elimination of 1 mol. of hydrogen chloride from the intermediate α -chloroacetyl derivatives by treatment with anhydrous potassium carbonate in acetone:

$CH_2Cl \cdot HO \cdot CR \rightarrow CH_2 \cdot O \cdot CR$
 $CO \cdot NPh \cdot N \rightarrow CO \cdot NPh \cdot N$. Thus,

α -chloroacetyl- β -acetylphenylhydrazine, m. p. 131°, affords Δ^2 -5-keto-4-phenyl-2-methyl-1:3:4-oxiazine, m. p. 65°; α -bromoacetyl- β -isobutyrylphenylhydrazine yields Δ^2 -5-keto-4-phenyl-2-isopropyl-1:3:4-oxiazine,

m. p. 40°, and β -benzoyl- α -chloroacetylphenylhydrazine, m. p. 198°, gives Δ^2 -5-keto-2:4-diphenyl-1:3:4-oxiazine, m. p. 96°, either by treatment with potassium carbonate or by the action of concentrated ammonia solution. The methyl and isopropyl derivatives are hydrolysed by aqueous-alcoholic sulphuric acid to phenylhydrazine and β -isobutyrylphenylhydrazine, respectively, whilst the diphenyl derivative is unaffected. This last compound is soluble in sodium hydroxide solution, reacting in its enol form.

α -N-Phenylaminoacetyl- β -acetylphenylhydrazine, m. p. 140°, is hydrolysed by aqueous-alcoholic sulphuric acid to α -N-phenylaminoacetylphenylhydrazine, m. p. 157° (benzylidene derivative, m. p. 194.5°). β -Benzoyl- α -N-phenylaminoacetylphenylhydrazine has m. p. 159°.

H. BURTON.

Catalytic dehydrogenation of nicotine. J. P. WIBAUT and J. OVERHOFF (Rec. trav. chim., 1928, 47, 935—939).—When nicotine is passed over platinised asbestos at 320—350° a 72—73% yield of N-methyl-2-(3'-pyridyl)pyrrole [picrate, m. p. 168—169° (lit. 163—164°)] is obtained.

H. BURTON.

Alkaloids of *Hyoscyamus reticulatus*, L. R. A. KONOVALOVA and O. J. MAGIDSON (Arch. Pharm., 1928, 266, 449—452).—The root contains about 1% of s-tetramethyldiaminobutane, b. p. 166—167° (picrate, m. p. 198—200°; chloroaurate, m. p. 200—205°; chloroplatinate, m. p. 224°), identical with that isolated by Willstätter and Heubner, (A., 1907, i, 959) from *H. muticus*, and a trace of hyoscyamine. No volatile, nitrogenous bases are present in *H. pusillus*, *Datura violaceum*, *D. stramonium*, and mandragora.

S. COFFEY.

Chloroarsinosoquinine. III. F. X. ERBEN (Ber., 1928, 61, [B], 2106—2108; cf. A., 1927, 265).—Dissolution of well-dried dehydroquinine in an excess of warm arsenic trichloride and preservation of the solution at the atmospheric temperature for about 6 months leads to the production of chloroarsinosodiquinine, $(C_{20}H_{22}O_2N_2)_2AsCl$, distinguished from chloroarsinosoquinine by its solubility in warm nitrobenzene. The sulphate of chloroarsinosoquinine is converted by sodium sulphite into chloroarsinosodiquinine sulphite.

H. WREN.

Tests for morphine and related alkaloids. C. C. FULTON (J. Lab. Clin. Med., 1928, 13, 750—762).—The "iodic acid-peroxide" test for morphine is described; the Pellagri test is improved. Tests are based on the formation of a dehydration product obtained by heating the alkaloid with concentrated sulphuric acid at 40—50°. CHEMICAL ABSTRACTS.

Cresolarsinic acids. C. FINZI (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1302—1311; Chem. Zentr., 1928, i, 2173—2174).—Four new cresolarsinic acids are added to the four out of ten already known; Christiansen's compound (A., 1923, i, 500) is 6-hydroxy-2-methylphenylarsinic acid, not 2-hydroxy-4-methylphenylarsinic acid. Bart's method was employed for 2-hydroxy-3-methyl- and 2-hydroxy-5-methyl-phenylarsinic acid with limited success; generally the diazotised aminomethylphenylarsinic acid was heated. The following compounds

are described: 2-hydroxy-3-methylphenylarsinic acid, m. p. (slow heating, froth) 200—205°, (rapid heating) 205°; 3-hydroxy-4-methylphenylarsinic acid, m. p. 174—175° (?-nitro-derivative, m. p. 237° [decomp.]); 2-hydroxy-4-methylphenylarsinic acid, m. p. (rapid heating) 125° (?-nitro-derivative, m. p. 193°, sinters 120°); 2-hydroxy-5-methylphenylarsinic acid, softens at 90—100°; after solidifying, m. p. 218° (frothing); 5-hydroxy-2-methylphenylarsinic acid, m. p. 184—185° (frothing); 3:3'-dihydroxy-4:4'-dimethylarsenobenzene, m. p. 192—197°; 2:2'-dihydroxy-4:4'-dimethylarsenobenzene, decomp. 108—110°; (?)-dinitro-derivative, m. p. 191° (decomp.).

A. A. ELDRIDGE.

Preparation of 4-chaulmoogrylaminobenzene-arsinic acid. M. M. DEWAR (U.S. Pub. Health Service Bull., 1927, No. 168, 31—32).—4-Chaulmoogrylaminobenzene-arsinic acid, from chaulmoogryl chloride and arsanilic acid, decomposes at 230°.

CHEMICAL ABSTRACTS.

Manufacture of new substituted 5:5'-[di]acylamido-4:4'-dihydroxyarsenobenzenes. I. G. FARBERIND. A. G.—See B., 1928, 837.

Friedel and Crafts' reaction and the organo-metallic compounds of aluminium. P. LEONE (Atti II Cong. Naz. Chim. Pura Appl., 1926, 1332—1337; Chem. Zentr., 1928, i, 2174).—The view that organo-metallic compounds are formed on admixture of aromatic hydrocarbons and aluminium chloride is supported; the position of equilibrium is, however, far to one side, so that only traces are formed. Aluminium phenyl iodide reacts with alkyl iodides forming benzene homologues; methyl iodide yields benzene, toluene, and xylene, ethyl iodide yields benzene, ethylbenzene, diethylbenzene, and higher homologues, propyl iodide yields isopropylbenzene (not propylbenzene), whilst isoamyl iodide yields small quantities of isoamylbenzene. Ketone synthesis cannot, however, be effected with aluminium organic compounds.

A. A. ELDRIDGE.

Structure of silk fibroin. E. ABDERHALDEN and H. MAHN (Z. physiol. Chem., 1928, 178, 253—275).—Silk fibroin dissolved in 50% lithium bromide solution was treated with bromine in chloroform, and thus separated into a soluble and an insoluble portion. The two products were hydrolysed. In the insoluble portion, which had taken up bromine, were found glycine, alanine, serine, and 2:5-dibromotyrosine. The smaller soluble portion contained glycine and probably alanine and serine. Silk fibroin in 50% lithium bromide was exposed for varying lengths of time to N-alkali. The quantity of bromine absorbed was fairly constant, but the amount of precipitate varied with the time of alkali action.

The breakdown of the protein by alkali was very rapid. Untreated and treated silk fibroin was stable to pepsin; it was hydrolysed by mixed pancreatic enzymes. The fibroin is probably partly broken down on dissolution in lithium bromide.

J. H. BIRKINSHAW.

Structure of proteins. E. ABDERHALDEN and W. KRÖNER (Z. physiol. Chem., 1928, 178, 276—290).—An attempt was made to find a general method for the isolation of the polypeptide break-

down products of proteins. Benzoylation of the esters followed by high-vacuum distillation led to decomposition except in the case of benzoyl-dl-leucylglycine ethyl ester. An attempted fractionation of the benzoylated polypeptide esters from caseinogen by means of solvents was no more successful. A separation was finally attained by repeated precipitation of the butyl alcohol extract with much water. A solid product was obtained which on hydrolysis gave benzoyl-leucine and glutamic acid in theoretical yield.

J. H. BIRKINSHAW.

Treatment of dipeptide or peptone with sugar, hexosediphosphate, and methylglyoxal. C. NEUBERG and M. KOBEL (Biochem. Z., 1928, 200, 459—467).—Small changes in optical rotation are obtained on mixing alanylalanine or silk fibroin peptone with solutions of dextrose, laevulose, or methylglyoxal. Mixing magnesium hexosediphosphate with alanylalanine gave practically no change of rotation.

P. W. CLUTTERBUCK.

Degradation of gelatin and gelatin-peptone with acetic anhydride. Isolation of associated polypeptides. A. FODOR and C. EPSTEIN (Biochem. Z., 1928, 200, 211—222).—The various fractions obtained in the author's previous work with gelatin (this vol., 435) have been analysed and the observations extended to gelatin-peptone.

P. W. CLUTTERBUCK.

Degradation of gelatin by glycerol under various conditions. Isolation of a non-colloidal intermediate product hydrolysable by pepsin. A. FODOR and R. SCHOENFELD (Biochem. Z., 1928, 200, 223—235).—Gelatin is converted by glycerol at 130° into a product, soluble in water and insoluble in alcohol, which gives the biuret and ninhydrin reactions, which has the same mol. wt. (406) as gelatin-peptone (400), which gives the same value (2/3) for the ratio "amino-N/total-N," and is hydrolysed by both pepsin and trypsin. The process is carried much further by heating at 180°, and fractionation of the product indicates the formation of lower polypeptide anhydrides.

P. W. CLUTTERBUCK.

Products of hydrolysis of proteins. J. TILLMANS, P. HIRSCH, and F. STRACHE (Biochem. Z., 1928, 199, 399—433; cf. this vol., 436).—The apparent dissociation constants (cf. Bjerrum, A., 1923, i, 444) of various di- and tri-peptides and of asparagine have been determined electrometrically; the values obtained both for acid and basic constants are greater than those obtained in the same way for simple amino-acids, those for tripeptides being a little greater than those for dipeptides. Both acidic and basic groups become progressively stronger as the length of the peptide chain increases, but the strength does not increase indefinitely. The simple diketopiperazines, whether in strongly acid or strongly alkaline solutions, do not combine with alkali or acid. Asparagine in strongly acid solution acts as if it has only one basic group. The hydrolysis of proteins with sodium hydroxide proceeds at first rapidly, then much more slowly, probably because some parts of the protein molecule are much more readily attacked than others. These facts strengthen

the formerly expressed opinion favouring the ring structure of proteins. For characterising and identifying the various proteins it is better to hydrolyse for 4 hrs. at 100° with 0.5*N*-sodium hydroxide or for 24 hrs. at 100° with 0.5*N*-hydrochloric acid than to use the methods of hydrolysis formerly employed. The curves of "molecular binding power" of the chief proteins found in foods have been plotted. These curves show that, in this connexion, there are no great differences between the various proteins. Such differences as are found appear gradually in passing through the series of proteins. A process is described by means of which, from the curve of "molecular binding power" of a mixture, the amounts of the separate constituents can be deduced, provided that the dissociation constants of the separate constituents are known. From such curves it is evident that, in the hydrolysates, a considerable part of the nitrogen present occurs in an "acidimetrically inactive" form. Since the products of alkaline hydrolysis when afterwards treated with acid exhibit decreasing "molecular binding powers," it is possible that diketopiperazines may undergo keto-enol transformations. W. McCARTNEY.

Compounds of albumin and metallic salts. H. BECHHOLD (Biochem. Z., 1928, 199, 451–458).—Methods of washing-out and of differential ultra-filtration have been applied to the study of mixtures of solutions of albumin with solutions of salts of heavy metals. It is probable that the complex compound of albumin and the chlorides of calcium, strontium, or barium is decomposed during the washing-out process, for these chlorides are completely removed from the albumin. Salts of nickel and of cobalt are also completely removed, but neither anion nor cation is removed, under the same conditions, from albumin solutions treated with the chlorides of zinc, aluminium, chromium, or iron (ferric) and, in the case of the first three of these metals, a constant ratio of albumin to metallic salt is found. It is not probable, however, that this constant ratio is due to the formation of actual chemical compounds. The product of interaction of ferric chloride and albumin (Liquor ferri albuminati) is a hydrosol of iron oxide dispersed in an exceedingly fine condition in albumin. Gold chloride closely resembles ferric chloride in its behaviour with albumin, but silver, in the form of silver nitrate, seems to form a water-soluble undissociated silver-albumin (1:5200) compound. These compounds are all soluble in water and, in aqueous solution, are hydrolytically or electrolytically dissociated. If the metal forms an insoluble hydroxide this may remain with the albumin after the washing-out, so forming an apparent compound containing metal and albumin in constant proportions. W. McCARTNEY.

Investigation of solutions containing albumin and metallic salts by the washing-out method. H. SCHORN (Biochem. Z., 1928, 199, 459–467; cf. preceding abstract).—A method for the preparation, by electro-ultra-filtration, of egg-albumin free from electrolytes is described. The existence of the lower zone of precipitation of albumin by salts of heavy metals is due to the presence in the albumin of

calcium salts: in albumin free from calcium this zone is absent. Water-soluble compounds of albumin with silver, zinc, chromium, and aluminium or their salts can be prepared. In these compounds the ratio of metal to albumin is 1:5100 to 1:5200. The reaction between ferric chloride and albumin is quite different from that between the salts of the other metals and albumin, the difference apparently being due to complications caused by hydrolysis.

W. McCARTNEY.

Equilibria between albumin and metallic salts (silver nitrate, ferric chloride, gold chloride). E. HEYMANN and F. OPPENHEIMER (Biochem. Z., 1928, 199, 468–497; cf. preceding abstracts).—In solutions containing metallic salts and albumin in different proportions the amount of uncombined metallic salt which is in equilibrium with the compound of metallic salt and protein has been determined by analysis of the intermicellar liquid, and the curves of combination of silver nitrate, ferric chloride, and gold chloride with highly-purified albumin have been studied. The maximum amounts of combined silver nitrate and ferric chloride are independent of the absolute concentrations of the albumin and of the salt, but the maximum for ferric chloride is greater than that for silver nitrate. With silver nitrate, in mixtures in all proportions, cations and anions are combined with albumin in equivalent amounts, whereas with ferric chloride this occurs only when the ratio is high. When the ratio is low more iron than chlorine is combined, and for gold chloride analogous results are found. The ways in which the metallic salts may be combined with albumin are discussed and the existence of molecular compounds is assumed, although the possible formation of adsorption compounds is not denied. W. McCARTNEY.

Bromine uptake of caseinogen and of caseinogen keratin hydrolysates. F. LIEBEN and R. MÜLLER (Biochem. Z., 1928, 197, 119–135).—When caseinogen is treated with a large excess of bromine or of bromine in aqueous or alkaline solution 5–6% of bromine is adsorbed. Tyrosine, histidine, and cystine are chiefly responsible for the bromine consumption of protein hydrolysates, and take up, respectively, per mol. 4, 4, and 10 atoms of bromine, both when treated separately and when present together. Large amounts of bromine partly oxidise tyrosine and produce melanin. Further, tyrosine and cystine react rapidly with bromine, whilst histidine reacts slowly, and hence, according to the amount of bromine added and to the duration of the experiment, the uptake of bromine may deviate from the requirements of the three acids. The distribution of bromine in protein hydrolysates was investigated by means of phosphotungstic acid precipitation. Histidine which has reacted with bromine is no longer precipitated by this acid. In the case of keratin there is increased bromine uptake after reduction of the hydrolysate, corresponding with the conversion of 1 mol. of cystine into 2 mols. of cysteine. Nascent iodine reacts only to a slight extent with protein hydrolysates. W. McCARTNEY.

Effect of X-rays on tyrosine and cystine. W. STENSTRÖM and A. LOHMANN (J. Biol. Chem., 1928,

79, 673—678).—Tyrosine in dilute solution (0.01% or less) is decomposed to a considerable extent by exposure to X-rays; cystine is not affected.

C. R. HARRINGTON.

Determination of tyrosine in proteins. M. T. HANKE (J. Biol. Chem., 1928, 79, 587—609).—The value of the author's method (A., 1926, 633) for the determination of tyrosine in protein hydrolysates is confirmed, although the values then obtained were 0.3—0.6% low on account of loss of tyrosine with the silver precipitate of histidine; it is better to precipitate the tyrosine directly from the hydrolysis mixture by the author's method and then to determine it by the method of Folin and Ciocalteu (A., 1927, 892). The criticisms of Looney (A., 1926, 1050) are answered on the ground that he employed too much tyrosine. Slight variations were observed in the tyrosine content of different samples of the same protein, according to the age and the method of drying of the sample.

