BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1929.

General, Physical, and Inorganic Chemistry.

Nomenclature and symbolism for the spectra of diatomic molecules. O. W. RICHARDSON (Trans. Faraday Soc., 1929, **25**, 628—633).—A notation is described, having regard to existing usages, and those for line spectra, suitable for the quantum treatment of the molecule as a whole, and of the individual electron, and the specification and quantum interpretation of molecular spectra. Standard symbols for important molecular constants are proposed.

N. M. BLIGH.

Detailed electronic structure of diatomic molecules, with special reference to carbon monoxide. R. C. JOHNSON (Trans. Faraday Soc., 1929, **25**, 649—668).—The present knowledge of general molecular structure gained from a study of electronic band spectra and the recent extensions of the methods of line spectra interpretation to the study of the electronic structure of molecules by Hund, Mulliken, and others are discussed. The mechanism of molecule formation is investigated from a consideration of atoms in an electric field; the resulting quasi-molecular states are tabulated for atoms of the first short period. The states of a molecule composed of two of these atoms are illustrated for the BeO molecule. About 16 band systems are known for the neutral CO molecule and three for the CO^+ ion. The known levels and transitions are given diagrammatically. The third positive carbon bands show the first recorded case of a quintuplet level in band spectra. The nature of the ground state is discussed, and the structure of the CO molecule and the interpretation of the electronic states are examined.

N. M. BLIGH.

Band spectra and atomic nuclei. R. S. MULLIKEN (Trans. Faraday Soc., 1929, **25**, 634—645).—Mainly mathematical. Alternating intensities and alternate missing lines in band spectra are explained on the assumption that a molecule must be antisymmetrical in all electrons, as confirmed by line spectra, and also in all protons. This rule for protons is examined theoretically for hydrogen and is confirmed by specific heat and band spectrum data. The theory is extended to molecules with complex nuclei, existing data are tabulated, and some difficulties are discussed. In agreement with theory, alternating intensities have not been found in molecules with unequal nuclei. N. M. BLIGH.

Term representation in complex spectra. O. LAPORTE (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 128—133; Chem. Zentr., 1929, i, 2617).—A discussion. A. A. ELDRIDGE.

Line structure. D. G. BOURGIN (Physical Rev., 1928, [ii], **31**, 704).—A discussion. L. S. THEOBALD.

Second order Stark effect in Balmer lines. M. KIUTI (Z. Physik, 1929, **57**, 658—666).—The second order Stark effect for the fine components of the H_β and H_γ lines has been determined quantitatively by Lo Surdo's method in fields up to 575,000 volts/cm. The results are in good agreement with the values required by quantum mechanics.

J. W. SMITH.

Doublet separation of Balmer lines and the molecule of hydrogen in relation to the electromagnetic quantum theory. C. L. SAGUI (Physical Rev., 1928, [ii], **31**, 715).—Theoretical. The doublet separation of the Balmer lines of hydrogen has been calculated, using the electromagnetic quantum theory, and good agreement found. The continuous and infra-red spectra have also been studied.

L. S. THEOBALD.

Hydrogen absorption [in the ultra-violet]. J. J. HOPFIELD (Physical Rev., 1928, [ii], **31**, 918).—The ultra-violet absorption systems have been extended to include the bands A_0—B_{17} and A_0—C_{10}, bringing both systems near the converging limit. From the data the heat of dissociation of H_2 with excitation of one of the atoms to the two quantum orbit can be calculated. Further experiments with less hydrogen in the receiver show that the absorption limit previously used by Dieke and Hopfield in connexion with the heat of dissociation of H_2 is not real; it marks the beginning, apparently, of new and stronger absorption band systems probably related to still higher electronic excitation. L. S. THEOBALD.

Infra-red emission of hydrogen. E. D. MCALISTER (Physical Rev., 1928, [ii], **31**, 917).—A shift of intensity as a function of pressure is indicated by thermocouple observations of emission from a long hydrogen tube of the Wood type. At low pressure and with high dispersion the third member of the Brackett series has been observed.

L. S. THEOBALD.

Atomic absorption coefficients. R. M. LANGER (Physical Rev., 1928, [ii], **31**, 1114).—The atomic absorption coefficients of normal hydrogen atoms for the first lines of the Lyman and the Balmer series calculated by means of the new mechanics are all high. L. S. THEOBALD.

Non-metastability of the 2s level in atomic hydrogen. V. ROJANSKY and J. H. VAN VLECK (Physical Rev., 1928, [ii], **32**, 327).—Theoretical.

L. S. THEOBALD.

Light excitation in the negative glow of a helium discharge. Y. TAKAHASHI (Ann. Physik, 1929, [v], **3**, 49—57).—The different modes of excitation possible for foreign atoms in the negative glow (inside a cylindrical cathode) of a helium glow discharge are discussed. An intensity anomaly is found in the Cd II series, but similar anomalies are much less evident for Zn II and Hg II. In addition to electrons, excitation may be due to metastable 2^3S and 2^1S states of the helium atom and helium ion He^+.

R. A. MORTON.

Intensity variation at critical points in the helium spectrum. I. CORNOG, J. T. LAY, and C. B. BAZZONI (Physical Rev., 1928, [ii], **31**, 1109).—A marked minimum of intensity appears near 54 volts for all lines in general; variations in the rate of change of intensity in different series are recorded.

L. S. THEOBALD.

Effect of pressure and current density on the spectrum of helium. A. C. HODGES (Physical Rev., 1928, [ii], **32**, 319).—The intensities of helium lines have been directly compared with the same wave-lengths from a standard tungsten filament. The relative intensities of the higher members of the various series increase with a decrease of pressure or current density. L. S. THEOBALD.

Structure of the band spectrum of helium. VI. W. E. CURTIS and A. HARVEY (Proc. Roy. Soc., 1929, **A**, **125**, 484—506; cf. A., 1928, 449; this vol., 1).—The rotation term differences for all the states of the He_2 molecule are tabulated, and it appears that in the same electronic sequence for a given value of j they tend towards a definite limiting value as n increases. These limiting values are identical in all cases and are the same for o-He_2 and p-He_2; they must evidently be those characteristic of the He_2^+ ion, since they correspond with the complete removal of an electron. The observed regularities are of great assistance in the further analysis of the spectrum and lead to a classification of the term sequences in agreement with that proposed by Dieke (A., 1928, 677). Details are given of the eight new bands: $4^3S \longrightarrow 2^3U$, $4^3Z \longrightarrow 2^3U$, $4^3X \longrightarrow 2^3U$, $4^3Y \longrightarrow 2^3U$, $4^3Y \longrightarrow 2^3P$, $5^3Y \longrightarrow 2^3P$, $5^3X \longrightarrow 2^3P$, and $4^1D_b \longrightarrow 2^1P$. This completes the theoretical term scheme for o-He_2.

L. L. BIRCUMSHAW.

Vacuum spark spectra in the extreme ultra-violet down to 100 A. B. EDLÉN and A. ERICSON (Nature, 1929, **124**, 688—689).—Wave-length standards from 1215·68 to 192 Å. have been determined. In the spectrum of Li II the first three lines of the principal series $1S-mP$ have the wave-lengths 199·263, 177·99, 171·54 Å., respectively. Hence the ionisation potential of Li II is $75·282 \pm 0·012$ volts. The spectrum of Be III has been extended to 100·25 Å.; the ionisation potential of Be III is calculated as $153·10 \pm 0·10$ volts. A. A. ELDRIDGE.

Beryllium hydride bands. M. PETERSEN (Physical Rev., 1928, [ii], **31**, 1130).—The spectrum of a beryllium arc run in hydrogen at 5—15 mm. pressure shows a strong band group near 5000 Å. This consists of several overlapping sets of three-branch bands, of which the earliest lines are narrow doublets, and apparently embraces part of a band system attributable to BeH with its origin at 20,032 cm.$^{-1}$, the head of the strongest Q branch. Six P and R branches can be detected. A moment of inertia of $3·53 \times 10^{-40}$ and, assuming BeH origin, an internuclear distance of $1·54 \times 10^{-8}$ cm. have been calculated. L. S. THEOBALD.

New absorption bands in nitrogen. J. J. HOPFIELD (Physical Rev., 1928, [ii], **31**, 1131).—Two new band systems or a system of double bands have been observed, together with two prominent isolated bands at λ 1518·8 and 1437·2 Å. The bands are diffuse and appear to be due to a modification of nitrogen. L. S. THEOBALD.

Alternating intensities in the spectrum of nitrogen. F. RASETTI (Nature, 1929, **124**, 792—793).—Results already reported (this vol., 975) have been confirmed. For oxygen the electronic wave function of the normal $^3\Sigma$ state is antisymmetrical, and oxygen nuclei, as expected, satisfy the Bose–Einstein statistics. A. A. ELDRIDGE.

Absorption of ultra-violet light by oxygen, water vapour, and quartz. L. P. GRANATH (Physical Rev., 1929, [ii], **34**, 1045—1048).—Measurements were made in the spectral region 1850—2300 Å. by means of a quartz spectrograph and a recording densitometer. Oxygen at atmospheric pressure in tubes up to 5 metres in length showed the peaks of absorption due to the Schumann–Runge band system below 1970 Å.; from 2000 to 2100 Å. the absorption appeared continuous with no marked peaks, the absorption coefficient α being 0·00025, 0·00032, and 0·0005 at 2100, 2050, and 2000 Å., respectively. Values of α for saturated water vapour at 25° were 0·0005, 0·0013, 0·003 at 2050, 1950, and 1900 Å., and for crystalline quartz 2·5 cm. thick, 0·086, 0·11, 0·13, and 0·17 at 2040, 2000, 1940, and 1870 Å., respectively. N. M. BLIGH.

Spectra of high-frequency discharge in oxygen and carbon monoxide. R. W. WOOD (Phil. Mag., 1929, [vii], **8**, 207—210).—An extension of previous work (A., 1927, 1008) on high-frequency discharges in very highly exhausted tubes. Application of the current by means of a single loop of wire round the tubes gives a bluish discharge exhibiting the secondary spectrum of hydrogen. In a few minutes this gives place to the greenish-yellow discharge of oxygen showing the characteristic four negative bands. After 4—5 min. operation the walls of the tube show a pink fluorescence which becomes ruby-red accompanied by an increase in the oxygen pressure. The luminous gas masses were spherical instead of streamlined and their positions were very sensitive to the position of the electrode. The spectrum of the light from the spheres and the adjacent regions showed both lines and bands, the bands appearing greatly enhanced in the spectral image of the spheres. The appearance of the spheres is therefore associated with gas molecules and not with atoms. The bands have been identified with the "comet tail" bands characteristic of discharges in carbon monoxide at very low pressures. A. E. MITCHELL.

Corona discharge in neon. L. G. H. HUXLEY (Phil. Mag., 1929, [vii], **8**, 128—129).—In reply to

the suggestion by Penning (Phil. Mag., 1928, [vii], **7**, 632) that the discrepancies between the results of Penning and of Huxley (A., 1928, 567) were due to impurities in the gas employed by the latter, the methods adopted to assure the purity of this gas are described. Experiments are recorded which claim to show that impurities would tend to accumulate in Penning's apparatus. It is impossible to estimate the effects of these on the potentials required to produce discharges. A. E. MITCHELL.

Magnetic rotation lines in the red sodium bands. W. R. FREDRICKSON (Physical Rev., 1928, [ii], **31**, 1130—1131).—The heads of the red absorption bands of sodium have been remeasured. They can be represented by the formula $\nu=15006{\cdot}68+(115{\cdot}22n'-0{\cdot}384n'^2)-(157{\cdot}14n''-0{\cdot}423n''^2)$. The magnetic rotation lines have been photographed at high dispersion and many new strong lines accompanied by weak ones have been detected. Absorption and magnetic rotation data have been correlated. L. S. THEOBALD.

Afterglow spectrum of argon. C. KENTY and L. A. TURNER (Physical Rev., 1928, [ii], **31**, 710).—The arc spectrum of argon persists approximately 0·001 sec. after an arc of 0·5 amp. at 0·5 mm. pressure is stopped, but since the D lines present in the arc itself are absent in the afterglow the spectrum is not due to direct excitation by electrons. Comparative photographs show that in the afterglow lines involving jumps from high s and d states are much stronger with respect to $1s-3p$ lines than in the arc. It is suggested that the afterglow spectrum results from recombination. L. S. THEOBALD.

Zeeman effect in the calcium hydride A band. P. S. DELAUP (Physical Rev., 1928, [ii], **31**, 1130).—The calcium hydride A band at 7000 Å. has been photographed with field strengths from 9000 to 23,000 gauss. At low fields the $Q_1(1)$, $Q_1(2)$, and $P_1(4)$ lines were resolved into doublets having a separation equal to twice that of the normal Zeeman separation. This agrees with Van Vleck's formula (A., 1927, 87) for the case of loose coupling of the spin axes. At low or medium fields the separation increases linearly with the field. L. S. THEOBALD.

Intensity relations in the spectra of titanium. III. Intensities in super-multiplets of Ti I. G. R. HARRISON (J. Opt. Soc. Amer., 1929, **19**, 109—133; cf. this vol., 860).—The intensities of 93 lines of the complex super-multiplet of Ti I, $^5D'FG'-{}^5H'GF'DP'$, arising from the transition $[(3d)^24s]4p-4d$, parent term a^4F', have been measured, and also those of 31 lines of the simple super-multiplet $^5D'FG'-{}^5F'$ arising from the transition $[(3d)^24s]4p-5s$, the intensities of which were found to be normal (multiplet ratios 8·95 : 7·00 : 5·30, theory requiring 9 : 7 : 5). The complex super-multiplet has abnormal intensities; in no multiplet is the summation rule obeyed. For the super-multiplet as a whole no single temperature effects agreement with the rule either horizontally or vertically, the nearest approach being given by a temperature of 2080° Abs. The total intensities of each multiplet after application of the excitation correction agree but roughly with Konig's formula. Inclusion as far as possible of the corresponding multiplets in the triplet system, and of all inter-system lines, effects but little improvement, and it is concluded that at least all the lines originating from the parent term a^4F' by the addition of an electron undergoing the transition $4d-4p$ must be included. Besides the intensities the intervals are in some cases abnormal, and there is an intermingling of the various levels of the upper states with one another (cf. Houston, this vol., 480). C. A. SILBERRAD.

Spectra of doubly-ionised vanadium, V III, and triply-ionised chromium, Cr IV. H. E. WHITE (Physical Rev., 1928, [ii], **32**, 318).—Doublet and quadruplet terms of the electron configurations $3d^3$, $3d^24s$, and $3d^24p$ have been determined for V III and Cr IV. Terms determined for $3d^24p$ combine with the lowest energy levels in the spectrum, $3d^3$, to give strong lines in the region 1100 Å. for V III and 600 Å. for Cr IV; the ionisation potentials computed for V III and Cr IV are 30 and 52 volts, respectively. L. S. THEOBALD.

Arc spectrum of nickel, Ni I. H. N. RUSSELL (Physical Rev., 1929, [ii], **34**, 821—857).—Tables are given of the energy levels recognised and their designations; terms and their combinations; the terms which have been assigned to each configuration, with the leading energy level and the separations between the remaining components in order of decreasing j; the quantum defects, and a table of the wave-length, intensity, and designation of almost all the known lines (1071) of Ni I. Included are 66 lines from the solar spectrum not yet found in the laboratory. The spectrum is regular, and in accordance with Hund's theory. A few of the predicted terms have not been found, but their combinations should be very faint. The principal ionisation potential of the neutral Ni atom is calculated to be 7·606 volts, corresponding with a double electron change from the configuration d^8s^2 to d^9. N. M. BLIGH.

Absorption spectrum of nickel vapour. New multiplet of nickel. R. G. LOYARTE and A. T. WILLIAMS (Physikal. Z., 1929, **30**, 634—640).—The absorption spectrum of nickel vapour has been studied at 2500° Abs. and earlier results (A., 1927, 5, 395, 396, 607, 910) have been confirmed and extended. Some terms in the arc spectrum of nickel have been classified and five new multiplets recognised. The application to nickel of the equation $N'/N=e^{-E/RT}$ has been considered (N'/N is the ratio of excited atoms to total atoms for deep levels). Atoms like nickel, in which the deep levels show two different configurations the term values of which overlap, require the modified formula $N'/N=e^{-(E+\Delta E)/RT}$, ΔE being the energy necessary for the transition from one configuration to another (cf. this vol., 366). R. A. MORTON.

First spark spectra of zinc and cadmium. Y. TAKAHASHI (Ann. Physik, 1929, [v], **3**, 27—48; cf. Paschen, A., 1928, 97; this vol., 365).—The spectra of Zn II and Cd II have been photographed with quartz and vacuum grating spectrographs, using the negative glow of a helium discharge, small quantities of the metal vapours being present. Analogies with Cu I and Hg II have assisted in the analysis of the spectra, the liberation of a d-electron from the tenth shell playing an important part. Wave-lengths, term

values, and combinations are tabulated. In Cd II the higher terms of series are greatly enhanced, indicating preferential excitation of the metal atom by means of helium ions, whereas the transformation energy of the metastable helium atom in the 2^3S state cannot be drawn on for this purpose (cf. also von Salis, A., 1925, ii, 334). R. A. MORTON.

First spark spectrum of arsenic, As II. C. W. GARTLEIN (Physical Rev., 1928, [ii], **32**, 320).—The spark spectrum of arsenic below 2300 Å. has been photographed, using various amounts of inductance in series with the spark. The As II lines were present even with large amounts of inductance, but lines from higher states decreased in intensity with an increase in inductance. The spectrum was also characterised by "long lines" due to glowing arsenic vapour. All terms of $(4p)^2$ and $4p5s$ have been identified as well as some from the configuration $4p4d$, and parts of the terms due to $4p5p$ have been identified by lines in the visible spectrum due to transitions into the levels of $4p5s$. L. S. THEOBALD.

Second spark spectrum of selenium. A. S. RAO (Z. Physik, 1929, **58**, 251—254).—The second spark spectrum of selenium has been mapped and analysed. A. J. MEE.

New cadmium hydride bands in the ultra-violet. E. BENGTSSON and R. RYDBERG (Z. Physik, 1929, **57**, 648—657).—New CdH^+ bands have been found over the wave-length range 2200—2700 Å., and the conditions under which these bands are excited have been investigated. The separate bands may be divided into simple *P*- and *R*-branches, and the system is ascribed to $^1\Sigma' \longrightarrow {}^1\Sigma'$ electron jumps of the ionised cadmium hydride. The intensity distribution in these bands is discussed. The dissociation energies of the two electronic states are calculated as 2·5 volts and 1·9 volts, respectively, and the ionisation potential of the neutral cadmium hydride molecule as 7·8 volts. J. W. SMITH.

Carrier of the absorption and fluorescence bands observed in cadmium vapour. W. KAPUŚCIŃSKI and A. JABLOŃSKI (Z. Physik, 1929, **57**, 692—695).—It is claimed that the absorption band system in the region 2590—2825 Å. attributed by Walter and Barratt (this vol., 237) to the CdO molecule is really due to the cadmium Cd_2 molecule, as stated by Jabłoński (this vol., 1) and by Winans (this vol., 481). Experiments carried out on the absorption spectrum of CdO vapour over the temperature range 500—800° showed no signs of these bands. The energy of dissociation of the Cd_2 molecule as calculated from these bands supports the view of the authors. J. W. SMITH.

Doublets and quadruplets of doubly-ionised silver, Ag III. R. C. GIBBS and H. E. WHITE (Physical Rev., 1928, [ii], **32**, 318—319).—When for a sequence of isoelectronic systems starting from any element in the periodic table the energy levels representing possible electron configurations are plotted on a Moseley type of diagram, the lines connecting corresponding terms of each successive element will be practically linear. Further, the radiated frequencies resulting from electron transitions involving no change in total quantum number are displaced to higher frequencies by a constant value. Application of these considerations to the arc spectrum of Rh I and the first spark spectrum of Pd II has enabled some of the doublet and quadruplet terms arising from $4d^9$, $4d^85s$, and $4d^85p$ of the second spark spectrum of silver to be determined. The ionisation potential of Ag III is calculated to be 34 volts approximately. L. S. THEOBALD.

Unclassified lines of the indium arc spectrum. J. G. FRAYNE (Physical Rev., 1928, [ii], **31**, 152).—Four of the five unclassified lines previously reported are now classified; the line 2858·30 Å. remains unclassified. L. S. THEOBALD.

Arc spectrum of antimony. J. B. GREEN and R. A. LORING (Physical Rev., 1928, [ii], **31**, 707).—The Zeeman effect has been studied for all of the stronger lines between 2500 and 4033 Å., and the *g* values of the terms have been computed. L. S. THEOBALD.

Structure of praseodymium lines. A. S. KING (Physical Rev., 1928, [ii], **32**, 319).—The complex structure of praseodymium lines has been examined in greater detail using high dispersion; 400 lines approximately from λ 3100 to 6800 Å. have been listed as complex, the complexity varying from double to six-component lines. Lines compared in furnace, arc, and spark spectra apparently retain their structures unchanged. L. S. THEOBALD.

Platinum term values and classification. P. J. OVREBO (Physical Rev., 1928, [ii], **31**, 1123).—Forty new intermediate and upper levels together with three new low levels have been found for platinum. Combinations of these and previous levels give 142 lines; 200 lines remain to be classified, excepting those of low intensity. L. S. THEOBALD.

Quadruplet structure of the first spark spectrum of mercury, Hg II. S. M. NAUDÉ (Ann. Physik, 1929, [v], **3**, 1—26).—Paschen (this vol., 365) in his work on the doublet system of the first spark spectrum of mercury found $^2D_{3/2,5/2}$ terms analogous to those known for Au I and Cu I. The conditions for maintaining a satisfactory discharge in mercury vapour have been worked out so that the unclassified lines are markedly enhanced in intensity. Spectra have been recorded over the range 890—8000 Å. for mercury vapour alone, and in the presence of helium under conditions facilitating the recognition of a number of multiplets belonging to the quadruplet system. The analogous spectrum of copper confirms the classification. Wave-lengths and intensities of lines obtained with or without helium are tabulated together with term schemes and a comparison of excitation potentials corresponding with the strongest lines, with measurements based on electron collisions. R. A. MORTON.

Densitometer curves for the green mercury line. R. W. WOOD (Phil. Mag., 1929, [vii], **8**, 205—207).—An examination of densitometer curves for the green mercury line taken from spectrograms made at right angles to and end on to the source show that the satellite at +0·124 is absorbed to a much smaller degree than that at +0·128, which is again less absorbed than that at +0·085. The satellites at

—0·102 and —0·07 are nearly equalised by absorption, whilst that at —0·237, in confirmation of the results of Metcalfe and Venkatesachar (A., 1921, ii, 669), shows no absorption. There is evidence of the unsymmetrical reversal of the main component.

A. E. MITCHELL.

Effect of mercury vapour on the continuous spectrum of hydrogen. H. JEZEWSKI (Spraw. Prace Polsk. Towarz. Fizycz., 1927, **3**, 161—173; Chem. Zentr., 1929, i, 2857).—In the presence of mercury vapour the intensity of the continuous spectrum of hydrogen is diminished. Temperature changes do not affect the distribution of the bands. The dissociation potential of hydrogen, 2·5 volts, given by Schüler and Wolf's theory (which is criticised) is too small.

A. A. ELDRIDGE.

Self-reversed lines in the spectrum of mercury. L. H. DAWSON and W. H. CREW (Physical Rev., 1928, [ii], **31**, 308; cf. this vol., 1).—Spectrograms of the region 6000—1860 Å. have been made of a mercury arc operating at the ordinary pressure and excited by a condensed discharge. Eleven arc and two spark lines were self-reversed and all of the arc lines, except 2536 Å., represent electron transitions originating on the 2^3P levels, the lowest energy levels of the excited mercury atom. Six of these lines start at 2^3P_1, two at 2^3P_0, and two at the 2^3P_2 level, indicating an accumulation of electrons on the supposed least stable orbit. The arc when excited by 4000, 8000, and 16,000 kilocycles at 5, 1, and 0·5 amp., respectively, gives sharp atomic lines as well as molecular bands coincident with those usually observed in fluorescing mercury vapour.

L. S. THEOBALD.

Nature of the production of one of the spark lines of mercury and the determination of mean life. L. R. MAXWELL (Physical Rev., 1928, [ii], **31**, 1110).—The variation of intensity of the line 4797 Å., measured for different positive-ion currents, is the same for all points along the line and is approximately proportional to the ion current, indicating that the line results from a single electron collision with the neutral atom. The mean life is of the order 10^{-7} sec.

L. S. THEOBALD.

Voltage-intensity relations of 29 lines of the mercury spectrum. P. B. TAYLOR (Physical Rev., 1928, [ii], **31**, 1135).—Data for the variation in intensity with voltage of 29 lines between 2378 and 4108 Å. are given.

L. S. THEOBALD.

Critical potentials below 4·7 volts for negative ion formation in mercury vapour. W. M. NIELSEN (Physical Rev., 1928, [ii], **31**, 1134).—The critical potentials observed below 4·7 volts are 0·4, 0·8, 1·4, 1·8, 2·3, and 2·7 volts, and are ascribed to the mercury molecule. The magnitude of such negative-ion currents increases faster than the first power of the vapour pressure.

L. S. THEOBALD.

Continuous spectrum of mercury. L. H. DAWSON and W. H. CREW (Physical Rev., 1928, [ii], **32**, 1109).—Band maxima observed in an arc at atmospheric pressure, excited by high voltage and low current density, are at 4500, 3300, and 2350 Å.; no continuous radiation is emitted in the region 2535—2350 Å. under these conditions, but on increasing the current the bands broaden in both directions to fill this gap.

L. S. THEOBALD.

Intensities of the lines of the mercury spectrum. E. O. HULBURT (Physical Rev., 1928, [ii], **31**, 1109).—The total radiation measured with a thermocouple in the region 6000—2300 Å. from a quartz mercury lamp filled with vapour at the ordinary pressure was $1{\cdot}54\times10^8$ erg sec.$^{-1}$. This gives about 50 quanta emitted per atom per second. The line intensities were measured. The temperature of the excited atoms derived graphically was of the order of 10^3 degrees.

L. S. THEOBALD.

Turning impulse and effective cross-section in chemical reactions. H. BEUTLER and E. RABINOWITSCH (Z. Elektrochem., 1929, **35**, 623—625).—Theoretical. The bands of mercury hydride and the cyanogen spectra are discussed.

H. T. S. BRITTON.

Excitation of radiation by metals by afterglowing mercury vapour. K. NARKIEWICZ-JODKO (Spraw. Prace Polsk. Towarz. Fizycz., 1928, **3**, 257—266; Chem. Zentr., 1929, i, 3068).—The following lines were observed with various metals or their salts: sodium 5895·9, 5889·9; potassium 7699, 7665, 4047, 4044; lithium 6707·8, 6104, 4602; cæsium 4593, 4555; strontium 6892, 4607; rubidium 7950, 7811, 6298·5, 6206·5, 4215·5, 4201·8; barium 5536; cadmium 6438·5, 4799·9, 4678·1; thallium 3775; calcium 6572, 4226·7 Å.

A. A. ELDRIDGE.

Total emissive power of bismuth. W. DEL REGNO (Atti R. Accad. Lincei, 1929, [vi], **10**, 77—83).—Measurements of the total emissivity of bismuth have been made at temperatures between 40° and 250°. The theoretical formulæ which express the emissivity of metals in terms of their specific electrical resistance do not hold in the case of bismuth. The experimental values of the total emissivity are much smaller and of the reflecting power greater than the theoretical values. These differences are due to divergences in the expression for the emissivity $e=KT^m$ of the K term, which is a function of the specific resistance. The experimental and theoretical values of the exponent m show good agreement. The larger experimental value of the reflecting power compared with the theoretical indicates that in the case of bismuth not only the free electrons, but also those in the atoms of the lattice take part in the phenomenon of reflexion.

O. J. WALKER.

Zeeman effect of hyperfine structure and magnetic moment of the bismuth nucleus. E. BACK and S. GOUDSMIT (Physical Rev., 1928, [ii], **31**, 1125; cf. A., 1928, 340).—Analysis of the hyperfine structure of the bismuth lines and energy levels shows that the bismuth nucleus probably possesses a mechanical moment of momentum, and an undetected magnetic moment. The nuclear moment is probably not produced by moving or spinning electrons in the nucleus but by positive particles.

L. S. THEOBALD.

High-frequency spark discharge in air. T. NISHI and Y. ISHIGURO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 817—830).—The characteristics of spark discharges in air between electrodes of various

shapes have been studied at frequencies of 91,000 and 196,000 cycles. At the higher frequency the corona becomes shorter and the sparking potential is in many cases increased. In many ways high-frequency spark discharges resemble low-frequency arc discharges. H. F. GILLBE.

Mechanism of spark discharge in air at the ordinary pressure. L. B. LOEB (Science, 1929, **69**, 509—512; J. Franklin Inst., 1928, **205**, 305).—Theoretical. Townsend's theory is discussed in the light of recent work and a new mechanism suggested. L. S. THEOBALD.

Spark spectrum of thallium, Tl II. Term analysis. Fine structure of lines. J. C. MCLENNAN, A. B. MCLAY, and M. F. CRAWFORD (Proc. Roy. Soc., 1929, **A**, **125**, 570—578; cf. this vol., 366).—The study of the thallium spark spectrum has been extended from the ultra-violet to the visible and near infra-red regions. Spectra of the spark in air between thallium metal electrodes were photographed from 8500 to 1850 Å. with Hilger glass and quartz prism spectrographs, and spectra of a condensed oscillatory discharge between aluminium terminals in an evacuated quartz tube containing heated thallium vapour were photographed also from 7000 to 2100 Å. The wave-lengths in the latter case were exceptionally clear. Many of the Tl II lines showed fine structure, the magnitudes of the line separations in numerous cases being much greater than any hitherto reported in an atomic spectrum. A few fine-structure term intervals are deduced directly by a wave-number analysis of the line components, and a number of fine-structure patterns are interpreted on the basis that the Back–Goudsmit vector relation $F=J+I$ is valid, that the selection rule $\Delta F=\pm 1$ or 0 holds, and that $I=0{\cdot}5$ for Tl II; The ionisation potential is estimated to be approximately 20·5 volts. L. L. BIRCUMSHAW.