C. R. HARRINGTON.

Micro-determination of halogens and sulphur in organic substances, especially chromium compounds. F. HEIN, K. HOYER, and K. KLAR (Z. anal. Chem., 1928, 75, 161—164).—For the micro-determination of halogens 20 mg. of substance and 0.18 g. of sucrose are intimately mixed with 2—2.5 g. of sodium peroxide in a Pringsheim crucible and covered with 2 g. of sodium peroxide, and the mixture is ignited by a hot wire etc. The heated and filtered solution of the mass is acidified with nitric acid and heated with sulphurous acid, and hydrogen peroxide solution, followed by nitric acid, is added. After dilution, an excess of 0.02N-silver nitrate solution and a few c.c. of ether are added and the excess of silver is titrated with 0.02N-thiocyanate solution, using iron alum as indicator.

For the determination of sulphur the alkaline solution is acidified with hydrochloric acid and

chromate reduced by heating with alcohol and sodium nitrite. The resulting solution and a faintly ammoniacal solution of barium chloride are added through capillary tubes to a boiling solution of ammonia, which is afterwards acidified with hydrochloric acid.

J. S. CARTER.

Determination of sulphur in organic compounds. E. A. SMITH and J. W. BAIN (Canadian Chem. Met., 1928, 12, 287—288).—The sulphur content of samples of barium lignosulphonate was determined by the following five methods: Eschka's method, fusion with sodium peroxide followed by gravimetric determination of sulphate, Klason's method in which the oxidation is carried out by the fumes from asbestos soaked in nitric acid in a combustion tube, Apitzsch's method using platinum gauze and oxygen, and Carius' method. The most consistent and highest results were obtained by Carius' method, which was closely approached by Apitzsch's method. Losses evidently occurred in the other methods, which gave very variable results.

C. IRWIN.

Colour reactions of the bile acids. L. CUNY (J. Pharm. Chim., 1928, [viii], 8, 358—364).—Seven colour reactions of the bile acids have been applied to each of the following substances: cholic, deoxycholic, anthropodeoxycholic, hyoglycodeoxycholic acids and the sodium salts of hyoglycodeoxycholic and hyocholic acids. In each reaction only cholic acid gave an intense colour and these colours have been spectroscopically examined. It is concluded that the colour reactions of the bile acids are due mainly to cholic acid, the accompanying acids having only a weak effect, and as the salts of cholic acid predominate in the human bile, these colour reactions still maintain their importance, but the presence of the related compounds should not be forgotten.

E. H. SHARPLES.

Biochemistry.

Modifications of the Haldane gas-analysis apparatus. V. DU VIGNEAUD (J. Lab. Clin. Med., 1927, 13, 175—180).

Apparatus for the continuous recording of the oxygen consumption of small animals. A. N. RICHARDS and L. W. COLLISON (J. Physiol., 1928, 66, 299—306).—The animal is placed in a closed chamber and the carbon dioxide and water which it produces are absorbed by soda-lime. Oxygen is bubbled in through paraffin oil to keep the pressure constant in the chamber. The oxygen consumption is determined and recorded automatically from the rate of formation of the bubbles.

B. A. EAGLES.

Effects of breathing carbon dioxide and oxygen mixtures on the carbon dioxide and oxygen tensions in the tissues. J. A. CAMPBELL (J. Physiol., 1928, 66, Proc. Physiol. Soc., i—ii).—The presence of carbon dioxide in no way prevents the entry of oxygen into the tissues.

B. A. EAGLES.

Influence of disodium hydrogen phosphate on gaseous exchange. E. SCHMUTZLER (Biochem. Z.,

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1928, 200, 407—413).—The effect of addition of phosphate to a carbohydrate diet in decreasing the respiratory quotient of rats and, to a diet of meat, in greatly reducing its specific dynamic action (Abelin, A., 1926, 539; 1927, 276) could not be confirmed with dogs. Addition of phosphate to a carbohydrate diet caused the R.Q. to increase somewhat more slowly at first, but after 1 hr. it attained the same value as the control, whilst addition of phosphate to a diet of meat caused the specific dynamic action of the meat to be slightly increased, but the increase was within experimental error.

P. W. CLUTTERBUCK.

Oxygen capacity of hæmoglobin. M. ABELOOS, J. BARCROFT, N. CORDERO, T. R. HARRISON, and J. SENDROY (J. Physiol., 1928, 66, 262—266).—The blood-gas pump and the Van Slyke constant-volume apparatus give concordant values, both for nitrogen and oxygen, in the analysis of hæmoglobin solutions.

B. A. EAGLES.

Combination of carbon dioxide in blood. I. Velocity of dehydration and hydration of carbonic

acid components of blood. II. Detection of quickly reacting, fixed carbon dioxide in hæmoglobin. III. Detection of a hæmoglobin-carbon dioxide complex in solutions of carbon dioxide and hæmoglobin. IV. Carbon dioxide combining power of reduced and oxy-hæmoglobin. V. Physiology of carbhæmoglobin. O. M. HENRIQUES (Biochem. Z., 1928, 200, 1—4, 5—9, 10—17, 18—21, 22—24).—I. The carbon dioxide exchange in the lungs cannot be explained as a simple dehydration of carbonic acid, since this process proceeds much too slowly.

II. Part of the carbon dioxide of blood is combined with hæmoglobin and this part is liberated much more readily than that combined as hydrogen carbonate.

III. The presence of "carbhæmoglobin" in solutions of hæmoglobin and carbon dioxide is detected by determining amounts of hydrogen carbonate and of free and total carbon dioxide.

IV. Up to pressures of about 100 mm., reduced hæmoglobin unites with much more carbon dioxide than does oxyhæmoglobin, but at higher pressures the amounts become equal.

V. Exchange of carbon dioxide proceeds in terms of the carbhæmoglobin content of the blood, and the hydrogen carbonate and carbonic acid play only a subsidiary rôle in respiration similar to that of the chlorine ion.

P. W. CLUTTERBUCK.

Gas and electrolyte equilibria in blood. XIV. Base bound by serum-albumin and -globulin. D. D. VAN SLYKE, A. B. HASTINGS, A. HILLER, and J. SENDROY, jun. (J. Biol. Chem., 1928, 79, 769—780).—Over the range p_H 6.8—7.8 the relationship between the p_H and the base bound by protein is linear for serum-albumin and -globulin, the numerical value of the milliequivalents of base per g. of protein-nitrogen being 0.78 (p_H 5.16) in the first case and 0.48 (p_H 4.89) in the second.

C. R. HARRINGTON.

Gas and electrolyte equilibria in blood. XV. Line charts for graphic calculations. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1928, 79, 781—798).—Nomographic charts, based on data previously obtained, are given for the application of the Henderson-Hasselbalch equation to blood-plasma, and for the calculation of the factor for conversion of whole blood carbon dioxide into carbon dioxide of serum or plasma.

C. R. HARRINGTON.

Colloid-chemistry of hæmoglobin. II. B. JIRGENSONS (Biochem. Z., 1928, 200, 331—338).—The effect of organic substances on the spectrum and on the colloidal stability of oxyhæmoglobin (this vol., 537) is due to the capillary activity of these substances. Inorganic salts alone have no such influence, but the effect of organic substances is intensified by the presence of salts. Thus with salts and alcohol the bands are displaced towards the violet and the spectrum of cathæmoglobin is obtained. With small concentrations of magnesium chloride and alcohol almost complete coagulation of oxyhæmoglobin sol is obtained, but if both are in high concentration no coagulation occurs. Rise of temperature favours both precipitation and spectroscopic changes.

P. W. CLUTTERBUCK.

Basic amino-acids of horse hæmoglobin. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, 79, 377—388).—From crystalline horse hæmoglobin there have been isolated, by methods described in earlier papers (this vol., 1121), histidine 7.64%, arginine 3.32%, and lysine 8.10%.

C. R. HARRINGTON.

Globin and denatured globin. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1928, 5, 213—222).—Details are given for the preparation of globin from hæmoglobin. By titrating a given weight of hæmatin with varying quantities of globin solution and converting the methæmoglobin formed into oxyhæmoglobin it is calculated that the chemical equivalent of globin is the same as that of globin present in natural oxyhæmoglobin, namely about 16,000. Under conditions limited by the concentration of reagents suitable for the optical instruments used, a weight of denatured ox globin equal to one equivalent weight of ox globin combines with 6 mols. of reduced hæmatin. The observation of Wu and Lin (cf. A., 1927, 688) has been confirmed that if methæmoglobin was converted into acid hæmatin and globin and the solution neutralised at once, almost all the acid hæmatin is reconverted into methæmoglobin, whereas in the case of oxyhæmoglobin only about two thirds reversion takes place. Oxyhæmoglobin is decomposed into hæmatin and globin more slowly and at a lower p_H than is methæmoglobin. Denatured horse- or ox-globin has a much higher rotation than the corresponding native globin. Denatured globin freshly prepared by the Schulz method often contains a small amount of globin.

W. O. KERMACK.

Photochemical dissociation of iron-carbonyl compounds (carbon monoxide-hæmochromogen, carbon monoxide-ferrocysteine) and the law of photochemical equivalence. O. WARBURG and E. NEGELEIN (Biochem. Z., 1928, 200, 414—458).—Continuing the authors' attempt to calculate the absorption spectrum of the respiratory enzyme from the photochemical dissociation of its carbonyl compound (cf. A., 1927, 1221; this vol., 537, 549, 851), a considerable amount of theoretical and experimental work is described in which are investigated the photochemical dissociation of carbon monoxide-hæmochromogen and of carbon monoxide-ferrocysteine and the influence of the pressure of carbon monoxide, of temperature, and of wave-length thereon. The light absorption coefficients of these two compounds are determined and the validity of Einstein's law is tested and the law confirmed.

P. W. CLUTTERBUCK.

Adsorption by erythrocytes. I. Adsorption of alanine. A. KULTJUGIN and N. IVANOVSKI (Biochem. Z., 1928, 200, 236—243).—Washed erythrocytes of cat, dog, and ox adsorb an amount of alanine, varying with its concentration, from solutions, the process being concluded in 30 min.

P. W. CLUTTERBUCK.

Erythrocyte as a colloidal system. III. Permeability of erythrocytes to electrolytes. IV. Mechanism of hæmolysis in hypotonic solutions. A. P. KONIKOV (Zhur. Exp. Biol. Med., 1928, 8,

480—487, 488—501).—Erythrocytes are permeable to both anions and cations of neutral salts; the ions also combine with the cell proteins, particularly hæmoglobin. The isoelectric point of erythrocytes is at p_H 6.8, that of hæmoglobin. The essential factor in hæmolysis is the osmotic condition of the hæmoglobin. The osmotic resistance increases with the alkalinity, being maximal at p_H 9.0; it depends on the inner state of the erythrocyte. The erythrocyte is regarded as a two-gel system consisting of stroma and hæmoglobin.

CHEMICAL ABSTRACTS.

Occurrence of lipase in polymorphonuclear leucocytes. W. FLEISCHMANN (Biochem. Z., 1928, 200, 25—28).—The presence of lipase is detected in the polymorphonuclear leucocytes of sterile peritoneal exudates (rabbit) by means of the manometric method of Rona and Lasnitzki (A., 1926, 866).

P. W. CLUTTERBUCK.

Micro-determination of the p_H of blood using an antimony electrode. R. BRINKMAN and F. J. J. BUYTENDYK (Biochem. Z., 1928, 199, 387—391).—By means of an antimony-coated platinum wire electrode the p_H of blood can be rapidly determined with sufficient accuracy for clinical purposes, using very small amounts of blood. W. MCCARTNEY.

Relation of p_H and changes in the buffer value of solutions of human serum. M. GEX (Compt. rend. Soc. Biol., 1927, 97, 1564—1567; Chem. Zentr., 1928, i, 2267).—The $t(=\Delta m/\Delta p_H)$, where m is the amount of alkali or acid added— p_H curves for normal and pathological sera and egg-albumin solutions, determined with the antimony electrode, have the same general character, but differ in the nature and position of the maxima and minima. Serum is a very complex system. Often the minima do not correspond with the principal isoelectric points.

A. A. ELDRIDGE.

Comparative determinations of proteins in horse-serum. D. VON DESEÖ (Biochem. Z., 1928, 200, 126—134).—The micro-method for the determination of protein of Howe (A., 1922, ii, 171, 172) in which the proteins are removed by precipitation with sodium sulphate gives results agreeing with those obtained by the gravimetric method after precipitation with saturated ammonium sulphate solution. The values so obtained for total protein agree with those obtained by Robertson's refractometric method (A., 1915, ii, 851), but the values for the albumin and globulin fractions do not agree and Robertson's method cannot be used for fractionation of horse-serum.

P. W. CLUTTERBUCK.

Isolation and determination of serum-globulin by means of electrodialysis. L. REINER and H. KOPP (Kolloid-Z., 1928, 46, 99—107).—The precipitation of globulin during electrodialysis depends on the ratio of protective matter to globulin and on the alterations of hydrogen-ion concentration and the velocity of removal of electrolytes. Among the substances which inhibit coagulation is heparin, which has also the effect of displacing the isoelectric point in the acid direction. Contrary to the assertions of Ettisch and Ewig, membranes coated with albumin are found to serve a useful purpose in electrodialysis.

The existence of an electrical polarisation in colloid membranes during electrodialysis is discussed.

E. S. HEDGES.

Determination of blood-calcium. E. M. WATSON (J. Lab. Clin. Med., 1928, 13, 670—671).—An apparatus for the micro-titration of calcium oxalate is described.

CHEMICAL ABSTRACTS.

Serum-calcium content of man. J. H. ROE and B. S. KAHN (J. Lab. Clin. Med., 1928, 13, 762—763).—Values varying from 9.0 to 11.6 mg. per 100 c.c. of serum (average 10.13 mg.) were obtained.

CHEMICAL ABSTRACTS.

Copper in human blood-serum. H. A. KREBS (Klin. Woch., 1928, 7, 584—585; Chem. Zentr., 1928, i, 2419).—A mixture of the fluid with cysteine and sodium pyrophosphate buffer is shaken with air, the oxygen used indicating the amount of copper present. Human blood-serum contains 0.62—1.24 (average 0.91) $\times 10^{-3}$ mg. per c.c.; higher values are observed in pregnancy, tuberculosis, and acute infections, and lower values in kidney disease.

A. A. ELDRIDGE.

Modification of the MacLean-Van Slyke method for the determination of chloride in blood. M. I. HANNA (J. Lab. Clin. Med., 1928, 13, 651—653).—The diluted oxalated blood (1 part with 7 parts of water) is shaken with 10% sodium tungstate solution (1 part) and 0.66N-sulphuric acid (1 part), and filtered; 10 c.c. of the filtrate are mixed with 10 c.c. of water and 5 c.c. of $M/29.35$ silver nitrate solution and filtered after 5 min.; 10 c.c. of the filtrate, after addition of 2 c.c. of starch-citrate-nitrite solution, are titrated with $M/73.1$ potassium iodide solution.

CHEMICAL ABSTRACTS.

Determination of plasma-chloride. A. E. OSTERBERG and E. V. SCHMIDT (J. Lab. Clin. Med., 1927, 13, 172—175).—The plasma (1 c.c.) is slowly mixed with nitric acid (1:3) with agitation, so that a white, flocculent precipitate of protein is obtained. $N/35.46$ silver nitrate solution (5 c.c.) is added, followed by ferric indicator, and the excess of silver titrated with $N/35.46$ thiocyanate.

CHEMICAL ABSTRACTS.

Iodometric micro-method for the determination of chloride. S. PRIKLADOWIZKY and A. APOLLONOV (Biochem. Z., 1928, 200, 135—144).—The chloride is precipitated with excess of silver nitrate and the excess determined by titration in acid solution with a standard iodine-iodide solution, using starch as indicator. A table is given from which the chloride is read off. The method is used with 0.1 c.c. of blood or plasma.

P. W. CLUTTERBUCK.

Determination of inorganic phosphate in blood-serum. S. L. LEIBOFF (J. Biol. Chem., 1928, 79, 611—619).—Proteins are removed from blood-serum with trichloroacetic acid; the filtrate is neutralised, re-acidified with acetic acid, and the phosphate precipitated as uranyl phosphate; the washed precipitate is dissolved in 20% trichloroacetic acid, treated with potassium ferrocyanide, and the resulting solution compared colorimetrically with one similarly prepared from a standard phosphate solution. The error of the method is $\pm 2.5\%$.

C. R. HARRINGTON.

Precipitation of phosphorus as strychnine phosphomolybdate (Embsen's method). Micro-determination of the various "forms" of phosphorus in blood and of combined phosphorus in various organic substances. J. ROCHE (Bull. Soc. Chim. biol., 1928, 10, 1061—1078).—The solution (3 c.c.) containing phosphate ions (about 0.02—0.15 mg.) is treated with a 16% solution of ammonium molybdate in dilute nitric acid and an equal volume of 1% strychnine nitrate in a centrifuge tube for 40 min. After threefold washing, the precipitate is dissolved in 0.025*N*-sodium hydroxide solution containing phenolphthalein. The boiling solution is then neutralised with hydrochloric acid of similar normality, a slight excess added (0.5 c.c.), and finally titrated again with sodium hydroxide. From these titres the weight of phosphorus may be calculated. Blood is first laked and deproteinised with trichloroacetic acid and the phosphorus determined in the filtrate. This gives the "free" phosphorus; the "acid-soluble" and the total phosphorus figures are obtained by oxidising respectively the above filtrate and the original sample with nitric and sulphuric acids.

G. A. C. GOUGH.

Determination of blood-bilirubin. L. JENDRASSIK and A. CZIKE (Deut. med. Woch., 1928, 54, 430; Chem. Zentr., 1928, i, 2192).—The serum or plasma (2 c.c.) is mixed with 0.5 c.c. of 50% sodium caffeine benzoate and 1 c.c. of diazo-mixture, followed in 5—10 min. by addition of 6.7 c.c. of 96% alcohol; a standard wedge is used for comparison of the filtrate.

A. A. ELDRIDGE.

Determination of cholesterol in blood. D. ACÉL (Deut. med. Woch., 1928, 54, 431—433; Chem. Zentr., 1928, i, 2192).—Autenrieth and Funk's method is simplified.

A. A. ELDRIDGE.

Alcohol content of blood and organs. I. P. FRAENCKEL (Deut. Z. ges. gerichtl. Med., 1928, 11, 129—133; Chem. Zentr., 1928, i, 2102).—Introductory.

A. A. ELDRIDGE.

Alcohol content of blood and organs. II. H. W. NICOLAI (Deut. Z. ges. gerichtl. Med., 1928, 11, 134—144; Chem. Zentr., 1928, i, 2102).—The alcohol is heated with a large excess of hydrogen iodide, the ethyl iodide collected in alcoholic silver nitrate solution, and the silver iodide weighed.

A. A. ELDRIDGE.

Determination of the reducing substances in blood. A. BAUDOUIN (Bull. Soc. Chim. biol., 1928, 10, 977—1049).—A critical survey of the more important methods and their modifications.

G. A. C. GOUGH.

Determination of lævulose in blood. S. VAN CREVELD (Arch. Néerland. Physiol., 1928, 13, 521—533).—The colour reaction given by lævulose with diphenylamine and hydrochloric acid has been applied to its determination in blood.

B. A. EAGLES.

Blood-sugar determination and separation of sugars with yeast. A. L. RAYMOND and J. G. BLANCO (J. Biol. Chem., 1928, 79, 649—655).—The value of the method of Somogyi (A., 1927, 1214) is confirmed; dextrose is adsorbed quantitatively by yeast from its solution in water or in blood; xylose,

ribose, arabinose, galactose, and lactose are not adsorbed from water or blood; lævulose, mannose, and sucrose are partly adsorbed; maltose is not adsorbed from water, but is so to the extent of 40% in presence of blood.

C. R. HARRINGTON.

Micro-determination of free and protein-sugar in blood-plasma. H. BIERRY and A. VOSKRESSENSKY (Compt. rend. Soc. Biol., 1928, 98, 744—747; Chem. Zentr., 1928, i, 2635).—The deproteinised blood (5 c.c.) is heated on a water-bath for 6 min. with 2 c.c. of alkaline copper salt and the cuprous oxide determined by the Mohr-Bertrand method.

A. A. ELDRIDGE.

Bunsen valve in blood-urea determinations. F. P. BROOKS (J. Lab. Clin. Med., 1928, 13, 668—670).—The simple Bunsen valve is used instead of Johnson's flutter valve, and paraffin is employed to prevent foaming.

CHEMICAL ABSTRACTS.

Catalase, anticatalase, and phylocatalase in animal tissue under various physiological and pathological conditions. I. Determination of catalase in blood. E. GAGARINA and W. JANKOWSKI (Zhur. exp. Biol. Med., 1926, 33—51).—Maintenance of diluted blood (1:25—1:50) for 30 min. at 37° with or without the addition of alcohol does not affect the catalase; catalase action is, however, diminished at a dilution of 1:500. The diminution can be prevented by ethyl alcohol even at a dilution of 1:50,000.

CHEMICAL ABSTRACTS.

Coagulation of fibrin as a process of micellar crystallisation and agglutination. E. HEKMA (Biochem. Z., 1928, 199, 333—365).—A review.

W. MCCARTNEY.

Hæmolysis by brilliant-green and serum. E. PONDER (Proc. Roy. Soc., 1928, B 103, 556—574).—When red blood-cells are sensitised with brilliant-green, a compound is formed between a protein component of the red-cell membrane and the dye. On the subsequent addition of serum, the serum-proteins react with the combined dye to form a hæmolysin which can react with the protein component of the red-cell membrane and thus bring about lysis. The kinetics of the reaction are discussed.

B. A. EAGLES.

Quinine hæmolysis; influence of carbon dioxide. W. WEISE (Abhandl. Geb. Auslandskunde, 1928, D, 26, ii, 5 pp.; Chem. Zentr., 1928, i, 2185).—Promotion of quinine hæmolysis by carbon dioxide takes place, if at all, only under extreme conditions. Inhibition by small acid concentrations, observed by Rusznyák, holds also for carbon dioxide. The intensity of the hæmolysis depends on the amount of quinine brought into contact with a single blood-corpuscle.

A. A. ELDRIDGE.

Hæmolytic action of irradiated ergosterol and cholesterol. R. FISCHER (Biochem. Z., 1928, 199, 294—297).—The substances formed from ergosterol and cholesterol when irradiated by sunlight or by ultra-violet radiation in the presence of oxygen act hæmolytically.

W. MCCARTNEY.

Halogen content of animal tissues. A. T. CAMERON and C. H. A. WALTON (Trans. Roy. Soc. Canada, 1928, [iii], 22, V, 1—11).—Results are given

of the determination by Van Slyke's method of the total chloride content of various tissues of man, cow, rat, and dog. No evidence could be obtained of the presence of chlorine in organic combination.

W. O. KERMACK.

Nuclear substance of liver cells. N. ISHIYAMA (Z. physiol. Chem., 1928, 178, 217—220).—The cell nuclei of fresh calf's liver had a phosphorus:nitrogen ratio of 1:4.81. The nucleic acid was isolated; the ratio in this case was 1:1.89. By difference the protein component of the nuclei would contain 12.4% of nitrogen, which does not correspond with protamines or histones.

J. H. BIRKINSHAW.

Cadmiphile cells of the lung. J. LECLOUX (Bull. Soc. Chim. biol., 1928, 10, 1091—1099).—The total thiol-compound content and the number of cadmiphile cells (determined by treatment with formaldehyde and cadmium chloride; Fauré-Frémiet, A., 1921, ii, 228) in the lungs of guinea-pigs and rats is unaffected by alteration of the sulphur content of the diet or by interperitoneal injection of colloidal sulphur. Whilst the number of cells varies greatly from animal to animal, these differences are not accompanied by corresponding variations in the thiol content. Irritation of the lung with chloroacetone causes an increase in the number of cells.

G. A. C. GOUGH.

Applicability of the Schiff reaction to the determination of thymus-nucleic acid. G. WIDSTRÖM (Biochem. Z., 1928, 199, 298—306).—The Schiff reaction can be applied to the colorimetric determination of thymus-nucleic acid in preparations containing nucleic acids but free or almost free from albumin. The method is accurate to within about 2% and the most suitable amount of thymus-nucleic acid for the determination is 0.5—2 mg. The preparation and the thymus-nucleic acid for comparison must be hydrolysed simultaneously for the same length of time, the hydrolysates must be of the same degree of acidity, and an equal, accurately measured quantity of the reagent must be added to each hydrolysate.

W. MCCARTNEY.

Occurrence and detection of a pigment resembling hæmochromogen in suprarenal glands. A. ROSENBOHM (Z. physiol. Chem., 1928, 178, 250—252).—The suprarenal glands of freshly-killed pigs, cattle, and white rats showed absorption bands corresponding with hæmochromogen. Oxidation with hydrogen peroxide gave a spectrum resembling that of oxyhæmoglobin.

J. H. BIRKINSHAW.

Distribution of creatine-phosphoric acid in various muscles and organs of the animal organism. D. FERDMANN and O. FEINSCHMIDT (Z. physiol. Chem., 1928, 178, 173—178).—White muscle of the rabbit and cock contains more creatine-phosphoric acid than red muscle. The creatine-phosphoric acid accounts for about 30% of the total creatine of white muscle; the percentage is much less in the case of red muscle. Creatine-phosphoric acid is also found in smooth muscle and in various organs, but not in the kidney.

J. H. BIRKINSHAW.

Creatine-phosphoric acid, creatine, and lactacidogen content of white and red muscles of the

guinea-pig. A. PALLADIN and S. EPELBAUM (Z. physiol. Chem., 1928, 178, 179—185).—White muscle (biceps femoris) of the guinea-pig contains more creatine-phosphoric acid, creatine, and lactacidogen than red muscle (semitendinosus), heart-muscle considerably less. The percentage of creatine bound as phosphagen approaches 30% in white muscle, but is much less in red and heart-muscle.

J. H. BIRKINSHAW.

Biocatalyst content of normal and pathological tissues. H. VON EULER and H. JOHANSSON (Z. physiol. Chem., 1928, 178, 209—216).—Human placenta is shown to contain considerable amounts of co-zympase. The activity coefficient (c.c. CO₂ per hour/g. dried substance) is about 70. The effect of co-zympase and zymophosphate on methylene-blue reduction and respiration of fresh and washed placental tissue and extract is examined.

J. H. BIRKINSHAW.

Amylase in pyloric cæca of *Seriola quinqueradiatus*. T. OYA and K. HARADA (J. Imp. Fish. Inst. Tokyo, 1926, 2, No. 1, 28—33).—The optimal p_H of the amylase is p_H 7, and optimal temperature 43°; sodium chloride (0.0125 mol.) accelerated its action, but more than 0.05 mol. retarded it.

CHEMICAL ABSTRACTS.

Biochemistry of *Centrina vulpecula*, Rond. M. KOLLMANN, F. VAN GAVER, and J. TIMON-DAVID (Compt. rend. Soc. Biol., 1928, 98, 776—777; Chem. Zentr., 1928, i, 2624).—Liver- and ovary-oil, respectively, had iodine value 73.4, 113.9; saponif. value 132.3, 133.7; d_{15}^{20} 0.9022, 0.9106; n_D^{20} 1.4689, 1.4744.

A. A. ELDRIDGE.

Thiazine dyes as biological stains. II. Influence of buffered solutions on staining properties. R. HAYNES (Stain Tech., 1928, 3, 131—139).—The intensity of staining fixed sections with thionine, azures-A, -B, and -C, and methylene-blue increases with increase of p_H . It is uncertain as to whether this effect is due to varying the p_H , to the alteration of the salt content of the solution, or to both. Between p_H 5 and 7 there are always more pronounced metachromatic effects than with either more acid or more alkaline buffer solutions.

H. W. DUDLEY.

Secretion of hydrochloric acid into the stomach. J. R. F. RASSERS (Arch. Néerland. Physiol., 1928, 13, 514—520).—A "lecithalbumin" obtained from the mucosa of pig's stomach is added to a solution of sodium chloride. As shown by titration, free hydrochloric acid is present in the solution. From this observation it is argued that the lecithalbumin of the stomach mucosa is capable of decomposing sodium chloride; the sodium is adsorbed and free hydrochloric acid is secreted into the stomach.

B. A. EAGLES.

Permeability of cells. XIV. Excretion of sugars by the salivary glands. J. JEANGROS (Biochem. Z., 1928, 200, 367—378).—Intravenous injection of different concentrations of sugar solutions with simultaneously increased secretion of saliva due to injection of pilocarpine did not cause any of the various sugars used to appear in the saliva, even when the condition of hydræmic plethora was also established by injection of warm physiological

saline. As these sugars appeared in the urine, the permeability of the salivary and renal cells must be regarded as quite different. P. W. CLUTTERBUCK.

Detection of dried saliva on cloth. B. MUELLER (Deut. Z. ges. gerichtl. Med., 1928, 11, 211—224; Chem. Zentr., 1928, i, 2434).—The test depends on the detection of ptyalin by incubation with toluene and neutral starch solution. A. A. ELDRIDGE.

[Determination of] urinary calcium. C. H. COLLINGS (Chem. News, 1928, 137, 263—265).—The method described is particularly applicable where calcium oxalate is present, but fails in the rare case where sulphate is in evidence. The urine is acidified with hydrochloric and phosphoric acids, the calcium precipitated as phosphate by adding dilute ammonia, and the precipitate is then converted into oxalate, which is determined by titration with 0.05N. potassium permanganate solution. S. COFFEY.

Determination of chloride in urine and blood by conductivity titration. L. BUDAY (Biochem. Z., 1928, 200, 166—175).—The chloride content of urine, serum, and plasma is determined by conductivity titration with silver nitrate after acidification with dilute nitric acid. With whole blood after hæmolysis and acidification, an increase of conductivity is first observed on adding silver nitrate, accompanied by a shift of p_H . P. W. CLUTTERBUCK.

Volhard-Harvey method for determination of chlorides in urine. W. H. JEFFERY (J. Lab. Clin. Med., 1928, 13, 687).—The ingestion of one aspirin tablet gives a brownish-violet colour characteristic of the reagents employed. CHEMICAL ABSTRACTS.

Urinary colloids and crystalloids as solvents for uric acid. R. ASCOLI (Biochem. Z., 1928, 200, 95—107).—By determination of the extent to which addition of urine, dialysed urine, and dialysate to solutions of uric acid which had been supersaturated by warming hindered the precipitation of the acid on cooling, it is shown that normal urine and dialysate but not the dialysed urine have considerable solvent power in respect to uric acid, and this is not directly dependent on the reaction of the urine. It is suggested that this power must be ascribed to the crystalloid substances of the urine. P. W. CLUTTERBUCK.

Pernicious anæmia. IV. Relationship between corpuscular hæmoglobin and chloride contents in the anæmias. A. T. CAMERON and M. E. FOSTER (Canad. Med. Assoc. J., 1928, 18, 673—677).—In pernicious anæmia the hæmoglobin content of a given volume of red blood-corpuscles is increased and the chloride content decreased. In secondary anæmias the chlorine content is usually high, but the hæmoglobin content variable. In anæmia from *Diphyllobotrium latum* high chlorine and low hæmoglobin values were observed.

CHEMICAL ABSTRACTS.

Blood regeneration in severe anæmia. XII. Influence of ash of apricots, liver, kidney, and pineapple. F. S. ROBSCHET-ROBBINS, C. A. ELDEN, W. M. SPERRY, and G. H. WHIPPLE. **XIII. Influence of copper salts.** C. A. ELDEN, W. M. SPERRY, F. S. ROBSCHET-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1928, 79, 563—576, 577—

586).—XII. The ash of apricots, when added to the diet of dogs rendered anæmic by hæmorrhage, may cause an increased output of hæmoglobin of as much as 45 g. per 14 days; the ash of pineapple has little effect, whilst that of liver and of kidney is active, although only to about half the extent of the whole organ. Copper and iron are relatively abundant in those ashes which are of therapeutic value.

XIII.—Copper salts have a favourable influence on the regeneration of hæmoglobin in anæmic dogs, but the influence is not so marked as that of iron; combinations of the two metals are usually simply additive in effect. C. R. HARRINGTON.

Chlorine content of blood. Distribution in hæmopathological, particularly anæmic, conditions. A. EUGSTER (Z. klin. Med., 1928, 107, 224—255; Chem. Zentr., 1928, i, 2185).—A fall in the hæmoglobin content is often accompanied by a rise in the chlorine content of the whole blood; the relationship in pathological conditions is considered.

A. A. ELDRIDGE.

Blood-phosphorus in health and disease. III. Alleged value of blood-phosphorus determinations in suspected malignant disease. Blood-phosphorus distribution in anæmia, polycythæmia, and leucæmia. F. B. BYROM and H. D. KAY (Brit. J. Exp. Path., 1928, 9, 72—81).—Changes in the amount of free phosphate, phosphoric esters hydrolysed or not by phosphatases, lipin-phosphate, and total phosphate are attributable to anæmia, and are not specific for cancer. The blood-lipin-phosphorus is increased in severe obstructive jaundice. In pernicious anæmia and anæmia of nephritis, but not in polycythæmia and simple secondary anæmia, the character and amount of the phosphorus compounds of the cell are changed. Leucocytes are relatively rich in phosphorus compounds; hence in leucæmia blood-phosphorus determinations give irregular results.