Spectra of metals in explosions of gaseous mixtures. S. KALANDYK, L. KOZŁOWSKI, and T. TUCHOLSKI (Spraw. Prace Polsk. Towarz. Fizycz., 1928, **3**, 241—255; Chem. Zentr., 1929, i, 3068—3069).—Mixtures of oxygen with hydrogen, carbon monoxide, or coal gas were exploded in presence of finely-divided metallic salts, and the spectra were examined. That of strontium chloride is identical with the spectrum of the salt in the hydrogen–oxygen flame. With calcium chloride the spark lines H and K are increased in intensity and the characteristic bands between 3969 and 3652 Å. disappear. With ferrous sulphate and cupric chloride the spectrum is almost identical with the flame spectrum. A. A. ELDRIDGE.

Intensity of the Stark effect in the direction of the lines of force. H. MARK and R. WIERL (Z. Physik, 1929, **57**, 494—500; cf. this vol., 963).—It is shown that the intensity distribution of the electric vector of the light along the electric field is asymmetrical. The longer wave-halves of the components are in good agreement with Schrödinger's theory. A. J. MEE.

Quantum mechanical problem of ionisation in the Stark effect. J. KUDAR (Z. Physik, 1929, **57**, 705—709).—Mathematical. J. W. SMITH.

Explanation of the spectrum of the aurora. V. M. SLIPHER and L. A. SOMMER (Naturwiss., 1929, **17**, 802—803).—In photographing the aurora spectrum a new line of wave-length 5206 Å. was found, in addition to the usual lines. This line can be explained in a similar way to the 5577·350 Å. line, viz., as a transition between deep metastable terms. It is a line of the spectrum of the neutral nitrogen atom. A. J. MEE.

Nucleus as radiator. W. M. HICKS (Phil. Mag., 1929, [vii], **8**, 108—114).—A general account is given of radiation phenomena the origin of which is considered to be in the nucleus of the atom. The general considerations are based on the classical electromagnetic theory of light. A. E. MITCHELL.

Second spark spectrum of lead. A. S. RAO and A. L. NARAYAN (Nature, 1929, **124**, 794).—Support is adduced for the authors' results (A., 1928, 1067). A. A. ELDRIDGE.

Total radiation from polished and soot-covered nickel. B. T. BARNES (Physical Rev., 1929, [ii], **34**, 1026—1030; cf. Utterback, this vol., 1212).—Total emissivity values for soot-covered nickel range from 0·92 at 400° Abs. to a minimum of 0·81 at 800° Abs., rising to 0·86 at 1100° Abs. The value for polished nickel was 0·205 at 1400° Abs.; at 400° Abs. it was 0·087 before heating to incandescence and 0·063 afterwards. At intermediate temperatures there were similar differences due to surface changes during the initial heating. N. M. BLIGH.

Single crystal cathodes. K. G. EMELÉUS and J. W. BECK (Phil. Mag., 1929, [vii], **8**, 121—125).—It has been shown that a single crystal of pyrites behaves similarly to an ordinary piece of polycrystalline metal when used as the cathode for glow discharges in various gases. It is therefore considered that the work function of a single crystal does not change, as suggested by Linder (A., 1928, 8), from one face to another. From the values of the normal cathode potential fall in various gases the work function of pyrites for electrons is calculated to be 4·8 volts. A. E. MITCHELL.

X-Ray diffracting power of copper and iron for molybdenum and copper radiation. (MISS) H. ARMSTRONG (Physical Rev., 1929, [ii], **34**, 931—936).—Ionisation spectrometer measurements were made of the intensity of reflexion of the $K\alpha$ doublet of molybdenum and copper from copper and iron powders. From the relative intensities of reflexion from the different planes of the powdered crystals the relative atomic scattering factors F for these reflexions were calculated, and referred to an absolute value through the (220) reflexion of sodium chloride. The absolute values of F are shown as functions of $\sin\theta/\lambda$, where θ is the angle of reflexion. The curves for copper and molybdenum are not coincident, which suggests that F_{220} for sodium chloride is not the same for copper as for molybdenum radiation, and that F is not independent of the wave-length. N. M. BLIGH.

Short exposure times with X-ray diagrams. H. MARK and G. VON SUSICH (Naturwiss., 1929, **17**, 803—804).—Special apparatus is used in order to

obtain X-ray diagrams with the shortest possible exposures. Examples are given of the application of the method to the determination of the structure of the diamond and pentaerythritol, and to following the progress of the action of sodium hydroxide on cellulose. A. J. MEE.

Total reflexion of long wave-length X-rays. M. SCHÖN (Z. Physik, 1929, **58**, 165—182).—An apparatus is described for measuring the angle of total reflexion of long wave-length X-radiation (3—13 Å.). Results are given for the total reflexion at glass, diamond, quartz, and aluminium surfaces. In the region of normal dispersion the limiting angles of total reflexion agreed with those calculated from the Drude–Lorentz theory. For aluminium in the region of the K-level anomalous dispersion was found. No quantitative results can be given in support of Fresnel's reflexion law, although there is qualitative agreement. A. J. MEE.

Reflexion of the $K\alpha$ line of carbon from glass. E. DERSHEM (Physical Rev., 1929, [ii], **34**, 1015—1020).—A vacuum spectrographic method is described by which the intensities of the rays of very soft monochromatic X-radiation (the $K\alpha$ line of carbon, 44·6 Å.) reflected from a mirror could be compared photographically for glancing angles of incidence from 1° to 8°. The reflected intensity at 8° was less than 4% of that at 1°. The reflexion intensity–glancing angle curve shows no sharp change of slope, indicating that absorption effects so modify the intensity of the reflected ray as to obscure any sudden change at the critical angle for this order of wave-length. N. M. BLIGH.

Reflexion of X-rays from platinum films sputtered on glass. H. E. STAUSS (Physical Rev., 1929, [ii], **34**, 1021—1025; cf. A., 1928, 574).—Using the method of Edwards (cf. A., 1927, 921) a variation of the critical angle of reflexion with the thickness of the platinum film was found as in the case of nickel. Variations were found in the critical angles of several silver films identically sputtered. On five photographic films corresponding with five sputtered films, four of platinum and one of nickel, the reflected beam was the limit of a much weaker beam. Angles of deviation from the primary beam of 1° 6′ to 1° 46′ were measured. N. M. BLIGH.

Fine structure of X-ray absorption edges. D. COSTER and M. WOLF (Nature, 1929, **124**, 652—653).—K-Absorption spectra of copper and zinc exhibit considerable differences; the former gives a complex fine structure, whilst the latter does not. With metallic or combined zinc the M-shell is complete, whilst this is not the case with copper. A. A. ELDRIDGE.

K X-Ray absorption edge of iron. H. R. VOORHEES and G. A. LINDSAY (Physical Rev., 1928, [ii], **31**, 306).—The iron in crystals of pyrite, hæmatite, arsenopyrite, epidote, or lepidomelane gives the characteristic K absorption edge without the use of any other absorbing screen. Screens of iron compounds and of electrolytic iron, using a sylvan crystal reflector, also gave the absorption, a complicated fine structure of the edge extending over 200 volts being observed. It is supposed that a part, at least, of the fine structure is due to simultaneous ejection of two or more electrons from the atom. L. S. THEOBALD.

Fine structure in the K series of molybdenum. B. DAVIS and H. PURKS (Physical Rev., 1928, [ii], **31**, 306).—The fine structures observed with the increased resolving power obtained by proper arrangement of the crystals in the double X-ray spectrometer are described. L. S. THEOBALD.

Reflexion of soft X-rays from aluminium. S. D. GEHMAN and C. B. BAZZONI (Physical Rev., 1928, [ii], **31**, 1117).—Soft X-rays of range 40—300 volts have been passed through a slit system and then reflected from a polished aluminium mirror in a high vacuum. The curves obtained by plotting reflecting power against voltage and against grazing angle are described. L. S. THEOBALD.

Indices of refraction of platinum for X-rays of long wave-length. E. DERSHEM (Physical Rev., 1928, [ii], **31**, 305).—The indices of refraction of platinum measured over the range 1·279—7·01 Å. have values from $27{\cdot}3\times10^{-6}$ to 663×10^{-6} for $1-\mu$. L. S. THEOBALD.

Refractive indices of silver in the wave-length range 2—7 A. E. DERSHEM (Physical Rev., 1928, [ii], **31**, 1117; cf. this vol., 747).—The dispersion curve obtained shows a depression in the values of δ on both sides of the L_{I} absorption limit wave-length, with a greater depression midway between the L_{II} and L_{III} limit wave-lengths. In all substances so far examined δ rises rapidly with increasing wave-length between 6 and 7 Å.; for silver it increases 54% to a value of 666×10^{-6} at 7 Å. L. S. THEOBALD.

Absorption coefficient of some gases for short-wave X-rays. K. SCHOCKEN (Z. Physik, 1929, **58**, 39—47).—The absorption coefficient of air, oxygen, nitrogen, and argon was measured for different wave-lengths. An apparatus for measuring the absorption of gases at high pressures is described. The results fit a formula only when the scattering absorption coefficient is assumed independent of wave-length. A. B. D. CASSIE.

Photo-ionisation in liquids and crystals and the dependence of the frequency of X-ray absorption edges on chemical constitution. L. PAULING (Physical Rev., 1929, [ii], **34**, 954—963).—A relation is found between the electron affinity E, the average potential energy of a free electron W_0 in the liquid or crystal, and the diamagnetic susceptibility. The value 3·81 volt-electrons is deduced for the electron affinity of water. Observed values of long wave-length limits for ultra-violet absorption leading to photo-ionisation in crystals of alkali halides give electron affinities for the crystals corresponding with $\alpha=0{\cdot}8$ in the relation $E=\alpha W_0$, from which it is found that the diamagnetic susceptibilities of the silver halides are of the order of magnitude to give electron affinities of the crystals sufficient to allow photo-ionisation of the halide ions by visible light, as in the primary photo-sensitisation of a photographic plate. Shifts in the K edge of chlorine in various crystals and of potassium in its halides are predicted, and found to agree well with those observed in the alkali halides, supporting the view that the main factors in

producing shifts of the edges in these cases are the electrostatic potential and the electron affinity of the crystals. N. M. BLIGH.

Ionisation of solid dielectrics by *X*-rays. Investigations on ceresin. D. NASLEDOV and P. SCHARAVSKI (Ann. Physik, 1929, [v], **3**, 63—90).—The processes occurring in ceresin when exposed to the action of *X*-rays are probably of ionic origin. The curve intensity/ionisation current is parabolic, indicating that the current is proportional to the square root of the intensity of the incident radiation. Over the range 322—1600 volts the ionisation current is strictly proportional to the voltage, but it is noted that other workers have not observed this strict validity of Ohm's law. Persistent after-effects have been recorded with ceresin and it is thought that the phenomena are due to the slowness of ionic processes in solids. Fatigue phenomena in the irradiation processes have been studied in some detail.

R. A. MORTON.

Photo-ionisation of potassium vapour. E. O. LAWRENCE and N. E. EDLEFSEN (Physical Rev., 1929, [ii], **34**, 1056—1060).—Using a space-charge-neutralisation method (cf. this vol., 1121) the variation with wave-length of the ionisation per unit light intensity in potassium vapour was studied. The ionisation efficiency shows a maximum at the series limit 2856 Å., and another three times as great at 2340 Å.; a minimum value is found near 2700 Å. Good agreement with former results (cf. A., 1925, ii, 831) is shown. Ionisation by wave-lengths longer than the series limit is probably due to the absorption of principal series lines. The increase of ionisation efficiency beyond the series limit is probably not a molecular phenomenon, the observed dependence on wave-length being most likely an atomic property of potassium. N. M. BLIGH.

Ionisation potential of hydrogen atoms from the point of view of the electromagnetic quantum theory and polarisation of light from canal rays. C. L. SAGUI (Physical Rev., 1928, [ii], **31**, 1110).—Theoretical. A hydrogen atom appears to result from a collection of about 1800 electrons distributed in 60 energy levels in which the density of the electrons is proportional to the energy of each level. The electrons of the level $R((1/3)^2-(1/4)^2)$ would be more easily ejected by bombarding electrons, and 13·78 volts is the ionisation potential found in this case. Polarisation of light from canal rays is attributed to a component of the oscillating electrons parallel to the motion of the hydrogen atoms; this would not be uniform, but would result in a kind of wave.

L. S. THEOBALD.

Critical potentials of metals. H. B. WAHLIN (Physical Rev., 1928, [ii], **31**, 155; cf. A., 1928, 1068).—Critical potentials in the vapours of copper, silver, and nickel in the regions 0—11, 0—8, 0—17 volts, respectively, have been found, and some of them identified as optical levels. L. S. THEOBALD.

Relation between the cathode fall of potential, the length of the dark space, and the current in the electric discharge through gases. (SIR) J. J. THOMSON (Phil. Mag., 1929, [vii], **8**, 393—409).—Mainly mathematical. Certain relations between the electron energy, ionisation potential, pressure, and current density are defined, by means of which the relation between the thickness of the dark space, cathode fall of potential, and current can be found both for the normal and abnormal discharge. In the latter, the *P.D.* increases and the thickness of the dark space diminishes as the current increases. A transverse magnetic field diminishes both the thickness of the dark space and the *P.D.* required to produce a very short spark. An experimental proof of the latter result is described. It is concluded that the electronic collisions, although sufficient to account for the greater part of the ionisation, require to be supplemented by other processes such as radiation. An experiment is described showing the great effect on the discharge produced by radiation from the negative glow.

N. M. BLIGH.

Photo-ionisation of cæsium vapour. F. L. MOHLER, C. BOECKNER, R. STAIR, and W. W. COBLENTZ (Science, 1929, **69**, 479).—The photo-ionisation of cæsium vapour has been redetermined using an ionisation chamber designed to reduce the surface photo-electric effect of the radiation to a minimum. The cæsium sensitivity has a maximum at 3184 Å. which falls rapidly to about 15% of this value at 2700 Å. The mercury line 3130 Å. has the greatest effect of all lines giving 78% of the photo-ionisation. The computed value of k_{3130} is $1{\cdot}85\times10^{-19}$ at pressures ranging from 0·005 to 0·06 mm. (corresponding with temperatures of 146° and 201°) and the value of k_{3184} derived from the spectral sensitivity curve is $2{\cdot}3\pm0{\cdot}2\times10^{-19}$. The disagreement with Little's value of $k_{3130}=2{\cdot}2\times10^{-21}$ is unexplained. L. S. THEOBALD.

Talbot's law in photo-electric cells. N. CAMPBELL (Phil. Mag., 1929, [vii], **8**, 63—64).—The results of Carruthers and Harrison (*ibid.*, **7**, 792) are discussed. It is suggested that the fatigue phenomena observed must be due to temperature changes, since these are mainly responsible for the redistribution of gas and metal films in the cell associated with these phenomena. It is also pointed out that near the sparking potential of a gas-filled cell the form of the voltage characteristic and the magnification due to ionisation by collision vary with the illumination and that under such conditions Talbot's law cannot be general. A. E. MITCHELL.

Talbot's law in photo-electric cells. T. H. HARRISON and W. S. STILES (Phil. Mag., 1929, [vii], **8**, 64—65).—The points raised by Campbell (cf. preceding abstract) are discussed and it is claimed that there is no essential difference in the points of view.

A. E. MITCHELL.

Mechanism of photo-electric emission. J. H. HSU (Physical Rev., 1928, [ii], **31**, 311).—Theoretical. On the assumption that when a quantum of radiation strikes an atom its energy content is shared by the valency electron and the core of the atom, a theory to explain the mechanism of photo-electric emission is put forward. According to this theory, the work function, $h\nu_0$, should, in general, be equal to the lowest resonance potential, and for weak illumination and long wave-length, the relation between photo-electric emission and the intensity of incident light should not be linear. L. S. THEOBALD.

Effect of toluene on the photo-electric behaviour of mercury. D. ROLLER (Physical Rev., 1928, [ii], **32**, 323).—The introduction of toluene vapour into an evacuated photo-electric cell containing freshly-distilled mercury increases the sensitivity, and shifts the threshold towards the red. L. S. THEOBALD.

Emission electricity by incandescent tungsten in iodine vapour. S. KALANDYK (J. Phys. Radium, 1929, [vi], **10**, 337—344).—Iodine vapour diminishes the positive emission of a new tungsten filament, but does not affect a previously heated one. It increases the negative emission from tungsten particularly at temperatures lower than incandescence. Whilst it diminishes the emission from thoriated tungsten it does not affect that from tungsten oxide.

W. E. DOWNEY.

Influence of outgassing the cathode on the cathode fall. G. BARTH (Ann. Physik, 1929, [v], **3**, 253—269).—The gas dissolved in the metal of the cathode is concerned in the processes occurring at the cathode of a glow discharge. The cathode fall increases with diminution of gas and decreases when the cathode is recharged with gas. Photo-electric measurements on heated metal foil indicate a connexion with the capacity of the cathode to emit secondary electrons. R. A. MORTON.

Effect of canal rays on alkali chlorides. N. EMBIRIKOS (Ann. Physik, 1929, [v], **3**, 91—111).—The bombardment of alkali chlorides by means of canal rays gives rise to the emission of both electrons and ions. The ion emission per positive particle increases with increasing velocity of the canal rays. Other things being equal, the ion emission increases with increasing atomic number of the metal. The emission of series lines at the surface of the salts requires a certain minimum current density of positive rays below which only the fluorescence effect for lithium and sodium chlorides can be detected. In addition to arc lines, a few metallic spark lines can be obtained for sodium and potassium chlorides, but the arc lines are much more intense than the spark lines. The arc lines are emitted, although weakly, from the gas space surrounding the brightly luminous layer of vapour, but the spark lines are localised in the glowing vapour. The intensity of the spark lines can be affected by an electric field, a field capable of accelerating the emitted ions enhancing the intensity of the spark lines with respect to the arc lines and a retarding field exerting the opposite effect. R. A. MORTON.

Polarisation of light from canal rays. F. G. SLACK (Physical Rev., 1928, [ii], **31**, 312).—The partial polarisation of light emitted at right angles to a stream of hydrogen canal rays is explained on the theory that an atom, excited to a state characterised by a combination of quantum numbers which places the centre of gravity of the electronic charge well away from the nucleus, favours a transition resulting in light polarised with the electric vector parallel to the axis connecting the nucleus and point of average charge, whilst an atom excited into the state of the same quantum number but with a combination placing the charge closer to the nucleus favours a transition which results in light polarised at right angles to this axis. L. S. THEOBALD.

Selective absorption and reflexion of slow electrons at metals. E. RUPP (Z. Physik, 1929, **58**, 145—164; cf. this vol., 862).—The absorption of slow-moving electrons (4—40 volts) is investigated and it is found that where there is good absorption there is also good reflexion. A selective absorption maximum corresponds, at equal voltage, with a selective reflexion maximum. The results are grouped according to the position of the metal in the periodic table. The shape of the absorption curve is characteristic for elements in each vertical series of the table. In such a series, the position of the maximum shows a progressive displacement with increase of atomic number. The absorption and reflexion decrease rapidly with increasing velocity of radiation. There is, therefore, a larger transmission through metals for slow electrons than for fast ones.

In deciding the shape of the absorption curves, the outer electrons of the atom play a great part, since there is similarity between the curves for elements in the same vertical series and because the number of maxima in the curves depends on the series of the element. Experiment shows that in the copper series there is one maximum, in the magnesium series there are two, and in the arsenic series three. Probably the absorption bands of the outer dispersion electrons of the atom, somewhat modified in their position owing to the shape of the lattice, are concerned.

A. J. MEE.

Diffraction of electrons by a single layer of atoms. C. DAVISSON and L. H. GERMER (Physical Rev., 1928, [ii], **31**, 155; cf. A., 1928, 1173).—The scattering of a homogeneous beam of electrons by a crystal of nickel differs from *X*-ray scattering in that the individual atom scatters the equivalent electron radiation more efficiently, and the radiation is more rapidly extinguished in the metal than is *X*-ray radiation. The intensity may be reduced by 30 or 40% by passing normally through a single layer of atoms. Diffraction is a result of this.

L. S. THEOBALD.

Investigation of adsorbed layers with electron-waves. E. RUPP (Z. Elektrochem., 1929, **35**, 586—590).—A method of investigating crystal surfaces, and layers adsorbed thereon, in which electron-waves are allowed to impinge on the surface and the reflected radiations are received and measured by means of a Faraday cage, is described. The electron-waves emerge from a glowing wire and thence pass through a slit on to the surface. The apparatus is so arranged that the angles of incidence and reflexion are equal, whilst the velocity of the incident waves is varied and the variations in the reflected waves, determined by the space lattice of the crystal surface, are recorded. The method has been tested with pure nickel and iron surfaces and also with adsorbed layers of gases, hydrogen, nitrogen, and hydrogen sulphide, on these metals. The nature of the layers formed when these metals are first subjected to hydrogen and then to nitrogen, and *vice versâ*, is demonstrated.

H. T. S. BRITTON.

Electron collisions with molecules and resultant quantum losses. R. WHIDDINGTON (Nature, 1929, **124**, 758).—The behaviour of an "electron gun" is described. A. A. ELDRIDGE.

Properties of the electron. R. D. KLEEMAN (Nature, 1929, **124**, 728).—The electrical field of an electron is shown to decrease during its mean free path. A. A. ELDRIDGE.

Motion of a Lorentz electron as a wave phenomenon. A. M. MOSHARRAFA (Nature, 1929, **124**, 726—727).

Efficiency of quenching collisions and the radius of the excited mercury atom. E. GAVIOLA (Physical Rev., 1929, [ii], **34**, 1049—1051; cf. this vol., 486).—An erroneous interpretation previously given to the reabsorption factor is corrected, and a revised treatment leads to values for the radius of the excited mercury atom of 3·4 and 5·7 Å. for hydrogen and carbon monoxide collisions, respectively. The efficiencies of collisions are 0·4 for water vapour, 0·2 for nitrogen, 0·05 for argon, and 0·005 for helium. N. M. BLIGH.

Reflexion of hydrogen atoms from crystals. T. H. JOHNSON (Physical Rev., 1928, [ii], **31**, 1122).—Evidence for the existence of waves of length $\lambda=h/mv$ associated with the hydrogen atom has been sought by reflecting atomic hydrogen from a Wood tube from crystal surfaces of ice, rock salt, quartz, and calcite. Freshly-cleaved, degassed rock salt reflects intensely with the angle of reflexion equal to that of incidence. The prismatic and hexahedral faces of quartz and freshly-cleaved calcite reflect, but in no preferred direction. L. S. THEOBALD.

Phase theory in thermionics. O. HALPERN (Monatsh., 1929, **53** and **54**, 822—824).—Theoretical. A metal is considered as a two-component system of ions and electrons. L. S. THEOBALD.

Relation between the variations with temperature and density of the coefficient of recombination of gas ions. A. M. CRAVATH (Physical Rev., 1928, [ii], **31**, 912).—On the assumption that the masses of ions do not change with moderate variation in temperature, the density variations of the coefficient of recombination of gas ions with temperature are represented by an equation involving mobilities of positive and negative ions and the gas density. L. S. THEOBALD

Value of the period of polonium at various places. L. B. BOGOIAVLENSKI (J. Phys. Radium, 1929, [vi], **10**, 321—326).—Determinations of the period of polonium at various places in Russia gave values ranging from 125·6 to 181·6 days. It is concluded that the variation is outside the experimental error. W. E. DOWNEY.

[Value of the period of polonium at various places.] (MME.) P. CURIE (J. Phys. Radium, 1929, [vi], **10**, 327—328; cf. preceding abstract).—It is contended that the author did not exercise sufficient control in obtaining his results. W. E. DOWNEY.

Invariability of radioactive constants. (MME.) P. CURIE (J. Phys. Radium, 1929, [vi], **10**, 329—336).—The attempts made by the author and her collaborators to control radioactive processes with a view of influencing the radioactive constants are summarised. No definite exception to the generally accepted laws has been found, although some points of detail still require explanation. W. E. DOWNEY.

Application of adiabatic microcalorimeter to measurements of the heats of radiation of uranium, thorium, and radioactive minerals. A. DORABIALSKA (Rocz. Chem., 1929, **9**, 494—503).—Values for heat of radiation in good agreement with those obtained by other authors using different methods, as well as with those theoretically derived, are obtained for the above substances, using Swientosławski and Dorabialska's adiabatic microcalorimeter (A., 1927, 1163). The entire heat effect of radiation is taken up by the substance examined, so that $Q=c.\Delta t$, where Q represents g-cal./g.hr. and c is the specific heat of the body. R. TRUSZKOWSKI.

Activation in rare gases. M. LAPORTE and L. GOLDSTEIN (Compt. rend., 1929, **189**, 689—691).—To test whether recoil atoms are all positively charged at the moment of formation the yield, *i.e.*, the ratio (Ra-A+-B+-C collected) : (total active deposit in equilibrium with amount of radon present) was determined in air and in pure argon (cf. A., 1926, 877) for pressures up to 85 cm. of mercury, using 3 millicuries of radon and a voltage of 85 between electrodes. The yield never exceeded 50%, and was uniformly less in argon than in air. Reasons for these results are suggested. C. A. SILBERRAD.

Close collision between an α-particle and a nitrogen nucleus. L. F. CURTISS (Physical Rev., 1928, [ii], **31**, 1128).—Approximately 83,000 α-ray tracks in air have been photographed and recorded. One fork involving a close collision between an α-particle and a nitrogen nucleus has been analysed. The α-particle was deflected through an angle $\phi=110°$ with its initial direction, and travelled 10·5 mm. after the collision; the nitrogen nucleus travelled 4·7 mm. at an angle $\phi=26·5°$ to the original direction of the α-particle. The velocity of the latter was $1·1\times10^9$ cm. per sec. at the moment of impact and $8·7\times10^8$ cm. per sec. after impact, and it has been calculated that the nearest approach of the α-particle was $0·5\times10^{-12}$ cm. from the centre of the nucleus. No evidence of the ejection of a proton was obtained in spite of the fact that the α-particle penetrated the nuclear structure with sufficient energy. L. S. THEOBALD.

Straggling of β-particles. E. J. WILLIAMS (Proc. Roy. Soc., 1929, **A**, **125**, 420—445).—Theoretical. A brief account is given of previous experimental work on the loss of energy by fast electrons in traversing matter (*e.g.*, White and Millington, A., 1928, 1302), with special reference to the effect of the complications introduced by "scattering." The inapplicability of Bohr's formula for the straggling of electric particles to β-particles is demonstrated, and a theory is developed whereby the complete curve representing the distribution of the energy losses by β-particles traversing thin foils may be calculated. A theory is also proposed according to which collisions in which a moving electric particle loses energy to an atomic electron are of two distinct types; one involves only the moving particle and the electron which acquires the energy, but in the second the whole atom is involved and the nucleus plays an essential part. L. L. BIRCUMSHAW.

Extreme ultra-violet spectra excited by controlled electron impacts. K. T. COMPTON and J. C. BOYCE (Physical Rev., 1928, [ii], **31**, 708).—Spectra photographed at low pressures and increasing voltages under conditions in which electrons make only one collision with a gas molecule show successive stages of excitation and ionisation brought about by single electron impacts. In helium ten members of the arc series have been observed from 584 to 507 Å. and five members of the spark series from 303 to 234 Å. In neon and argon the results of Dorgelo and Abbink have been generally confirmed and many additional lines observed. L. S. THEOBALD.

Inelastic collisions in mercury vapour. J. D. WHITNEY (Physical Rev., 1929, [ii], **34**, 923—930).—For the study of inelastic collisions through the residual energies of colliding electrons, a narrow beam of electrons from a hot cathode, after undergoing collisions in mercury vapour, passed to a high vacuum region and was separated by a magnetic field into a velocity spectrum. The intensities of components of the spectrum corresponding with energy losses equivalent to 4·9, 6·7, and 8·8 volts were measured as a function of the initial energy of the electrons. The intensity in each case reaches a distinct maximum within a few volts of the excitation potential of that component. Other energy losses were detected of such low intensities that they were not measured. N. M. BLIGH.

Attachment of electrons to neutral molecules. L. B. LOEB (Phil. Mag., 1929, [vii], 98—102).—The criticisms of Bailey (this vol., 231) of the results of Wahlin (A., 1922, ii, 608) and Loeb (Phil. Mag., 1922, [vi], **43**, 229) are discussed and it is shown that the discrepancies in the results on the formation of negative ions in ammonia attributed to the presence of impurities in the gas used by Wahlin and Loeb are unjustified and that under the different pressure and electrical conditions employed Bailey's results would not be expected to be the same as those of the other observers. A. E. MITCHELL.

Collision process accompanying the combination of nitrogen atoms in active nitrogen. B. LEWIS (Physical Rev., 1928, [ii], **31**, 314).—The necessity for a triple collision in the combination of nitrogen atoms is discarded. The nitrogen molecule may be formed in a two-body collision process. L. S. THEOBALD.

Active nitrogen. Z. BAY and W. STEINER (Z. Elektrochem., 1929, **35**, 733—738).—Spectroscopic evidence is advanced of the existence of unstable intermediate products between the inactive and active forms of nitrogen, the latter being atomic. The concentration of nitrogen atoms and the intensity of the after-glow are inter-related. A mild discharge weakens the intensity of the after-glow. H. T. S. BRITTON.