CHEMICAL ABSTRACTS.

Urine of carcinomatous rats. Y. KIMURA (J. Biochem. Japan, 1928, 8, 469—494).—The fresh urine is acid; the quantity is approximately proportional to the amount of chlorine excreted. With development of the tumour the total nitrogen, ammonia-nitrogen, and uric acid-nitrogen increase, but the percentages of the two fractions decrease. During active growth the amino-nitrogen diminishes but later increases. The allantoin-nitrogen, neutral sulphur, potassium, sodium, calcium, and magnesium increase. The sulphate varies with the ammonia, and the calcium with the sulphate. It is concluded that the tumour causes an increased splitting of body protein, especially of the nucleated cells; the increased protein cleavage is accompanied by insufficient oxidation. The softening of the tumour leads to a great increase in the salt content of the urine. Simultaneous formation of protein is indicated by the diminished excretion of amino-nitrogen.

CHEMICAL ABSTRACTS.

Mineral metabolism in coeliac disease. S. V. TELFER (Glasgow Med. J., 1928, 38, 306—313).—The existence of a grossly defective absorption of mineral elements and fats is indicated.

CHEMICAL ABSTRACTS.

Degradation of dextrose and l  vulose in normal and experimentally diabetic dog's blood. E. S. TURCATTI (Compt. rend. Soc. Biol., 1928, 98, 175—176; Chem. Zentr., 1928, i, 2512).—In normal blood, 27.59% glycolysis takes place in 6 hrs.; the action is less marked in diabetic blood. The effect of addition of dextrose and of l  vulose was examined.

A. A. ELDRIDGE.

Lactacidogen in experimental pancreas diabetes. M. VON FALKENHAUSEN and H. HIRSCH-KAUFFMANN (Z. ges. exp. Med., 1927, 58, 567—577; Chem. Zentr., 1928, i, 2420).—Lactacidogen metabolism (of dogs) is not disturbed by experimental pancreas diabetes.

A. A. ELDRIDGE.

Carbohydrate changes in epilepsy. C. J. MUNCH-PETERSEN (Compt. rend. Soc. Biol., 1928, 98, 891—893; Chem. Zentr., 1928, i, 2729).—Glycosuria was sometimes observed with a blood-sugar value which normally does not lead to glycosuria; in other cases expected glycosuria was not observed.

A. A. ELDRIDGE.

Plasma-chlorides in obstructive jaundice. I. S. RAVDIN and M. E. MORRISON (Arch. Int. Med., 1928, 42, 491—499).—A consistent reduction of the plasma-chloride of dogs was found in experimental jaundice after ligation of the common duct and cholecystectomy, but not after either of these operations alone.

H. R. ING.

Pancreatic fat necrosis. F. K. HERBERT (Brit. J. Exp. Path., 1928, 9, 57—63).—Soap is formed in the necrotic areas. More than one type of crystal is observed histochemically; possibly neutral fat, fatty acid, and soaps are all present. Analysis indicates acid hydrolysis of the fat, with little formation of soap.

CHEMICAL ABSTRACTS.

Significance of electrolytes for the organism. Parturient paresis in cows. B. SJOLLEMA (Biochem. Z., 1928, 200, 300—308).—The calcium, inorganic phosphorus, potassium, cholesterol, carbamide, chloride, dextrose, total acetone contents, and the alkaline reserve of the serum of cows in milk-fever, of healthy cows in full lactation or freshly calved, and of young animals are tabulated. The calcium and inorganic phosphorus contents of cows in milk-fever are abnormally low, the potassium content is either normal or high, the carbamide and acetone contents are often somewhat higher than normal, whilst the blood-sugar shows no regular variation.

P. W. CLUTTERBUCK.

Creatine metabolism in the brain of pigeons in hunger and in polyneuritis. T. LJUBARSKAJA (Pfl  ger's Archiv, 1928, 218, 627—634; Chem. Zentr., 1928, i, 2730—2731).—The spastic form of polyneuritis is associated with a diminution of total nitrogen and an increase of creatine in the brain; the paralytic form is associated with a greater diminution and smaller increase, respectively. In the chronic form and in hunger there is a small increase of creatine, the total nitrogen remaining unchanged.

A. A. ELDRIDGE.

Avitaminosis. X. Formation of acetaldehyde in the muscle of normal vitamin-lacking

and fasting pigeons. A. PALLADIN and A. UTEVSKI. XI. Influence of scurvy and fasting on the chemical composition, especially on the creatine content, of brain. A. PALLADIN and E. SAVRON (Biochem. Z., 1928, 200, 108—114, 244—249).—X. Acetaldehyde (4—9 mg./100 g. tissue) is formed during autolysis for 18 hrs. of the muscle (pectoral) of normal pigeons. The amount is decreased during avitaminosis and starvation. When boiled tissue of normal animals is added to that of starving or vitamin-lacking pigeons, the formation of aldehyde rises to normal amounts.

XI. The brain of guinea-pigs contains considerable amounts of creatine, the cerebellum being richer than the hemispheres. During scurvy the cerebellum and hemispheres become richer in water and total nitrogen and poorer in phosphorus, but the creatine content remains constant. P. W. CLUTTERBUCK.

In vitro respiration of the tissues of beri-beri pigeons. M. GUGLER (Biochem. Z., 1928, 200, 340—350).—The respiration, measured by Barcroft's method, of the breast muscle, before and after aqueous extraction, of 13 normal and 13 beri-beri pigeons and the effect of phosphate buffering and of alterations of the interval between the death of the animal and the determination of the respiration of the muscle are investigated. Washed muscle gave more constant results than the fresh tissue. The oxygen consumption of the tissue of the beri-beri animals is less than that of the washed or fresh tissue of normal pigeons, the reduction being with washed muscle about 25% and with fresh muscle about 10%. With phosphate buffering, the respiration values are higher than with hydrogen carbonate buffering and the difference between the respiration of the tissue of normal and beri-beri animals is greater. Washed muscle, however, respire equally well in both buffer solutions. The oxygen consumption is not strictly proportional to the weight of tissue and, to obtain constant results, the proportion of tissue to total fluid is important. The interval between the death of the animal and the beginning of the respiration experiment causes a decrease of respiration, but this is not proportional to the length of the time interval.

P. W. CLUTTERBUCK.

In vitro tissue respiration. E. SENNHAUSER (Biochem. Z., 1928, 200, 351—355).—The dinitrobenzene method of Lipschitz and the Barcroft method for the determination of tissue respiration are comparatively investigated. Comparable results are obtained by the two methods with fresh tissue of both healthy and beri-beri animals, but with washed muscle the increase of respiration on adding succinate measured by the dinitrobenzene method is only from the low value of washed up to that of fresh tissue, whereas when determined under the same conditions by the Barcroft method it is increased to 3—5 times that of fresh muscle.

P. W. CLUTTERBUCK.

Differentiation between normal and syphilitic sera by means of organic colloids. R. DOUBIS and J. BECK (Compt. rend., 1928, 187, 683—686).—When one volume of 2% sodium oleate (limpid solution at 45  ) and one of phosphoric acid (0.23%) are added to one volume of normal serum, the mixture

remains perfectly clear. Use of syphilitic serum gives opalescence within five minutes of mixing.

G. A. C. GOUGH.

Intermediate metabolism of rats infected with trypanosomes. G. SCHEFF (Biochem. Z., 1928, 200, 309—330).—The disturbance of carbohydrate, protein and fat metabolism, and of the acid-base equilibrium in trypanosomiasis are investigated in rats. The chief substances utilised by trypanosomes are carbohydrate and oxygen. The glycogen reserve is therefore gradually used up and a hypoglycæmia results which adrenaline cannot alleviate. Smaller disturbances of protein metabolism also occur, due partly to protein utilisation by the trypanosomes and partly to secondary disturbance of the liver. The utilisation of part of the available oxygen supply by the infecting organisms and the anæmia resulting from infection lead to deficient oxygen supply and a type of asphyxia. Both this and the metabolic changes result in acidosis. P. W. CLUTTERBUCK.

Amino-acids in blood in tuberculosis. L. HANTSCHMANN and M. STEUBE (Klin. Woch., 1928, 7, 637—638; Chem. Zentr., 1928, i, 2626).

A. A. ELDRIDGE.

Sulphuric acid reaction in deproteinised uræmic serum. K. MACHOLD (Wien. klin. Woch., 1928, 41, 447—449; Chem. Zentr., 1928, i, 2636).—In the determination of indicanæmia the filtrate (1 c.c.) of a mixture of the serum with 20% trichloroacetic acid solution (1 : 1) is treated, without mixing, with concentrated sulphuric acid (1 c.c.); a reddish-blue coloration at the interface reaches maximal intensity in 2 min. The colour can be extracted with amyl alcohol or chloroform, but not with ether.

A. A. ELDRIDGE.

Metabolism of mammalian tissues in different media. I. Respiration of explantates of rats' hearts, which had grown in the plasma of normal animals and of animals fed on a diet deficient in vitamin. K. BÖRNSTEIN (Biochem. Z., 1928, 200, 176—183).—The respiration of explantates of rat's heart grown in the plasma of animals fed on a diet free from vitamin-B was found to be decreased to less than one half of that of explantates of hearts of animals receiving a normal diet.

P. W. CLUTTERBUCK.

Development and metabolism of the kidney. P. GYÖRGY, W. KELLER, and T. BREHME (Biochem. Z., 1928, 200, 356—366).—The anaërobic glycolysis (Q_{N}) of the cortical tissue of the kidney both in young and adult animals is small but of the medullary tissue is 4—5 times as great, whilst the reverse is true of the respiration, the value Q_{O_2} for the cortical tissue being 4—5 times as great as for the medullary tissue. Warburg's excess fermentation $U = Q_{\text{N}} - 2Q_{\text{O}_2}$ is thus for cortical tissue negative, as is usual for all normal tissue except the retina, but for the medullary tissue is positive.

P. W. CLUTTERBUCK.

Acid-base relationships in the organism. Observations on a human case after removal of the stomach. P. ASCHMARIN and E. MARTINSON (Biochem. Z., 1928, 199, 307—325).—A woman from whom the stomach had been removed on account of

cancer was fed on 3 diets of which the first contained a moderate excess of acid (30 c.c. of *N*-acid), the second an excess of alkali (75 c.c. of *N*-alkali), and the third a large excess of acid (65 c.c. of *N*-acid). On the first diet a reduced ammonia value (Hasselbalch) was observed. On going over to the alkaline diet the p_{H} of the urine fell, and whilst on this diet very high values for the urinary acid-base difference were noted. After eating, the carbon dioxide tension of the alveolar air fell. These results are discussed in reference to the lack of normal gastric secretion.

H. W. DUDLEY.

Parallelism between creatinine excretion and basal metabolism. TAKAHIRA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551). CHEMICAL ABSTRACTS.

Availability of disulphide acids in replacing cystine of diet. II. α -Dihydroxy- β -dithiodipropionic acid. Oxidation of disulphide acids in animal organism. B. D. WESTERMAN and W. C. ROSE (J. Biol. Chem., 1928, 79, 413—421, 423—428).—Dithiodiglycollic acid, β -dithiodipropionic acid, and α -dihydroxy- β -dithiodipropionic acid cannot replace cystine in the diet of growing rats, although all these acids are readily oxidised in the organism of the rabbit.

C. R. HARRINGTON.

Nitrogen metabolism of chicken embryos. H. TARGONSKI (Bull. Acad. Polonaise, 1927, B, 1277—1300).—Analyses have been made on the amniotic and allantoic fluids from the chicken embryo with reference to the variation and distribution of the nitrogenous products of metabolism during development. The nitrogen metabolism of the developing embryo differs from that of the adult bird in the relatively small percentages of uric acid present in these two fluids. During the earlier stages of development the products of nitrogen metabolism accumulate in the amniotic fluid.

E. A. LUNT.

Detoxication process in the foetal organism. M. TAKAHASHI (Z. physiol. Chem., 1928, 178, 291—293).—The elimination of toxic substances by the embryo of the hen's egg was studied. There was a marked increase of ethereal sulphate in the allantoic liquid with the progress of incubation.

J. H. BIRKINSHAW.

Detoxication process in the foetal organism. II. Synthesis of ornithuric acid in the incubated hen's egg after injection of benzoic acid. M. TAKAHASHI (Z. physiol. Chem., 1928, 178, 294—297).—Benzoic acid injected into fresh eggs as sodium benzoate (0.005 g. per egg) is shown to be present as ornithuric acid in the allantoic liquid after 14 days' incubation, all the free benzoic acid having disappeared.

J. H. BIRKINSHAW.

Formation of hexone and purine bases during incubation of the hen's egg. J. SAGARA (Z. physiol. Chem., 1928, 178, 298—301).—Hens' eggs after 14 days' incubation showed a considerable increase in arginine and particularly in lysine content. Purine bases were also formed.

J. H. BIRKINSHAW.

Variations in metabolism during fast and on resumption of feeding. H. TAKAHIRA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment.,

1927, 15, 481—504, 524—551).—On resumption of feeding a large amount of nitrogen was fixed.

CHEMICAL ABSTRACTS.

Value of small quantities of whole cow's milk when fed to pigs. A. H. BLISSETT and J. GOLDING (J. Agric. Sci., 1928, 18, 642—648).—The addition of $\frac{1}{2}$ pint of full-cream milk per day to a complete basal diet for pigs increased the live weight of the animals from 8 to 10%, and decreased the ratio of dry matter consumed to live weight increase. When extracted soya-bean meal was included in the basal ration the effect of the added milk was slightly less marked.

A. G. POLLARD.

Digestibility trials with poultry. IV. Digestibility of certain varieties of oats. V. Digestibility and feeding value of Bulrush millet. VI. Influence of the size of the ration on its digestibility. E. T. HALMAN (J. Agric. Sci., 1928, 18, 634—641, 766—771).—IV. Feeding experiments with fowls show that Grey Winter oats have a better nutrient value than Black Bountiful or Scotch Potato oats. The preference is associated with the fibre content, the thinner-husked varieties giving the better results.

V. Bulrush millet (*Pennisetum typhoideum*) is a suitable feeding-stuff for poultry.

VI. The digestibility of nutrients is not materially affected by variations in the amount of food supplied.

A. G. POLLARD.

Effect of the degree of polishing of rice on its absorption. SUGIMOTO, HIGUCHI, MOMOYDEA, and TANAKA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551).—None of the constituents is completely eliminated; nitrogen decreases slightly, fat, ash, and fibre decrease considerably, whilst the phosphorus varies. The properties of oryzanin from common and glutinous rice are compared.

CHEMICAL ABSTRACTS.

Influence of methods of cooking on the absorption of rice. SUGIMOTO, FUJIMAKI, MOMOYEDA, TANAKA, and YASUDA (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551).

CHEMICAL ABSTRACTS.

Calorific value of soluble carbohydrates in feeding-stuffs. L. A. ALLEN (J. Agric. Sci., 1928, 18, 691—701).—Considerable variations exist in the calorific values of carbohydrates of feeding-stuffs, and the values are generally higher than those usually assigned to the simpler carbohydrates of known composition. The values obtained varied from 3800 to 4800 g.-cal. per g. with an average of 4310 g.-cal. The values for crude fibre were also higher.

A. G. POLLARD.

Nutritive value of linseed cake. J. STEWART (J. Agric. Sci., 1928, 18, 702—703).—The starch equivalent of linseed meal, calculated by means of Wood's curves from the experimental data of one lamb fed on linseed meal only, was in close agreement with Kellner's value.

A. G. POLLARD.

Effect of variations in vitamins, protein, fat, and mineral matter in the diet on the growth and mortality of eastern brook trout. C. M. McCAY, F. C. BING, and W. E. DILLEY (Trans. Amer. Fish. Soc., 1927, 57, 240—250). CHEMICAL ABSTRACTS.

Growth of black-beetles (*Periplaneta orientalis*, L.) and of cockroaches (*Blattella germanica*, L.) on artificial and on incomplete diets. J. ZABIŃSKI (Acta Biol. Exp., Warsaw, 1928, 2, 123—163).—The length of the normal development cycle of the black-beetle is 12 months; of the cockroach 3 months. More than one third of this time these animals grow equally rapidly whether on a normal or a "synthetic" diet. Black-beetle larvæ fed on synthetic diets attain only one third of their normal weight at the end of the period usually required for full development, and then die. If, however, they are put on an artificial diet at about one half the growth-period, they are able to attain sexual maturity. Cockroaches are able to pass through the entire growth-cycle on a synthetic diet, even when the only source of nitrogen given is glycine. They exhibit, however, symptoms of avitaminosis, such as matt-surfaced chitin, lack of mobility, small size, and sterility. The rate of growth can be controlled by limiting the nitrogen supply, and both of these animals are able to maintain their weight on a nitrogen-free diet over periods of time equal to those of the entire post-embryonic cycle. As soon as nitrogenous food-stuffs are again given, their development recommences at the point at which it was arrested, and normal adult insects are obtained. These animals cannot maintain life on a purely protein diet.