Change in the electrical state of metallic surfaces on charging with hydrogen ions and by the bombardment of electrons. R. SUHRMANN (Z. Elektrochem., 1929, **35**, 681—686).—If the surface of a metal be illuminated by a beam of light of sufficiently short wave-length, a limiting wave-length is emitted such that the quantity of electrons involved increases per unit of energy of incident light in the case of most metals as the emitted wave-length decreases. A method is described which enables the nature of a metal surface to be studied when it has been charged with hydrogen, by bombarding it with electrons and measuring the variation in photo-electric sensitivity. Several curves are given illustrating the dependence on the wave-length of photo-electric electron emission of gold and silver under different conditions. It is concluded that hydrogen in the adsorbed state is ionic. The importance of the method in the investigation of the surfaces of catalysts is emphasised and the possibility of "active centres" on metal surfaces is discussed. H. T. S. BRITTON.

Spectroscopic determination of the pressure in the calcium chromosphere. A. UNSÖLD (Astrophys. J., 1929, **69**, 209—226).—The average value of the partial pressure of the calcium ion calculated from observations of the emission and absorption spectra of the calcium chromosphere is 4×10^{-15} atm. The average velocity of the ions from Doppler measurements is 15 km./sec. Milne's theory that the radiation absorbed by the *H* and *K* lines is just sufficient to support the mass of the calcium ion in the chromosphere is fulfilled. L. S. THEOBALD.

Is there argon in the corona? H. N. RUSSELL and I. S. BOWEN (Astrophys. J., 1929, **69**, 196—208).—From a critical study of Freeman's work (A., 1928, 210), the authors conclude that he is in error in attributing lines in the solar corona to argon, and that there is no spectroscopic evidence of the presence of argon in the corona or elsewhere in the sun. L. S. THEOBALD.

Scattering of quanta with diminution of frequency. K. K. DARROW (Science, 1928, **68**, 488—490).—The four or five cases in which quanta appear to surrender a part but not all of their energy are discussed. L. S. THEOBALD.

General theory of the plasma of an arc. L. TONKS and I. LANGMUIR (Physical Rev., 1929, [ii], **34**, 876—922).—Theoretical. It is assumed that in a plasma each positive ion, instead of having a random velocity, starts from rest and subsequently possesses only the velocity which it acquires by falling through a static electric field which is itself maintained by the balance of electron and ion charges. On this view equations for the plasma-sheath potential distribution are formulated and solved for a number of important cases. The ion current equation gives a new method of calculating the density of ionisation; from the plasma balance equation the rate of ion generation can be calculated. Extensions and calculations from the equations are made and shown to be in agreement with experimental results. N. M. BLIGH.

Rôle of hydrogen in the oscillating arc. E. Z. STOWELL and H. E. REDEKER (Physical Rev., 1929, [ii], **34**, 978—983).—Attempts to produce radio-frequency oscillations in the Poulsen arc in atmospheres other than hydrogen were unsuccessful, except when this gas could be formed intermediately, and the presence of hydrogen is concluded to be essential. It was found that numerous elements, generally of even atomic number, could be used as cathodes. The spectrum of the oscillating arc shows the Balmer

series and the first spark spectrum of the cathode; when the latter is sufficiently hot the cathode lines disappear leaving a strong Balmer series on a continuous background. All oscillating arcs of the Poulsen type have about the same high-frequency limit of 5×10^6 cycles per sec. N. M. BLIGH.

Connexion between the quantum mechanics "uncertainty" and the structure of elementary particles, and a calculation of the masses of the proton and electron based thereon. R. FÜRTH (Z. Physik, 1929, 57, 429—446).—Theoretical. Whilst the radius of the electron has a definite meaning in the classical electron theory, matters become very complicated on applying quantum mechanics. The Heisenberg "uncertainty" relationship is applied first to a light quantum, and then to protons and electrons. The change of matter into radiation and inversely is considered, and the masses of the electron, proton, and neutron are obtained. Eddington's theory of the elementary quantum, in which it is described in 16-dimensional space, is also considered, and the above calculations are carried out. A. J. MEE.

Electron theory of ferromagnetism and electrical conductivity. F. BLOCH (Z. Physik, 1929, 57, 545—555; cf. Heisenberg, A., 1928, 1300; Dorfman and others, this vol., 751).—Mathematical. The possibility of accounting for ferromagnetism by considering the conductivity electrons is investigated. A. J. MEE.

Synthesis of elements. III. G. I. POKROVSKI (Z. Physik, 1929, 57, 560—565; cf. this vol., 623, 739, 973).—It has already been shown that an electron and a proton can combine together with emission of energy and loss of mass. For elements with atomic numbers greater than 120 the total loss of mass considerably exceeds the mass of a proton. There are, however, a number of facts which go to show that the heavier atomic nuclei are constructed from α-particles. It is shown that the same mechanism as that put forward for the construction of the lighter elements holds for these heavier ones, α-particles taking the place of protons. There is good agreement between the relative loss of mass calculated by this method and Aston's results. An upper limit is found for the loss of mass which enables a limit to be fixed for the number of protons in the nucleus. This number must be less than 240. A. J. MEE.

Electronic structure of some diatomic molecules. J. E. LENNARD-JONES (Trans. Faraday Soc., 1929, 25, 668—686).—Mathematical. The Schrödinger wave-equation is applied to diatomic molecules. N. M. BLIGH.

Wave-mechanical condition for the stability of the atomic nucleus. J. KUDAR (Z. Physik, 1929, 57, 710—712).—Mathematical. J. W. SMITH.

***B*-State of the hydrogen molecule.** C. ZENER and V. GUILLEMIN, jun. (Physical Rev., 1929, [ii], 34, 999—1009).—Mathematical. The *B*-state of the H_2 molecule dissociates adiabatically into a normal and a two-quantum hydrogen atom, the corresponding band system being the Lyman bands. The *B*-state is treated by wave mechanics. The form of the wave function indicates that the *B*-state is partly, but not wholly, polar. N. M. BLIGH.

Rotational instability and uncoupling of the electronic orbital angular momentum from the axis in diatomic molecules. W. W. WATSON (Physical Rev., 1929, [ii], 34, 1010—1014; cf. this vol., 1136).—Theoretical. The details of several diatomic hydride bands are discussed to illustrate a number of peculiar rotational phenomena exhibited by some molecular spectra, and attributed to uncoupling of the electronic orbital angular momentum from the nuclear axis, which would contribute to a condition of rotational instability. N. M. BLIGH.

Quantum of cosmic radiation and the relative mass of proton and electron. A. K. DAS (Naturwiss., 1929, 17, 841).—If r_Q, the radius of a photon, is equal to c/v the wave-length must be of the order of the radius of an electron. Cosmic radiation has a wave-length of this order, and is therefore regarded as composed of quanta made up of protons and electrons separated by a distance equal to the radius of an electron. It is hence shown that $m_P'+m_E'/m_E=1839$, m_P' and m_E' being the masses of proton and electron, respectively. Coulomb's law is assumed to be true for a distance of 10^{-13} cm., and if this assumption is valid, the quantum of cosmic radiation would seem to be a miniature hydrogen atom. R. A. MORTON.

Colour efficiency of artificial retina. F. WEIGERT and M. NAKASHIMA (Naturwiss., 1929, 17, 840—841).—Glass plates covered with gelatin layers containing visual purple from frog retinas (artificial retina) have been studied in relation to photodichroism (cf. this vol., 871, 894), the results being quite analogous to those obtained with other light-sensitive dyes and photo-chlorides. The spectral curves for the dichroism with white and monochromatic linearly polarised light are given and it is found that, apart from red light, the same after-effects are obtained in the dark in all cases. The data support Weigert's theory of colour vision and the work indicates a new method of physiological investigation. R. A. MORTON.

Heisenberg's indetermination principle and the motion of free particles. A. E. RUARK (Physical Rev., 1928, [ii], 31, 311).—Theoretical. Heisenberg's principle is concluded to be valid. L. S. THEOBALD.

Atomic structure factor and Fourier analysis. G. E. M. JAUNCEY and W. D. CLAUS (Physical Rev., 1928, [ii], 31, 1118; cf. A., 1928, 938).—Comparison of a U-curve obtained from a Fourier integral now derived with a similar curve from Compton's formula for a model Cl′ atom shows agreement between the positions of the maxima. A U-curve gives the electron distribution relative to a lattice point of a crystal and not relative to the centre of the atom. L. S. THEOBALD.

Rotational distortion and Zeeman effect of diatomic molecules in wave mechanics. C. ZENER (Physical Rev., 1928, [ii], 31, 1115).—Mathematical. L. S. THEOBALD.

Heats of condensation of electrons on platinum in ionised helium, nitrogen, and argon. C. C. VAN VOORHIS and K. T. COMPTON (Physical Rev., 1928,

[ii], **31**, 1122).—The following values for ϕ have been obtained: platinum in argon 5·20, in neon 5·00, and in helium 4·77 volts. Relatively the values are accurate, but the absolute values may be 5% high. The work function of the metal in these gases varies with the gas used; it is the ions rather than the neutral atoms which influence this function.

L. S. THEOBALD.

A gas in crossed fields according to the quantum mechanics. K. F. NIESSEN (Z. Physik, 1929, **58**, 63—74).—Mathematical.

Raman effect and hydrogen spectrum. D. B. DEODHAR (Z. Physik, 1929, **57**, 570—572).—The Raman effect has been observed in the multiple line spectrum of hydrogen. Allen (cf. this vol., 363) has noted the phenomenon for diminished frequency for five Balmer lines. A further investigation revealed a large number of Raman lines of higher as well as lower frequencies from ten members of the Balmer series. The results obtained are compared with those of Allen. The displacements correspond with the rotation spectrum of hydrogen.

A. J. MEE.

Raman spectrum and geometrical isomerism. The Raman spectrum of the two forms of dichloroethylene. G. B. BONINO and L. BRÜLL (Z. Physik, 1929, **58**, 194—199).—The Raman spectra of the *cis*- and *trans*-forms of dichloroethylene were found. The excitation was by mercury arc, apparatus similar to Wood's being used. The *cis*-form has m. p. 60·25°; the *trans*, 48·35°. A number of differences are observed in the Raman spectra of the two forms. For short wave-length infra-red absorption the lines fall almost together. The C–H bands for both forms are at 3·25 μ and 6·30 μ; the 7·25 μ line also is coincident, but the *trans*-form shows two lines corresponding with 7·85 μ and 13·12 μ which do not appear with the *cis*-form. This is the greatest difference between the two forms in the arrangement of Raman lines below 15 μ. Above 15 μ there are wide differences. The *trans*-form has only one band at 41·1 μ, whereas the *cis*-form has three important bands at 17·60, 24·50, and 58·50 μ. The intensities of the lines were also investigated. The effect of geometrical isomerism in this very simple case is most marked, and differences also appear in the infra-red absorption spectrum.

A. J. MEE.

Scattering of light in crystals at high temperatures. G. LANDSBERG and L. MANDELSTAM (Z. Physik, 1929, **58**, 250).—The dispersion spectrum of quartz at high temperatures (800—900°) was investigated.

A. J. MEE.

Raman effect on organic substances. I. Raman spectra of simple benzene derivatives. II. Influence of temperature on Raman lines. Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 205—222).—I. Tables of the Raman lines are given for benzene, toluene, chlorobenzene, bromobenzene, phenol, nitrobenzene, and anisole. The line corresponding with wave-number difference 3060 cm.$^{-1}$ was assigned by Pringsheim and Rosen (A., 1928, 1307) to the fundamental frequency of the CH group. The author contends that, although the 3060 cm.$^{-1}$ is the strongest Raman line, Pringsheim and Rosen's assignment is not in agreement with the results of infra-red spectroscopy, and he prefers to regard it as the first harmonic. The fundamental frequency (6·4 μ) corresponds with a Raman displacement of about 1600 cm.$^{-1}$; this line, although much more faint than the other, occurs in all the compounds examined. The line corresponding with wave-number difference of 2921·4 cm.$^{-1}$ is attributed to the vibration of the CH_3 group. The effect of the coupling force of the substituent group, the sharpness of the lines, and the polarisation of the lines are discussed.

II. The effect of raising the temperature is to make some of the Raman lines more diffuse; others remain unaltered. The diffuseness of Raman lines may be due to quantised motion and the rise in temperature may accelerate this motion and thereby increase the diffuseness.

W. R. ANGUS.

Raman effect from powdered crystals. R. BÄR (Nature, 1929, **124**, 692).—Powdered naphthalene gives Raman lines at wave-numbers 21541, 21637, 21910, 22170, 22420, 23320, 23682, 23950, and 24195 cm.$^{-1}$, all having been observed previously for the liquid or dissolved material. The mercury line 4358 Å., when scattered by ammonium nitrate, gives rise to two lines of almost equal intensity with wave-numbers 22232 and 21882 cm.$^{-1}$, respectively, by calcium nitrate one line with 21884 cm.$^{-1}$; with sodium nitrate a strong line at 21864 cm.$^{-1}$ was possibly associated with two weaker lines. Sodium nitrite crystal powder gave one line at 21605 cm.$^{-1}$, whilst sodium chloride, ammonium bromide, and solid carbon dioxide gave no lines.

A. A. ELDRIDGE.

Raman effect and electrolytic dissociation. I. R. RAO (Nature, 1929, **124**, 762).—Nitric acid (65%) shows nine Raman lines—three for water, three for the HNO_3 molecule, and three for the NO_3 ion; the last group is exhibited also by nitrates. Raman lines belonging to the HNO_3 molecule gradually disappear with dilution; those belonging to the nitrate ion increase in brightness up to a certain dilution and thereafter diminish. The three water bands become sharper with increasing concentration of the acid; one diminishes and one increases in intensity as the concentration of acid is increased.

A. A. ELDRIDGE.

Polarisation of Raman lines. A. C. MENZIES (Phil. Mag., 1929, [vii], **8**, 504—515).—Using a small source and a double-image prism the light scattered by some organic liquids at angles of 90° and 180° was investigated. The polarisation can be explained on the assumption that the direction of the initial vibration is parallel to that of the final vibration for plane-polarised lines, and perpendicular for unpolarised lines, with intermediate inclination for partly polarised lines. The Raman spectrum of quartz was measured for three orientations of the optic axis, and the state of polarisation of the lines was investigated. Some of the scattered lines change their direction of polarisation through an angle of 90° as the direction of the optic axis is similarly turned. Two lines remained plane-polarised parallel to, and two others perpendicular to, the direction of the unmodified lines. An energy level diagram co-ordinating the Raman and infra-red observations is given.

N. M. BLIGH.

Raman effect of some aqueous solutions. P. PRINGSHEIM and M. YOST (Z. Physik, 1929, **58**, 1—6).—Aqueous solutions of sulphuric acid (12%), ammonium sulphate, sodium thiosulphate, sodium dithionate, selenious acid, potassium selenite, and a concentrated solution of uranyl sulphate in sulphuric acid have been investigated. The frequency differences characteristic of the sulphate and thiosulphate ions are nearly the same and are in close agreement with the frequency differences attributed to the sulphite ion by Dickinson and Dillon (this vol., 741). No characteristic wave-number difference can be assigned to the ammonium ion. The binding of the two sulphur atoms in the $S_2O_3^{--}$ and $S_2O_6^{--}$ ions is different and this explains the dissimilarity in Raman spectra of aqueous solutions containing these ions. It is found with both sulphuric and selenious acid that the acid gives a more diffuse spectrum than an aqueous solution of a salt; a salt shows a line not found in the spectrum of the acid. Uranyl sulphate gives a line apparently characteristic of the UO_2 radical. The frequency difference of this line agrees with the results obtained from fluorescence spectra. W. R. ANGUS.

Line absorption spectra of solids at low temperatures in the visible and ultra-violet regions of the spectrum. S. FREED and F. H. SPEDDING (Physical Rev., 1929, [ii], **34**, 945—953; cf. this vol., 490).—The absorption spectra of the synthetic uniaxial crystal $GdCl_3,6H_2O$ were investigated down to the temperature of liquid hydrogen, and found to consist of very sharp lines, mainly in the ultra-violet; with reduction of temperature the lines showed a slight shift towards the red, and a greater separation between the lines of each multiplet, due primarily to the contraction of the crystal bringing the ions closer together. Complete results are tabulated, and a simple new method for growing crystals from solution is described. N. M. BLIGH.

Molecular scattering of light from solids: crystalline sulphates and their water solutions. A. HOLLAENDER and J. W. WILLIAMS (Physical Rev., 1929, [ii], **34**, 994—996).—The Raman spectra of the sulphates of calcium, barium, copper, potassium, and aluminium were investigated and results tabulated for the crystalline state and in aqueous solution. For the crystals, lines corresponding with infra-red absorption bands at 4·54, 6·5, and 5·95 μ, and broad and diffuse Raman lines corresponding with the region 14—16 μ were found. For each crystal and solution strong lines were found at 4552 and 4213 Å., corresponding with an infra-red band at 10·2 μ associated with the sulphate ion. N. M. BLIGH.

Proof of the Maxwell-Boltzmann law by intensity measurements of the Raman effect for carbon tetrachloride. L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1929, **57**, 539—544).—The method used by Einstein to derive the Planck law is here used to find the intensity ratio of the Stokes-Raman lines and the anti-Stokes-Raman lines. The formula derived is $J_S/J_{AS}=(\nu-\nu_1)/(\nu+\nu_1)e^{h\nu_1/kT}$, where J_S and J_{AS} are the intensities, and ν, ν_1 are frequencies corresponding with two states. In order to test this equation intensity measurements were made with the Raman lines shown by carbon tetrachloride. With this substance the transition frequency is small and this gives rise to relatively strong anti-Stokes lines, so that the ratio J_S/J_{AS} is never less than 12. Good agreement was found between experiment and theory. The method also enables the value of h/k to be obtained with accuracy. A. J. MEE.

Absorption of ultra-violet light by some organic substances. L. MARCHLEWSKI and J. MAYER (Bull. Acad. Polonaise, 1929, **A**, 169—202).—The quantitative spectral absorption of furfuraldehyde, furfuramide, furyl alcohol, furan-2-carboxylic acid, the three isomeric toluic, nitrobenzoic, aminobenzoic, and hydroxybenzoic acids, the three isomeric nitrotoluenes, α- and β-naphthaquinolines, and benzaldehyde is described. All these substances show complicated selective absorption and follow Beer's law. The *para*-derivatives absorb much more strongly than the corresponding *ortho*- and *meta*-isomerides. A. A. GOLDBERG.

Spectro-chemical study of amino-acid anhydrides. III. Light absorption of some *N*-substituted diketopiperazines and some other amino-acid anhydrides. T. ASAHINA (Bull. Chem. Soc. Japan, 1929, **4**, 202—209).—The spectral absorptions of the following substances have been measured, the results being plotted by the older method: *N*-phenylglycine, m. p. 123·5—124·5°, and its ethyl ester, m. p. 55·5—56·5°; *NN'*-diphenyldiketopiperazine, m. p. 265°; ethyl benzylaminoacetate, b. p. 137°/8 mm.; benzylamine, b. p. 182—183°; *NN'*-dibenzyldiketopiperazine; *NN'*-diacetyldiketopiperazine, m.p. 102·5°, from glycine anhydride and acetic anhydride; NN'-*dipropionyldiketopiperazine*, m.p. 114·5°, obtained by heating glycine anhydride with propionic anhydride at 130—140° for 5 hrs.; *NN'*-dichloroacetyldiketopiperazine, m. p. 169°, best prepared by heating glycine anhydride with chloroacetic anhydride at 100° for 1 hr.; *NN'*-dibenzoyldiketopiperazine, m. p. 137°; hydantoin, m. p. 215°, ethyl hydantoate, m. p. 137·5—138·5°, γ-phenylhydantoin, m. p. 155°, γ-phenylhydantoic acid, m. p. 192°, and phenylcarbamide, m. p. 146—147°; benzaldehyde azlactone, m. p. 164·5°, and furfuraldehyde azlactone, m. p. 170·5°. A. I. VOGEL.

Absorption spectra and the nature of the chemical combination in thallous halides in the vapour state. K. BUTKOW (Z. Physik, 1929, **58**, 232—249).—The absorption spectra of thallous chloride, bromide, and iodide were investigated over the spectral range from 7000 to 1900 Å. Term tables are drawn up for the chloride and bromide. The convergence limits and heats of dissociation for these two salts are also obtained. The heat of dissociation of the chloride is 87·0 kg.-cal./mol., and that of bromide 73·1 kg.-cal./mol. Considering the nature of the chemical combination of the elements in the thallous halides, it is shown that all the salts are decomposed by absorbed radiation into excited atoms. A decomposition into unexcited atoms which is characteristic of ionic compounds was not observed. The conclusion reached is that in the vapour state the molecules are atomic compounds. The electronic affinity of chlorine and bromine was found to be 91 and 86·5 kg.-cal./mol., respectively. A. J. MEE.

Ultra-violet absorption spectra of benzene and toluene in alcoholic solution. C. V. SHAPIRO and R. C. GIBBS (Physical Rev., 1928, [ii], **31**, 310).—Twenty-three new bands in benzene and 21 in toluene are reported in the absorption spectra of these substances in alcoholic solution. Many of the new bands are narrow and resemble those of the vapours, to which, however, they cannot be ascribed. With a possible exception in the case of benzene, all the bands can be arranged in a series by means of a simple mathematical expression derived from the theory of band spectra. The results of Smith, Boord, Adams, and Pease (A., 1928, 152, 1308), indicating a benzene-like structure for the absorption spectra of certain organic compounds, are due to the presence of benzene as an impurity. L. S. THEOBALD.

Absorption of the halogen ions in aqueous solution in the near Schumann ultra-violet (electron affinity spectra). G. SCHEIBE (Z. physikal. Chem., 1929, **B**, **5**, 355—365).—The absorption spectra of the chloride, bromide, and iodide ions in aqueous solution have been determined photometrically from about 1800 to 2100 Å. The extinction coefficient–wave-length curve for the chloride ion exhibits but one maximum, at about 1820 Å., which is, however, probably the result of two adjacent maxima, for the bromide ion two well-defined maxima at 1995 and 1900 Å., whilst for the iodide ion there is a maximum at about 1950 Å. and a minimum at about 2080 Å. The distances between the maxima are in accordance with the view that by separation of the electrons the halogen atoms exist both in the stable 2^2P_2 and the metastable 2^2P_1 states. H. F. GILLBE.

Rotation–vibration spectrum of ammonia. R. M. BADGER and R. MECKE (Z. physikal. Chem., 1929, **B**, **5**, 333—354).—The absorption spectrum of ammonia has been photographed from 10,000 to 5900 Å. with a dispersion of 216 Å./mm. Of the bands observed, at 8810, 7920, and 6450 Å., the last two are the fourth and fifth of the series arising from the N–H vibration. All the infra-red absorption bands are derived from the three fundamental vibrations $\nu_1=3396-60n$, $\nu_2=1630$, and $\nu_3=966$. Investigation of the fine structure of the band at 7920 Å. indicates that the molecule is somewhat unsymmetrical, probably as a result of nuclear vibration; the three moments of inertia are $2{\cdot}79\times10^{-40}$, $2{\cdot}74\times10^{-40}$, and $3{\cdot}40\times10^{-40}$ g./cm.^{2}, whilst the distance between the nitrogen and hydrogen atoms is $0{\cdot}977\times10^{-8}$ cm. and between the hydrogen atoms $1{\cdot}43\times10^{-8}$ cm.; the height of the pyramidal molecule is $0{\cdot}517\times10^{-8}$ cm. H. F. GILLBE.

Co-ordination of the potentials of halogen ions and their ultra-violet absorption in aqueous solution. G. SCHEIBE (Z. Elektrochem., 1929, **35**, 701—703).—Iodide and bromide ions have two maxima in the ultra-violet absorption spectra of solutions containing them corresponding with an energy difference between the stable and metastable ions. It is argued from theory that there should exist a parallelism between the ultra-violet spectra and the electrode potentials of the various halogen electrodes. Curves showing the variation in the absorption spectra of halide ions with temperature are compared with the potential measurements of Schmid ("Die Diffusionsgaselektrode," Stuttgart, 1923). H. T. S. BRITTON.

Molecular spectra. W. E. GARNER and J. E. LENNARD-JONES (Trans. Faraday Soc., 1929, **25**, 611—627).—A general survey of the present state of knowledge of molecular spectra with regard to the experimental technique of research in the infra-red, visible, and ultra-violet regions. The theoretical systematisation due to the introduction of wave mechanics, nature and origin of the spectra, notation employed, and results are explained and discussed. N. M. BLIGH.

Absorption spectrum of nitric oxide. M. LAMBREY (Compt. rend., 1929, **189**, 574—576).—Measurements for the band $0\longrightarrow0$ of the γ-system of nitric oxide (λ 2265 Å.) have shown that the apparent optical density is a function of lp^x, where l is the length of the absorption tube (0·75—1032 mm.), p the pressure, and x equals $1{\cdot}81\pm0{\cdot}03$. Although this is the resonance band of the NO molecule no selective diffusion was observed as in the case of the 2537 Å. mercury line. The effect of change of temperature (−80° to 300°) is in agreement with the classical laws of the distribution of intensities in band spectra. J. GRANT.

New spectrum of gaseous alkali halides, and its significance. K. SOMMERMEYER (Z. Physik, 1929, **56**, 548—562).—Diffuse bands appear at the long-wave limit of the continuous spectrum when the temperature of the salt is sufficiently high. Measurements of minima show convergence towards the red, showing these bands as due to different vibration levels of the unexcited molecule. Different vibration levels in the excited state seem too close to be resolved. This suggests that the normal electronic state always corresponds with ionic binding, the excited state with binding by polarisation; that is, the alkali halides are ionic molecules on Franck's classification. A. B. D. CASSIE.

Intensities of lines in the ammonia band at 2 μ, and the form of the ammonia molecule. E. F. BARKER (Physical Rev., 1928, [ii], **31**, 1131).—Intensity computations show the molecule to be oblate, and the distance from the nitrogen atom to the plane of the three hydrogen atoms is 0·06—0·1 of the distance between the hydrogen atoms. L. S. THEOBALD.

Effect of *X*-rays on the infra-red absorption of kunzite and hiddenite. P. L. BAYLEY (Physical Rev., 1928, [ii], **31**, 1132; cf. A., 1928, 1312).—The range of measurement of the spectral transmission of kunzite and hiddenite, before and after exposure to *X*-rays, has been extended to 4·5 μ. L. S. THEOBALD.

Infra-red investigations of molecular structure. III. Molecule of carbon monoxide. C. P. SNOW and E. K. RIDEAL (Proc. Roy. Soc., 1929, **A**, **125**, 462—483).—The vibration–rotation band ($n''=1/2\longrightarrow n'=3/2$) of carbon monoxide has been resolved, the measurements being made with the gas at a pressure of 11 cm. The band consists of P and

R branches only, the R branch being convergent, and its centre is at $2144 \pm 0{\cdot}4$ cm.$^{-1}$ The first overtone ($n''=1/2 \longrightarrow n'=5/2$), consisting of P and R branches, has been plotted and the P branch partly resolved. The centre of the band is at 4266 ± 1 cm.$^{-1}$ Almost all the results obtained agree with those calculated for the vibration–rotation bands of a molecule in a ^1S state, acting as an anharmonic oscillator, and with the actual experimental values for the vibration frequency and constant of anharmony obtained from the electronic bands. The following values are deduced: $\omega_0=2155$, $\omega_0 x=11$, $I=1{\cdot}50 \times 10^{-39}$ g.-cm.^{2}, and $r=1{\cdot}15 \times 10^{-8}$ cm. With a knowledge of the fine structure, the potential function can be completely expressed. The potential function can also be expressed as $V=e^2(C_1/r+C_2/r^4)$, and on this basis it is possible to describe the positions of the lines in the R and P branches of the fundamental by an expression involving only I, ω_0, and x. The subject of alternating intensities is briefly considered. It appears certain that there cannot be regular alternating intensities in any bands save those due to a completely symmetrical molecule X_2 (*e.g.*, acetylene and ethylene). L. L. BIRCUMSHAW.

Structure of OH bands. R. S. MULLIKEN (Physical Rev., 1928, [ii], **31**, 310).—Each band comprises six main branches, six weak series, and a further weak branch extending towards high frequencies from each band. The main branches ($\Delta j_k=\Delta j$) and four of the weaker agree completely with Hund's predicted structure for $^2S \longrightarrow$(inverted)^2P, except that the latter branches are stronger than predicted. The last-mentioned weak branch is identified as an R branch ($\Delta j=1$), but $\Delta j_k=2$, and a companion P branch, at present unknown, is expected. The occurrence of the R branch and the high intensity of the weak series show OH as a transition case between CH 3900 Å. and HgH. The ZnH bands lie between OH and HgH in all these features. Two of the six weak series have $\Delta j_k=\Delta j$ like main branches, but differ by forming the first known exceptions to the usual rules of σ-type doubling. L. S. THEOBALD.

Water absorption band at 9727 Å. J. E. LAMBLY (Physical Rev., 1928, [ii], **31**, 706).—The water absorption band in the near infra-red has been located at 9727 Å. for a temperature of 22° (cf. Collins, *ibid.*, 1927, **26**, 771). Photographic records of spectral intensity and density measurements have been made, and ratios were computed to determine absorption peaks which have been measured. The average of the three independent determinations made should be accurate to 10 or 12 Å.

L. S. THEOBALD.

Tesla-luminescence spectra. VI. Some phenolic compounds and their ethers. J. C. MACMASTER, A. RUSSELL, and A. W. STEWART (J.C.S., 1929, 2401—2407; cf. McVicker and others, A., 1925, ii, 630).—Photographs were obtained of the spectra emitted under the Tesla discharge by 41 phenols and phenolic ethers, and the wave-length limits of the continuous spectrum, region of maximum brilliancy, occurrence of a glow in the visible region, and the positions of bands are tabulated for each substance. The effect of substitution on the benzene ring, and similarities for ethers and corresponding chains composed entirely of hydrocarbon radicals, are discussed. Interrupted spectra characterised by a region of non-emission between two regions of emission are shown in the similar spectra of hydrindene and benzyl methyl ether, and of tetrahydronaphthalene and benzyl ethyl ether. This suggests a curving of the ether chains so as to make the ether molecule analogous to the closed-chain compounds. A fresh type of emission, or violet glow, was observed in several ether spectra. A band observed at 4315 Å. in several of the spectra is provisionally attributed to the decomposition of a complex ether with liberation of the alkyl group and a phenol. N. M. BLIGH.

Tesla-luminescence spectra. VII. Some aromatic aldehydes. A. RUSSELL and A. W. STEWART (J.C.S., 1929, 2407—2412; cf. preceding abstract).—Twenty aromatic aldehydes were examined, and out of 17 containing a single benzene nucleus 11 showed no detectable emission. Spectral details are given for benzaldehyde, 3- and 4-methylbenzaldehyde, 3 : 4-dimethylbenzaldehyde, 4-propylbenzaldehyde, anisaldehyde, and piperonal. All the emitting compounds showed the benzaldehyde blue band type of spectrum. The banding of the spectrum appears to be associated with the benzene ring and is deeply modified by substitution; a methyl group *ortho* to the aldehyde group extinguishes emission in the blue region; *p*-substitution reduces the number of detectable bands. The introduction of a hydroxyl group quenches the emission of the aldehydes, but methoxyl groups do not necessarily extinguish the blue band series. N. M. BLIGH.

High-frequency discharge in organic vapours. P. N. GHOSH and B. D. CHATTERJEE (Nature, 1929, **124**, 654).—The striated character of the electrodeless discharge is described. Vapours, *e.g.*, of propyl bromide, when thus ionised give rise to band spectra.

A. A. ELDRIDGE.

Foreign ion content of alkali halide phosphors. W. KOCH (Z. Physik, 1929, **57**, 638—647).—It is found that the foreign ion content of crystals of alkali halide phosphors is only 0·5—0·05 of that in the fused mass from which the crystals are prepared. The relation between the heavy metal content, as determined by direct analysis of the crystals, and the absorption at the absorption maximum has been followed. In the case of potassium chloride–thallium chloride phosphor the absorption constant rises almost linearly with the concentration of thallium ion, but potassium chloride–lead chloride was found to be non-homogeneous and no satisfactory data could be obtained. The absorption curves for different concentrations of foreign ion have also been followed. The absorption spectra of aqueous solutions of the chlorides and bromides of lead and thallium have also been investigated. The effect of addition of considerable quantities of potassium chloride on the absorption spectrum of lead chloride solution is also indicated. J. W. SMITH.

Efficiencies in luminescence accompanying electrolysis. R. T. DUFFORD (Physical Rev., 1928, [ii], **31**, 157; cf. A., 1928, 994).—The luminescence

at the electrodes accompanying electrolysis has been studied for many solutions with different metals as electrodes, the chief cases being those of aluminium in sodium phosphate or carbonate solutions, and almost any metal in anhydrous ethereal solutions of Grignard reagents. The brightness ranges from 6×10^{-9} to 10^{-5} lambert, and generally increases with applied *P.D.* Efficiency increases and then decreases with an increase in voltage, but is practically unaffected by changes in concentration and is the same for chemically similar solutions. L. S. THEOBALD.

Metallic reflexion from rock-salt and sylvite in the Schumann region. A. H. PFUND (Physical Rev., 1928, [ii], **31**, 315; cf. A., 1928, 934).—The maxima of reflexion lie near 1600 Å. for rock-salt and near 1625 Å. for sylvite, with indications of further maxima near 1000 Å. L. S. THEOBALD.

Dielectric constant and electric moment of some alcohol vapours. J. B. MILES, jun. (Physical Rev., 1929, [ii], **34**, 964—971).—By using a new method of measuring the pressure of the hot vapour, the dielectric constant of the vapours of methyl, ethyl, *n*-propyl, and *n*-butyl alcohols was measured at several temperatures. Good agreement was found with Debye's equation for the dielectric constant of gases at higher temperatures where there is no association. Association is discussed theoretically. The calculated electric moments $\times10^{-8}$ are respectively 1·68, 1·69, 1·65, and 1·65. N. M. BLIGH.

Dielectric constants and molecular structure of carbon disulphide and nitrous oxide. P. N. GHOSH, P. C. MAHANTI, and B. C. MUKHERJEE (Z. Physik, 1929, **58**, 200—204).—The dielectric constants of carbon disulphide and nitrous oxide determined by the usual balance method are respectively 1·002912 and 1·001050. The electric moments were calculated from the Debye equation, and the Debye function, y, is plotted against temperature. The curves show that neither substance possesses a definite dipole moment, and the Maxwell relationship holds, *i.e.*, the dielectric constant is equal to the square of the extrapolated refractive index for infinitely long waves. The non-polar nature of nitrous oxide is also shown by its relatively weak Kerr effect. The observations show that the molecules of nitrous oxide and carbon disulphide are linearly symmetrical. A. J. MEE.

Dielectric polarisation potential and the law of superposition for hard rubber. H. H. RACE and J. R. CAMPBELL, jun. (Physical Rev., 1929, [ii], **34**, 1031—1034).—A sample of hard rubber (ebonite) was subjected to several similar conditions of charge at a constant potential of 884 volts per cm., and to different conditions of discharge at potentials from 829 to 882 volts per cm. Results indicate that the polarisation potential built up during a long-time charge is approximately equal and opposite to the charging potential. The current–time curve predicted from Curie's law of superposition with data previously obtained for the sample was in close agreement with the actual curve. N. M. BLIGH.

Dielectric constants of benzene, carbon disulphide, and carbon tetrachloride, and of dilute solutions of alcohols in these solvents. J. D. STRANATHAN (Physical Rev., 1928, [ii], **31**, 156; cf. A., 1928, 576).—The dielectric constants of benzene, carbon disulphide, and carbon tetrachloride have been determined at temperatures between the f. p. and b. p. by means of a high-frequency beat method, and also of dilute solutions of methyl alcohol in benzene and in carbon tetrachloride, and of amyl alcohol in benzene. The electric moments of methyl and amyl alcohols (in benzene) obtained by a graphical method are $1·66\times10^{-18}$ and $1·65\times10^{-18}$ e.s.u., respectively. For methyl alcohol in carbon tetrachloride, the results are inconsistent with the Debye theory, possibly owing to association. The calculated moment of the alcohol molecule in this case is $1·65\times10^{-18}$, assuming that there is no association at the b. p. L. S. THEOBALD.

Nature of the general polarisation effect in aromatic molecules. W. A. WATERS (Phil. Mag., 1929, [vii], **8**, 436—441).—The general polarisation effect in aromatic molecules may be correlated with the dipole moment μ of the substituent group. From $\log K_s/K_u \propto \mu$, where K denotes the reaction velocity coefficients of the substituted and unsubstituted compound, the relative orders of magnitude of the reaction velocities of all *meta*-substituted aromatic compounds can be predicted from the electrical dipole moments of the substituent groups, and *vice versâ*. The prediction is less certain for *para*-compounds, and is not possible for *ortho*-compounds. N. M. BLIGH.

Time-lag differences of the Faraday effect in several mixtures and compounds. F. ALLISON (Physical Rev., 1928, [ii], **31**, 313).—The time-lag previously observed (*ibid.*, 1927, **30**, 66) has been studied with mixtures of liquids and with certain chemical compounds. Each liquid retains its own lag on mixing. Lags for various wave-lengths have been measured in ethyl alcohol, acetic acid, and ethyl acetate; the last-named shows two time-lag differences, those of the alcohol and the acid, for each wave-length used. Similar results are obtained with acetic acid, amyl, *n*-butyl, and methyl alcohols, and the corresponding esters, the esters showing no specific lag. L. S. THEOBALD.

Calculation of the number of dispersion centres in sodium. W. K. PROKOFIEV (Z. Physik, 1929, **58**, 255—267; cf. Sugiura, A., 1927, 1004).—The calculation carried out by Sugiura for the first two doublets of the principal series of sodium is repeated. The calculation is simplified and extended. In the first place the potential energy of the valency electrons of sodium is calculated. The determination of the characteristic function of the Schrödinger wave equation is then carried out, and the probability of switch and number of dispersion centres are obtained from it. The calculation can be applied in an easy way to the third and fourth doublets of the principal series and some of the first doublets of the secondary and combination series. A. J. MEE.

Magneto-optical dispersion of some organic liquids in the ultra-violet region of the spectrum. C. C. EVANS and E. J. EVANS (Phil. Mag., 1929, [vii], **8**, 137—158).—The magneto-optical rotations of *iso*propyl alcohol, allyl alcohol, methyl acetate, and

ethyl acetate have been determined for wave-lengths in the violet and longer ultra-violet spectral regions. The refractive indices of *iso*propyl alcohol, methyl acetate, and ethyl acetate have been determined for the same wave-lengths. The values of ϕ ($=n\delta\lambda^2$) for the respective compounds are given by $5{\cdot}5526\times 10^{-3}\{\lambda^2/(\lambda^2-0{\cdot}1137^2)\}^2$, $7{\cdot}24\times10^{-3}\{\lambda^2/(\lambda^2-0{\cdot}1372^2)\}^2$, $4{\cdot}587\times10^{-3}\{\lambda^2/(\lambda^2-0{\cdot}1117^2)\}^2$, and $4{\cdot}825\times10^{-3}\{\lambda^2/(\lambda^2-0{\cdot}1140^2)\}^2$, where n=refractive index, δ=Verdet's constant in minutes per cm. gauss for wave-length λ and the wave-lengths of the absorption bands controlling the magneto-optical rotations of *iso*propyl alcohol, allyl alcohol, methyl acetate, and ethyl acetate are respectively 0·1137 μ, 0·1372 μ, 0·1117 μ, and 0·1140 μ. A. E. MITCHELL.

Refractive indices of calcite in the wave-length range of 2—6 Å. E. DERSHEM (Physical Rev., 1928, [ii], **31**, 916).—For calcite the reflexion method gave $1-\mu=17{\cdot}8\times10^{-6}$ at 1·98 Å. and 137×10^{-6} at 6·00 Å., in good agreement with the values calculated from the Drude–Lorentz formula. Within 0·2 or 0·3 Å. of the calcium absorption limit the values of $1-\mu$ are depressed on both sides of the absorption edge as required by quantum theories of *X*-ray dispersion. L. S. THEOBALD.

Interferometric experiments on liquids in an electric field. K. SCHAUM and E. WALTER (Z. wiss. Phot., 1929, **27**, 109—112).—An experimental method is devised for the separate determination of the optical changes produced by the thermal and electric effects. With certain organic liquids, such as *tert.*-amyl chloride and *o*-nitrotoluene, the thermal effect is greater than the electric effect from the commencement of excitation by the electric field, or at least after a time of excitation of 1 second. For other substances, however, such as nitrobenzene and ethyl phenylacetate, the electric effect predominates for a certain time. J. W. GLASSETT.

Surface tension. IV. Mechanics of drops pendant from cylindrical tubes. A. W. PORTER (Phil. Mag., 1929, [vii], **8**, 180—186).—The mechanics of the formation of sustained drops for cylindrical tubes is discussed. It is shown that assuming conditions such that contact between the drop and a tube of infinitely thin wall is made above the end of the tube, then for a given material one and only one weight of pendant drop can be in equilibrium near the end of a tube of given outside radius of curvature, the weight being determined by the expression $W/\pi\sigma a=1+a/c$, where W=weight of drop, σ=surface tension, a=radius of tube to the outside, and c=radius of curvature at the point of contact between liquid and tube. Values calculated from this expression are in fair agreement with those determined by Rayleigh and by Harkins and Brown. A. E. MITCHELL.

Interpretation of the temperature coefficient of surface tension. N. K. ADAM (Phil. Mag., 1929, [vii], **8**, 539—547; cf. Hunten and Maass, this vol., 252).—On the view that the rate of decrease of surface tension with temperature is the rate of increase of the thermal bombardment pressure exerted by the surface molecules, parallel to the surface on a barrier in the surface, a number of factors, some at present undeterminable, affecting the value of the Eötvös constant are considered. The temperature coefficient of surface tension of four homologous aliphatic series is considered, and new data are presented for long-chain compounds. There is nearly complete orientation of the surface molecules when the chains are ten carbon atoms or more long, if the molecules have a polar group at one end; the hydrocarbons are probably not fully oriented until double this length of chain. The intensity of vibration of the molecules of the triglycerides appears to be somewhat less than that of three chains separately, although the chains move independently in some degree. N. M. BLIGH.

Determination of the orientation of a crystal from a Laue photograph. K. YAMAGUCHI and S. TOGINO (Bull Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 603—608).—Details are given of a "crystallometric globe" by which the orientation of a crystal axis may be obtained mechanically after the type and co-ordinates of the face have been determined from a Laue photograph. With a globe of 6 cm. radius the limit of error is less than 0·1°. F. G. TRYHORN.

Supposed effect of *X*-rays in crystal rectifiers. S. OBERTO (Atti R. Accad. Lincei, 1929, [vi], **10**, 89—92).

Significance of *X*-ray analysis of alkali sulphates. A. E. H. TUTTON (Phil. Mag., 1929, [vii], **8**, 195—201).—The classical optical and morphological constants of the series of alkali sulphates are discussed in the light of the results of *X*-ray analysis, and it is pointed out that in this series of eutropic isomorphous compounds the whole of the morphological and physical properties of their crystals are functions of the atomic numbers and atomic weights of the interchangeable family-group elements giving rise to the series. This result is considered to afford a proof of the law of Haüy that to every definite chemical substance crystallising in any but the cubic system there is a particular crystalline form (or forms if polymorphous) peculiar to and characteristic of the substance. A. E. MITCHELL.

***X*-Ray analysis of chromium–nickel alloys.** F. C. BLAKE, J. O. LORD, W. C. PHEBUS, and A. E. FOCKE (Physical Rev., 1928, [ii], **31**, 305; cf. A., 1928, 1313).—Etching, photomicrographs, and *X*-ray analysis show the presence of a third, rhombohedral phase in nickel–chromium alloys. This rhombohedral lattice, together with the body-centred lattice, is present in alloys containing 65—85% Cr. L. S. THEOBALD.

Interpretation of *X*-ray crystal photographs. II. Complete rotation photographs. W. H. GEORGE (Phil. Mag., 1929, [vii], **8**, 442—456; cf. this vol., 381).—A mathematical instrument is described which directly interprets the principal axis, and complete rotation of cubic, tetragonal, hexagonal, and trigonal crystals. In combination with the previously described grid method of measuring *X*-ray photographs, the method is independent of the nature of the spectrometer, the wave-length of the *X*-rays, or the size of the unit cell of the particular substance. Some applications are described, and some tables of constants are given for use in connexion with reciprocal

lattice methods for interpretation of rotation photographs. N. M. BLIGH.

Fine structure of the absorption bands of crystals. H. M. RANDALL and H. H. NIELSEN (Physical Rev., 1928, [ii], **31**, 1131).—A fine structure with the lines spaced approximately 23 Å. apart has been developed in the band of calcium carbonate at 3·5 μ. L. S. THEOBALD.

***X*-Ray investigation of the structure of naphthalene and anthracene.** J. M. ROBERTSON (Proc. Roy. Soc., 1929, **A**, **125**, 542—569).—The crystal structures of naphthalene and anthracene, examined by the rotating-crystal method, are found to be closely similar. The former has *a* 8·34, *b* 5·98, *c* 8·68, β 122° 44′, *d* 1·152; the latter *a* 8·58, *b* 6·02, *c* 11·18, β 125° 0′, *d* 1·250. The space-group is C_{2h}^5 in each case and there are two molecules in the unit cells, which must therefore possess a centre of symmetry. A geometrical structure factor is developed for these conditions. A study of the relative intensities of reflexion at various planes indicates that there is a fundamental periodicity along the *c* axis of amount 1·28 Å. in both naphthalene and anthracene, and that the scattering centres lie nearer the *ac* than the *bc* planes. Since the molecules do not exhibit even an approximate plane of symmetry in the *ac* planes, it is assumed that the scattering centres lie in two rows parallel to the *c* axes, forming a chain-like structure. With this limitation, a compact geometrical structure factor is developed for the general case of *n* scattering centres (each regarded as a carbon atom with its attendant hydrogen atom, if any), and a detailed examination of the parameters leads to values which account for the intensity distribution in the various spectra of the two crystals. The structures are found to be alike, within the limits of experimental error. The dimensions of the molecules differ very little from those of Bragg's tetrahedral structure, and the chain structure, moreover, is shown to be closely related in many of its dimensions to that of the hydrocarbon $C_{29}H_{60}$ (Müller, A., 1928, 1176). This affords strong evidence that the tetrahedral properties of the carbon atom are maintained in aromatic structures. L. L. BIRCUMSHAW.

Quantitative study of reflexion of *X*-rays from crystals of aluminium. R. W. JAMES, G. W. BRINDLEY, and R. G. WOOD (Proc. Roy. Soc., 1929, **A**, **125**, 401—419; cf. James and others, A., 1928, 225, 462).—By means of the method previously used for crystals of rock-salt and sylvine (*loc. cit.*), measurements have been made of the intensity of reflexion of *X*-rays by single crystals of aluminium at the ordinary temperature and at the temperature of liquid air. The temperature factor deduced from the results is in close agreement with that predicted by the Debye–Waller theory, and the absolute values of the atomic scattering power *F*, corrected by means of the measured temperature factor, agree with those calculated theoretically from the Schrödinger charge-distributions, assuming the existence of zero-point energy. L. L. BIRCUMSHAW.

Precision measurements of *X*-ray reflexions from crystal powders. M. L. FULLER (Phil. Mag., 1929, [vii], **8**, 585—586; cf. Brentano and Adamson, this vol., 493).—A discussion of the relative accuracy of available data for the lattice parameter of cadmium oxide. N. M. BLIGH.

Spinning target *X*-ray generator and its input limit. A. MÜLLER (Proc. Roy. Soc., 1929, **A**, **125**, 507—516).—Mathematical. In an ordinary *X*-ray tube a limit for the specific input is soon reached owing to the intense heating of the focus and the consequent deterioration of the target surface, but by keeping the target moving this limitation may be avoided. An estimate is made of the extent to which the specific input may be increased by this means. L. L. BIRCUMSHAW.

Systematics of the types of binding of diatomic molecules. H. LESSHEIM and R. SAMUEL (Naturwiss., 1929, **17**, 827).—The relations between the two deepest electron terms of diatomic molecules have been investigated with reference to their potential curves. Analysis of the different possibilities indicates a definite correlation between the potential curves and the types of binding. Normal molecules in the chemical sense, whether atom- or ion-molecules, are merely those in which the union of two unexcited atoms or ions leads to a state possessing greater energy of dissociation than that resulting from the combination of one excited and one unexcited entity. R. A. MORTON.

Term resolution in crystals. H. BETHE (Ann. Physik, 1929, [v], **3**, 133—208).—The influence of an electrical field of known symmetry (crystal field) on an atom has been treated by the methods of wave-mechanics. R. A. MORTON.

Chemical binding. F. HUND (Trans. Faraday Soc., 1929, **25**, 646—648).—The properties which enable atoms to form bindings are investigated and discussed, and their relation to London's analogy between chemical valency and some quantum properties of atoms is considered. London's work appears to give a quantum theoretical explanation of valency by the energies arising from the disappearance of the exchange degeneracy. N. M. BLIGH.

Structure of diatomic molecules. G. HERZBERG (Z. Physik, 1929, **57**, 601—630).—By extensions of the methods of Mulliken (A., 1928, 1067; this vol., 116) and of Hund (this vol., 117) an attempt is made to explain the disagreements obtained when the stable electronic states of a diatomic molecule are calculated by different methods. The theory developed is applied to the calculation of the heats of dissociation of a large number of diatomic molecules for which suitable data are available. J. W. SMITH.

Molecular structure of the silicotungstates and related compounds. L. PAULING (J. Amer. Chem. Soc., 1929, **51**, 2868—2880).—The principles previously enunciated (this vol., 748) are used to determine the structures of silicododecatungstic acid and analogous acids. The structures proposed lead to the formula $H_x[MO_4,W_{12}O_{18}(OH)_{36}]$, where $x=3, 4, 5, 6$, respectively, when M=P, Si, B, H_2. This formula is in complete agreement with the known properties of these complex acids. Structures are also proposed for *iso*silico- and for *iso*boro-dodecatungstic acids, which correspond respectively with the formulæ

$H_4[SiW_{12}O_{40}],15H_2O$ and $H_5[BW_{12}O_{40}],15H_2O$; suggested structures are also given for some unsaturated (or condensed) heteropoly-acids. S. K. TWEEDY.

Structure of crystal hydrates. A. KAPUSTINSKY (Z. physikal. Chem., 1929, **144**, 187—196).—A study of the heats of hydration for the addition of successive water molecules to salts which have an odd number of molecules of hydration, and of the molecular heats of these compounds, indicates that the first molecule of water is bound in a different way from the rest. Ions such as those of zinc, magnesium, manganese, copper, lanthanum, iron, and nickel, which form such hydrates, have average ionic radii and charge densities sufficient in general for the attraction of water, and consequently for the formation of crystal hydrates, but insufficient for hydrolysis. The hypothesis here put forward, that in these crystal hydrates the first water molecule is bound constitutionally (*i.e.*, the metal combines with the hydroxyl group and the anion with the hydrogen ion), is in accord with Werner's theory and with the electrostatic theory of chemical affinity. Structural formulæ for these and other hydrates are suggested. F. L. USHER.

Chemical combination as an electrostatic phenomenon. II, III. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, **26**, 114—118, 146—149).—II. The electrostatically stable arrangement of the ions in various types of molecules is described with reference to the periodic classification, and the varieties of ion which can be formed are classified: Six classes of positive ion are recognised: (1) the hydrogen ion; (2) ions with the helium configuration; (3) ions with eight outer electrons, derived from elements following the inert gases by loss of electrons up to eight in number, *e.g.*, ruthenium and osmium; (4) ions with eight outer electrons but containing more electrons than the corresponding inert gas; (5) ions with eighteen outer electrons, derived from elements following nickel, palladium, platinum; (6) ions of a lower degree of symmetry in which the highest valency is not attained, *e.g.*, iron, cobalt, nickel, rhodium, palladium, iridium, and platinum.

III. The space configuration of the ions in molecules containing from 1 to 4 negative ions attached to a positive nuclear ion is discussed. From the similarities of, *e.g.*, lithium hydride with the halides of the alkali metals and of boron hydride, B_2H_6, with the boron halides it is suggested that in such compounds the hydrogen is present as a negatively charged ion. This view is supported by the behaviour of the hydrocarbons towards substituents and by the contrasts between the properties of halides in various groups of the periodic classification. The manner in which crystal lattices are built up from polar molecules is described. H. F. GILLBE.

Molecular linking and other properties of the hydrogen halides. R. T. BIRGE and O. R. WULF (Physical Rev., 1928, [ii], **31**, 917).—Theoretical. Energy level diagrams for hydrogen fluoride, chloride, bromide, and iodide have been devised, using recent data. These substances appear to exist with atomic linking in the non-vibrational state, but a dissociation into ions is also indicated. The heat of dissociation of these molecules in the ionised condition is approximately zero or negative. L. S. THEOBALD.

Dissociation of molecules by rotation. O. OLDENBERG (Z. Physik, 1929, **56**, 563—575).—The curves connecting potential energy with nuclear distance, when modified to include rotational energy, explain the sudden disappearance of rotational levels, and show that the energy of the last discrete level is not the energy of dissociation. Diffuse lines are expected near this critical edge. An example is mercurous hydride. A. B. D. CASSIE.

Gas content, crystal structure, and hydrogen absorption of sputtered nickel films. L. R. INGERSOLL and J. D. HANAWALT (Physical Rev., 1929, [ii], **34**, 972—977).—By using a special deposition tube to allow withdrawal of the cathode without altering vacuum conditions, films of nickel were sputtered in hydrogen, helium, nitrogen, and argon, and their gas content was investigated. The gas is emitted just below the baking temperature range for which the films become magnetic and better conducting. In addition to the influence of crystal structure, evidence indicates that the gas, by keeping the atoms apart, is mainly responsible for the abnormal magnetic properties of the films. Evaporated films contained much less gas than the sputtered, even when produced at the same gas pressure, the gas being excited or activated during the sputtering process, and its occlusion promoted; the evidence pointed to the production of nickel hydrides and nitrides. The films showed a high absorption for hydrogen above a critical temperature depending on the previous heat treatment. N. M. BLIGH.

Crystal disintegration and formation. P. P. VON WEIMARN (Kolloid-Z., 1929, **49**, 149—150).—A summary of previously published work on the conditions of formation and disintegration of small crystals. E. S. HEDGES.

Crystal structure of *m*-iodobenzoic acid. H. P. KLUG, E. MACK, jun., and F. C. BLAKE (J. Amer. Chem Soc., 1929, **51**, 2880—2888).—Assuming β to be 91° 29·5′ (Groth), the axial ratio of *m*-iodobenzoic acid is $a:b:c=1{\cdot}3252:1:5{\cdot}5824$, and the unit cell, which contains 4 mols., has a_0 6·206, b_0 4·683, and c_0 26·14 Å. The space-group is C_{2h}^5, in the monoclinic prismatic group. The parameters of the molecules in the unit cell were determined; the structure embodies a "puckered" benzene ring. The use of absorbing filters in Laue spot *X*-ray photography is discussed briefly and justified. S. K. TWEEDY.

Crystallographic and optical properties of diaminozinc chloride formed in the Leclanché cell. K. CHUDOBA (Zentr. Min. Geol., 1929, **A**, 139—143; Chem. Zentr., 1929, i, 2865).—In addition to the compound $ZnCl_2,6NH_3$, *d* 1·50, *H* 1, n_ω 1·539±0·002, the compound $ZnCl_2,2NH_3$, which appears in three habits, was observed. A. A. ELDRIDGE.

Crystal structure of strontium oxide. T. A. WILSON (Physical Rev., 1928, [ii], **31**, 1117).—The pattern of the oxide has been isolated from spectrograms of a mixture of the oxide and carbonate. The

lattice is of the sodium chloride type with 5·073±0·01 Å. length of cube edge, and d 5·235.

L. S. THEOBALD.

Crystal structure of potassium dithionate. M. L. HUGGINS and G. FRANK (Physical Rev., 1928, [ii], **31**, 916).—X-Ray spectra from rotating crystals show the space-group to be $D_3^1(3D-1)$ of the hexagonal system. The unit structure has a_0 9·8, c_0 6·45 Å., and contains 6K, 6S, and 18 oxygen atoms. The sulphur atoms are in pairs on the three-fold symmetry axes, each sulphur atom having 3 oxygen atoms placed symmetrically around it. L. S. THEOBALD.

Crystalline structure of bromides of bivalent metals. A. FERRARI and F. GIORGI (Atti R. Accad. Lincei, 1929, [vi], **9**, 1134—1140).—The bromides of cobalt, ferrous iron, magnesium, and manganese possess structures of the cadmium iodide type. The characteristics of these substances, in the above order, are: a 3·685, 3·740, 3·815, 3·820 Å.; c 6·120, 6·171, 6·256, 6·188 Å.; c/a 1·66, 1·65, 1·64, 1·62; d 5·072, 4·790, 3·876, 4·549. F. G. TRYHORN.

Vanadium-carbon system. S. OYA and A. OSAWA (J. Study Met., 1928, **5**, 434—441).—Vanadium has a body-centred cubic lattice, a 3·024 Å. Vanadium–carbon alloys contain (α) a phase consisting mainly of vanadium, (β) a phase having a close-packed hexagonal lattice with axial ratio 1·59, and (ε) a phase having a face-centred cubic lattice. The effect of varying amounts of carbon on the lattice has been examined. The β-phase consists of the compound V_5C, and the ε-phase of the compound V_4C_4. CHEMICAL ABSTRACTS.

Electrical and optical behaviour of half conductors. I. Hall effect and conductivity of silver sulphide. F. KLAIBER (Ann. Physik, 1929, [v], **3**, 229—253).—The Hall effect has been determined for both modifications of silver sulphide in the form of plates prepared in different ways from pure materials. The Hall constant and the conductivity have been measured at temperatures between 160° and 225°, the results for different specimens agreeing within a few per cent. The transformation: β-Ag_2S (rhombic) $\longrightarrow$ α-Ag_2S (regular) at 179° is accompanied by a change in Hall constant from 20 cm.^{3}/amp. sec. to about 0·6 cm.^{3}/amp. sec.; the conductivity of 1·5 ohm^{-1} cm.$^{-1}$ increases 310 times, so that α-Ag_2S at the transformation point has a conductivity of $4{\cdot}7\times10^2$ ohm^{-1} cm.$^{-1}$, *i.e.*, about 100 times as great as that of the best molten electrolytes. The product of the Hall constant and the conductivity for both modifications of silver sulphide lies between the limits observed for metals. No Hall effect could be observed for solid, regular silver iodide (α-AgI). The interpretation of the results is discussed.

R. A. MORTON.

Variations of the Hall coefficient, of the thermoelectric power, and of the resistance with the magnetic field in ordinary and compressed bismuth. R. FEDELE (Atti R. Accad. Lincei, 1929, [vi], **10**, 83—89).—Measurements of the above three quantities have been made with varying magnetic fields for crystalline bismuth and for bismuth tablets made by compressing the finely powdered metal. Modifications in the structure of the bismuth, even if these are produced by the magnetic field, have no influence on the variation of the Hall effect, of the thermoelectric power, or of the resistance with the magnetic field. These variations are due solely to electrodynamic action. O. J. WALKER.