R. TRUSZKOWSKI.

Calcium metabolism with diet rich in vitamin but deficient in mineral constituents. H. ZIMMER (Z. ges. exp. Med., 1927, 58, 362—369; Chem. Zentr., 1928, i, 2420).—A negative calcium balance was observed; no definite relation between excreted calcium and the urinary C : N coefficient was found.

A. A. ELDRIDGE.

Rôle of calcium in the nutrition and some biological processes of the animal organism. A. POPOV (Arch. Sci. Biol. Moscow, 1927, 27, 377—391; Chem. Zentr., 1928, i, 2185).—Guinea-pigs deprived of vitamin-C show no disturbance of blood-calcium. Experiments with rats indicate the significance of lipoids in calcium assimilation. Administration (oral or subcutaneous) of calcium chloride in milk did not affect the calcium equilibrium in health.

A. A. ELDRIDGE.

Formation of glycogen in the wall of the intestine. K. LANG (Biochem. Z., 1928, 200, 90—94).—The intestinal wall has the power of synthesising glycogen from dextrose and much less readily from lævulose. In the depancreatized dog, the power is retained, but to a much smaller extent. Insulin assists the synthesis.

P. W. CLUTTERBUCK.

Metabolism of hearts of cold-blooded animals. Dextrose utilisation with varying amounts of work. G. EISMAYER and H. QUINCKE (Z. Biol., 1928, 88, 139—144).—A preparation of the frog's ventricle allows simultaneous determination of the work done and the dextrose consumed. The heart uses dextrose in amount increasing with the time, but the large and unknown amounts of reserve glycogen prevent accurate comparison of metabolism with the output of work.

E. BOYLAND.

Sugar metabolism. Lactose, galactose, and xylose. J. G. BLANCO (J. Biol. Chem., 1928, 79, 667—672).—After oral administration to normal rabbits, lactose and galactose failed to appear in the blood, whilst xylose was present for a prolonged period; after subcutaneous injection, lactose caused an increase in lactose and a more marked and persistent increase in dextrose of the blood, galactose showed an initially high concentration in the blood which steadily fell and was accompanied by little change in the dextrose, and similar, but less uniform results were obtained with xylose. After intravenous injection of all three sugars a simultaneous increase in the dextrose of the blood was observed.

C. R. HARRINGTON.

Coefficient of diffusion of lactic acid through muscle. G. P. EGGLETON, P. EGGLETON, and A. V. HILL (Proc. Roy. Soc., 1928, B, 103, 620—628).—The coefficient of diffusion of lactic acid through muscle is not independent of the state of fatigue of the muscle. This difference is not due simply to concentration of lactic acid; a muscle after heat rigor with a high concentration of lactic acid shows a higher diffusion constant. It is likely that the change in diffusion constant with fatigue is due to an alteration in the lymph inter-spaces of the tissues.

B. A. EAGLES.

Concentration and diffusion of phosphate in muscle. G. STALLA (J. Physiol., 1928, 66, 19—31).—Inorganic phosphate is able to pass freely by diffusion into or out of a muscle immersed in Ringer's solution containing phosphate. The diffusion constant is the same for a resting or a fatigued muscle and is nearly the same for a muscle in rigor. A hypothesis calling for a change in the permeability to phosphate of the muscle fibres is unnecessary.

B. A. EAGLES.

Inorganic phosphate content of resting mammalian muscle. J. SACKS and H. A. DAVENPORT (J. Biol. Chem., 1928, 79, 493—498).—The muscle of the anaesthetised animal was frozen and minced, and the proteins were removed by treatment with trichloroacetic acid at 0°; the inorganic phosphate in the filtrate was precipitated with magnesia mixture and then determined by the method of Fiske and Subbarov (A., 1926, 443). By this method the inorganic phosphate content of the resting muscle of various mammals was found to be close to 20 mg. %.

C. R. HARRINGTON.

Muscular contraction. I. Lactic acid content. H. A. DAVENPORT, H. K. DAVENPORT, and S. W. RANSON (J. Biol. Chem., 1928, 79, 499—505).—The lactic acid content of muscles in a state of permanent contraction resulting from tetanus intoxication is not markedly different from that of normal muscles.

C. R. HARRINGTON.

Lactic acid formation in muscular contraction. O. MEYERHOF (Z. physiol. Chem., 1928, 178, 306—310).—A comment on the work of Embden and Lehnartz (this vol., 1049).

J. H. BIRKINSHAW.

Lactic acid formation in muscular contraction. G. EMBDEN and E. LEHNARTZ (Z. physiol. Chem., 1928, 178, 311—315).—A reply to Meyerhof (preceding abstract).

J. H. BIRKINSHAW.

Feeding rats with oils and fats. E. FRIEDBERGER and S. SEIDENBERG (Biochem. Z., 1928, 200, 289—297).—By feeding growing rats with oats and bread mixed with olive and cod-liver oils, considerable inhibition of growth occurs when compared with rats fed on the same diet but without addition of oil. Lard and butter had a similar but smaller effect.

P. W. CLUTTERBUCK.

Action of formaldehyde on lecithin. Formation of methylated compounds in the organism. W. R. WITANOWSKI (Acta Biol. Exp., Warsaw, 1928, 2, 61—72).—Further quantities of choline are produced by the action of formaldehyde on commercial lecithin containing cephalin, pointing to the partial conversion of the latter into lecithin by methylation of its free amino-group. This increase in choline content varies from 10 to 53% of the original quantity. The optimum pH of the reaction lies between 5 and 7. The quantity of additional choline produced does not correspond with the number of free amino-groups present in commercial lecithin, indicating either that the reaction does not proceed to completion or that amino-group-containing impurities other than cephalin are present. The addition of calf-liver extract does not increase the yields of choline obtained.

R. TRUSZKOWSKI.

Relation of bile acids to food cholesterol. K. LOEFFLER (Z. physiol. Chem., 1928, 178, 186—191).—Cholic acid when fed to mice and rabbits along with cholesterol produces a much more marked accumulation of cholesterol in the liver than does deoxycholic acid.

J. H. BIRKINSHAW.

Origin of bile acids. IV. Researches in dogs with complete bile fistula and reversed Eck fistula. E. ENDERLEN, S. J. THANNHAUSER, and M. JENKE (Arch. exp. Path. Pharm., 1928, 135, 131—136).—The technique previously described (this vol., 788, 789) has been modified. A dog is employed having a reversed Eck fistula as well as a complete bile fistula so that cholesterol injected intravenously passes through the liver and is not immediately taken up by the lung, as is the case when the animal has no reversed Eck fistula. Under these conditions it is found that the production of bile acids is not increased by the administration either of cholesterol or of the oxidation product of cholesterol, but that it is very definitely increased after administration of *allo*-cholesterol. It is suggested that *allo*-cholesterol may be an intermediate product between cholesterol and the bile acids and that this compound may be present in animal tissue.

W. O. KERMACK.

Origin of bile acids. V. Is there a relation between breakdown of fatty acids and formation of bile acids? E. ENDERLEN, S. J. THANNHAUSER, and A. DISTL (Arch. exp. Path. Pharm., 1928, 135, 137—142).—The administration of triolein intraperitoneally or of oleic acid intravenously to a dog with complete bile fistula does not increase the production of bile acids. There is no decrease in the production of bile acids when the spinal column is sectioned in such a way that the mobilisation of fat from the peripheral depôts is inhibited.

W. O. KERMACK.

Relation between bile and glycogen formation in rabbit's liver. E. FORSGREN (Skand. Arch. Physiol., 1928, 53, 137—151; Chem. Zentr., 1928, i, 2422).—A high glycogen content of rabbit's liver is associated with a low content of bile constituents. The function of the liver is periodic, with a glycogen maximum in the morning and minimum later. The results are considered in relation to the general problems of metabolism. A. A. ELDRIDGE.

Effect of alcohol on the absorption of dextrose. II. N. EDKINS and M. M. MURRAY (J. Physiol., 1928, 66, 102—108).—Alcohol accelerates the rate of absorption of dextrose from the alimentary canal into the blood. B. A. EAGLES.

Action of glucosone on animals. P. T. HERRING and A. HYND (J. Physiol., 1928, 66, 267—273).—The injection of glucosone produces in mice, white rats, rabbits, guinea-pigs, and cats a train of symptoms which closely resemble, but are not identical with, those which follow the injection of insulin. It is suggested that glucosone arises from the action of insulin on the blood-dextrose. Glucosone may be regarded as an important intermediate substance in carbohydrate metabolism. B. A. EAGLES.

Influence of arsenic on the magnitude of the carbon and oxidation quotients of the urine. L. KOROWITSKY (Biochem. Z., 1928, 199, 366—376).—Oral or subcutaneous administration of therapeutic or toxic doses of arsenic in inorganic or organic combination usually leads to increase of the carbon and oxidation quotients of the urine, but, exceptionally, in the case of toxic doses the quotients sometimes decrease and in the case of therapeutic doses, sometimes remain unaltered. The alterations in the two quotients generally run parallel. Occasionally, although the administration of arsenic continues, the quotients cease to increase or even fall. W. MCCARTNEY.

Absorption and excretion of boric acid in man. L. KAHLENBERG and N. BARWASSER (J. Biol. Chem., 1928, 79, 405—408).—Boric acid can be detected in the urine within 1 min. after immersion of the feet in a saturated solution of the acid at 45°. C. R. HARRINGTON.

Effect of administration of iron on the iron reserve. C. S. WILLIAMSON and P. EWING (Arch. Int. Med., 1928, 42, 600—606; cf. this vol., 199).—96 young rats were fed on a standard caseinogen diet, and an equal number received a similar diet with addition of ferric citrate. The average hæmoglobin concentration of the latter group after 90 days was still equal to that of the former. Ferric citrate was shown not to increase the iron reserve available for hæmoglobin formation by bleeding both groups at this date, when it was found that the hæmoglobin regeneration after 28 days was approximately equal in the two groups. H. R. ING.

Toxicology of lead and its compounds. VI. P. W. DANCKWORTT and E. JÜRGENS (Arch. Pharm., 1928, 266, 492—501).—A study has been made of the distribution of lead in the organs, and particularly the bones of the dog. The bones were dissolved in nitric acid, the solution was evaporated, and the residue

ashed. The lead was precipitated as chromate. In this way 2 mg. of lead per 100 g. of bone could be accurately determined. The greater part of the lead was found in the bones, flat bones having a higher content than round bones, but where insufficient time had elapsed for all the lead to be carried to the bones, relatively large amounts were also discovered in the liver, heart, and brain. The lead content of ordinary water has no effect on the life of fish. S. COFFEY.

Fatal case of acute lead poisoning. A. BRÜNING and B. KRAFT (Arch. Pharm., 1928, 266, 501—504).—In cases of lead poisoning chemical examination of the organs is essential. When administered orally, lead is found chiefly in the stomach and intestines. Fühner's method of analysis (A., 1918, ii, 240) was employed. S. COFFEY.

[Detection of chronic lead poisoning.] TIMM (Deut. Z. ges. gerichtl. Med., 1928, 11, 185—188; Chem. Zentr., 1928, i, 2434).—A spectrographic method of examining the constituents of organs is described. Lead is retained for a long time by the living organism. A. A. ELDRIDGE.

Determination of silver in biological fluids and tissues. [Disappearance of silver from, and re-appearance in, the blood of dogs.] E. STERKIN (Biochem. Z., 1928, 199, 392—398).—Organic matter in the material under investigation is destroyed, any chloride present being removed as hydrogen chloride by nascent hydrogen generated from zinc and acid. The silver is then determined volumetrically by the thiocyanate method. When colloidal silver is administered intravenously to dogs the metal at once disappears from the blood and cannot be detected by analysis except when the dose is sufficient to produce poisoning or death. Silver is then always found in the blood. The time at which the symptoms of poisoning appear always coincides exactly with that at which silver can first be detected. In cases where the animal, although poisoned, does not die, the silver again disappears from the blood. W. MCCARTNEY.

Detection of uranium and localisation of uranium in the animal organism after uranium poisoning. H. EITEL (Arch. exp. Path. Pharm., 1928, 135, 188—193).—The tissue is incinerated and the residue is then either treated with nitric acid and the liquid evaporated, or heated with borax to 800—900°. Both these methods restore the fluorescence of the uranium present, which is then observed in ultra-violet light. After fatal poisoning with uranium the metal is present in the kidney cortex but not in the medulla or in any other organ. W. O. KERMAK.

Toxicity of anæsthetics containing bromine and chlorine. G. H. W. LUCAS (J. Pharm. Exp. Ther., 1928, 34, 223—237).—Experiments on rabbits indicate that the administration of anæsthetics containing bromine is followed by the presence of bromides in the liver, and consequent damage to this and other tissues. Experiments *in vitro* have shown that liver pulp can decompose chloroform and bromoform with liberation of the corresponding halogen ion. E. A. LUNT.

Micro-chemical detection in urine of some derivatives of barbituric acid. O. EHRLSMANN and

G. JOACHIMOGLU (Biochem. Z., 1928, 199, 272—275).—The barbituric acid derivative, extracted from urine in the usual way, is heated electrically at 70—130° for 8—20 hrs. in a micro-sublimation apparatus the temperature in which is automatically controlled to within $\pm 2.5^\circ$. The sublimate is identified by their appearances, which are quite distinct, but the pure substance is always sublimed at the same time and under the same conditions in the same apparatus. For "veronal," "luminal," and "dial" the lowest amount detectable is 0.5 mg. W. McCARTNEY.

Mechanism of action of hydrocyanic acid; functional significance of glutathione. I. H. HANDOVSKY (Arch. exp. Path. Pharm., 1928, 135, 143—154).—In the muscles of rabbits poisoned by hydrocyanic acid there is observed an increase of free glutathione and also of lactic acid. At a later stage the total carbohydrate content is increased, but is finally decreased, the decrease occurring in the glycogen fraction, whilst the lower carbohydrates are increased. The glutathione content of the livers of guinea-pigs shows a seasonal variation. W. O. KERMACK.

Action of histamine on the cholesterol content of the blood of normal and splenectomised dogs. A. TANGL and S. RECHT (Biochem. Z., 1928, 200, 190—193).—The cholesterol content of the blood of normal dogs on injection of histamine at first rises and then falls to the normal value, whereas that of splenectomised dogs at first falls and then rises to normal values. P. W. CLUTTERBUCK.

Chloride, base, and nitrogen content of gastric juice after histamine stimulation. W. S. POLLAND, A. M. ROBERTS, and A. L. BLOOMFIELD (J. Clin. Invest., 1928, 5, 611—637).—The titratable acid is increased. CHEMICAL ABSTRACTS.

Effect of sympathetic and parasympathetic poisons on the content of creatine in muscle. H. AKATSUKA (J. Biochem. Japan, 1927, 8, 57—77).—Formation of creatine is increased by adrenaline and decreased by ergotoxin. Physostigmine accelerates the transformation of creatine into creatinine. Curarised animals are not affected. In homeothermic animals cooling causes over-secretion of adrenaline and an increased creatine content of muscle. In poikilothermic animals the muscle-creatine content is not appreciably influenced. CHEMICAL ABSTRACTS.

Myrtillin. F. M. ALLEN (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1927, 81, 462).—Myrtillin reduces adrenaline hyperglycemia and accelerates oxygen consumption after carbohydrate ingestion in normal and diabetic subjects.

CHEMICAL ABSTRACTS.

Blood-sugar level in nicotine poisoning. A. I. BURSTEIN and J. D. GOLDENBERG (Biochem. Z., 1928, 200, 115—125).—Acute nicotine poisoning with small, medium, and large doses is accompanied by increase of blood-sugar occurring in 15—30 min. after injection of nicotine, reaching its maximum in the first hour and decreasing to normal again in 3—3.5 hrs. No decrease of glycolysis could be detected. In chronic nicotine poisoning, no permanent increase in blood-sugar occurred. The increase is conditioned by an accompanying increased secretion of adrenaline. P. W. CLUTTERBUCK.

Digitalis uptake and digitalis action in warm-blooded animals. I. Effective dose of various digitalis glucosides for the heart. H. WEESE (Arch. exp. Path. Pharm., 1928, 135, 228—244).—The ratio of the glucoside taken up by the heart to that taken up by the rest of the body has been determined in the cases of digitoxin, strophanthin, and scillaren (B) and it appears that the heart takes 4—9% of that circulating in the blood. Digitoxin and strophanthin are not destroyed by blood, but scillaren is hydrolysed by the blood and heart. The mammalian heart can accumulate the same amount of glucoside independent of the concentration and quantity used. The rate of action is a simple linear function of the concentration of the glucoside.