Discontinuities of magnetisation in iron and nickel. C. W. HEAPS and J. TAYLOR (Physical Rev., 1929, [ii], **34**, 937—944).—The discontinuities of magnetisation (Barkhausen effect) in iron and nickel were recorded photographically, and the dependence of their number on the rapidity of change of the magnetising force was determined. More and smaller discontinuities were found at high than at low speeds of magnetisation. By varying the size of the specimen the length of the portion of material involved in one of the discontinuities was estimated at 2—3 mm., and the volume of the order 10^{-7} c.c. A method for determining the hysteresis loop of very small specimens is described. It is suggested that in different portions of the material different magnetostrictive effects may occur, the strains thus set up, when relieved discontinuously, producing the jumps of induction. N. M. BLIGH.

Effective and reversible permeability. G. J. SIZOO (Ann. Physik, 1929, [v], **3**, 270—276).—Using an iron–silicon alloy (3% Si) it is shown that as the amplitude of the superposed field becomes increasingly small, the identification of measured effective permeability and reversible permeability becomes increasingly trustworthy. Gans' generalisation, that permeability is a true function of magnetisation, and that the experimental deviations are due to inhomogeneity of material, is valid only in the limiting case of an infinitely small amplitude for the magnetisation process. If Gans' law is a criterion of reversibility, the magnetisation can be reversible only in the limiting case. R. A. MORTON.

Saturation magnetisation of ferro-cobalts and atomic moments of iron and cobalt. P. WEISS and R. FORRER (Compt. rend., 1929, **189**, 663—666; cf. A., 1928, 454).—The saturation magnetisation of 25 iron–cobalt alloys (0—100% Co) has been determined at the ordinary temperature, and the variation with temperature down to that of liquid air. From these figures absolute saturation at absolute zero has been calculated. It is deduced that the atoms of iron and cobalt can exhibit magnetic moments of varying multiples of the magneton, usually integral, *e.g.*, 11 and 15 for Fe-α, 14 for Fe-γ, 17 and 9 for Co-α, but sometimes apparently fractional. The revised value 1125·6 is given for the gram-magneton.

C. A. SILBERRAD.

Application of thermomagnetic analysis to the study of oxides and minerals of iron. J. HUGGETT (Ann. Chim., 1929, [x], **11**, 447—510; cf. A., 1928, 503, 841).—Apparatus is described by means of which variations in the magnetic properties of oxides of iron with temperature can be employed to establish their presence in mixtures or minerals, and to indicate the occurrence of chemical changes. The results of independent experiments on pure oxides and their mixtures under various conditions have been applied to the investigation of various materials containing iron oxides. Martite and hæmatite are always

found to contain a small quantity of magnetic oxide, whilst gœthite and lepidocrocite give on dehydration a certain amount of Malaguti's oxide, this substance also being formed superficially when magnetite is heated in air. Metallic iron, after long immersion in aërated water, forms a mixture of magnetite and rust, and the latter gives a thermomagnetic curve resembling completely that of lepidocrocite.

F. L. USHER.

Electrical phenomena of crystals floating on a saturated aqueous solution. N. KATOH (Nature, 1929, **124**, 653—654).—Experiments with acetanilide are described. A. A. ELDRIDGE.

Electrical resistance and magnetic permeability of iron wire at radio frequencies. G. R. WAIT, F. G. BRICKWEDDE, and E. L. HALL (Physical Rev., 1928, [ii], **31**, 303).—No critical change in high-frequency resistance or critical variation in permeability could be observed. L. S. THEOBALD.

Effect of boundary distortion on the surface energy of a crystal. (MISS) B. M. DENT (Phil. Mag., 1929, [vii], **8**, 530—539; cf. this vol., 17).—A method of evaluating the effect of surface distortion on the surface energy of polar crystals is described, and illustrated by results for the halides of sodium and potassium. The distortion decreases the surface energy by about 20%, the effect being due almost entirely to the polarisation of the surface ions. N. M. BLIGH.

Variation with temperature of the critical stress of cadmium crystals. W. BOAS and E. SCHMID (Z. Physik, 1929, **57**, 575—581; cf. this vol., 374).—The initial plastic deformation of cadmium crystals on stretching has been investigated over the temperature range 20—585° Abs. In the lower portion of this temperature range the critical stress of the translation system decreases nearly linearly with rise of temperature, but from about 450° Abs. to the m. p. it is almost constant at about 20·2 g./mm.^{2} The results are compared with those for zinc.

J. W. SMITH.

Slip bands of compressed aluminium crystals. I. Distortion by single slipping and a tentative theory of work-hardening of metal. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 223—241).—An analysis of distortion when the specimen slips on one plane is made on the assumption that distortion is perfect simple shear on the slip plane to the direction of slip which was obtained from the condition of maximum shear stress. The stress-strain curve obtained is decidedly below the theoretical curve, due probably to inclusion in the sample of small unabsorbed grains. Imperfect slipping influences the direction of the actual slip bands with compression. A tentative theory of work-hardening of metal is put forward based on the mechanism of the self-stopping of the slip. W. R. ANGUS.

Fracture of iron at low temperatures. F. SAUERWALD and K. A. POHLE (Z. Physik, 1929, **56**, 576—578).—Fracture was studied at −10°, −20°, −80°, and −170°. A. B. D. CASSIE.

Defects in crystal structure and heterogeneous catalysis involving active centres. A. SMEKAL (Z. Elektrochem., 1929, **35**, 567—573).—Defects, *e.g.*, cavities, may be formed in the interior of crystals, depending on the way in which they were prepared, and so give rise to active centres on the surfaces of the crystals. Previous work has shown that these defects affect the physical properties of the crystals (cf. this vol., 753, 871).

H. T. S. BRITTON.

Physical identity of enantiomerides. A. N. CAMPBELL (Nature, 1929, **124**, 792).—It appears that chemical combination can take place between dextro- and lævo-forms, and that this action differs from that between molecules of the same form producing association. Hence a difference in chemical, and therefore in physical, nature is to be postulated; measurements of f. p., solubility, and specific rotation, *e.g.*, of the esters of tartaric acid, are desirable.

A. A. ELDRIDGE.

Polymorphism of zinc. W. GUERTLER and L. ANASTASIADIS (Z. Metallk., 1929, **21**, 338).—Differential thermal analysis of pure zinc (99·999% Zn) fails to show the presence of any of the three transformation points observed by previous investigators. Their results are attributed to the presence of impurities. A. R. POWELL.

Effect of iron on the magnetic susceptibility of aluminium. R. B. MASON (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).—Comparative measurements of the magnetic susceptibility of aluminium and its alloys have been made. Pure aluminium (99·97% Al) is shown to be definitely paramagnetic. The susceptibility is increased only slightly by the presence of iron up to 8%. This result is due to the iron existing in the form of an intermetallic compound. On treatment with sodium hydroxide solution to break up the compound and liberate free iron on the surface of the sample, there is a very marked increase in the magnetic susceptibility. The method can be employed for the approximate determination of iron in aluminium in the absence of other impurities. Manganese appears to increase the magnetic properties of aluminium to a greater extent than iron. H. J. T. ELLINGHAM.

Magnetic susceptibility of halogen ions. K. RIECHENEDER (Ann. Physik, 1929, [v], **3**, 58—62).—The magnetic susceptibilities of hydrochloric, hydrobromic, and hydriodic acids in aqueous solution have been determined. Assuming $\chi_{acid}=(\chi_a)_H+(\chi_a)_{ion}$ and putting $(\chi_a)_H=0$, the atomic susceptibilities of the ions are: $Cl^-=-21·9$, $Br^-=-32·5$, $I^-=-50·2\times10^{-6}$. The results are in good agreement with Ikenmeyer's data based on measurements with alkali halides (this vol., 247). R. A. MORTON.

Conductivity of ionised air at high frequency. (FRL.) A. SZÉKELY (Ann. Physik, 1929, [v], **3**, 112—132).—The conductivity of ionised air in the negative glow has been determined for frequencies $1—5\times10^6$ Hertz (wave-lengths between 242 and 58 m.). In agreement with the requirements of theory the resistance increases as the square of the frequency. The conductivity is due to electrons which are approximately in thermal equilibrium with the gas molecules. The confirmation of the theory concerning the behaviour of ionised gases subjected to

high frequencies in the range of wireless telegraphy is of special interest, since it applies to pressures and ionisation of the type and strength to be expected in the Heaviside layer at 60—80 km. height.

R. A. MORTON.

Ionic magnetic moments. E. C. STONER (Phil. Mag., 1928, [vii], **8**, 250—266).—Previous theories of ionic magnetic moments are reviewed in conjunction with the experimental results. The difference in the magnetic behaviour of the first transition series of ions and the rare-earth series is discussed. The difference is attributed to the fact that in the former the incomplete group of electrons belongs to the group of highest total quantum number, whilst in the latter the incomplete group belongs to an inner group and that interaction between an ion and its neighbours affects mainly the electrons of highest quantum number. The rare-earth ions behave magnetically as free, the moment expressed in Weiss magnetons being given by $p=4{\cdot}97g\sqrt{j(j-1)}$, where g is the Landé splitting factor and j the inner quantum number characterising the state. In the first transition series the orbital moment l and the spin moment s require separate consideration. The orbital moment is partly ineffective owing to the interaction field, which is treated as equivalent to an initial magnetic field the general effect of the character of which on the measured susceptibility is considered. The limits of the value of p for these ions is shown to be between $4{\cdot}97\sqrt{4s(s+1)}$ and $4{\cdot}97\sqrt{4s(s+1)+l(l+1)}$, there being a tendency to the former value at low temperatures and to the latter at high temperatures.

A. E. MITCHELL.

Influence of particle size on diamagnetism. V. I. VAIDYANATHAN (Nature, 1929, **124**, 762).—The diamagnetic susceptibility of graphite or antimony falls with diminution of particle size.

A. A. ELDRIDGE.

Electroaffinity of gases. M. A. DA SILVA (Ann. Physique, 1929, [x], **12**, 99—168).—The ionisation current (produced by α-particles) in pure argon reaches saturation under atmospheric pressure at direct-current voltages much smaller than are needed for air. The negative ions formed in argon consist of free electrons. The ionisation current obtained with alternating current (200—1000 volts) consists of a practically constant flow of negative charges equal to one half the saturation current obtained with direct current. The effects of adding small increasing quantities of oxygen and water vapour have been studied. With oxygen 0·06% of added gas is necessary before the ionisation curve is definitely affected, whilst with water 0·004% suffices. The electronic affinity of water vapour is therefore at least ten times as great as that of oxygen. The mobility of positive ions in argon is 2·2 cm./sec. at atmospheric pressure. Methods which served to show that the electron affinity of argon is zero were applied to nitrogen and hydrogen, and it is found that although the values for these gases are small, the electron affinity is not zero. At the same time, the results for hydrogen might be interpreted by assuming the existence of very rapid (mobility $>$ 11 cm./sec.) positive ions.

The experimental results have been compared with the hypotheses of J. J. Thomson and of Wellisch to account for the formation of negative ions in gases. It is shown that Wellisch's hypothesis can be rejected. By measuring the ionisation currents in pure argon, the period of decay of polonium is found to be 140·2 days.

R. A. MORTON.

Electrocapillary curve of mercury and its dependence on temperature. Absolute values of electrochemical potentials. O. KOENIG and E. LANGE (Z. Elektrochem., 1929, **35**, 686—695).—Theoretical. Reference is made to the contact potential between mercury and metals in *E.M.F.* measurements.

H. T. S. BRITTON.

Aluminium electrolytic condenser. R. E. W. MADDISON (Phil. Mag., 1929, [vii], **8**, 29—55).—A general account of the theory and properties of the aluminium electrolytic condenser is given and the bearing of these on its applications is discussed.

A. E. MITCHELL.

Thermoelectric power of selenium crystals. R. M. HOLMES and A. B. ROONEY (Physical Rev., 1928, [ii], **31**, 1127).—Crystals of selenium were formed by slow condensation of the vapour in an evacuated tube heated at a constant temperature at one end. The thermal *E.M.F.* in millivolts against copper is given by the equation $E=1{\cdot}10t+0{\cdot}00017t^2$ between 0° and 180°. An *E.M.F.* is developed in some crystals by the absorption of light when the circuit is at a uniform temperature.

L. S. THEOBALD.

Absorption of ultrasonic waves by some gases. T. P. ABELLO (Physical Rev., 1928, [ii], **31**, 157; cf. A., 1928, 828).—Measurements of the absorption by carbon dioxide and hydrogen using a new method confirm the dependence on concentration previously observed.

L. S. THEOBALD.

Velocity of sound in liquids. L. G. POOLER (Physical Rev., 1928, [ii], **31**, 157).—A resonance method for determining the velocity of sound in liquids with a high degree of precision has been developed. The velocity of sound in air-free, distilled water at 25° is found to be $1493{\cdot}2\pm2{\cdot}3$ m./sec., and the rate of change of velocity with temperature is 2·2 m./sec. per degree between 25° and 30°, decreasing to 0·4 m./sec. per degree between 60° and 70°.

L. S. THEOBALD.

Physico-chemical properties of ethanesulphonic and methanesulphonic acids. A. BERTHOUD (Helv. Chim. Acta, 1929, **12**, 859—865).—The densities at 0—90°, viscosities, refractive indices, heats of dissolution in water, and conductivities in aqueous solution of the above acids have been determined. Surface tension measurements show the acids to be associated in the liquid state. From the f.-p. curves of aqueous solutions the existence of the *compounds* $Me{\cdot}SO_3H,H_2O$, m. p. 11°, $Me{\cdot}SO_3H,3H_2O$, m. p. −51·7°, and $Et{\cdot}SO_3H,H_2O$, m. p. 5·4°, is deduced.

R. CUTHILL.

Intensively dried carbon tetrachloride. S. LENHER (J. Amer. Chem. Soc., 1929, **51**, 2948—2950).—Intensive drying does not affect the b. p. and mol. wt. (determined by V. Meyer's vapour density method) of carbon tetrachloride.

S. K. TWEEDY.

Superheating and the intensive drying of liquids. S. LENHER (J. Physical Chem., 1929, **33**, 1579—1582; cf. A., 1928, 1189).—Details of results previously announced (this vol., 872) are given and objections are raised to the hypothesis that prolonged drying changes the degree of association of a liquid. The conditions for superheating of liquids are considered. L. S. THEOBALD.

Specific heat of gases at medium and high pressures. I. [With K. VON LÜDE.] Specific heats of air, nitrogen, carbon monoxide, carbon dioxide, nitrous oxide, and methane between 0° and 220°. II. [With G. HOFFMANN.] Specific heat of chlorine between −30° and 180°. A. EUCKEN (Z. physikal. Chem., 1929, **B**, **5**, 413—441, 442—451).—I. The specific heats at constant pressures of a number of gases have been determined between 0° and 200° by a modification of the Lummer–Pringsheim method. The observed variations of C_p with temperature for carbon monoxide, carbon dioxide, and nitrous oxide are in good agreement with those calculated from the Planck–Einstein function by employment of spectroscopically determined values for the intramolecular characteristic frequencies, but for nitrogen and oxygen frequencies some 13% greater than the observed values must be employed. In the case of methane the semi-empirical formula of Eucken and Fried is applicable.

II. Application of the Planck–Einstein function yields results for chlorine in good agreement with those experimentally determined with a modified apparatus. Measurements of the vapour pressure of chlorine at −28° have been made and the temperature variation of the second virial coefficient has been calculated from −29° to 184°.

H. F. GILLBE.

Properties of para-hydrogen. K. L. BONHOEFFER and P. HARTECK (Z. Elektrochem., 1929, **35**, 621—623).—At the ordinary temperature hydrogen comprises a mixture of one part of parahydrogen to three parts of orthohydrogen, at the temperature of liquid air the ratio is about 1 : 1, whilst at 20·4° Abs. it is practically pure hydrogen. The m. p. of normal hydrogen at 760 mm. is 20·39° Abs., whereas that of parahydrogen is 20·26° Abs. The triple points of the two forms are slightly different, as also are physical properties such as specific heat and thermal conductivity. H. T. S. BRITTON.

Metastability of matter and our physical "constants." E. COHEN (Z. Elektrochem., 1929, **35**, 620—621).—The necessity of using physically pure substances, and not mixtures of metastable modifications, for the determination of their physical constants is emphasised. H. T. S. BRITTON.

Fusion curve of helium. F. SIMON (Z. Elektrochem., 1929, **35**, 618—619).—The fusion curve of solid helium can be represented with considerable accuracy by $\log_{10}(p+171)$ kg./cm.^{2} $=1{\cdot}5544 \log_{10} T+1{\cdot}236$, so that at the ordinary temperature the pressure at which melting occurs is of the order of 100,000 kg./cm.^{2} H. T. S. BRITTON.

M. p. of palladium. F. H. SCHOFIELD (Proc. Roy. Soc., 1929, **A**, **125**, 517—531).—The basis of the "International temperature scale" up to the m. p. of gold is the gas thermometer, and beyond this temperature the Wien or Planck law of radiation. At present, the radiation scale is defined by the values assigned to the constant c_2 and a fixed point on the thermodynamic scale, as given by the gas thermometer, viz., the m. p. of gold. With the object of recording another fixed point on the radiation scale a determination has been made of the m. p. of palladium, the measurements taking the form of a determination of the current in a pyrometer lamp required to give a match in brightness, at a particular wave-length, with a black body held at the m. p. of gold, and a similar measurement in the case of palladium, employing a rotating sector to reduce the brightness to about the same intensity as at the gold point. Full details are given of the experimental procedure used to obtain black-body radiators at the two m. p., three methods of realising a black body being adopted. Taking c_2 as 1·432 cm. degrees and the m. p. of gold as 1063°, the value found for the m. p. of palladium is 1555°, to the nearest 1°, in good agreement with previous determinations. L. L. BIRCUMSHAW.

Method of reducing heat losses during gaseous explosions and its use in a new method of determining the specific heat of water vapour. K. WOHL and G. VON ELBE (Z. Elektrochem, 1929, **35**, 644—648; cf. Wohl, A., 1924, ii, 600).—A method is described by which the mean specific heat of water vapour, between the ordinary temperature and that at which a mixture of the constituent gases used in the process explodes, can be found. A mixture of oxygen with excess of hydrogen was exploded in a hemispherical vessel of about 10 litres capacity, and the pressures before and after explosion were recorded by means of a membrane indicator. More accurate results were obtained by using wet gases (cf. Pier, A., 1909, ii, 789).

H. T. S. BRITTON.

Entropy and probability. W. S. KIMBALL (J. Physical Chem., 1929, **33**, 1558—1578).—Mathematical. L. S. THEOBALD.

Molecular forces. II. Temperature variation of the second virial coefficient of some organic vapours. A. EUCKEN and L. MEYER (Z. physikal. Chem., 1929, **B**, **5**, 452—466).—The second virial coefficients [B in the expression $pV=n(RT+Bp)$] of benzene, carbon tetrachloride, ethyl ether, methyl alcohol, acetone, and nitromethane have been calculated as functions of the temperature from measurements of the vapour pressure in the neighbourhood of 60—110°. The theoretical significance of the results is discussed. H. F. GILLBE.

Vapour pressure and heat of vaporisation of iron pentacarbonyl. M. TRAUTZ and W. BADSTÜBNER (Z. Elektrochem., 1929, **35**, 799—802).—The vapour pressure of iron pentacarbonyl has been measured between 47·56° and 104·26°, using the apparatus of Trautz, Baisch, and Dechend (A., 1908, ii, 569). Calculations of the heat of vaporisation, using the Clausius–Clapeyron equation, showed that it gradually decreased from 9·65 kg.-cal. at 23·78° to 8·79 kg.-cal. at 98·98°. From the pressures at 0° and 104·2°, a value of 9·38 kg.-cal. is obtained—a

value much higher than that of Dewar and Jones (A., 1906, ii, 89). The lower values corresponding with the higher temperatures are attributed to the presence of $Fe_2(CO)_9$ dissolved in the pentacarbonyl, reducing its vapour pressure and raising its b. p.

H. T. S. BRITTON.

Vapour pressure of mercury and some mercury compounds at low temperatures. A. STOCK and W. ZIMMERMANN (Monatsh., 1929, **53** and **54**, 786—790).—The vapour pressure of mercury has been determined by saturating at the ordinary pressure a large quantity of air with mercury vapour, removing the mercury by means of liquid air, converting it into mercuric chloride, and finally weighing it after electrodeposition on a gold wire or determining its amount colorimetrically. The saturation pressures found are $5{\cdot}50\times10^{-4}$, $1{\cdot}79\times10^{-4}$, $3{\cdot}3\times10^{-5}$, and $4{\cdot}9\times10^{-6}$ mm. at 10°, 0°, —20°, and —60°, respectively, which are, in general, higher than the values obtained by previous investigators. The corresponding pressures, obtained at 0° in a similar manner, are for mercuric chloride, iodide, and oxide $1{\cdot}1\times10^{-6}$, $3{\cdot}5\times10^{-7}$, and $4{\cdot}1\times10^{-6}$ mm., respectively. Mercuric sulphide was not volatilised by this treatment, and mercury should be changed into this compound when it is desirable to avoid any harmful physiological effects of the vapour.

L. S. THEOBALD.

Equation of state of a mixture determined from the equations of state of its constituents, and its application in determining the physical and chemical properties of a mixture in terms of those of the constituents. R. D. KLEEMAN (Physical Rev., 1928, [ii], **31**, 311).—The equation of state of a mixture and the equations of the isolated constituents have the functional forms $p=\psi[(A_1M_a+B_1M_a+\ldots)/v,\ (A_2M_a+B_2M_a+\ldots)/v\ldots]$; $p_a=\psi(A_1M_a/v, A_2M_a,\ldots)$; $p_b=\psi(B_1M_b/v,\ B_2M_b/v,\ldots)$, where M_a, M_b, . . . denote the masses in g.-atoms of the constituents a, b, c . . ., respectively, p, p_a, p_b, . . . the pressures of the mixture and isolated constituents, respectively, and A_1, B_1, . . . are functions of T. The exact form of ψ is unknown. The equations form the theoretical basis for expressing the purely physical properties, such as optical, magnetic, and electric, of a complex substance in terms of those of its constituents.

L. S. THEOBALD.

Volume changes during the solidification of metals and alloys of low m. p. W. E. GOODRICH (Trans. Faraday Soc., 1929, **25**, 531—569).—The volume changes which occur during the solidification of tin, lead, bismuth, and zinc and a number of binary and ternary alloys have been investigated. The alloys were prepared and filtered in a vacuum, and the volume changes determined in an atmosphere of nitrogen. Minimal contraction (2·28%) of lead–tin alloys takes place in the alloy containing 48% Pb, 52% Sn. The bismuth in bismuth–tin alloys expands 3·47% during solidification, so that the expansion or contraction of these alloys is determined by the proportion of the constituents. The solidification of any primary antimony-rich crystallites from molten binary antimony alloys containing either zinc or tin is not marked by any sudden volume changes, neither is there any change in the direction of the specific volume–temperature curve when they begin to solidify. The addition of copper to an alloy of constant tin–antimony ratio increases the contraction, and especially when it has become greater than 1·5%. Pure zinc on solidification contracts 4·48%, and expands on melting by 4·69%. These figures can be considerably increased by alloying small amounts of copper and tin with the zinc, although when aluminium is substituted for the tin the changes in volume are very much reduced.

H. T. S. BRITTON.

Heat capacity of toluene from 14° to 298° Abs. Entropy and free energy of formation. K. K. KELLEY (J. Amer. Chem. Soc., 1929, **51**, 2738—2741).—The specific heat of toluene is recorded down to 14° Abs. The molal heat of fusion at the m. p., 177·95° Abs., is 1582 g.-cal. The molal entropy is 52·4 g.-cal./1° at 298·1° Abs., and the molal free energy 24,300 g.-cal. For *m*-xylene, the provisional molal entropy of 60·3 g.-cal./1° and molal free energy of 24,000 g.-cal. are recorded. These results, taken in conjunction with the values for benzene, support the conclusions previously reached with regard to the entropy and free energy difference in successive members of an homologous series (cf. this vol., 635).

S. K. TWEEDY.

Mass of the normal litre of ammonia. E. MOLES and T. BATUECAS (Montash., 1929, **53** and **54**, 779—785).—The value of L_0 for ammonia (prepared by three methods) is 0·77170, after the correction for absorption by the glass vessel used has been made. The value is considerably higher than other published values, but agrees with that of Leduc.

H. BURTON.

Movement of gases around electrically heated wires. S. LENHER and G. B. TAYLOR (J. Amer. Chem. Soc., 1929, **51**, 2741—2744).—A periodic pressure change occurs in vessels containing an axially-placed electrically heated wire, which change attains a maximum when the vessel is tilted at about 45°. The change is observed with a nearly horizontal wire in air, nitrogen, argon, and carbon dioxide, but not in hydrogen or helium, and the effect decreases in air with a pressure decrease from 2 atm. to 0·25 atm. Introduction of a mist into the gas revealed the formation of a mist-free zone around the wire, which appears to be the conduction zone which has previously been postulated. The size of this zone increases with rising wire temperature. The periodic pressure change synchronises with visible periodic turbulence in the convection currents revealed by the mist.

S. K. TWEEDY.

Intermolecular forces in liquids. J. H. HILDEBRAND (Physical Rev., 1929, [ii], **34**, 984—993).—An expression is deduced for the volume energy of liquids, in terms of attractive and repulsive forces, and is tested by the use of thermodynamic data, and energy of vaporisation for a number of liquids. Using the values found for the constants of the expression, the energy-volume coefficient for ether is calculated and plotted as a function of the volume.

N. M. BLIGH.

Azeotropism in binary systems containing hydroxyl compounds. M. LECAT (Atti R. Accad.

Lincei, 1929, [vi], **9**, 1121—1128).—A discussion of the nature of the azeotropism in systems in which one component is an alcohol, a phenol, or an acid, and the other a hydrocarbon, halogen derivative, ester, amine, ketone, nitro-compound, or oxide.

F. G. TRYHORN.

Molecular orientation and the partial vapour pressures of binary mixtures. I. Systems composed of normal liquids. II. Systems containing an alcohol. C. P. SMYTH and E. W. ENGEL (J. Amer. Chem. Soc., 1929, **51**, 2646—2660, 2660—2670).—I. The vapour pressures below 100° of hexane, ethyl iodide, butyl chloride and bromide, heptane, carbon tetrachloride, and ethyl alcohol and of binary mixtures of some of these with one another and with ethyl bromide were investigated by Sameshima's dynamic method (A., 1918, ii, 429). The data indicate that Langmuir's theory of molecular surface energies is approximately applicable, deviation from the theoretical behaviour being attributed to the presence of electric doublets in the molecules.

II. Binary systems containing either butyl or ethyl alcohol were investigated. Deviation from Raoult's law is very considerable. The results do not conform to Langmuir's theory. The orientation of the alcohol molecules relative to one another appears to be more important in determining the behaviour of the system than their orientation relative to the molecules of the other component or the orientation of the molecules of the other component relative to one another. The deviations from Langmuir's theory are qualitatively explained in terms of the forces acting between the molecular dipoles.

S. K. TWEEDY.

Methods of determining heats of vaporisation of liquid mixtures. V. KIREJEV (Z. Physik, 1929, **57**, 403—410).—The heat of vaporisation of liquid mixtures may be derived from the heats of vaporisation of the pure components and the heat of dissolution, and also from the corresponding vapour-pressure data for the mixture. The theories of these methods as well as the definitions of the quantities used have been treated differently by different observers, leading to contradictory results. The results obtained by both the indirect methods are compared with the direct experimental results. The values derived from vapour-pressure data show large deviations. The magnitude of the heat of vaporisation of single components of a mixture may be very different from that of the components in the pure state.

A. J. MEE.

Vaporisation of binary mixtures. I. Method of determining heats of vaporisation of pure liquids and solutions. M. S. VREVSKI (Z. physikal. Chem., 1929, **144**, 244—252).—A new method for determining heats of vaporisation at constant temperature has been worked out and applied to water and a solution of sulphuric acid. A knowledge of this constant is essential to the understanding of dissolution processes from an energetic point of view.

F. L. USHER.

Viscosity and m. p. of the system ethylenediamine–water. M. S. ELGORT (J. Russ. Phys. Chem. Soc., 1929, **61**, 947—959).—A study of the viscosity isotherms and m. p. of the above system shows the existence of *ethylenediamine dihydrate*, m. p. —10°. The eutectic point is —53° at 83·2 mol.-% H_2O.

R. TRUSZKOWSKI.

M. p. of mixtures of *cyclo*hexane and benzene. I. SETO (Bull. Centr. Res. Inst. S. Manchuria Rly. Co., 1928, **13**, 123—125).—Maximal expansion was observed at 55·56% of *cyclo*hexane. The m.-p. curve shows the existence at —41·9° of a eutectic containing 74·44% of *cyclo*hexane.

CHEMICAL ABSTRACTS.

Refraction of alcohol–water mixtures. N. SCHOORL (Pharm. Weekblad, 1929, **66**, 905—920).—The data recorded in the literature for the refractive indices of absolute alcohol and of alcohol–water mixtures are found to be unsatisfactory for the analysis of mixtures. Tables are given of data obtained with the Eykman and Pulfrich–Zeiss refractometers. For analytical purposes the mixture should contain about 30 wt.-% of alcohol, as in this region the refractive index alters most rapidly with the composition.

S. I. LEVY.

***X*-Ray investigation of palladium–silver–hydrogen alloy. I.** Å. OSAWA (J. Study Met., 1928, **5**, 443—454).—Palladium and silver both have a face-centred cubic lattice with lattice constant 4·069 and 3·86—3·874 Å., respectively, and form a solid solution for all ranges of composition. Saturation of palladium with hydrogen increases the lattice constant by 3·6—3·87%. Palladium–silver alloys absorb hydrogen well. The expansion coefficient increases from an alloy containing 30% Pd to a maximum at 100% Pd.

CHEMICAL ABSTRACTS.

Elastic constants, lattice constants, and densities of metallic solid solutions. Z. NISHIYAMA (J. Study Met., 1929, **6**, 17—41).—Binary solid solutions of nickel, silicon, aluminium, cobalt, vanadium, tungsten, chromium, and manganese with iron; of aluminium, tin, zinc, manganese, and nickel with copper; of iron and copper with nickel; and of zinc and manganese with aluminium were studied.

CHEMICAL ABSTRACTS.

Special properties of eutectic and eutectoid alloys in binary metallic systems. P. J. SALDAU (J. Russ. Phys. Chem. Soc., 1929, **61**, 837—882).—Reheated eutectic alloys of the pairs tin–zinc, tin–antimony, tin–zinc, gold–zinc, and gold–cadmium, as well as reheated eutectoid carbon steel, show greater hardness and a smaller electrical conductivity and temperature coefficient than alloys of different composition. It follows that the physical and mechanical constants of reheated eutectic alloys do not lie on the curves obtained for mechanical mixtures which would be obtained by the fusion together of the given components of a system. Eutectic and eutectoid alloys show either a maximum or a minimum value. This relation persists at all temperatures below the m. p. in the case of eutectic alloys or below the transition point in the case of eutectoid alloys, and is restored on cooling should the alloys have been heated above these temperatures. The presence in excess of one of the eutectic phases is essential for the process of coalescence in reheated eutectic alloys.

R. TRUSZKOWSKI.

Systems formed by certain tetrahalides. P. A. BOND and W. R. STEPHENS (J. Amer. Chem. Soc., 1929, **51**, 2910—2922).—The miscibility of the tetrachlorides of titanium and of silicon with liquid sulphur dioxide has been examined. The results accord with theory as regards polarity etc. The solubility of zirconium tetrachloride in liquid sulphur dioxide between 0° and 20° was determined by a method specially adapted for measuring solubility in highly volatile solvents; the results agree with the principles governing solubility where there is a large difference of polarity. The *compound* $ZrCl_4,SO_2$ was isolated in the form of colourless plates, stable at and below 0°.

S. K. TWEEDY.

Solubility of ethylene glycol. H. M. TRIMBLE and G. E. FRAZER (Ind. Eng. Chem., 1929, **21**, 1063—1065).—Ternary systems of ethylene glycol and acetone with xylene (25°), toluene (27°), chlorobenzene (23°), bromobenzene (25°), nitrobenzene (22°), and benzene (27°), and of glycol and alcohol with xylene (26°), toluene (25°), benzene (25°), and nitrobenzene (29°), have been investigated at the temperatures indicated. In each case a single binodal curve is obtained. Tie-lines are shown for all the systems containing acetone.

C. W. GIBBY.

Solubility of ether in concentrated solutions of mineral acids. C. MARIE and G. LEJEUNE (Monatsh., 1929, **53** and **54**, 69—72).—The solubility curves for ether in various concentrations (2—11*M*) of perchloric, hydrochloric, sulphuric, and phosphoric acids have been determined at 18° and 25°. The solubility is greatest in perchloric acid; a maximum is shown at 6·5—7*M*. In general, an increase in the concentration of the acid of 1 mol. per litre (at the concentrations where solubility is of a measurable order) causes an increase of the solubility of ether by 20, 1·8, 2·25, and 7·5 mols., respectively, for the above order.

H. BURTON.

Limit of solubility of copper in reversible ferro-nickels. P. CHEVENARD (Compt. rend., 1929, **189**, 576—578).—Dilatometric observations show that ternary austenite is formed in the presence of small amounts of copper. A second constituent rich in copper appears in the austenite when the proportion of copper is increased, but this disappears on tempering. The logarithmic contraction–time curve (cf. A., 1923, ii, 166) associated with the precipitation of Mg_2Si from hyper-tempered aluminium–magnesium–silicon alloys (isothermal recovery) has been confirmed.

J. GRANT.

Solubility of nitric oxide in carbon tetrachloride, benzene, and nitrobenzene. A. KLEMENC and E. SPITZER-NEUMANN (Monatsh., 1929, **53** and **54**, 413—419).—Determination of the Ostwald solubility coefficients for nitric oxide in benzene and carbon tetrachloride at 8·8—34·6° shows that these rise with the temperature for each solvent. With nitrobenzene at 20—90° the coefficient is the same at all temperatures. The free energy of the dissolution process decreases with rising temperature. Nitric oxide dissolves in benzene and carbon tetrachloride with a small negative heat of dissolution.

H. BURTON.

Solubility of sodium thiocyanate in water and in organic solvents. O. L. HUGHES and T. H. MEAD (J.C.S., 1929, 2282—2284).—The solubility of sodium thiocyanate in water has been measured between 10·7° and 101·4°; a hydrate $NaCNS,H_2O$ is formed below 30·4°. The solubilities have also been determined in methyl alcohol from 15·8° to 52·3°, in ethyl alcohol from 18·8° to 70·9°, and in acetone from 18·8° to 56° (*compound* $NaCNS,COMe_2$).

C. W. GIBBY.

Solubility of sodium ferrocyanide in water between 0° and 104°. J. A. N. FRIEND, J. E. TOWNLEY, and R. H. VALLANCE (J.C.S., 1929, 2326—2330).—The solubility of sodium ferrocyanide in water has been determined by a gravimetric method. Above 65° the results diverge from those of previous workers (cf. Conroy, A., 1899, i, 2; Farrow, A., 1926, 236).

C. W. GIBBY.

Hydrates of lithium sulphate and their solubility in water between —16° and 103°. J. A. N. FRIEND (J.C.S., 1929, 2330—2333).—The solubility of lithium sulphate in water has been determined between —16° and 103°. A break in the curve was found at —8°. A dihydrate is possibly formed at lower temperatures.

C. W. GIBBY.

Solubility of benzidine sulphate and benzidine hydrochloride in hydrochloric acid solutions. W. B. MELDRUM and I. G. NEWLIN (Ind. Eng. Chem. [Anal.], 1929, **1**, 231).—The solubility of benzidine sulphate in hydrochloric acid at 25° increases rapidly with the acidity, and attains a maximum of about 1·93 g. per litre in 3·5*N*-acid, thereafter decreasing slowly. The solubility of benzidine hydrochloride under similar conditions decreases rapidly from 5·34 g. per litre in pure water to 1·24 g. per litre in 5·6*N*-acid, remaining constant at this value for higher concentrations of acid up to 10*N*.

H. F. HARWOOD.

Connexion between velocity of dissolution and solubility. General equation for solubility. I. W. JACEK (Rocz. Chem., 1929, **9**, 472—492).—If k is the thickness of the layer of saturated solution which would be obtained by the concentration of the dilute solution formed in unit time by the immersion of the solute, the surface of which is taken as constant, and ρ' the thickness of the layer of solute dissolved in unit time by the pure solvent, then $\rho'\delta/k\Delta=C'$, where δ is the density of the solute, Δ that of the saturated solution, and c' the solubility expressed per unit weight of saturated solution. A further expression, $s=\rho'\delta/\xi\delta'$, is derived, in which s is the solubility per unit weight of solvent, δ' the density of the solvent, and ξ is the thickness of the layer of pure solvent corresponding with ρ'. The value of ρ' is determined for sylvine, sodium chloride, alabaster, potassium sulphate and dichromate, alum, tartaric acid, and sucrose, for temperatures between 0° and 50°. The relation between ρ' and temperature, T, is given by $\rho'\delta=e^{-A_1/T+B_1}$, where the constant B_1 depends on the rate of stirring. A general equation for the solubility is given by $s=e^{-(A_1-A_2)T+(B_1-B_2)+(C_1-C_2)\log_e T+(G_1-G_2)}$. The terms (A_1-A_2), (B_1-B_2), (C_1-C_2), and (G_1-G_2) depend on the heat of dissolution of the given solute and on the nature of both components of the solution,

and may have positive, negative, or zero values, and the differences observed between the solubility curves of various substances are due to the differential nature of these terms. R. TRUSZKOWSKI.

Adsorption of air and water vapour on rock-salt surfaces. J. H. FRAZER (Physical Rev., 1929, [ii], **34**, 644—648).—By a method previously used (cf. this vol., 503) the adsorption of air on rock-salt surfaces has been measured at various temperatures, and the temperature at which complete outgassing occurs determined. The thickness and approximate speed of formation of the film are estimated. Exposure to water vapour has no permanent effect on the surface so long as the partial pressure of the water vapour is less than that of the saturated solution at the same temperature. This is true only of cleavage surfaces; polished surfaces are less stable against the action of water vapour. N. M. BLIGH.

Sorption of vapours from circulating gas by solid absorbents and the adaptation of activated charcoal and silica gel to the determination of small quantities of vapours in exhaled breath. W. PONNDORF and H. W. KNIPPING (Beitr. Klin. Tuberk., 1928, **68**, 751—806; Chem. Zentr., 1929, i, 2904).—The principle of the process is discussed, and curves illustrate the effect of the form of the absorbent layer, the temperature, and the pressure. Silica gel is preferable for the absorption of water and active charcoal for that of acetone and other organic substances. Acetone can be quantitatively absorbed from large volumes of moist air. A. A. ELDRIDGE.

Temperature coefficient of the saturation maximum in gaseous adsorption. F. J. WILKINS and A. F. H. WARD (Z. physikal. Chem., 1929, **144**, 259—268).—Theoretical. The temperature variation of the value of the saturation maximum expected from Langmuir's and other theories is discussed. The basis of the alteration is to be sought, not in a change of the adsorbing surface, as Zeise supposes, but rather in the adsorbed gas layer. From the conception of lateral diffusion of the adsorbed unimolecular gas layer, the saturation pressure is found to be independent of the temperature, whilst the temperature coefficient of the adsorption maximum is equal to the coefficient of expansion of a gas at constant pressure. This conclusion is supported by the available experimental data. F. L. USHER.

Linear adsorption. R. S. BRADLEY (Phil. Mag., 1929, [vii], **8**, 202—204).—The thermodynamic surface activity is given by the expression $RT \log a_s = F' - F'_0 = RT \log F + BF$, where a_s is the surface activity, B is a constant and the standard state for F', the free energy per g.-mol. in the surface being defined by the limits $F' \longrightarrow F'_0$ when $A - B/A \longrightarrow 1$, $A \longrightarrow RT/F$, and $a_s \longrightarrow F$, where A is the area per g.-mol. Applying this to a two-dimensional gas the Langmuir isotherm becomes constant$/p = 1/s$—constant, where p is the pressure and s is the surface concentration, the substance distributing itself between the two regions according to the distribution law $p/\{s/(1-SB)\}$=constant, $S/(1-SB)$ being the effective surface concentration. Similar application to adsorption at a line gives $RT \log a_l = RT \log RTL' + RTB^{\frac{1}{2}}L'$, where a_l is the linear activity and L' is the effective linear concentration$=L/(1-LB^{\frac{1}{2}})$, where L is the linear concentration. The approximate distribution law between a line and a surface then becomes L'/S'=constant$=e^{\Delta F_0/RT}$, where $S' = S/(1-SB)$ and ΔF_0 is the free energy increase for the change line$\longrightarrow$surface in the standard states. A. E. MITCHELL.

Heat of adsorption of gases by solids. K. F. HERZFELD (J. Amer. Chem. Soc., 1929, **51**, 2608—2621).—Theoretical. On the assumption that the adsorbing forces are purely of electrical nature, the adsorption of a gas without permanent dipoles on the surface of a heteropolar salt is investigated mathematically and it is shown that the positive or negative increase in the heat of adsorption with the amount adsorbed can be explained by the interaction of the dipoles set up in neighbouring molecules by the adsorbing forces. The association of a large free energy change during adsorption with a small total energy change is best explained (but not with complete satisfaction) by assuming that the adsorbed molecules cohere together into groups. The extent of the difference between the amounts of two gases (having the same heat of adsorption) adsorbed on the same adsorbent under the same external pressure is discussed briefly. S. K. TWEEDY.

Mixed adsorbents. N. SCHILOV, M. DUBININ, and S. TOPOROV (Kolloid-Z., 1929, **49**, 120—126).—A method for the preparation of an intimate mixture of silica and wood charcoal for adsorption purposes is described. This mixed adsorbent is more active than wood charcoal alone in the adsorption of ammonia, chlorine, steam, and benzene vapour and in the adsorption of iodine from solution in water, alcohol, or benzene. The maximum activity is attained when the adsorbent contains 60—70% of carbon. Although silica gel adsorbs iodine negatively, it increases the adsorption by carbon. Coarse mixtures of silica and wood charcoal have less adsorbent capacity than wood charcoal alone. E. S. HEDGES.

Adsorption velocity of water and benzene vapours. H. ISOBE and S. MORI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 801—804).—Activated charcoal adsorbs more benzene than water from air saturated with both substances, whereas for acidic clay the reverse is true; with both adsorbents the adsorption of benzene is more rapid than that of water. Density measurements indicate that activated charcoal possesses a greater surface than non-activated charcoal. H. F. GILLBE.

Adsorption and gas-friction. C. DRUCKER (Z. Elektrochem, 1929, **35**, 640—644).—Expressions are obtained by which the coefficient of friction of mixtures of gases, *e.g.*, helium and hydrogen, carbon dioxide and hydrogen, hydrogen chloride and hydrogen, can be calculated with fair accuracy. With the help of these formulæ, it is possible to determine the adsorption of the gases by the glass walls of the containing vessel. H. T. S. BRITTON.

Process of adsorption. H. KALBERER, H. MARK, and C. SCHUSTER (Z. Elektrochem., 1929, **35**, 600—602).—The adsorbing surfaces of silica gel and

aluminium oxide have been calculated from an expression involving the heat of adsorption, the thickness of the adsorbed layer, and the volume occupied by the adsorbed gas. The different values obtained for the surface of an adsorbent when different gases are used is attributed to differences in the adsorption potential which the active places in the surface have for the particular gases (see Kälberer and Schuster, this vol., 757). The dependence of the volume of adsorbed gas on the temperature is also discussed. H. T. S. BRITTON.

Adsorption of complex platinum compounds by carbon. I. I. SHUKOV and O. P. SCHIPULINA (Kolloid-Z., 1929, **49**, 126—133).—The adsorption of a number of complex platinum compounds by wood charcoal has been studied. The compounds were decomposed on adsorption and the adsorbability depends on the electronic configuration of the compound, no relation being found between adsorbability and solubility. The adsorbability is influenced by isomerism only so long as a change in electrical configuration is involved. Of the compounds examined, the non-electrolytes were adsorbed more strongly than the electrolytes. Optically active complex platinum compounds cannot be resolved into their isomerides by adsorption on charcoal.

E. S. HEDGES.

Precipitation and adsorption of small quantities of substances. III. The adsorption law, applications, results, and conclusions. O. HAHN and L. IMRE (Z. physikal. Chem., 1929, **144**, 161—186; cf. A., 1926, 1092).—The authors distinguish between the co-precipitation of small amounts of a substance with a bulky precipitate and the adsorption of the substance by the precipitate, and the two laws previously put forward are restated and confirmed by new data. In the present work the adsorption of hydrolysing and non-hydrolysing cations by two types of lattice, polar and non-polar, is considered. The polar lattices studied were those of the silver halides, the non-polar those of the mercurous halides. The adsorbed substances were the short-lived radio-elements thorium-*B*, thorium-*C*, and polonium (hydrolysing ions), radium and thorium-*C''* (non-hydrolysing), chosen for convenience in detecting small amounts, but the results are generally applicable. The difference between the behaviour of non-hydrolysing and hydrolysing cations is striking, inasmuch as the latter show "colloid adsorption," and an excess of the precipitating anion is not necessary for considerable adsorption to occur. Appreciable adsorption occurs only under special conditions on non-polar precipitates such as the mercurous halides, since they lose their charge much more readily than the analogous silver compounds, but under these conditions Hahn's adsorption law is followed. The results of ionic and colloid adsorption on polar and non-polar lattices are summarised. The earlier results of Fajans are in agreement with the authors' views on adsorption processes. A possible extension of the adsorption law to readily soluble but weakly dissociating compounds is indicated. F. L. USHER.

Influence of adsorbed ions on the absorption spectrum of metal halides. K. FAJANS and G. KARAGUNIS (Z. physikal Chem., 1929, **B**, **5**, 385—405).—Measurements with silver iodide analogous to those previously conducted with silver bromide (this vol., 625) show that adsorbed silver ions produce up to 40% increase in the intensity of the band with its maximum at 4200 Å., without, however, influencing the position of the maximum. Adsorbed iodine ions produce a decrease of absorption on the long wave-length side of the maximum. These results are in accordance with the colour variations exhibited by the iodide when precipitated in presence of an excess of iodide or of silver ion. Mercuric iodide emulsions show a general decrease of absorption when treated with a solution of a mercuric salt or of a soluble iodide on account of the formation of non-absorbing complex ions. The energy quantum of the primary process of the photochemical decomposition of silver iodide is not altered by the presence of adsorbed silver ions, but the number of elementary processes is increased.

H. F. GILLBE.

Lyosorption. WO. OSTWALD and W. HALLER (Kolloidchem. Beih., 1929, **29**, 354—395).—When powders are shaken with liquids in which they are insoluble and are then allowed to settle, the volume of the sediment varies with different liquids. A technique for the examination of this phenomenon is developed, the essential conditions being constant temperature and a long duration of experiment. The sedimentation volumes of powdered talc, fuller's earth, alumina, silica, magnesium oxide, calcium carbonate, ferric oxide, graphite, and norit stand in the same order for all the liquids tested, being greatest for carbon tetrachloride and decreasing in the order hexane, benzene, chloroform, ether, acetic acid, alcohol, acetone. Some irregularities can be traced to chemical reaction or some other secondary influence. The variation in sediment volume is caused by the binding of a layer of liquid by the surface of the powder. The volume can be reduced by mechanical pressure or by centrifuging, and is smaller at higher temperatures. By centrifuging the sediment a constant final volume is attained, which, although smaller than the sedimentation volume, varies in the same order throughout the series of liquids. Lyosorption produces an increase in viscosity of the suspension, which is dependent on the velocity of flow, the viscosity falling with increasing velocity. The influence of moisture and of heating the powder has been examined and the result varies with the different systems; graphite and norit give smaller sedimentation volumes after heating, but talcum gives the same volume after heating at 350°. In an investigation of the relation between lyosorption and chemical constitution of the liquid, experiments have been carried out with two powders and about 50 different organic liquids and a relation between lyosorption and the dielectric properties of the liquid has been established. Lyosorption values and the dielectric constants of the liquids vary antibatically and it is inferred that the force involved in lyosorption is of electronic nature. E. S. HEDGES.

Activation process at boundary surfaces. M. POLANYI (Z. Elektrochem., 1929, **35**, 561—567).—Theoretical. H. T. S. BRITTON.

Ring method for determining surface tension. A. H. NIETZ and R. H. LAMBERT (J. Physical Chem., 1929, **33**, 1460—1467).—The influence of the thickness and diameter of the ring and of the contact angle on determinations of surface tension has been investigated. The pull on the ring for a given diameter is a linear function of the size of the wire, and *vice versâ*. The classification of the ring method as one independent of the angle of contact is erroneous, since it has been shown that the pull on the ring is related to the angle of contact between the material of the ring and the liquid. The relationship $F = 2lT(1+\cos\theta)^n$, where F is the force in dynes required to remove the ring, l is the average perimeter of the ring, and θ is the angle of contact, holds over a limited range of size of wire. L. S. THEOBALD.

Calculation of surface tension from drop weight. T. IREDALE (Z. physikal. Chem., 1929, **144**, 158—159).—Comments on a paper by Palitzsch (this vol., 257). F. L. USHER.

Unimolecular films of cyclic ketones. E. H. BÜCHNER, J. R. KATZ, and P. J. P. SAMWEL (Z. physikal. Chem., 1929, **B**, **5**, 327—332).—Unimolecular films on water of a number of cyclic ketones have been prepared and their thicknesses per molecule determined. The results indicate that the molecules of these substances are formed of two parallel carbon chains, in accordance with the view of Ruzicka (cf. A., 1928, 642, and earlier abstracts).

H. F. GILLBE.

Structural changes produced in colloidal films by stretching. J. TRILLAT (J. Phys. Radium, 1929, [vi], **10**, 370—384).—The structural changes produced when films of cellulose nitrate and acetate are stretched have been followed by means of X-ray diffraction photographs taken in three directions: along the axis of stretching and also the two axes perpendicular to this. When the extension of the film is slight normal circular diffraction haloes are obtained which are more or less intense in certain directions. As the extension is increased the film becomes anisotropic, for the haloes obtained from two of the three directions studied possess a marked increase in intensity at the equator. The long molecules constituting the film appear therefore to arrange themselves in a direction parallel to the axis of stretching. At very great extensions the haloes are deformed into ellipses. A comparison of these diffraction patterns with those given by the substances in the crystalline state indicates that in these highly stretched films incipient crystallisation is taking place. A nematic phase is therefore transformed by stretching into a pseudocrystalline phase. These results are applied to the consideration of the properties of "cold-worked" films. F. J. WILKINS.

Electrical conductivity caused by insoluble unimolecular films of fatty acid on water. J. W. MCBAIN and C. R. PEAKER (Proc. Roy. Soc., 1929, **A**, **125**, 394—401).—The possibility of the dissociation of unimolecular films of insoluble fatty acids on water with formation of free hydrogen ions in the latter is investigated. A special form of conductivity cell is described which enables measurements to be made of (*a*) the conductivity of the water alone, (*b*) that of the water after introduction of the fatty acid but with the surface far removed from the electrodes, (*c*) that of the water when the surface is brought to the level of the tops of the electrodes, and (*d*) that of the water with the surface in the same position after the introduction of the fatty acid. A modified form of the conductivity bridge described by Jones and Josephs (A., 1928, 595) is employed. The specific surface conductivity (*i.e.*, the conductivity in reciprocal ohms between two parallel electrodes 1 cm. long placed 1 cm. apart on the surface) at 25° in the region of the unimolecular film of stearic acid is $3{\cdot}5\times10^{-8}$ mho. This corresponds with a dissociation of about one ninth of the total stearic acid in the unimolecular layer on water of conductivity $1{\cdot}2\times10^{-6}$ mho. The surface conductivity is ascribed to the presence of independent mobile hydrogen ions dissociated from the fatty film, which is thus left with an equal and opposite electric charge. This conception lends support to the view that the Helmholtz double layer is not responsible for the electrokinetic phenomena, and that the classical formulæ are not strictly applicable owing to the existence of unbalanced charges on the interface. L. L. BIRCUMSHAW.

Stability of sub-microns. Dissolution of crystals and their formation. J. TRAUBE (Z. Elektrochem., 1929, **35**, 626—627).—The dissolution of crystalline substances begins at definite points on their surfaces, leading thereby to pearl-like cellular structures, which subsequently collapse to form sub-microns, and finally dissolve. The rate of dissolution can be decreased in the presence of gelatin. The reverse order has been observed in the building-up of crystals from sub-microns. A cinematograph was used in the experimental part of the work.

H. T. S. BRITTON.

Insoluble sulphates and passivity. L. MCCULLOCH (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 4 pp.).—Attention is directed to the difficulty with which anhydrous chromic, ferric, and nickel sulphates dissolve in dilute sulphuric acid and it is suggested that passivity may be due to films of these anhydrous salts. H. J. T. ELLINGHAM.

Periodic precipitations with diffusion. H. RYAN and R. J. DOYLE (Nature, 1929, **124**, 762).—The authors' objection to Ostwald's theory (this vol., 1144) is invalid. A. A. ELDRIDGE.

Velocity of transference of water through a semi-permeable wall by osmotic pressure. S. RAY (Z. anorg. Chem., 1929, **182**, 351—352).—An expression for the rate of osmotic flow of solute through a semi-permeable membrane is derived.

H. F. GILLBE.

Penetration of electrolytes. W. J. V. OSTERHOUT (Proc. Soc. Exp. Biol. Med., 1928, **26**, 192—197).—For a time-curve of penetration (of living cells by weak electrolytes) of the first order, the high electrical resistance of the protoplasm in *Nitella* and *Valonia* suggests that when a binary electrolyte is largely ionised there is very little penetration. If the external concentration remains constant while the p_H value changes so as to decrease the concentration of undissociated molecules, the rate of penetration

will diminish even when the protoplasm is permeable to ion pairs only. Strong electrolytes may enter largely as undissociated molecules formed at the surface by collision of ions. CHEMICAL ABSTRACTS.

Electro-stenolysis and electrolytic membrane processes. K. SÖLLNER (Z. Elektrochem., 1929, **35**, 789—799).—The effects produced when currents are passed through certain porous membranes and precipitates, on each side of which are solutions of salts of heavy metals, may be divided into two classes, viz., (1) membranes to which only small *P.D.* may be applied (2—3 volts), resulting in the deposition within the membrane of a precipitate containing the metal, *e.g.*, the oxide, (2) membranes to which a *P.D.* of at least 20 volts must be applied to effect the precipitation of the metal itself within the pores of the membranes ("electro-stenolysis"). Hypotheses to account for these effects are advanced. H. T. S. BRITTON.

Unequal distribution of ions in a collodion cell. J. H. NORTHROP (J. Gen. Physiol., 1929, **13**, 21—25).—A "dry" collodion membrane containing sodium thiosulphate solution immersed in a solution of iodine in potassium iodide gradually becomes richer in iodine ions until all the free iodine outside has been converted into iodide ions within the cell. As the membrane, although permeable to iodine, is impermeable to iodide ions, comparatively high concentrations of iodide ions inside the membrane may be attained. With a membrane containing sodium chromate immersed in a solution of mercuric chloride and sodium sulphate, the mercury is gradually precipitated as mercuric chromate. In this case the membrane is permeable to mercuric chloride, but not to sodium or other chlorides. Acetate ions are concentrated in a cell originally containing a suspension of calcium carbonate and immersed in acetic acid. These experiments show that artificial systems may be made which resemble living cells. W. O. KERMACK.

Preparation of colloidal gold solutions by the use of alkaloids. M. O. CHARMANDARJAN (Kolloid-Z., 1929, **49**, 133—135).—Colloidal solutions of gold are obtained when small quantities of brucine or nicotine are added to a boiling dilute solution of chloroauric acid acidified with hydrochloric acid. Brucine gives a yellowish-orange sol and nicotine a blue sol. E. S. HEDGES.

Viscosity of hydrophilic colloids. H. FICKENTSCHER and H. MARK (Kolloid-Z., 1929, **49**, 135—148).—The relation between mol. wt. of colloids and viscosity is discussed and leads to the rule that at constant temperature and in solutions of polymeric homologous series of the same viscosity the square of the mol. wt. varies inversely as the concentration. In Einstein's modified equation, $z=1+a\,.\,cb/(100-cb)$, where b is the volume in which 1 g. of substance is dispersed, it is shown that $\sqrt{b}$ is proportional to the mol. wt. The values calculated by the two methods show good agreement and are independent of temperature. E. S. HEDGES.

Nephelometric study of colloidal solutions of metallic sulphides. M. WATANABE and C. NAKAU (J. Petrol. Min. Ore Dep., 1929, **1**, 61—64).—When dilute solutions of metallic salts are precipitated with an excess of sodium sulphide in dilute solution the colloidal sulphide does not easily coagulate. A study of the relation between the coagulation time and the relative concentrations shows that at an initial period the turbidity increases, is then constant for a time, and on coagulation decreases suddenly. CHEMICAL ABSTRACTS.

Scattering of light in colloidal solutions and gels. K. KRISHNAMURTI (Nature, 1929, **124**, 690—691).—In the ageing of silicic acid sols formed by the hydrolysis of methyl silicate the primary particles form larger aggregates after some time, the rate of formation being determined by an increase in the number of effective collisions between the particles and a decrease in the number of the original particles. An explanation of similar results obtained with gelatin sols is offered. With sodium oleate solutions supersaturation with formation of colloidal particles is observed on cooling. A. A. ELDRIDGE.

Electrolytic dissociation of colloidal solutions. I. K. TAKATA (Hokkaido J. Med., 1928, **6**, 577—586).—In 0·00001—0·001*N*-hydrochloric acid or sodium hydroxide solution containing mastic sol there is a discrepancy between the calculated and experimental p_H values which shows that hydrogen or hydroxyl ions are combined with the mastic. The electrical conductivity decreases with addition of mastic. CHEMICAL ABSTRACTS.

Organophilic colloids. G. S. WHITBY, J. G. MCNALLY, and W. GALLAY (Coll. Symp. Mon., 1928, **6**, 225—236).—The smaller the amount of solvent bound in a sol, the smaller is the quantity of precipitant needed to produce separation. Various properties are considered. CHEMICAL ABSTRACTS.

Influence of electrolytes and non-electrolytes on optical activity and relative resistance to shear of gelatin systems. J. R. FANSELOW (Coll. Symp. Mon., 1928, **6**, 237—252).—The behaviour of gelatin systems can be better explained by the laws for highly dispersed heterogeneous systems than by the classical laws of stoicheiometry. CHEMICAL ABSTRACTS.

Emulsions. II. System xylene–phenol–sodium oleate–water. J. WEICHHERZ (Kolloid-Z., 1929, **49**, 158—173; cf. this vol., 260).—A study has been made of the phase relations between water and a mixture consisting of 79·94% of xylene, 12·91% of phenol, and 7·15% of sodium oleate. With increasing amounts of water, the initial homogeneous phase is followed by a heterogeneous region of water-in-oil emulsions, then by a second homogeneous region, and finally by a heterogeneous region of oil-in-water emulsions. Rise of temperature displaces all the regional limits in the direction of smaller quantities of water: the first homogeneous region and the region of water-in-oil emulsions become narrower, whilst the second homogeneous region and the region of oil-in-water emulsions become more extensive. The transformation of the system sodium oleate dispersion in xylene–phenol into the system sodium oleate dispersion in water occurs at a lower water content the higher the temperature. Measurements were made of

the viscosity of the system xylene–phenol–sodium oleate–water at different temperatures. With increasing water content, the viscosity rises to a maximum, then falls, and again rises. E. S. HEDGES.