W. O. KERMACK.

Intensity of the action of quinine salts in relation to their fluorescence. E. MILANESI (Arch. Farm. speriment., 1928, 46, 29—32, 33—43).—The exposure of solutions of quinine salts to ultra-violet rays has no effect on the paralysing influence of these solutions towards *Paramaecium* and *Vorticella*. That quinine hydrogen sulphate is more active in this respect than the other quinine salts tested may be due to its more marked fluorescence.

T. H. POPE.

Cardiovascular action of tropinonesemicarbazone and tropinone and ψ -pelletierine oximes. R. HAZARD and J. LÉVY (Compt. rend., 1928, 187, 676—678).—Whilst tropinonesemicarbazone possesses an enhanced cardiovascular action similar to that of the parent ketone, the corresponding oxime and that of ψ -pelletierine are devoid of such action.

G. A. C. GOUGH.

Action of ultra-violet rays on the migration of pigment from the blood of normal and splenectomised dogs. G. FARKAS and H. TANGL (Biochem. Z., 1928, 200, 184—189).—Irradiation inhibits excretion of pigment by normal animals. Similar inhibition is obtained in splenectomised animals.

P. W. CLUTTERBUCK.

Activator of malt amylase. S. NISHIMURA (Biochem. Z., 1928, 200, 81—89).—The malt amylase complex does not consist of two enzymes but of one enzyme, amylase, which can attack starch slowly, and an activator which accelerates the liquefaction and hydrolysis of starch. The activator is inactivated at pH 3.0, but regains its activity at 7.4, and, whilst the enzyme is considerably injured at 70°, the activator is quite stable at that temperature.

P. W. CLUTTERBUCK.

Invertase. E. CANALS and (Mlle.) P. GOMBERT (Bull. Soc. chim., 1928, [iv], 43, 1137—1144).—Invertase, after precipitation with alcohol, contains less magnesium and exhibits diminished activity in neutral or acid solution. The activity is partly restored by the addition of magnesium ions (as sulphate). Dialysed invertase, almost entirely free from electro-positive magnesium, contains non-dialysable electro-negative magnesium, which migrates with and carries the same kind of charge as the enzyme. Magnesium forms an integral part of the invertase micelle.

R. BRIGHTMAN.

Stereochemical specificity of ketone-aldehyde mutase. C. NEUBERG and E. SIMON (Biochem. Z.,

1928, 200, 468—472).—Under the same experimental conditions *Mucor javanicus* converts methylglyoxal into *D*-lactic acid, whilst *M. stolonifer* yields *DL*-lactic acid.

P. W. CLUTTERBUCK.

Decomposition of β -hydroxybutyric acid by liver enzymes. I. Preparation and properties of the enzyme. Detection of the products of decomposition. II. Oxidation intensity of the system. J. KÜHNAU (Biochem. Z., 1928, 200, 29—60, 61—80).—I. A method is described for the preparation of an enzyme solution free from protein which can oxidise β -hydroxybutyric acid, the action taking place both aerobically and anaerobically and being activated by methylene-blue without decolorisation occurring. *D*- β -Hydroxybutyric acid is oxidised 3 to 4 times as quickly as the *L*-isomeride. The following oxidation products were detected: aldol, acetoacetic acid, α -butylene glycol, acetaldehyde, succinic, fumaric, and malic acids, and traces of acetic and pyruvic acids. The importance of this work in regard to the possible conversion of fat into carbohydrate is discussed.

II. With the help of Clark's indicator method, the intensity of oxidation at p_H 7 of the enzyme system was determined. Under anaerobic conditions, the reduction-oxidation potential is not constant, but decreases in 10—15 hrs. from r_H 23 to a constant final value of r_H 17.6—17.7, the time taken to attain this value being longer the longer is the contact of the enzyme extract with oxygen before the experiment. The influence of aldol on the oxidation intensity is investigated. Methylene-blue is not reduced by the enzyme-hydroxybutyric acid system, since its potential is lower than that of the enzyme system, but the reduction-oxidation intensity of this dye is responsible for an increase in the oxidation of the acid.

P. W. CLUTTERBUCK.

Properties of emulsin prepared twenty-three years ago. M. BRIDEL and (MLLE.) M. DESMAREST (Bull. Soc. Chim. biol., 1928, 10, 1056—1060).—See this vol., 1157.

Enzymic proteolysis. II. P. RONA and E. MISLOWITZER (Biochem. Z., 1928, 200, 152—165).—During peptic digestion of caseinogen the breakdown into large fragments without increase of amino-nitrogen previously observed (this vol., 923) during the early stages of tryptic digestion does not occur. More prolonged hydrolysis does result in breakdown, but the amino-nitrogen appearing is entirely present in the non-colloidal fraction.

P. W. CLUTTERBUCK.

Specificity of animal proteases. XIV. Structural requirements of the specific fission of proteolytic substrates. Specificity of trypsin, trypsin-kinase, and intestinal erepsin. E. WALDSCHMIDT-LEITZ, W. KLEIN, and A. SCHÄFFNER (Ber., 1928, 61, [B], 2092—2096; cf. this vol., 673).—Observations are recorded of the action of trypsin, trypsin-kinase, and intestinal erepsin on benzoyl-glycylglycine, benzoylalanyldicarboxyleucine, bromo- α -hexoyl-diglycine and -glycyltyrosine, chloroacetyl-phenylalanine and -tyrosine, carbethoxyglycyltyrosine, benzoylglycyltyrosine, 2-naphthalenesulphonyl-glycyltyrosine, -tyrosylglycine, and -tyrosine, phenyl-

alanylarginine, and histidylglycine. The previous hypothesis (*loc. cit.*) that a certain electronegative character of the substrate is necessary for its hydrolysis by trypsin and that a free carboxy-group in the former is necessary for addition of the enzyme is confirmed, particularly by the behaviour of the halogenoacyl compounds which are not attacked by erepsin. It is remarkable that the hydrolytic activity of trypsin is greatly increased after activation of the enzyme by enterokinase, the effect depending probably on a change in the mechanism of the reaction. The hypothesis that dipeptides occupy a peculiar position among proteolytically hydrolysable substrates and that they must be regarded as specific substrates of erepsin whatever is the nature of the amino-acids from which they are derived (*loc. cit.*) cannot be completely maintained, since glutamyltyrosine and phenylalanylarginine are appreciably attacked by pancreatic trypsin.

H. WREN.

Influence of bile acids on nuclease action in the intestine and liver. T. OKAMURA (J. Biochem. Japan, 1928, 8, 391—396).

Crystalline urease. III. Variations in Jack bean meal. J. B. SUMNER and R. G. HOLLOWAY (J. Biol. Chem., 1928, 79, 489—492).—Crystalline urease cannot be obtained by the author's method (A., 1926, 1061, 1176) unless the dilute acetone extract of the Jack bean meal contains more than 7 units of the enzyme per c.c.; certain samples of meal have been encountered from which dilute acetone and alcohol fail to extract the enzyme in high concentration, and these are useless for the preparation of the crystalline material.

C. R. HARRINGTON.

Influence of ions on action of urease. E. M. MYSTKOWSKI (Acta Biol. Exp., Warsaw, 1928, 2, 211—224).—The influence of a number of sodium salts on the action of urease on urea was studied. Where inhibition takes place this is proportional to the concentration of salt added, and inversely proportional to the concentration of urease present. Certain salts which at low concentrations accelerate the action of urease in every case retard its action at higher concentrations. In unbuffered solutions the influence of the salts used, at molecular concentrations, is in the order of intensity acetate > sulphate > iodide > thiocyanate > tartrate > citrate > nitrate > chloride, whilst in buffered solutions the order is acetate > sulphate > iodide > thiocyanate > chloride > nitrate > citrate > tartrate. The influence of fluoride is specific, the inhibition curve obtained by adding increasing concentrations of this salt being of the adsorption type, pointing to the inactivation of urease by adsorption of fluoride on its surface.

R. TRUSZKOWSKI.

Action of uricase. Properties of uricase. S. J. PRYZLECKI and R. TRUSZKOWSKI (Compt. rend. Soc. Biol., 1928, 98, 789—790, 790—792; Chem. Zentr., 1928, i, 2725).—It is not possible partly to deactivate uricase. It is inactivated by mercurous chloride, sodium fluoride, and alcohol.

Uricase is an oxidising enzyme, probably with a heavy metal as active agent. Colloidal and active substrates are differentiated. Uricase contains sulphur, nitrogen, and traces of phosphorus; it has

no reducing properties. Solutions give faintly the biuret, Millon, xanthoproteic, and Hopkins tryptophan reactions. A. A. ELDRIDGE.

Preparation of uricase. S. PRZYLECKI (Compt. rend. Soc. Biol., 1928, 98, 787—788; Chem. Zentr., 1928, i, 2725).—Uricase was obtained from frog's tissue, the liver and kidneys of mammals, and from grain. The preparation from tissue by extraction with glycerol, chloroform, and water, precipitation with alcohol, dissolution of the dried residue in sodium chloride solution, filtration, and treatment with acetone, is described. A. A. ELDRIDGE.

Relation of co-zymase to phosphatase activity. A. L. RAYMOND (J. Biol. Chem., 1928, 79, 637—648).—Removal of co-zymase from zymine preparations greatly reduced the capacity of the latter to hydrolyse hexosediphosphate, and, to a smaller extent, its capacity to hydrolyse the hexosemonophosphates of Neuberger (A., 1918, i, 423) and of Robison (A., 1923, i, 86), whilst addition of co-zymase to such washed zymines restored their phosphatase activity. The best preparations of co-zymase were obtained by extraction of fresh yeast with cold water and toluene. C. R. HARRINGTON.

Hexosephosphates and alcoholic fermentation. A. L. RAYMOND and P. A. LEVENE (J. Biol. Chem., 1928, 79, 621—635).—The effect on a series of hexosemonophosphates and on dihydroxyacetone monophosphate was observed of a preparation of zymine showing an induction period which was completely abolished by the presence of 0.005*M*-hexosediphosphate. No lowering of the induction time was produced by any synthetic ester except α -lactulose- α -phosphate, which, as also the esters of Neuberger (A., 1918, i, 423) and Robison (A., 1923, i, 86), decreased the induction period, but to a much smaller extent than the diphosphate. During the induction period the rate of hydrolysis of the esters was greater than the rate of fermentation when sufficient ester was present to abolish the induction, whence it is concluded that the esters are first hydrolysed and the hexose is subsequently fermented; the rates of hydrolysis and fermentation were considerably greater with the natural than with the synthetic esters. Arsenate increased the rate of fermentation of the natural esters but had little effect on the synthetic. C. R. HARRINGTON.

Phosphorylation and alcoholic fermentation of sugars. C. NEUBERG and M. KOBEL (Annalen, 1928, 465, 272—282).—The rate of evolution of carbon dioxide from sugars fermented with dried yeast or maceration juice in presence of potassium phosphate and traces of magnesium hexosediphosphate and of toluene is compared with that from sodium hexosemonophosphate similarly treated. The curves for dextrose, α -lactulose, and sucrose are very similar, but the induction period is much longer with the first. The fermentation of the hexosemonophosphate, however, begins only slightly more rapidly, and is soon retarded in such a way that after a few hours it has proceeded to a much smaller extent than has that of the uncombined sugars. These results are obtained with yeasts and sugars of varying sources, and show that a hexosemonophosphate cannot be, at least in

its normal stable form, an intermediate compound in the fermentation of sugars (cf. Neuberger, A., 1920, i, 582; Meyerhof and Lohmann, A., 1927, 697; Euler and Myrbäck, *ibid.*, 794). E. W. WIGNALL.

Mechanism of alcoholic fermentation. A. LEBEDEV (Biochem. Z., 1928, 200, 149—151).—Polemical. P. W. CLUTTERBUCK.

Activator Z. IV. Specific accelerator of fermentation by fresh yeast. H. VON EULER, E. BRUNIUS, and S. PROFFE (Z. physiol. Chem., 1928, 178, 202—208).—Attempts were made to purify "Z," which is contained in boiled yeast juice. In the most successful method, precipitation with mercuric nitrate gave a filtrate with eight times the activity of the original juice (comparing the dry weights). J. H. BIRKINSHAW.

Specificity of carboxylase. C. NEUBERG and F. WEINMANN (Biochem. Z., 1928, 200, 473—476).—Samples of top and bottom yeast which were able to break down pyruvic acid in the normal way were unable to decarboxylate trimethylpyruvic acid. P. W. CLUTTERBUCK.

Proteolytic enzymes from bacteria; influence of p_H on proteolysis. MOYCHO (Compt. rend., 1928, 187, 681—683).—Filtrates of cultures of *B. prodigiosus* and *B. pyocyaneus* on peptone water are adjusted to varying p_H values and allowed to act on films of sterile gelatin of corresponding p_H . The intensity of the proteolytic activity is measured by the depth of the gelatin liquefied in a given time. The maximum action takes place at p_H 8 in each case; at p_H 4 the former liquid has a very slight action, whilst the latter is inactive. G. A. C. GOUGH.

Decomposition of olive oil by micro-organisms; conversion of oleic into ketostearic acid. G. PIGULEVSKI and M. CHARIK (Biochem. Z., 1928, 200, 201—210).—A ketostearic acid, m. p. 79—80°, has been isolated. P. W. CLUTTERBUCK.

Growth of *Bacterium radiculicola*. S. SNIESZKO (Bull. Acad. Polonaise, 1928, B, 55—74).—*B. radiculicola* from kidney bean, red clover, cultivated pea, and hairy vetch does not grow on a synthetic medium of p_H above 7.0 or below 4.5. The hydrogen-ion concentration exerts considerable influence on the morphological changes observed in *B. radiculicola*. B. A. EAGLES.

Mechanism of cellulose digestion in the ruminant organism. II. Transformation of cellulose into dextrose by the agency of cellulose-splitting bacteria. H. E. WOODMAN and J. STEWART (J. Agric. Sci., 1928, 18, 713—723).—A cellulose-splitting organism showing optimum activity at 65° was isolated and is described. Little or no dextrose appeared in the media after the normal fermentation process at 65°, but if the fermentation was checked by the addition of toluene when the organisms were in the most active condition, considerable amounts of dextrose accumulated. It is suggested that the production of dextrose is the result of enzymic activity, masked during normal fermentation by the further utilisation of dextrose by the organism as fast as it is formed. A. G. POLLARD.

Sulphate reduction by bacteria, with cellulose fermentation products as source of energy. L. RUBENTSCHIK (Zentr. Bakt. Par., 1928, II, 73, 483—496; Chem. Zentr., 1928, i, 2266).—In the methane fermentation of cellulose on Omelianski's medium a halophilic (opt. 5—7% of sodium chloride) desulphurising *Microspira* was found. Acetic and butyric acids are sources of energy for the organism, which produces up to 83 mg. of hydrogen sulphide per litre.

A. A. ELDRIDGE.

Metabolism and distribution of fermentation-sarcina (*S. ventriculi*, Goodsir, and *S. maxima*, Lindner). J. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 421—432).—The limiting p_H values suitable for the cultivation of *S. ventriculi* and *S. maxima* have been determined (cf. Ned. Tijdschr. Hyg., 1927, 1, 201; 2, 210). The values vary with the acid. For hydrochloric acid the minimum p_H is 0.8 for pure cultures, for nitric acid 1.5, lactic acid 2.9, and phosphoric acid 1.45. On the alkaline side the limit is p_H 9.8. *S. maxima* differs from *S. ventriculi* only in the cellulose reaction with iodised zinc chloride, which is negative for the former and positive for the latter, and in the products of fermentation. *S. ventriculi* produces, in such substances as egg-white or yeast water, with a little sugar, besides carbon dioxide and hydrogen, a large quantity of ethyl alcohol with a smaller proportion of acetic acid and sometimes formic and lactic acids. *S. maxima*, on the other hand, gives no ethyl alcohol, but considerable quantities of butyric acid, more lactic acid, and some succinic acid, besides similar quantities of acetic and formic acids. A number of samples of soil, sludge, and sand from different parts of the world, not necessarily from cultivated regions, have been found to contain *S. ventriculi*. It is also found in the stomach, but not when this is healthy. It is most easily cultivated from samples of sand. *S. maxima* appears to be found only in clays in which cereals are grown. The life-history and distribution of the sarcina have been studied.