Rôle of dielectric constants, polarisation, and dipole moment in colloid systems. VII. Swelling of cellulose acetate in binary mixtures. III. I. SAKURADA (Kolloid-Z., 1929, 49, 178–184 ; cf. this vol., 1234).—Experiments have been conducted on the swelling of cellulose acetate in binary liquid mixtures where both the components are polar. No simple relation between swelling and polarisation, such as is observed where only one component is polar, could be recognised. The curves are greatly influenced by the presence of small amounts of additional polar substances. Data are listed in an attempt to show the relations between swelling, molecular polarisation, vapour pressure, and viscosity of solutions of cellulose acetate in binary liquid mixtures where one or both of the components are polar. E. S. HEDGES.

Wo. Ostwald's solid-phase rule and the solubility of casein in sodium hydroxide. A. VON BUZÁGH (Kolloid-Z., 1929, 49, 185—188).—An explanation is given of the different results obtained by Sörensen and Sládek (this vol., 1230) and by von Buzágh (A., 1927, 310) on the solubility of casein in solutions of sodium hydroxide. E. S. HEDGES.

Solid-phase rule in the production of protein sols. WO. OSTWALD (Kolloid-Z., 1929, 49, 188—209).—The essential differences in the solubility relations of colloids and molecularly dispersed substances are defined. The dependence of the solubility of molecularly dispersed tartaric acid in sodium hydroxide solutions on the amount of the solid phase (Sörensen and Sládek, this vol., 1230) is shown to bear no analogy with the solid-phase rule recognised in colloid systems. The maximum of solubility in this system is caused by the formation and precipitation of a new solid phase consisting of an acid tartrate. The solubility of globulin in solutions of neutral salts is discussed from the same point of view. Numerous other arguments are advanced against Sörensen's views on the molecular relations of protein sols. E. S. HEDGES.

Theory of colloid osmosis. W. HALLER (Kolloid-Z., 1929, 49, 74—83).—The osmotic pressure of colloidal solutions does not conform to the law $P=cRT$. Secondary influences causing deviation are discussed, but it is also shown on theoretical grounds that molecular-kinetic processes must lead to deviations from van 't Hoff's equation, which only represents a special case. Whilst in the case of the osmotic pressure of molecular solutions only a translatory motion of the molecule is concerned, in the treatment of colloids it is necessary also to consider movements of oscillation and rotation. The following equation for total osmotic pressure is developed : $P=c'RT+c'^2RT(0{\cdot}46N_Lv\phi)$, where c' is the concentration in g.-mol. per litre, v is the number of degrees of freedom of oscillation of a micelle, and ϕ is the amplitude. E. S. HEDGES.

Action of sodium hydroxide on stannic acid sol. I, II. B. N. GHOSH (J.C.S., 1929, 2290—2297, 2298—2304).—I. Measurements have been made on the membrane equilibria and osmotic pressures of stannic hydroxide sols containing sodium hydroxide. In mixtures in which the ratio $SnO_2 : Na_2O$ varied from 17·2 to 0·5 the amount of diffusible stannic oxide never exceeded 19%. The membrane potential calculated on the assumption that all the diffusible ions are univalent agrees with the observed value. The dissociation of the colloidal complex of the two oxides is small.

II. Measurements have been made of the hydroxyl-ion concentration, f.-p. lowering, and conductivity of five sols in which the ratio $Na_2O : SnO_2$ varied from 2 to 0·25. At higher values of the ratio the greater part of the added alkali is uncombined, but this fraction diminishes as the ratio becomes smaller. The f.-p. depressions are due mainly to the free sodium hydroxide, and diminish as the ratio $Na_2O : SnO_2$ diminishes. The degree of dissociation of the colloid diminishes rapidly as the proportion of stannic oxide increases. Conductivity measurements indicate that the greater part of the conductivity is due to the free sodium hydroxide. C. W. GIBBY.

Acidity–dilution and neutralisation curves for a sol of arsenious sulphide and a suspension of gamboge. A. BOUTARIC and (MLLE.) G. PERREAU (Bull. Soc. chim., 1929 [iv], 45, 701—706).—In the determination of the acidity–dilution curves a sol containing 18·6 g. of arsenious sulphide per litre was diluted with water up to 32 vols., and a suspension of 6·124 g. of gamboge up to 4 vols. For neutralisation the sol contained 1·55 g. per litre, the suspension 1·225; in both cases equal volumes of a solution of potassium hydroxide of normality varying from 2 to 200×10^{-4} for the sol, and from 1 to 100×10^{-4} for the suspension were added. The p_H was determined with a quinhydrone electrode—for the sol immediately, and after 3 days, for the suspension after 3 days only. The intermicellary liquid of the sol, obtained by filtration through collodion, was similarly examined; the dilution curve was quite similar, but that of neutralisation indicated that the presence of the granules increased the buffer effect in the mixture of sol and base. In both cases the behaviour is that of a weak acid such as acetic, but the equilibrium takes some time to establish itself, the change on keeping being consistent with the hypothesis of a slight dissociation of the "acid." C. A. SILBERRAD.

Physico-chemical behaviour of lecithin. I. Capillary activity of lecithin as a function of p_H. H. I. PRICE and W. C. M. LEWIS (Biochem. J., 1929, 23, 1030—1043).—The capillary behaviour of egg-lecithin has been studied and the surface tension–p_H curves for aqueous dispersions and aqueous-alcoholic dispersions are compared. According to these curves the isoelectric point is 2·6 in both sets of dispersions. An explanation of the surface tension–p_H curves is offered on the basis of simple orientation. The influence of salts such as sodium chloride and calcium chloride on the surface tension–p_H relation for dispersions of lecithin has been examined. The effects are of a complex character. The mol. wt. of egg-lecithin is found to be 797 in ethyl alcohol and 3388

in benzene. The egg-lecithin was prepared by Levene and Rolf's method. S. S. ZILVA.

Osmotic pressure of crystalline egg-albumin. J. MARRACK and L. F. HEWITT (Biochem. J., 1929, **23**, 1079—1089).—In moderate concentrations of sodium acetate and sodium chloride, isoelectric egg-albumin has the same osmotic pressure as in medium concentrations of ammonium sulphate. Different values are obtained in concentrated solutions of sodium chloride and in dilute solutions of sodium acetate, but the deviations are less than those shown by ammonium sulphate solutions. The mol. wt. calculated from the authors' figures and from those of Sörensen is 43,000. Electrodialysed egg-albumin gives a slightly higher figure. There is no fall of osmotic pressure on the acid side of the isoelectric point in the presence of sodium chloride and sodium acetate. At p_H 6·7—8·0 the osmotic pressure–concentration curve of egg-albumin resembles that of serum. The influence of ammonium sulphate on the activity of egg-albumin cannot be explained entirely in terms of the salting-out effect. S. S. ZILVA.

Lyophilic colloids. III. Gum arabic sol. H. R. KRUYT and H. J. C. TENDELOO (Kolloidchem. Beih., 1929, **29**, 396—412).—Sols of gum arabic exhibit the properties typical of lyophilic colloids. Measurements were made of the viscosity of the sol at different concentrations and in presence of varying amounts of electrolytes. Poiseuille's law is obeyed. The effect of electrolytes is to lower the viscosity, and the first small amounts produce the greatest effect; at higher concentrations of electrolyte the particles of sol become partly dehydrated, and when dehydration and electrical discharge occur simultaneously (as by adding alcohol and an electrolyte) the sol is coagulated. Small quantities of electrolyte raise the charge on the particles. It is maintained that the stability of lyophilic colloids is conditioned by capillary electric charge and hydration of the particles. E. S. HEDGES.

Lyophilic colloids. IV. Charge, hydration and particle-size in sols of starch, gum arabic, gelatin, and casein. H. R. KRUYT and H. J. C. TENDELOO (Kolloidchem. Beih., 1929, **29**, 413—431).—A method for measuring the cataphoretic migration velocity of the particles of colourless sols is described. Measurements of the viscosity, electrical conductivity, and cataphoretic migration velocity of starch sols give a mean particle size of 9 $\mu\mu$ for the hydrated particles and 4 $\mu\mu$ for the dehydrated particles. In sols of gum arabic the ζ-potential passes through a maximum with increasing electrolyte concentration, whilst the viscosity falls continuously. Hydration and electric charge vary simultaneously in sols both of gum arabic and of gelatin. E. S. HEDGES.

Lyophilic colloids. V. H. R. KRUYT (Kolloidchem. Beih., 1929, **29**, 432—435).—A discussion of previously published work having a bearing on the four preceding parts of the series. E. S. HEDGES.

Lyophilic colloids. VI. Electroviscous effect with two hydrophilic sols which do not obey Poiseuille's law: linseed and carragheen. H. G. B. DE JONG and O. S. GWAN (Kolloidchem. Beih., 1929, **29**, 436—453).—Sols of linseed and carragheen possess an unusually high viscosity even at low concentrations. Poiseuille's law does not hold either for the sols alone or in presence of electrolytes. The sols are very sensitive to traces of electrolytes, 1 milliequiv. of electrolyte lowering the viscosity considerably, but similar concentrations of a non-electrolyte such as alcohol produce no effect. The valency of the cation determines the type of viscosity lowering. Electrolytes with ter-, quadri-, and sexa-valent cations fall into two groups: complex salts, which lower the viscosity in the normal sequence, and cations the salts of which are readily hydrolysed (lanthanum, aluminium, thorium) which in low concentrations produce much less lowering of viscosity than is to be expected. E. S. HEDGES.

Lyophilic colloids. VII. Capillary electric charge and hydration as characteristics of hydrophilic gels: reversible volume changes of agar gel. H. G. B. DE JONG (Kolloidchem. Beih., 1929, **29**, 454—482).—An apparatus for the measurement of small dimensional changes in a gel is described. At the ordinary temperature, a 2·2% gel of agar does not swell in distilled water, but undergoes syneresis. All neutral electrolytes in small concentrations cause the gel to shrink, the maximal linear change being 1%. Non-electrolytes have no influence. The shrinkage is a capillary electrical phenomenon which is determined solely by the valency of the cation; the nature of the cation or the valency and nature of the anion have no influence. Sexavalent cations produce their maximal effect at so low a concentration as 1·5 milliequiv. per litre and the contraction produced at higher concentrations is less, although whether this is due to a reversal of charge is not clear. The contraction is reversible, for the gel increases in volume again when the electrolyte is washed out; exchange-adsorption of the cations can also take place. Alcohol in high concentrations causes a linear contraction of 7%, which is reversible and is due to dehydration of the units of the structure. High concentrations (up to 5N) of magnesium chloride do not cause greater shrinkage than small amounts, but with magnesium sulphate a greater shrinkage (4%, linear dimensions) is observed the higher is the concentration; the difference is that magnesium chloride is unable to dehydrate the particles of gel, whilst magnesium sulphate does so readily. E. S. HEDGES.

Slow change in mixtures of colloidal solutions recalling anaphylactic effects. A. BOUTARIC and M. DUPIN (Compt. rend., 1929, **189**, 754—757; cf. A., 1928, 360).—Contrary to the effect of repeated additions of small quantities of an electrolyte to a colloidal solution, the successive addition of small quantities of a second sol causes complete flocculation with a smaller total amount of the second sol than when this is added in one lot. The phenomenon is illustrated by the addition of a sol of arsenious sulphide to one of ferric hydroxide and *vice versa*. The possible bearing of this result on the phenomenon of anaphylaxy is pointed out. C. A. SILBERRAD.

Electrical excitation and the possible structure of the plasmatic membrane. H. H. DIXON and

T. A. BENNET-CLARK (Nature, 1929, **124**, 650—651).—In electrical excitability there is a marked similarity between oil-in-water emulsions, *e.g.*, olive oil 50 c.c., water 25 c.c., oleic acid 1 c.c., sodium hydroxide 0·08 g. (or calcium oxide 3·0 g.), and living tissues. The relation between the voltage applied to a given emulsion and the change of resistance produced is of the same type as that obtained with living tissues. It is believed that the plasmatic layer of the living cell is a water-in-oil emulsion close to its inversion point. A. A. ELDRIDGE.

Growth of colloidal silver in gelatin layers. H. ARENS and J. EGGERT (Z. Elektrochem., 1929, **35**, 728—733).—The growth of silver particles embedded in gelatin layers has been investigated in its dependence on the initial size of particles and also on the silver concentrations, and this has been compared with the growth occurring in the blackening of a photographic plate. H. T. S. BRITTON.

Reactions between hydrophilic sols. I. Gelatin and silicic acid. W. J. LESLEY (Trans. Faraday Soc., 1929, **25**, 570—579).—Determinations of the p_H values of acid and alkaline solutions of gelatin or silicic acid, or both, were made under varying conditions. Co-precipitation of the two colloidal substances appears to be at a maximum at the isoelectric point of the gelatin. Addition of silicic acid sol to an acid solution of gelatin causes practically no change in p_H value, although precipitation occurs in many cases. Various precipitates obtained from hydrochloric acid solutions in the neighbourhood of the gelatin isoelectric point were of approximately constant composition, although in all cases the silicic acid was completely precipitated. A series of experiments with decreasing ratio of gelatin to silicic acid showed that when the ratio was less than about 0·07 the precipitation of silicic acid ceased to be complete and, instead of precipitation, opalescence alone ensued. H. T. S. BRITTON.

Coagulation of hæmoglobin. I. S. L. PUPKO (Kolloid-Z., 1929, **49**, 150—153).—The coagulation of aqueous hæmoglobin solutions in presence of ethyl alcohol and potassium chloride and bromide has been investigated viscosimetrically. The greater is the amount of added electrolyte, the smaller is the amount of alcohol required for coagulation. The product of the volume of alcohol just insufficient to cause coagulation and the concentration of the electrolyte is constant. Potassium chloride and bromide have equal effects. E. S. HEDGES.

Coagulation and separation into two liquid layers. Systems gum arabic–gelatin. H. G. B. DE JONG and W. A. L. DEKKER (Biochem. Z., 1929, **212**, 318—336).—In mixtures of some hydrophilic sols, *e.g.*, gum arabic and soluble starch, gum arabic and agar, the viscosity relationships are almost exactly additive. With gelatin–gum arabic mixtures, additive relationships are obtained outside the p_H range 4·8—1·2, but within this range the additivity curve shows a minimum corresponding with optimal separation into two layers. Capillary electric charges also have an influence on the separation into liquid layers. At p_H 4·7, gelatin is faintly positively and gum arabic strongly negatively charged; as the p_H decreases the charges are reversed, gelatin becoming strongly positively and the gum weakly negatively charged. At p_H 1·2 when the gelatin has lost much of its positive charge and the gum arabic is very slightly negatively charged, separation into liquid layers ceases. Over the same p_H range in presence of 0·15*N*-potassium chloride, the viscosity again shows additive relations. In equivalent concentrations the return to additivity is the more pronounced the greater is the valency of the anions, increasing, *e.g.*, with KCl, $\frac{1}{2}K_2SO_4$, $\frac{1}{3}K_3Fe(CN)_6$, and the same holds for increasing valency of cations. The same behaviour is obtained with gelatin and mucilages of linseed, Iceland moss, althæa root, tragacanth, and carragheen as with gum arabic. P. W. CLUTTERBUCK.

Effect of proteins on the coagulation of bentonite suspensions by electrolytes. B. N. GHOSH (J.C.S., 1929, 2285—2290).—The addition of small quantities of gelatin accelerates the coagulation of bentonite suspensions by sodium or barium chloride, but larger quantities retard coagulation and finally cause protection. The protective action of a given weight of gelatin is the greater the more dilute is the suspension. Casein and egg-albumin behave similarly, but the protective action of the latter is less than that of the two former. On the acid side of their isoelectric points the proteins coagulate the suspensions without addition of electrolytes. C. W. GIBBY.

Precipitations in gels. I. Influence of an electric field on rhythmic precipitation. II. Single ring precipitation. B. KISCH (Kolloid-Z., 1929, **49**, 154—156, 156—158).—I. Experiments are described on the formation of Liesegang rings of silver chromate under the influence of an electric field. When a *P.D.* of 0·1 volt was applied, the anode being in the centre of the drop of diffusing silver nitrate and the cathode in the gelatin beyond the edge of the drop, more rings are formed in the direction of the cathode and they are more strongly marked and broader. If instead of a point-cathode a platinum ring is used so as to encircle completely the drop, diffusion occurs more quickly and broad rings are formed, but if the outer circular electrode is made the anode, the diffusion field is much smaller and no rings are formed.

II. When a drop of a concentrated solution of potassium iodide is placed on a gelatin or agar gel containing 1% of mercuric chloride, a single ring of mercuric iodide is produced instead of the usual series of concentric rings, and the boundary of the drop moves as the potassium iodide diffuses outwards. This is because the ring of precipitate is soluble in excess of the reagent. E. S. HEDGES.

Effect of potassium alum on gelatin. A. LOTTERMOSER and W. MATTHAES (Kolloid-Z., 1929, **49**, 103—118).—The changes in certain properties of gelatin after treatment with solutions of potassium alum have been examined. The gelatin was allowed to swell in water, a solution of the alum was added, and the viscosity of the mixture measured 5 min. after the addition. These values of the "initial viscosity" increase with the amount of swelling

undergone by the gelatin before the addition of alum and also reach a maximum at a concentration of 11% of potassium alum. The high initial viscosity falls with time, ultimately reaching a value close to that of untreated gelatin solutions. Heating the solution reduces the initial viscosity and this change is irreversible. The viscosity of gelatin solutions treated with alum is also reduced by pressure, although such a change is not observed in untreated solutions. The m. p. of gelatin gels is at a maximum after treatment with 3% of potassium alum and the value is reduced by heating the mixture; when the gel is kept, the m. p. rises. The temperature of setting increases with the concentration of both the gelatin and the alum. The "Abschwimmtemperatur," at which a gelatin film ceases to adhere to the base on which it has been formed, increases with the amount of alum added: for ordinary gelatin solutions this value lies below the m. p., but for solutions treated with alum it is always above the m. p. and is more readily reproducible; the value also depends on the drying treatment. The surface tension of the solutions, as determined by a stalagmometric method, is raised by the addition of alum, but is reduced when the solution is heated. The addition of potassium alum reduces the swelling of gelatin. The mechanical strength of gelatin gels is at a maximum after addition of 3% of potassium alum, coinciding with the maximum of m. p. E. S. HEDGES.

Diffusion of methylene-blue in gelatin gels. K. SCHULTZE (Kolloid-Z., 1929, **49**, 118—120).—The gradual disappearance of colour at the boundary of a gelatin gel and a solution of methylene-blue which is allowed to diffuse into it, described by Mokruschin (A., 1928, 238), does not occur when all the apparatus and materials used are carefully sterilised, but may be brought about by the subsequent addition of certain bacteria. It is inferred that the explanation given by Mokruschin is not valid, and that the disappearance of colour is due to some reducing substance in the gelatin which may be produced by bacterial decomposition. E. S. HEDGES.

Effect of hydrogen carbonate ions on the swelling of gelatin. E. G. MILLER, jun. (Biochem. J., 1929, **23**, 876—879).—The influence of hydrogen carbonate concentration and p_H on gelatin swelling (over a limited range) is of the same order of magnitude as the corresponding influence of the chloride ion. S. S. ZILVA.

Vapour-pressure diminution of rubber jellies. P. STAMBERGER (J.C.S., 1929, 2318—2326).—Measurements have been made of the vapour pressure of rubber jellies in benzene, chloroform, and carbon disulphide, particularly at low concentrations. Up to a certain concentration the vapour-pressure lowering is inappreciable, but increases rapidly above that. The solvation of the jellies is discussed. C. W. GIBBY.

Ionisation currents from zinc oxide smokes. H. P. WALMSLEY (Phil. Mag., 1929, [vii], **8**, 553—568; cf. A., 1927, 287; this vol., 869).—Using the method previously described (cf. A., 1926, 654) the ionisation currents from clouds or smokes of zinc oxide particles were investigated. The smoke was produced in a cistern from an electric arc between zinc electrodes, whilst in a second case zinc oxide was dispersed by the decomposition of diluted zinc ethyl vapour passed into the cloud chamber. The initial ionisation and its changes with time were measured. The cloud particles in both cases are crystalline, with the internal structure of zincite. The clouds from the arc are ionised on formation; those from the zinc ethyl are not. There is a spontaneous production of ions in the clouds as they age; in those from zinc ethyl, ionisation increases from zero to a maximum and then diminishes. Qualitatively the intensity increases with the amount of material dispersed and with the degree of dispersion. The initial ionisation in clouds from the arc is attributed to thermoelectric emission of charges at the high temperature of formation. With arc clouds of low concentration this diminishes with time. The coefficient of recombination of these ions is of the same order of magnitude as the coagulation constant of similar clouds. With increasing concentration of dispersion the two effects are superposed. N. M. BLIGH.

Derivation of the law of mass action. R. D. KLEEMAN (Phil. Mag., 1929, [vii], **8**, 267—269).—Further to a previous paper (cf. A., 1928, 1315) in answer to Goldstein's criticism of the derivation of the modified law of mass action (this vol., 881), it is pointed out that the ordinary (and Goldstein's) derivation of the law involves constraints which do not allow of molecular dissociation, whilst in the revised derivation no constraints are applied. It is pointed out that under conditions of constraint the process of the van 't Hoff cycle cannot be considered as isothermal. A. E. MITCHELL.

Velocity law of gas molecules. G. JÄGER (Monatsh., 1929, **53** and **54**, 199—202).—Mathematical. For values between u and $u+du$ the velocity component of a gas molecule depends only on u and not on any other arbitrarily-assumed quantities. L. S. THEOBALD.

Derivation of the Boltzmann entropy law by means of the conception of material waves. A. HAAS (Monatsh., 1929, **53** and **54**, 165—174).—Mathematical. The Boltzmann entropy law can be deduced from the Gibbs formula for energy distribution. It is now shown that the logarithm of the probability equals $E-\Psi/\Theta$, where E is the total energy and Θ the distribution modulus which is proportional to T; by using the conception of material waves the function Ψ is identified with the free energy F. From these results the Boltzmann entropy law is derived and applied to vibrating quantum systems. L. S. THEOBALD.

Equilibrium between the mono-, di-, and tri-oxides of nitrogen. E. ABEL and J. PROISL (Z. Elektrochem., 1929, **35**, 712—715).—The equilibria involved in the decomposition of nitrogen trioxide at 8·1° and 34·8° have been investigated: from the results it is calculated that nitrogen trioxide at 25° and 760 mm. is 89·5% dissociated into the monoxide and dioxide, at 50°, 94·2%, and at 100°, 98·8%. H. T. S. BRITTON.

Equilibrium of carbon dioxide decomposition of formic acid and its potential. G. BREDIG, S. R. CARTER, and M. ENDERLI (Monatsh., 1929, **53** and **54**, 1023—1030).—The equilibrium constants for the formation of formic acid from carbon dioxide and hydrogen in presence of water and palladium-black (cf. Bredig and Carter, A., 1914, i, 377) at 20—90° and 60—117 atm. have been determined. From these constants and those for the water-gas reaction (*loc. cit.*) the equilibrium constants for the formation of formic acid from carbon monoxide and water in aqueous solution are calculated; these agree with the values obtained by Branch (A., 1915, ii, 742). The vapour pressures of 0·0306—0·0641*M*-solutions of formic acid in water at 20—90° have been determined by Zawidzki's method (A., 1901, ii, 6). From these results the equilibrium constants for the formation of formic acid from either carbon dioxide and hydrogen or carbon monoxide and water were calculated for the gaseous phase. The normal potential for the formation of aqueous formic acid in *N*-hydrogen-ion solution from carbon dioxide at 1 atmosphere pressure is calculated to be approximately −0·12 volt at 20° and −0·18 volt at 90°. H. BURTON.

The p_H value of water. A. KLING and A. LASSIEUR (Compt. rend., 1929, **189**, 637—639; cf. this vol., 240, 355).—The p_H of water determined by means of the cell $H_2|Aq-Hg_2Cl_2|Hg$ and a Moulin quadrant electrometer is "about 5·6." A more accurate method, using two hydrogen electrodes, one containing the water under examination, the other a liquid of known p_H adjusted until the *E.M.F.* of the combination vanishes, gave p_H 5·8. C. A. SILBERRAD.

Ebullioscopic determination of equilibrium constants. W. SWIENTOSLAWSKI, Z. BLASZKOWSKA, and E. JÓZEFOWICZ (Bull. Acad. Polonaise, 1929, **A**, 149—167).—See this vol., 396.

Electrolytic dissociation. C. DRUCKER (Monatsh., 1929, **53** and **54**, 62—68).—The saturation concentrations of benzoic, *o*-nitrobenzoic, oxanilic, and picric acids in dilute sulphuric, hydrochloric, and nitric acids decrease with increasing concentration of the inorganic acid. The specific conductivity of the solutions increases with diminishing values of the saturation concentrations. With benzoic, *o*-nitrobenzoic, and oxanilic acids in dilute picric acid solution, the saturation concentration first diminishes and then increases with increasing concentration of picric acid. This increased solubility is doubtless due to the formation of additive compounds. The anionic mobilities of the above organic acids in the same acid solutions have been determined electrometrically, using either hydrogen–iridium or quinhydrone–gold electrodes, and are found to be approximately the same. The results given for picric acid alone do not agree with those of von Halban and Ebert (A., 1924, ii, 826). All measurements were carried out at 25°. H. BURTON.

Dissociation constant of nitrous acid. A. KLEMENC and E. HAYEK (Monatsh., 1929, **53** and **54**, 407—412).—When carbon dioxide is passed through a 0·06*M*-solution of sodium nitrite at the rate of 170 c.c. per min. at 12·5°, the amount of nitrite decomposed in accordance with $3NaNO_2+2CO_2+H_2O=2NaHCO_3+NaNO_3+2NO$ reaches a limiting value (cf. Baur, A., 1906, ii, 649). If sodium hydrogen carbonate is first added to the nitrite solution no decomposition occurs on passing carbon dioxide. The conductivities of dilute solutions of nitrous acid (from barium nitrite and sulphuric acid) have been determined at 0° and 12·5°, using platinum electrodes. The equivalent conductivities (λ) at v=411·2 and 822·4 litres are 84·3 and 106·5 at 0° and 122·7 and 155·1 at 12·5°, respectively. Extrapolation of the values of λ for potassium nitrite gives λ_∞=115·7 (±0·5) at 12·5°. From the above data, the accessible transport numbers, and the heat of dissociation (ΔH=4480 g.-cal.) the dissociation constants of nitrous acid at 0°, 12·5°, and 30° are found to be $3{\cdot}2(\pm0{\cdot}3)\times10^{-4}$, $4{\cdot}6(\pm0{\cdot}4)\times10^{-4}$, and $6{\cdot}0(\pm0{\cdot}6)\times10^{-4}$, respectively H. BURTON.

Ionisation constant of *p*-cyanobenzoic acid. E. P. VALBY and H. J. LUCAS (J. Amer. Chem. Soc., 1929, **51**, 2718—2720).—An improved method of preparing *p*-cyanobenzoic acid is described. The conductivity at 25° of solutions of the acid up to 0·007446 mol./litre is recorded. Assuming the limiting conductivity to be 377 ohm^{-1}, *i.e.*, the same as that of *m*-cyanobenzoic acid, the Ostwald ionisation constant is $3{\cdot}1\times10^{-4}$. The electron attraction of the ·CN radical appears to exceed that of the $\cdot SO_2\cdot NH_2$ group and to be less than that of the $\cdot NO_2$ group. The equivalent conductivity of the *p*-cyanobenzoic ion is 27. S. K. TWEEDY.

Dissociation constants of valine and glutamic acid. L. J. HARRIS (J. Biol. Chem., 1929, **84**, 179—181).—The criticism by Kirk and Schmidt (this vol., 397) of the values obtained by the author for the dissociation constants of valine and glutamic acid is based on a mistaken reference. C. R. HARINGTON.

[Physico-chemical] study of bromosuccinic acid. I. Ionic product of water and some other dissociation constants. A. ÖLANDER (Z. physikal. Chem., 1929, **144**, 49—72).—When bromosuccinic acid is hydrolysed two simultaneous reactions occur, giving as end-products fumaric and maleic acids. Fumaric acid can be accurately determined in the presence of the other constituents by precipitation as mercurous fumarate dihydrate. Analytical details are given. Existing data for the ionic product of water, the p_H of standard buffer mixtures, and dissociation constants as determined conductometrically are critically discussed. The value 2·093 is selected as being the most trustworthy for the p_H at 18° of the mixture 0·01*N*-HCl+0·09*N*-KCl, which has been used as a standard in conjunction with a quinhydrone electrode in the potentiometric determination of the dissociation constants of acids, for which the following values are given, in the form of negative logarithms: succinic acid, 4·22; bromosuccinic acid, 2·69; phthalic acid, 3·00; acetic acid, 4·79. The above are the first dissociation constants at 50°. The second dissociation constant of succinic acid is pk_2=5·73 at 50°. The apparent second dissociation constant of sulphuric acid at ionic strength 0·25

is $pk_2=1\cdot68$ at 50°. Activity coefficients at various ionic strengths have been determined for acetate, primary phthalate, and primary and secondary succinate ions. A table of values of the ionic product of water between 0° and 50°, calculated from the formula of Lewis and Randall, is given.

F. L. USHER.

Acidity of mannitol. P. TERECHOV (Coll. Czech. Chem. Comm., 1929, **1**, 551—559).—It is suggested that mannitol (M) behaves as a weak acid and that in the presence of hydroxyl ions a complex M·OH′ is formed thus: M+OH′=M·OH′. The constant of the reaction has been determined (*a*) from cryoscopic measurements with sodium hydroxide solutions of concentrations varying between 0·1401*N* and 0·4102*N* and found to be 4·2 at 0°, (*b*) from the solubility in sodium hydroxide of various concentrations, the value found being about 8 in dilute solutions and decreasing in more concentrated solutions, the variation being attributed to the salting-out effect, (*c*) from potentiometric measurements with mercuric oxide and platinum electrodes of the activity of hydroxyl ions in the presence of mannitol, which lead to a value of 4·2 at 0° and 5·0 at 22°, and (*d*) from conductivity measurements of ammoniacal solutions containing mannitol which lead to values of 4·20 and 4·24 at 0° and 25°, respectively. The fact that the constant appears to be independent of the temperature is claimed to support the view of complex formation. The mass law constant is calculated to be 0·42 and $2\cdot4\times10^{-4}$ at 0° and 25°, respectively, when the values 0·1 and $1\cdot0\times10^{-14}$, respectively, are employed for the ionic product of water at these two temperatures.