M. S. BURR.

Muller's phenomenon. Distant punctate hæmolytic of blood agar by staphylococci. F. M. BURNET (Austral. J. Exp. Biol., 1928, 5, 205—212).—The conditions have been investigated which favour the appearance of Muller's phenomenon, that is, the occurrence of discrete regions of hæmolytic in a human blood agar medium on which staphylococcus is grown. Some constituent of blood-serum associated with the globulin is an important factor; only human erythrocytes are effective, whilst the strain of staphylococcus and the type of agar used are also of importance.

W. O. KERMAK.

Chemical changes accompanying the growth of tubercle bacilli on Long's synthetic medium. T. B. JOHNSON and A. G. RENFREW (Amer. Rev. Tuberculosis, 1928, 17, 508—519).—During growth the inorganic ammonia content and the p_H of the medium change, constant values being attained when growth ceases. The sudden change in p_H at the end of 4 weeks' growth is accompanied by the appearance of reducing substances, possibly sugars.

CHEMICAL ABSTRACTS.

Chemospecific antigens. I. A. KLOSTOCK and G. E. SELTER (Z. Immunitätsforsch., 1928, 55, 118—141; Chem. Zentr., 1928, i, 2267—2268).

Reactions of basic dyes with cyclic derivatives of an acid character. W. C. HOLMES and R. M. HANN (Stain Tech., 1928, 3, 122—130).—The actual staining agent in the Ziehl-Neelson technique is an additive product of the phenol and the basic dye employed. The following phenol-dye complexes were therefore studied: phenol-rosaniline hydrochloride; resorcinol- and quinol-fuchsin hydrochloride; resorcinol-, quinol-, pyrocatechol-, chloroquinol-, pyrogallol-, and phloroglucinol-crystal-violet hydrochloride; β -naphthol-crystal-violet; resorcinol-methylene-blue hydrochloride. Various salts of dyes were prepared: rosaniline phenoxide; crystal-violet picrate (insoluble in water), hydrogen phthalate, α -naphthol-4-sulphonate, and 8-amino- α -naphthol-3:6-disulphonate; methylene-blue salicylate, acetylsalicylate, and *o*-toluate; tetrachlthionine acetylsalicylate; azure-C acetylsalicylate. Some of these compounds may be useful as stains for pathological organisms.

H. W. DUDLEY.

Wright's stain as a differential spore stain. L. O. DUTTON (Stain Tech., 1928, 3, 140—142).—A method of differential spore-staining with Wright's stain diluted 5 times in a phosphate buffer of p_H 7.6 is described. Spores are stained a deep blue, whilst the cytoplasm of the sporangium is stained a pinkish-red.

H. W. DUDLEY.

Mechanism of action of adrenaline. I. S. EDLBACHER and J. KRAUS (Z. physiol. Chem., 1928, 178, 239—249).—Adrenaline was found to catalyse the oxidation of glycine to ammonia and carbon dioxide by oxygen or air. From no other amino-acids tested, with the possible exception of cystine, was ammonia evolved in the same manner. The catalytic action seems to be a specific property of two phenolic hydroxyl groups in the *ortho*-position, since pyrocatechol has the same action as adrenaline, but resorcinol, ephedrine, and ephedrine are inactive; quinol has a slight catalytic effect.

J. H. BIRKINSHAW.

Isolation of secretin: chemical and physiological properties. J. MILLANBY (J. Physiol., 1928, 66, 1—18).—Fresh pig's duodenal mucosa is extracted with absolute alcohol. After removal of the alcohol and fats and soaps the secretin is adsorbed from aqueous solution on precipitated bile acids. This precipitate is dissolved in absolute alcohol. Secretin is precipitated on the addition of acetone and is further purified by dissolution in water and reprecipitation by dilute acetic acid. It is a polypeptide containing phosphorus and is rapidly destroyed by pepsin or trypsin.

B. A. EAGLES.

Physiological response of rabbits to insulin. M. SAHYUN and N. R. BLATHERWICK (J. Biol. Chem., 1928, 79, 443—460).—A greater dose of insulin is necessary to produce convulsions in rabbits when it is given intravenously than when given subcutaneously or intraperitoneally, although the onset of convulsions is more rapid in the first case; the difference is ascribed to increased mobilisation of the liver-glycogen after administration of insulin intravenously.

The sensitivity of rabbits towards insulin is increased by previous treatment with adrenaline and by section of the splanchnic nerves, and is diminished by feeding with a diet rich in carbohydrate.

C. R. HARRINGTON.

Hormonal sterilisation of female animals with insulin. E. VOGT (*Vox medica*, 1928, 7, 384—388; *Chem. Zentr.*, 1928, i, 2728).—Treatment of rabbits with insulin affects the fertility. Insulin and the female sexual hormone appear to be closely related.

A. A. ELDRIDGE.

Dihydroxyacetone and insulin hypoglycæmia. P. A. LEVENE and J. G. BLANCO (*J. Biol. Chem.*, 1928, 79, 657—666).—Unimolecular dihydroxyacetone was prepared from the commercial product "oxantin" by distillation under diminished pressure; the substance could be determined in blood by application of the method of Hagedorn and Jensen (*A.*, 1923, ii, 265, 440) after removal of dextrose by adsorption with yeast. Dihydroxyacetone showed a reducing power 1.6 times as great as that of dextrose. Injection of dihydroxyacetone into animals suffering from insulin convulsions generally produces temporary recovery; in all cases of recovery there is increased dextrose, and in most cases increased dihydroxyacetone, in the blood.

C. R. HARRINGTON.

Influence of insulin on the blood-sugar of animals after removal of the kidneys. H. GNOINSKI (*Compt. rend. Soc. Biol.*, 1928, 98, 785—786; *Chem. Zentr.*, 1928, i, 2728).—Nephrectomised animals behave normally towards insulin. Animals ligatured after section of the ureter showed hyperglycæmia 24 hrs. after injection of insulin.

A. A. ELDRIDGE.

Influence of insulin on the blood- and urine-phosphoric acid. A. BOLLIGER (*Z. ges. exp. Med.*, 1928, 59, 717—723; *Chem. Zentr.*, 1928, i, 2419).—Insulin lowers the phosphate value of the blood, but phosphate changes in the blood and urine are not specific for the hormone.

A. A. ELDRIDGE.

Action *in vitro* of insulin and of normal and diabetic dog's muscle on dextrose. T. J. C. COMBES (*Compt. rend. Soc. Biol.*, 1928, 98, 174—175; *Chem. Zentr.*, 1928, i, 2511).—Normal dog's muscle diminishes the rotation of dextrose solutions; diabetic muscle reduces it less or not at all. The rotation is diminished by addition of insulin.

A. A. ELDRIDGE.

Insulin does not increase the fixation of blood-sugar by lymphocytes. G. FONTÈS and L. THIVOLLE (*Compt. rend. Soc. Biol.*, 1928, 98, 847—849; *Chem. Zentr.*, 1928, i, 2625).

Effect of internal secretions and temperature on the metabolism of amino-acids and simple sugars by animal cells. W. E. BURGE, A. M. ESTES, G. C. WICKWIRE, and M. WILLIAMS (*Proc. Amer. Physiol. Soc.*, *Amer. J. Physiol.*, 1927, 81, 468).—Cultures of *Paramœcium* utilised (in diminishing order) dextrose, lævulose, and galactose; the rate of utilisation was increased by insulin or pituitrin, but decreased by thyroxine. The utilisation of amino-acids was slightly increased by adrenaline or thyroxine, but unaffected by insulin or pituitrin.

CHEMICAL ABSTRACTS.

Oxidation-promoting action of thyroxine. K. DRESEL (*Klin. Woch.*, 1928, 7, 504—505; *Chem. Zentr.*, 1928, i, 2184).—Thyroxine, on subcutaneous injection into rats, led to increased hepatic, and particularly renal, oxidation.

A. A. ELDRIDGE.

Evaluation of thyroid preparations. J. R. MØRCH (*Dansk Tidsskr. Farm.*, 1928, 2, 281—307).—Determination of the iodine content of thyroid preparations does not afford a satisfactory measure of their therapeutic values, a biological method being necessary. If white mice are dosed with thyroid extract an increased production of carbon dioxide results, and a method for computing the values of the different preparations has been based on this. The mice must be fed on a standard diet, and after 8 days have elapsed the normal amount of carbon dioxide produced by respiration during five successive periods of 24 hrs. each is determined. The subsequent increase in carbon dioxide due to the administration of a daily dose of thyroid extract may require 3 weeks to reach a constant value, hence the comparison must not be made until after the lapse of that time. During the whole of the experimental period the animals should be kept at a temperature of 23°. As the weight of the mice frequently alters during this time, small doses of extract leading to an increase in weight, large doses to the reverse, it is necessary to refer the carbon dioxide production to the same unit. In the former case it has been found that the carbon dioxide production is proportional to the superficial area of the animal (which in the case of mice can be calculated from the formula $A = 11.36 \times \text{weight}^{2/3}$) and in the latter case to its weight. The best results are obtained when the quantity of thyroid extract administered is sufficient to cause an increase in carbon dioxide production not exceeding 35%; it is practicable to distinguish with certainty between the effects of two doses differing by 33%. It is suggested that the values of thyroid preparations should be expressed in terms of a unit, which is defined as that amount of a preparation which, when administered in food to white mice daily for 3 weeks, and calculated per 1000 g. weight of animal, is sufficient to cause a 15% increase in carbon dioxide production. Of other biological methods, the acetonitrile process of Hunt and Seidell gives values proportional to the iodine content of the preparations, and is consequently of little value. The axolotl method of Jensen possibly gives values proportional to the content of therapeutically active substances present, but has not yet been compared with the above method.

H. F. HARWOOD.

Bio-assay of preparations of ovarian follicular hormone. E. P. BUGBEE and A. E. SIMOND (*J. Amer. Pharm. Assoc.*, 1928, 17, 962—966).

Preparation of female sexual hormone from urine, particularly in pregnancy. B. ZONDEK (*Klin. Woch.*, 1928, 7, 485—486; *Chem. Zentr.*, 1928, i, 2184).—Urine is extracted with a lipin solvent, the hot residue from the solvent is treated with alkali, the aqueous solution of the residue is extracted with ether, the ethereal residue dissolved in hot water or dilute acetic acid, and the solution containing the hormone is filtered.

A. A. ELDRIDGE.

Female sexual hormone, menoformone. IX. Action on the mammary gland. E. LAQUEUR, E. BORCHARDT, E. DINGEMANSE, and S. E. DE JONGH (Deut. med. Woch., 1928, 54, 465—467; Chem. Zentr., 1928, i, 2184).—A study of menoformone as the hormone of the normal development of the mammary gland. A. A. ELDRIDGE.

Colorimetric determination of vitamin-A. B. VON EULER and H. VON EULER (Svensk Kem. Tidskr., 1928, 40, 242—244).—Ox blood-serum was extracted with twice its volume of ether and the latter distilled off, when an orange-yellow fatty residue was obtained, from which lipochromes crystallised; 0.14 g. of the residue (from 100 g. of serum) was dissolved in 2.5 c.c. of chloroform, and 0.2 c.c. of this solution was mixed with 2 c.c. of a 30% solution of antimony trichloride in chloroform and determined colorimetrically. It gave 7 Lovibond units.

For carrots, 100 g. of the dried pulp were shaken for 3 hrs. with 300 c.c. of ether and the latter was distilled off, leaving a deep red, fatty residue. On dissolving in carbon disulphide and precipitating with alcohol, crystals of carotin were obtained which gave the Carr-Price reaction with antimony trichloride.

These experiments confirm the view that there is a connexion between the carotinoid content of food-stuffs and the presence of vitamin-A.

S. J. GREGG.

Vitamin-A deficiency and calcification of the renal epithelium. E. C. VAN LEERSUM (J. Biol. Chem., 1928, 79, 461—463).—Rats suffering from deficiency of vitamin-A frequently show calcification of the renal tubules; this represents the origin of the urinary calculi found in such animals (this vol., 332).

C. R. HARRINGTON.

Dietary sterility associated with vitamin-A deficiency. B. SURE (J. Agric. Res., 1928, 37, 87—92).—Rats fed on a diet of skim-milk powder, agar-agar, dextrin, ferric citrate, Harris yeast, and wheat oil developed in the second and third generations a sterility characterised by the reabsorption of the foetus during gestation. It is concluded that this sterility is associated with vitamin-A deficiency.

E. A. LUNT.

Biochemical relationships of phenols. II. Effect of quinol on vitamin-A content of stored oils. R. C. HUSTON, H. D. LIGHTBODY, and C. D. BALL, jun. (J. Biol. Chem., 1928, 79, 507—518).—Small amounts of quinol when added to butter and cod-liver oil act as preservatives of the vitamin-A in these materials.

C. R. HARRINGTON.

Vitamin-A content of wheat oil. B. SURE (J. Agric. Res., 1928, 37, 93—99).—A dose of 0.05 c.c. per rat per day maintains good growth for 10—16 weeks. Vitamin-A deficiency is accompanied by inanition.

E. A. LUNT.

Vitamin-A and -B content of the pigeon pea (*Cajanus indicus*). C. O. MILLER (J. Agric. Sci., 1928, 18, 569—573).—Meal prepared from the leaves of the pigeon pea proved a good source of vitamin-A for rats. The vitamin-A content of the seeds was poor. Both leaves and seeds were valuable sources of vitamin-B.

A. G. POLLARD.

Vitamin content of barley germ (malt dust). A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1928, 58, 645—661; Chem. Zentr., 1928, i, 2415).—Vitamins-A, -B, -D, and -E were detected.

A. A. ELDRIDGE.

Complex nature of vitamin-B. I. Evidence for a third factor. C. H. HUNT (J. Biol. Chem., 1928, 79, 723—731).—Vitamins-B₁ and -B₂ were separated by treatment of a yeast autolysate with fuller's earth, which adsorbed the former; the two fractions supplemented each other in maintaining the growth of rats, but failed to produce so good an effect as an equivalent amount of fresh yeast. The existence of a third factor, which appears to be contained in the yeast residue, is deduced.

C. R. HARRINGTON.

Antineuritic and antipellagic potency of cow's milk. C. H. HUNT and W. E. KRAUSS (J. Biol. Chem., 1928, 79, 733—738).—Milk from winter-fed cows is rich in vitamin-B₂ and poor in vitamin-B₁.

C. R. HARRINGTON.

Concentration of vitamin-B. IV. Concentration and separation of the two components of vitamin-B. P. A. LEVENE (J. Biol. Chem., 1928, 79, 465—470).—Treatment of yeast extract at p_H 3.0 with silica gel (cf. A., 1926, 760, 1279) causes preferential adsorption of vitamin-B₁; preliminary deamination followed by adsorption results in a preparation completely free from vitamin-B₂.

C. R. HARRINGTON.

Excretion of vitamin-B in urine. SUGIMOTO (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The urine of normal men contains a substance which stimulates the growth of yeast, but the presence of vitamin-B is doubtful.

CHEMICAL ABSTRACTS.

Avitaminosis. IX. Influence of the character of the food on the blood-sugar curve in experimental scurvy and on the sensitivity of guinea-pigs to insulin. A. PALLADIN and A. UTEWSKI (Biochem. Z., 1928, 199, 377—386).—The characteristic changes which take place in the sugar content of the blood of guinea-pigs are the same when the food which the animals receive is free from vitamins-A, -B, and -C as when it is free from vitamin-C only. When the animals are scorbutic the reaction of the food they receive does not affect the course of these changes, but alkaline food causes the hyperglycemia to increase more rapidly than does acid food. When scorbutic guinea-pigs are transferred from one vitamin-free diet to another the change from acid to alkaline food causes a second short period of hyperglycemia. Guinea-pigs which have received alkaline food are much more sensitive to insulin than those which have received acid food. W. MCCARTNEY.

Properties of vitamin-D. SAIKI and FUJIMAKI (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551).—Vitamin-D is not destroyed by heating at 115° for 1.5 hrs., slightly at 140° for 1.5 hrs., 40—50% destroyed in 45 min. at 150—155°, and almost completely in 1.5 hrs. at 165—170°. It is not destroyed in 1 hr. at -60°, but largely destroyed in 1 hr. at 100° in 0.1N-acid or alkali.

CHEMICAL ABSTRACTS.

Formation and destruction of vitamin-D during irradiation of ergosterol. D. VAN STOLK, E. DUREUIL, and HEUDEBERT (*Compt. rend.*, 1928, 187, 854—856).—An alcoholic solution of pure ergosterol shows absorption maxima at 2932, 2815, 2700, and 2600 Å. Irradiation by the light of a mercury-vapour lamp from which all radiations shorter than 2550 Å. have been removed shows a very slow formation of the vitamin. Irradiation by the total light of a hydrogen lamp in an atmosphere of nitrogen results in the disappearance of the first three bands, an increase in the intensity of the fourth, the appearance of bands at 2503 and 2405 Å., and the formation of much vitamin-D. It is suggested that the destruction of the vitamin is due to oxidation and not to deleterious radiations (cf. Morton, Heilbron, and Kamm, A., 1927, 948). G. A. C. GOUGH.

Physical and biological properties of irradiated sterols. R. FABRE and H. SIMONNET (*Bull. Soc. Chim. biol.*, 1928, 10, 1100—1110).—Chiefly a discussion of work already published. A 0.01% alcoholic solution of ergosterol after 10—30 min. exposure to the light of a mercury-vapour lamp exhibits maximum absorption at 2825 and 2725 Å.: a pronounced general absorption is observed in the shorter wave-band. G. A. C. GOUGH.

Fractionation of the antirachitic vitamin. E. M. KOCH and M. H. CAHAN (*Proc. Inst. Med. Chicago*, 1926, 1—4).—Lecithin, oleic acid, stearic acid, and tyrosine, when irradiated with ultra-violet light, did not, like cholesterol, acquire antirachitic properties. These properties were possessed to an important extent by a yellow, resinous material extracted from the irradiated cholesterol, or from the unsaponifiable fraction of cod-liver oil, with liquid ammonia. CHEMICAL ABSTRACTS.

Vitamin effects produced by steryl phosphates and by sterols from erythrocytes. H. VON EULER, B. VON EULER, and M. RYDBOM (*Biochem. Z.*, 1928, 199, 276—293).—Diergosteryl phosphate (cf. Euler and Bernton, A., 1927, 1066) irradiated in hydrogen or in air has an antirachitic power as great as that of irradiated ergosterol and it also promotes growth in rats in doses of 0.0002 mg. per day. A sterol, or mixture of sterols, isolated from blood-corpuseles and having physical constants very close to those of cholesterol also exhibited antirachitic power, especially when irradiated. Although this material was repeatedly recrystallised, it probably contained about 1% of ergosterol or of a sterol which can be activated by ultra-violet radiation. W. MCCARTNEY.

Hypervitaminosis by large doses of vitamin-D. H. KRETTMAIR (*Münch. med. Woch.*, 1928, 75, 637—639; *Chem. Zentr.*, 1928, i, 2626).—Hypervitaminosis, caused by overdosing with vitamin-D, is associated with increased metabolism, particularly of calcium. A. A. ELDRIDGE.

Hydrogen-ion concentration of plant-tissues. VII. Buffers of sunflower stem and root. VIII. Buffers of bean stem and root. S. H. MARTIN (*Protoplasma*, 1928, 3, 273—281, 282—301).—VII. The normal reactions of the sap of mature sunflower stems and roots are buffered by a small amount of

inorganic phosphate present in solution in the cell sap.

VIII. The sap exhibited a higher buffer capacity than that due to the inorganic phosphate; the buffer value increased with titration to an arbitrary end-point, usually pH 6.8. The action of oxalates, malates, and carbon dioxide is considered.

CHEMICAL ABSTRACTS.

Hydrogen-ion concentration of plant-tissues. IX. Improved technique for the range indicator method. C. T. INGOLD and J. SMALL (*Protoplasma*, 1928, 3, 458—468).—Standard alcoholic indicators are diluted to an alcohol content not greater than 10% with conductivity water; aqueous indicators are preferred, and a minimal immersion period is employed. The indicators are brought as near as possible to their neutral point. CHEMICAL ABSTRACTS.

Positive, non-, and negative antagonism of binary mixtures of electrolytes [in their toxic action towards plants]. L. MAUME and J. DULAC (*Compt. rend.*, 1928, 187, 668—670).—Binary mixtures of electrolytes containing a common ion and consisting of two salts in which this ion is dissociated to different degrees show an ionic concentration and a toxicity value towards certain plant roots below that indicated by the mixture law (calcium chloride and magnesium chloride; calcium nitrate and sodium nitrate). Mixtures of salts (ammonium, potassium, and sodium chlorides) of approximately the same dissociation constant follow the mixture law in both respects, whilst salts containing no common ion (potassium sulphate and sodium chloride) give enhanced values owing to the formation of the several types of dissociated and undissociated molecules. G. A. C. GOUGH.

Correlation between positive antagonism and absorption by plants. L. MAUME and J. DULAC (*Compt. rend.*, 1928, 187, 769—771; cf. preceding abstract).—When wheat was grown in a series of solutions containing calcium chloride and varying amounts of a second salt (sodium chloride, sodium nitrate, or potassium sulphate) it was found that the second salt had an inhibitory effect on the absorption of calcium by the plants which increased with concentration. R. K. CALLOW.

Influence of the soil reaction on the ionisable constituents of the tomato as determined by electro-dialysis. E. S. HABER (*J. Agric. Res.*, 1928, 37, 101—114).—Tomato plants have been grown in soils to which varying amounts of acid or basic ions have been added in the form of lime or hydrochloric acid, and the resulting plants have been analysed by the method of electro-dialysis to determine the effect on the ionisable constituents in the plant ash. E. A. LUNT.

Carbon dioxide nutrition of the forest. II. D. FEHÉR and G. SOMMER (*Biochem. Z.*, 1928, 199, 253—271; cf. A., 1927, 385).—The production of carbon dioxide by the soil in woods directly affects the amount of this gas in the air of the woods. This production, in its turn, is influenced by such factors as the number and activity of the micro-organisms in the soil, the temperature of the soil and of the

air, the respiration of the trees, the atmospheric conditions, and the physical and chemical condition of the soil. The extent of the influence of these and other factors has been measured.

W. McCARTNEY.

Effect of freezing on the respiration of the apple. D. B. CARRICK (Cornell Agric. Exp. Sta. Mem., 1928, No. 110, 1—28).—The speed of autolysis varied directly with the degree of freezing. Apples (Winesap, McIntosh, Baldwin) when frozen for 3 or 6 hrs. after ice formation at -7.5° to -8.5° showed an increased respiration at 0° of 85%, the acceleration gradually declining after several days. Apples frozen sufficiently to kill 80% of the cells excreted at 0° only one third of the normal amount of carbon dioxide. The invasion at 20° of frozen apples by *Penicillium* markedly increased the production of carbon dioxide.

CHEMICAL ABSTRACTS.

Nitrogen metabolism of *Pyrus malus*, L. IV. Effect of sodium nitrate applications on the total nitrogen and its partition products in the leaves, new and one-year branch growth. W. THOMAS (Plant Physiol., 1927, 2, 245—271).—During the most rapid absorption of nitrate there is a large increase in total water-soluble and non-protein nitrogen, with concomitant increase in amino-, amide, basic, and residual nitrogen. A larger amount of nitrogen is stored in the autumn, as amide nitrogen and residual nitrogen compounds, chiefly in the one-year branch growth.

CHEMICAL ABSTRACTS.

Nitrogen and carbon nutrition of plants. BORNEMANN (Fortschr. Landwirts., 1928, 3, 250—252; Chem. Zentr., 1928, i, 2415).—It is considered that plants are unable to utilise urea directly; the urea increases the activity of soil bacteria which, by producing more carbon dioxide, increase assimilation by the plant.

A. A. ELDRIDGE.

Sachs' method applied to the determination of the migration of [nitrogenous] substances [in plants]. R. COMBES (Compt. rend., 1928, 187, 666—668).—After avoiding the sources of error already indicated by Brown and Escombe (A., 1905, ii, 849) and by Thoday (A., 1913, i, 1425), the method of Sachs is still found to yield untrustworthy results when applied to the migration of nitrogenous substances in green and autumnal leaves. The source of error is unknown.

G. A. C. GOUGH.

Rôle of iron in the formation of chlorophyll. T. N. GODNEV (Bull. polytech. inst. Ivanovo-Vosniesensk, 1927, No. 10, 87—92).—In the absence of iron, magnesium pyrrole-2-carboxylate is harmful to chlorotic leaves (cf. Deuber, Amer. J. Bot., 1926, 13, 276).

CHEMICAL ABSTRACTS.

Potassium and sodium in sea-weeds. G. BERTRAND and M. ROSENBLATT (Bull. Soc. chim., 1928, [iv], 43, 1133—1137).—See this vol., 1059.

Formation of iodine in *Laminaria*. P. FREUNDLER (Bull. Soc. Chim. biol., 1928, 10, 1123—1128).—Chiefly a reply to Dangeard (this vol., 562, 1061); it is denied that previous figures are invalidated by errors arising from volatilisation of iodine. The volatile iodine is probably evolved in

greatest amount in the spring, whilst in the autumn the amount generated is almost negligible.

G. A. C. GOUGH.

Iodine content of Cape Cod cranberries. F. W. MORSE (J. Biol. Chem., 1928, 79, 409—411).—Three samples of cranberries from the neighbourhood of Cape Cod had iodine contents of 26—35 parts per billion.

C. R. HARRINGTON.

Increase of the iodine content of plants after application of iodine. K. SCHARRER and A. STROBEL (Angew. Bot., Z. Erforsch. Nutzpflanzen, 1927, 9, No. 2, 187—199; Chem. Zentr., 1928, i, 2442).—Application of iodine (0.25—2.5 kg. per hectare) with sodium nitrate to beet markedly increased the iodine content of roots and leaves. Similar increase was observed with lucerne, clover, false-oat-grass, and fox-tail, and the straw, but not seed, of barley, oats, and peas.

A. A. ELDRIDGE.

Iodine as a biogenic element. XVIII. Liberation of iodine by soils. K. SCHARRER and J. SCHWABOLD (Biochem. Z., 1928, 200, 258—272; cf. this vol., 787).—Acid mineral soils do, but neutral or alkaline soils do not, liberate iodine from added iodide. Moorland soils do not show iodine liberation because any iodine liberated becomes immediately combined with organic matter. Of mineral soils of the same acidity, loam and clay soils show a higher iodine liberation than sandy soil. The power to liberate iodine is lost by drying at 100° and by sterilising for 3 hrs. at 160° , but is increased by treatment with phenol and aluminium chloride solutions. Iodine liberation occurs only at a pH below 7 and is generally more pronounced the more acid is the soil and the greater is the content of colloids and iron and manganese compounds.

P. W. CLUTTERBUCK.

Phosphorus distribution in grains. J. E. WEBSTER (J. Agric. Res., 1928, 37, 123—125).—Analyses were made of the phosphorus distribution of a number of seeds. There appears to be no relation between the total phosphorus content of the seeds and that of any of the fractions, nor could any comparable variation be detected among the different fractions.

E. A. LUNT.

Microchemical detection and change of the organic phosphorus in plants. G. KLEIN (Planta, 1926, 2, 497—506).—Mandel and Neuberg's method has been adapted to micro-chemical determinations. Changes in the form of phosphorus in seedlings of *Phaseolus multiflorus* and *Zea mays* were studied.

CHEMICAL ABSTRACTS.

Variations of water and dry matter in the leaves of Pima and Acala cotton. R. S. HAWKINS (Ariz. Agric. Exp. Sta. Tech. Bull., 1927, 17, 419—444).—Acala cotton leaves contain more water than Pima. The amount of dry matter increased during the day more rapidly in the latter, but during drought in the former.

CHEMICAL ABSTRACTS.

Metabolism of conifer leaves. J. DOYLE and P. CLINCH (Proc. Roy. Irish Acad., 1928, B, 38, 116—127).—Peroxidase, sometimes accompanied by an alcohol-soluble inhibitor, has been identified as the sole oxidising enzyme in the leaves of conifers.

Experiments have failed to establish a relationship between the p_H and the water-soluble pentosan fraction of the leaves.

E. A. LUNT.

Catalase content of conifer leaves. J. DOYLE and P. CLINCH (Proc. Roy. Irish Acad., 1928, B, 38, 128—147).—The seasonal variation in the catalase content of conifer leaves is described and appears to be associated with the corresponding variation in starch content. The variations of the initial rate of the catalase activity with temperature, enzyme and substrate concentration have also been determined.

E. A. LUNT.

Rice; oxidase. HIGUCHI (Imp. Japanese Inst. Nutrition; Bull. Soc. hyg. aliment., 1927, 15, 481—504, 524—551).—The catalase was determined as follows: 100 grains were ground and suspended in water (100 c.c.) and the mixture was filtered; 25 c.c. were kept for 1 hr. at 25° after admixture with 10 c.c. of neutral 0.05% hydrogen peroxide solution, and the excess was titrated with permanganate after addition of sulphuric acid. The results for catalase and peroxidase are parallel to those for oxidase. Variations with the quality and origin of the rice are described.

CHEMICAL ABSTRACTS.

Composition of tobacco leaves. A. I. SMIRNOV [with M. A. DRBOGLAV and L. S. ERYGIN] (U.S.S.R. State Inst. Tobacco Invest., 1928, Bull. 46, 1—59).—The variation in tobacco leaves with age has been determined with reference to the following: dry weight, rate of respiration, total carbohydrate, sucrose, maltose, starch, dextrin, invertase, amylase, total nitrogen, protein, nicotine, amide nitrogen, and hydroxy-acid contents.

E. A. LUNT.

Enzymes of wheat flour. N. NEUENSCHWANDER (Biochem. Z., 1928, 199, 445—450).—The flour, alone or in the presence of co-zyrnase, decolorises methylene-blue very slowly. In the presence of zymophosphate there is even a retardation of the decolorising process. The enzymic activity is enormously increased, however, when an activator (co-zyrnase) and a hydrogen donator (zymophosphate) are present together and decolorisation proceeds very rapidly. Dry flour when heated for 15 min. at 85° does not lose its enzymic activity. The enzyme content of extracts of flour so treated as well as of untreated flour is very low. The greater the degree of fineness of a flour the greater is its apparent content of oxidising-reducing enzymes. The content also varies in flours of the same degree of fineness but derived from different varieties of wheat. No differences are observed in the oxygen consumptions of flours of different degrees of fineness. In addition, the differences in oxygen consumption by flours from different varieties of wheat do not agree qualitatively with the differences in rate of decolorisation of methylene-blue by these varieties.

W. MCCARTNEY.

Influence of flour on the reaction of liquid in which it is soaked. S. KOEHLER (Bull. Acad. Polonaise, 1927, B, 951—963).—Flour from rye, wheat, barley, and oats was shaken with solutions of

dilute hydrochloric acid or sodium hydroxide of varying hydrogen-ion concentration. At first contact with a slightly acid solution there is an immediate increase in acidity, followed by a lessened acidity at the end of 3 hrs. These changes of acidity indicate the presence of two types of compounds in flour: the more acid ones act immediately on the reaction of the liquid and are readily soluble, the other type of compound slowly decreases the acidity produced by the first type and is sparingly soluble in slightly acid solution.

B. A. EAGLES.

Colouring matter of cottonseed hulls. A. H. GILL and H. W. GREENUP (Oil and Fat Ind., 1928, 5, 288—294).—No colouring matter could be isolated from cottonseed soap stock or foots. The hulls afforded no carotin or xanthophyll and only a negligible amount of gossypol. A resinous or pectin-like substance, charring at 320°, approximating to $C_{19}H_{33}O_{21}$, which formed an additive compound with copper nitrate, was isolated from the aqueous extract.

S. COFFEY.

Gum arabic. L. AMY (Bull. Soc. Chim. biol., 1928, 10, 1079—1090).—Gum arabic contains a water-insoluble substance which remains as a gel when a solution in cold water is filtered, colloidal arabic acid (partly present as salts), and dialysable acids. The last two constituents are separated by dialysis in the middle chamber of a bath which is divided into three portions by cellophane sheets and contains water in the end chambers. In order to avoid acidification of the arabic acid, an electric current is passed through the bath; strips of copper and platinum serve respectively as anode and cathode. By means of electrometric titration the purified, non-crystalline arabic acid is shown to be a strong monobasic acid, mol. wt. about 1600. The titration curve indicates that it is probably homogeneous. Heating at 100° causes it to develop reducing properties, which are originally absent, and to be partly transformed into an insoluble acid. In the anode chamber of the bath a small amount of a non-reducing acid is found. This acid, which is unstable both to anodic oxidation and to heating at 100°, may be obtained by the addition of sodium carbonate to the anode liquid.

G. A. C. GOUGH.

Coarse ultra-filters. H. BECHHOLD and K. SILBEREISEN (Biochem. Z., 1928, 199, 1—7).—An improvement on a previous method (Bechhold and Gutlohn, A., 1924, ii, 621) for the production of collodion ultra-filters when wide pores are desired consists in using aqueous acetic acid up to 82% concentration as coagulant for the collodion-acetic acid solution. With increasing concentration of coagulant acid the size of the pores increases.

J. H. BIRKINSHAW.

Electro-dialysis or electro-osmosis. G. LASCH and J. REITSTÖTTER (Biochem. Z., 1928, 199, 216—217).—A reply to Reiner (this vol., 543). The full advantages of electro-dialysis are gained only when relatively strong currents are used.

J. H. BIRKINSHAW.