A. I. VOGEL.

Viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. G. JONES and M. DOLE (J. Amer. Chem. Soc., 1929, **51**, 2950—2964).—The viscosity, η, at 25° of barium chloride solutions varying in concentration from 0·005 to 0·99*M* was determined in a Washburn viscosimeter. The results are given to within 0·03% by the equation $\eta_{H_2O}/\eta=1-0\cdot02013\sqrt{c}-0\cdot20087c$. Equations of this general type are shown to represent accurately the available trustworthy viscosity data for salt solutions. The coefficient of $\sqrt{c}$ is negative for strong electrolytes and zero for non-electrolytes. It represents the stiffening effect on the solution of the electric forces between the ions which tend to maintain a space-lattice structure; this effect is the cause of the negative curvature in viscosity–concentration curves. The coefficient of *c* is negative for those salts which increase the viscosity of water at all concentrations; the equation of the given type is then valid up to *M*. For salts which decrease the viscosity of water this coefficient is positive and the type of equation is valid only up to 0·2*M*. It is predicted from the equation type that at very low concentrations the viscosity of solutions of all strong electrolytes will be greater than that of water.

S. K. TWEEDY.

Dependence of the molecular refraction of acids in aqueous solutions on concentration. H. KOHNER and M. L. GRESSMANN (Z. physikal. Chem., 1929, **144**, 137—146; cf. A., 1928, 477, 1320; this vol., 258).—Measurements of the molecular refraction of sulphuric, acetic, perchloric, and benzenesulphonic acids are recorded. The occurrence of a well-defined maximum at 18 mol.-% of perchloric acid is confirmed. The molecular refraction of benzenesulphonic acid increases regularly with dilution within the range 22·6—3 mol.-%, and no indication of the attainment of a constant value at 12·5 mol.-%, as recorded by Hantzsch and Düringer, has been observed (cf. following abstract).

F. L. USHER.

Chemical changes of acids and salts in solution based on refractometric data. II. A. HANTZSCH and F. DÜRINGER (Z. physikal. Chem., 1929, **144**, 147—157; cf. A., 1928, 834, 1089).—Polemical against Fajans and co-workers (cf. preceding abstract). The authors' theoretical conclusions are in no way invalidated by the fact that other workers have based different interpretations on data obtained by the use of more refined methods. The scale used by Fajans and others in illustrating their results is adversely criticised, as is also their practice of making dilutions from a standard concentrated solution without checking the final concentrations by analysis.

F. L. USHER.

Landolt and Oudemans' law in non-aqueous solutions. P. WALDEN (Monatsh., 1929, **53** and **54**, 14—38).—The rotatory powers of tetraethylammonium α-bromocamphor-π-sulphonate, the free acid, and the acid chloride in non-aqueous solvents have been determined at dilutions varying from 10 to 500 litres per mol. of solute. The values of $[M]_D^{18}$ for the camphorsulphonate in methyl, ethyl, *n*- and *iso*-butyl alcohols, acetonitrile, chloroform, chloroform+benzene, acetic anhydride, and ethylene dichloride vary from 297° to 332° (water, 273°), but dilution has no effect on the value for any one solvent. For the acid chloride the values vary from 390° to 438° (same solvents), and dilution has no effect. The ratio $[M]_{chloride}/[M]_{salt}$ for all the solvents is approximately 1·31. The values do not appear to be related to the dielectric constants of the solvents; in acetonitrile and chloroform almost identical values are obtained. An approximate parallelism between rotatory power and refractivity in individual solvents is noticed. The values of $[M]$ for the free acid in various solvents are the same as the values for the camphorsulphonate. From the results it is concluded that not only free ions in the salt (or acid), but also the latent or not yet dissociated ions in the heteropolar linking, are responsible for the constant values.

H. BURTON.

Alteration of the optical absorption in the visible and ultra-violet regions through aggregation processes in alkaline and acid solutions of amphoteric hydroxides. G. JANDER and T. ADEN (Z. physikal. Chem., 1929, **144**, 197—212).—When aqueous solutions of alkali stannates or tungstates are gradually acidified, the formation of the final product is preceded by that of anions of progressively higher mol. wt. In the case of stannic, tungstic, chromic, or vanadic acid this process is accompanied by a displacement of the beginning of the optical absorption towards the longer wavelengths. At the same time any maxima or minima

tend to become flattened and are usually shifted in the direction of shorter wave-length.

F. L. USHER.

F.-p. measurements in very dilute solutions of strong electrolytes in *cyclo*hexanol. E. SCHREINER, O. E. FRIVOLD, and F. ENDER (Phil. Mag., 1929, [vii], **8**, 669—680).—Deviations from the ideal values of the f. p. of very dilute solutions of uni-univalent salts in *cyclo*hexanol (A., 1926, 1208) are in close agreement with the Debye–Hückel theory, in spite of the low dielectric constant, 15·0, of *cyclo*hexanol. Similar experiments have now been carried out with uranyl acetate, lanthanum nitrate, and mixtures of lanthanum nitrate and lithium chloride. So far as it is possible to judge from the experiments the deviations do not conform so closely with the Debye–Hückel law as in the case of a uni-univalent salt alone. The discrepancies, however, appear to be in the direction indicated by the modifications introduced into the theory by Müller (A., 1927, 626; 1928, 590), and by Gronwall, LaMer, and Sandved (A., 1928, 841).

M. S. BURR.

Dielectric constants of electrolytic solutions for various concentrations. A. P. CARMAN and C. C. SCHMIDT (Physical Rev., 1928, [ii], **31**, 157).—The dielectric constants of solutions of sodium, potassium, and barium chlorides, and of copper sulphate have been measured for equivalent concentrations up to 0·02, 0·01, 0·022, and 0·026, respectively. The graph of ε against concentration shows for sodium chloride a decrease in ε up to a concentration of 0·012, followed by an abrupt increase, and for concentrations greater than 0·016, the value of ε is greater than that of water. Solutions of potassium chloride give a similar curve, but the curves for barium chloride and copper sulphate show two minima, the values for ε in each case being greater in the more concentrated solutions than that for water. Walden (A., 1925, ii, 773) predicted part of these results, but not the occurrence of the minima.

L. S. THEOBALD.

Static balance electrometer method for measuring dielectric constants of electrolytes. A. P. CARMAN, O. B. YOUNG, and K. O. SMITH (Physical Rev., 1929, [ii], **34**, 1040—1041).—Carman's differential electrometer method (cf. A., 1928, 106) has been adapted to take readings with conducting electrolytes by static balance, the thermal disturbances being controlled by a special cooling water-jacket round the vessel containing the tested solution.

N. M. BLIGH.

Dielectric constants of three electrolytes by a static balance electrometer method. A. P. CARMAN and K. O. SMITH (Physical Rev., 1929, [ii], **34**, 1042—1044; cf. preceding abstract).—Values of the dielectric constants of solutions of potassium chloride, copper sulphate, and barium chloride were measured for concentrations from 0·001*N* to 0·024*N*, at temperatures between 25° and 26°, in fields of about 26·7, and were found to increase at first above that of water, and later to decrease; in the case of copper sulphate, the values are greater than that of water.

N. M. BLIGH.

Thermodynamic requirements of concentrated solutions. R. FRICKE and J. LÜKE (Z. Elektrochem., 1929, **35**, 631—640).—To test the validity of Kirchhoff's equation connecting the heat of dilution with the vapour pressures of solvent and of solution, an improved method was used for determining vapour pressures (cf. Fricke and Havestadt, A., 1928, 134). Solutions of the following were investigated: thorium nitrate, ammonium nitrate, glycerol, carbamide, sodium hydroxide, sodium acetate, magnesium chloride, and zinc chloride.

H. T. S. BRITTON.

Activity of hydrogen ion in concentrated hydrofluoric acid. E. R. B. PRIDEAUX and J. N. MILLOTT (Trans. Faraday Soc., 1929, **25**, 579—581).—Measurement at 18° of the *E.M.F.* of cells of the type: quinhydrone|HF sol.|sat. KCl, Hg_2Cl_2|Hg, in which the acid is 33·5*M* and 3·485*M*, respectively, give 0·179 and 0·106 for the activity coefficient. Taken in conjunction with the data of Wynne-Jones and Hudleston (A., 1924, ii, 470), it appears that the graph of the activity coefficient of hydrofluoric acid against concentration passes through a minimum at about 1·5*M*.

H. T. S. BRITTON.

Activity coefficients of cadmium chloride and bromide. W. W. LUCASSE (J. Amer. Chem. Soc., 1929, **51**, 2597—2604).—*E.M.F.* measurements at 25° on cells of the type Hg,Cd|CdX_2,xM|AgX|Ag are recorded, with x=0·01—6 when X=Cl, and x=0·01—3 when X=Br. The data do not fit the functions of Brönsted and of Hückel, probably owing to complex ion formation. The activity coefficients, γ, of the cadmium halides have been computed by utilising the standard potential of the cadmium electrode. These are given by $\log \gamma = aM - bM^c$, where a, b, and c are 0·6, 1·75, and 0·38, respectively, for the chloride and 0·2, 1·48, and 0·308 for the bromide. The activity coefficients of these salts decrease with increase in concentration much more rapidly than the coefficients of typical strong electrolytes; the results indicate that cadmium chloride and bromide cannot be regarded as completely dissociated in solution.

S. K. TWEEDY.

Activity coefficients of electrolytes. III. Principle of specific interaction in mixtures of high valency electrolytes. V. K. LAMER and R. G. COOK (J. Amer. Chem. Soc., 1929, **51**, 2622—2632).—The validity of Brönsted's principle of specific interaction (A., 1922, ii, 699) has been tested for salts of higher valency by measuring the effects of various salts (*e.g.*, nitrates and chlorides of potassium, magnesium, and lanthanum) on the solubility at 25° of two ter-univalent and two uni-univalent cobalt-ammines. The principle holds for solvents of higher valency provided that comparisons are restricted to types in which the ratio of the ionic strengths remains unaltered when changes are made in the common solvent ion at the same equivalent concentration. Even at very low concentrations, the Debye limiting law is not obeyed by these solvent salts (cf. LaMer and Mason, A., 1927, 314, whose work is confirmed).

S. K. TWEEDY.

Activity coefficients of electrolytes. IV. Solubilities of lanthanum and thallous iodates

in aqueous salt solutions and the principle of specific interaction. V. K. LAMER and F. H. GOLDMAN (J. Amer. Chem. Soc., 1929, **51**, 2632—2645).—The solubility of lanthanum iodate and of thallous iodide in aqueous salt solutions (*e.g.*, magnesium sulphate, lanthanum nitrate, etc.) has been determined. The Debye–Hückel limiting law is not obeyed, so that this disagreement is not peculiar to the cobaltammines. The conclusions stated in the preceding abstract with regard to the validity of Brönsted's theory of specific interaction are substantiated. The individual specific interactions appear to be restricted to the ions of opposite sign at least up to 0·1*N*. The solubility ratios for thallous chloride and for thallous iodate in various salt solutions conform to Brönsted's principle up to 0·3*N*. The data of Harkins and Pearce (A., 1917, ii, 77) for the solubility of lanthanum nitrate in ammonium nitrate solutions, recalculated according to modern theory, show excellent agreement with the principle of ionic strength. S. K. TWEEDY.

Perylene and its derivatives. XXVI. Heats of combustion of perylene and its derivatives. A. PONGRATZ and F. GRIENGL (Monatsh., 1929, **53** and **54**, 256—262).—The heats of combustion of several perylene derivatives have been determined using the micro-apparatus described by Roth, Ginsberg, and Lassé (A., 1924, ii, 748). The molecular heats of combustion (kg.-cal. 15°), the values being based on that for benzoic acid [6324 g.-cal.^{15}/g. (air)], are: perylene, 2333·0; 3 : 9-diacetyl-, 2780·5; 3 : 9-dipropionyl-, 3079·6; 3 : 9-dibutyryl-, 3395·4; 3 : 9-dibenzoyl-, 3878·0; 3 : 9-di-*o*-toluoyl-, 4213·0, and 3 : 9-dicyano-perylene, 3156·0. Perylene-3 : 10- and -1 : 12-quinones give values of 2158·8 and 2213·3, respectively. H. BURTON.

Thermochemistry of the compounds in the system $CaO-Al_2O_3,SiO_2$. I. Heat of dissolution of calcium oxide in hydrochloric acid. T. THORVALDSON, W. G. BROWN, and C. R. PEAKER (J. Amer. Chem. Soc., 1929, **51**, 2678—2682).—The heat of dissolution of calcium oxide in the solution $HCl,200H_2O$ at 20° is 828·9 g.-cal. (20°) per g., independent of the ignition temperature of the oxide between 800° and 1200°. S. K. TWEEDY.

Solubility and energy of reciprocal transformation of different forms of calcium sulphate. P. N. LASCHTSCHENKO and A. I. MOROZOVA (J. Russ. Phys. Chem. Soc., 1929, **61**, 962—976).—The solubility at 25° of gypsum is 2·209 g./litre. That of anhydrite, as expressed by the electro-conductivity of the solution, rises to a maximum in 6—7 days as a result of hydration. The solubility of polyhydrate falls from 7·48 g./litre 10 min. after dissolution to 2·15 g./litre 48 hrs. later, whilst constant values for the conductivity of saturated polyhydrate solutions are attained 7 hrs. after their preparation. The process of setting of plaster of Paris is supposed to consist of a rapid process of hydration of anhydrite with the formation of metastable β-gypsum (dihydrate), which is then gradually converted into ordinary gypsum. The initial conductivity of saturated solutions of gypsum rises from $26·5\times10^{-4}$ in the case of gypsum previously heated at 110° to $62·4\times10^{-4}$ for material heated at 230°; when higher temperatures are used, the initial conductivity gradually falls to $13·1\times10^{-4}$ for 1100°. The final conductivity is 22·8—22·3 for gypsum heated at 110—285°; above 285° it rises to 29·4 for 600°, falling again to 24·5 for 1100°. These results indicate a maximum formation of soluble anhydrite at 230°, following which the yield of insoluble anhydrite becomes increasingly large. The energy of transformation, E, of one form of calcium sulphate into another is given by $E=2RT\log_e K_2/K_1$, where K_1 and K_2 are the specific conductivities of saturated solutions of the respective forms. The results obtained by substitution in this formula of values for the interconversion of the various forms are in good agreement with those obtained by using van 't Hoff's formula. R. TRUSZKOWSKI.

Formation of gaseous gold hydride. A. FARKAS (Z. physikal. Chem., 1929, **B**, **5**, 467—475).—The vapour pressure of gold at 1400° is $9·1\times10^{-3}$ mm., and of the hydride AuH $7·8\times10^{-2}$ mm. The equilibrium constant of the reaction $2Au+H_2\longrightarrow 2AuH+Q$ is $1·04\times10^{-2}$, whilst Q has the value 43,500 kg.-cal. At 1100° the vapour pressure of silver is $3·8\times10^{-2}$ mm. and of silver hydride $1·1\times10^{-2}$ mm. The equilibrium constant of the reaction $2Ag+H_2\longrightarrow 2AgH$ is 14·5, and the heat of dissociation of the hydride 67,500±6300 kg.-cal. The absorption spectra of gold and silver hydrides at 1400° and 1100°, respectively, have been examined and the results compared with those given by Birge and Sponer's extrapolation method. H. F. GILLBE.

Decomposition of thallic oxide. A. B. F. DUNCAN (J. Amer. Chem. Soc., 1929, **51**, 2697—2705).—From the oxygen pressures set up in the decomposition of thallic oxide between 670° and 770° the amount, x, of thallous oxide present in the fused mass has been derived. The m. p. of thallic oxide is 717°±5°; this cannot be determined in air, since p is 25·5 cm. at 720°. For a given temperature p is a linear function of x, the isotherms being inclined to the composition axis. Raoult's law is apparently obeyed. The heat and free energy of the reaction $Tl_2O_3=Tl_2O+O_2$ are calculated from the equilibrium constant of the reaction. S. K. TWEEDY.

Hydrates of lithium thiocyanate. V. I. NIKOLAEV (J. Russ. Phys. Chem. Soc., 1929, **61**, 939—945).—The equilibrium diagram for the system lithium thiocyanate–water shows two *hydrates*, $LiCNS,H_2O$, m. p. 60·5°, and $LiCNS,2H_2O$, m. p. 34°; the existence of a trihydrate is excluded. The eutectic point of the system is −33° at 88% of water. R. TRUSZKOWSKI.

Additive compounds of lithium halides with methyl and ethyl alcohols. Existence rule in homologous series of complex compounds. G. F. HÜTTIG [with F. OSCHATZ] (Monatsh., 1929, **53** and **54**, 299—304).—The heats of formation (kg.-cal.) of the following alcoholates are: LiCl,MeOH, 13·4; LiCl,3MeOH, 13·2; LiCl,EtOH, 12·9; LiCl,4EtOH, 12·8; LiBr,MeOH, 14·6; LiBr,3MeOH, 14·15; LiBr,EtOH, 14·05; LiBr,4EtOH, 13·45; LiI,MeOH, 14·8; LiI,3MeOH, 13·4; LiI,4MeOH, 13·2. The three halides form mono-, di-, and tri-hydrates; the

iodide gives also a hemihydrate. Revised values for the heats of formation of lithium halide ammines are given (cf. Biltz and Hansen, A., 1923, ii, 760), and also the values for the analogous compounds with mono-, di-, and tri-methylamine (Simon and Glauner, this vol., 431). In a homologous series the tendency towards the formation of additive compounds diminishes with increasing mol. wt. of the addendum.

H. BURTON.

Dissociation of the compounds $HgBr_2,2NH_3$ and $HgCl_2,2NH_3$. M. FRANÇOIS (Compt. rend., 1929, **189**, 583—585).—The temperatures at which the dissociation pressures are equal to 760 mm. are 186° and 239°, respectively. J. GRANT.

System leucite–diopside. N. L. BOWEN and J. F. SCHAIRER (Amer. J. Sci., 1929, [v], **18**, 301—312).—Leucite (m. p. 1686±5°) and diopside (m. p. 1391·5°) form a eutectic at 1300±2° containing 61·5% of diopside. The liquidus curve of leucite is concave upwards at high temperatures and convex at lower temperatures. C. W. GIBBY.

System water–carbon dioxide–ammonia. E. JÄNECKE (Z. Elektrochem., 1929, **35**, 716—728).—The binary systems ammonium hydrogen carbonate–ammonium carbamate, ammonium carbamate–ammonia have been investigated. Solubility determinations at various temperatures have also been carried out on the ternary systems: ammonium hydrogen carbonate–ammonia–water, and ammonium carbamate–ammonia–water. The solubilities of ammonium hydrogen carbonate in ammonia solutions are recorded for temperatures below 0°. The solubilities of carbon dioxide in concentrated solutions of ammonia at 1 atm. and over an extensive range of temperature are also given. H. T. S. BRITTON.

Equilibrium in the reduction of silver sulphide by hydrogen. M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 708—713).—The reduction of silver sulphide by hydrogen between 453° and 704° has been studied. The equilibria can be represented by the equation $\log K_p = 125{\cdot}44/T - 0{\cdot}6499$.

C. W. GIBBY.

Equilibrium between water and the nitrates and chlorides of sodium and potassium. E. CORNEC and H. KROMBACH (Caliche, 1928, **10**, 153—161; Chem. Zentr., 1929, i, 2740—2741).—The limits of the sodium nitrate field only have been investigated, and the results include solutions saturated with respect to this salt as well as potassium nitrate or sodium chloride or both at temperatures from 0° to 100°. The deviations from earlier work are considerable. The four saturation fields of the nitrates and chlorides meet at the two ternary points KNO_3–$NaNO_3$–NaCl and KNO_3–KCl–NaCl. The diagrammatic representation of the results is described. The ternary point shows a minimum solubility for sodium chloride at 75°. L. S. THEOBALD.

Equilibrium between water and the nitrates, chlorides, and sulphates of sodium and potassium at 75°. E. CORNEC and H. KROMBACH (Caliche, 1928, **10**, 250—259; Chem. Zentr., 1929, i, 2741; cf. preceding abstract).—The equilibria which obtain between water and these salts at 75° have been investigated. Their representation in a geometrical manner is described. Thirty invariant points occur.

L. S. THEOBALD.

Quaternary system water–sodium nitrate–sodium chloride–sodium sulphate. A. CHRÉTIEN (Ann. Chim., 1929, [x], **12**, 9—155).—The binary systems sodium nitrate–water, sodium chloride–water, and sodium sulphate–water have been investigated, with results in general agreement with those of other workers. The system sodium nitrate–sodium chloride–water has been studied at various temperatures between −24·3° and 119·8°. No double salts are formed. In the system sodium sulphate–sodium chloride–water, of which isotherms have been determined between −10·6° and 100°, no solid phases other than the simple salts and their hydrates have been found. The system sodium sulphate–sodium nitrate–water was investigated between −18° and 120°. Darapskite, $Na_2SO_4,NaNO_3,H_2O$, is stable between 13° and 74°; solutions in contact with it are incongruently saturated. The preparation of darapskite is discussed. Dehydration of darapskite between 92° and 112° gives rise to an anhydrous double salt, $Na_2SO_4,NaNO_3$. The quaternary system has been investigated between −24·4°, the temperature of the quaternary eutectic, and 121·7°. No further complex salts are formed. C. W. GIBBY.

System $AlCl_3$–$FeCl_3$–KCl–HCl–H_2O at 25°. G. MALQUORI (Gazzetta, 1929, **59**, 556—563).—Phase studies have been made of the systems $FeCl_3$–KCl–HCl–H_2O and $AlCl_3$–KCl–$FeCl_3$–H_2O and the results applied to the elucidation of the system $AlCl_3$–$FeCl_3$–KCl–HCl–H_2O. In the latter, the following sets of solid phases are capable of independent existence: $AlCl_3,6H_2O$–KCl; $FeCl_3,2KCl,H_2O$–KCl–$AlCl_3,6H_2O$; $FeCl_3,2KCl,H_2O$–KCl; $FeCl_3,2KCl,H_2O$–$FeCl_3,6H_2O$–$AlCl_3,6H_2O$; $FeCl_3,2KCl,H_2O$–$FeCl_3,HCl,2H_2O$–$AlCl_3,6H_2O$–$FeCl_3,2H_2O$; $FeCl_3,HCl,2H_2O$–$FeCl_3,2H_2O$–$AlCl_3,6H_2O$; $FeCl_3,HCl,2H_2O$–$FeCl_3,2KCl,H_2O$–$FeCl_3,2H_2O$. The study of the above system shows the possibility, exemplified in the practical application of the Blanc process, of obtaining good yields of potassium and aluminium chlorides of high purity from the fractional crystallisation of the liquors resulting from the treatment of leucite with hydrochloric acid.

F. G. TRYHORN.

Heat of formation of sulphur dioxide. J. R. ECKMAN and F. D. ROSSINI (Bur. Stand. J. Res., 1929, **3**, 597—618).—Since a variable small quantity of sulphur trioxide is formed when sulphur burns in an excess of oxygen the heat of formation of sulphur dioxide has been determined by causing oxygen to react with an excess of hot sulphur vapour in a specially-designed reaction chamber. No trace of trioxide is formed and difficulties associated with the analysis of the combustion gases are thereby obviated. The mean value of the heat of formation from solid rhombic sulphur and gaseous oxygen at 25° is 70,940±50 g.-cal. A. R. POWELL.

Energy of hydration of hydroxyl ion and the lattice energies of alkali hydroxides. F. J. GARRICK (Phil. Mag., 1929, [vii], **8**, 102—107).—The total energy of hydration of the ions of water is deter-

mined from the cycle Aq $\longrightarrow$ $(H_2O)_{gas}$ $\longrightarrow$ $(H^+ + OH^-)_{gas}$ $\longrightarrow$ $(H^+_{aq} + OH^-_{aq})$ $\longrightarrow$ Aq, employing accepted values for the heat of evaporation of water and the heat of neutralisation of strong acids and bases and the mean of the values of Senftleben (A., 1926, 768) and Hund (Z. Physik, 1925, **32**, 1) for the work of ionisation of water vapour. The existence of H_3O^+ as postulated by Volmer is accepted and it is assumed that H_3O^+ and OH^- have nearly the same energy of hydration. Then taking the mean of the values of Hund (*loc. cit.*) and of Grimm (Z. Elektrochem., 1925, **31**, 474) for the heat of formation of H_3O^+ from water vapour and a proton, the heat of hydration of OH^- is found to be 94 kg.-cal., whilst that of H^+ becomes 255 kg.-cal., in good agreement with the results of Fajans and Webb. A similar cycle is employed to calculate the lattice energies of alkali hydroxides, the results obtained being in agreement with those obtained by the method of Hund (*loc. cit.*). These values combined with those of Fajans and Born and of Webb for the heat of hydration of H^+ lead to the mean value of 92 kg.-cal. for the heat of hydration of OH^-. A. E. MITCHELL.

Vapour pressure and heat of dilution. VI. Heat of dilution of hydrochloric acid, sodium hydroxide, and acetic acid. R. C. PAYN and E. P. PERMAN (Trans. Faraday Soc., 1929, **25**, 599—610).—The heats of dilution of aqueous solutions of hydrochloric acid, acetic acid, and sodium hydroxide over wide ranges of dilution have been measured at temperatures ranging from 20° to 70° by means of the apparatus of Harrison and Perman (A., 1927, 207). Hydrochloric acid solutions gave no positive values, but small positive heats were observed in the case of dilute sodium hydroxide solutions at the lower temperatures. The higher concentrations of acetic acid gave large positive values, but these became slightly negative in the more dilute solutions. The heat of dilution of acetic acid at any particular concentration is found to be a linear function of the temperature. It is not possible to correlate the heats of dilution with the nature and constitution of the solutions. H. T. S. BRITTON.

Individuality of the integral heats of dilution of strong electrolytes. E. LANGE and J. MEIXNER (Physikal. Z., 1929, **30**, 670—678).—The Debye-Hückel theory has been examined by reference to integral heats of dilution, and certain simplifications in the formulæ have been introduced. A more exact calculation of the heats of dilution, which takes account of the higher terms, leads to the conclusion that the heat of dilution is equal to the difference of the electrical potential energies at the initial and final concentrations multiplied by a factor $1+TdD/DdT$ which depends on the solvent (D=dielectric constant). The case of a symmetrical z-z-valent electrolyte with equal apparent cross-sections for both ions is discussed in relation to theoretical equations and experimental data, the degree of agreement for small concentrations showing an improvement as compared with previous work. Alternative methods for considering the case of unsymmetrical valencies are suggested. R. A. MORTON.

Revision of thermal data. I. W. A. ROTH (Z. physikal. Chem., 1929, **144**, 253—258).—The need for a thorough revision of existing thermochemical data by means of fresh and more trustworthy experiments is pointed out. The connexion between atomic number and heat of formation furnishes a convenient check on the results. The heats of formation of silicon and aluminium oxides have been found by the calorimetric bomb method to be $204{\cdot}0 \pm 2{\cdot}1$ and $380{\cdot}8 \pm 0{\cdot}4$ kg.-cal. per g.-atom, respectively, at constant pressure. These results are higher than the values generally accepted. F. L. USHER.

Thermochemistry of iron, manganese, and nickel. W. A. ROTH (Z. angew. Chem., 1929, **42**, 981—984).—The following heats of formation derived from combustion experiments in a bomb calorimeter are recorded: $FeO=+64{\cdot}0$, $Fe_3O_4=+265{\cdot}7$, $Fe_2O_3=+197{\cdot}6$, $Fe_3C=-5{\cdot}4$, $Fe(CO)_5=+54{\cdot}4$, $NiO=+58{\cdot}6$, $Ni_3C=-9{\cdot}2$, $Mn_3O_4=+343{\cdot}8$, $MnO=+96{\cdot}2$, $Mn_3C=+23$ (kg.-cal./mol. at constant volume). The values are higher than those usually recorded. C. IRWIN.

Heat of decomposition and of activation of some oxides and sulphides. K. FISCHBECK (Z. Elektrochem., 1929, **35**, 607—610).—The work involved in the various stages of the formation of oxides and sulphides, *e.g.*, the formation of oxygen atoms from oxygen molecules and their transference to the surface of the oxide layer and subsequent diffusion through the oxide layer to, and reaction with, the metal, is discussed. A method, in which metal oxides are allowed to react with liquid sulphur between 150° and 200° and so to produce sulphur dioxide at measurable velocities, is described; from these observations the heats of activation of oxides may be derived. H. T. S. BRITTON.

Heat of dissociation of some strong electrolytes in benzonitrile and their calculation from molecular structure. A. R. MARTIN (Phil. Mag., 1929, [vii], **8**, 547—552).—The dissociation constants of strong electrolytes in benzonitrile can be calculated from measurements of the dielectric constant of the solvent and from conductivity data (cf. this vol., 143); values are tabulated for the iodides of lithium, sodium, and potassium, lithium bromide, and silver nitrate. The heat of dissociation of an electrolyte in any solvent can be calculated, the dissociation being regarded as taking place in three stages, for each of which the energy changes are found from the dielectric constant of the solvent and the ionic and molecular constants of the solute. Values are tabulated for sodium and potassium iodide. N. M. BLIGH.

Heats of hydrolysis of the amides. Acetamide. E. CALVET (Compt. rend., 1929, **189**, 530—533).—The heat change in the hydrolysis of acetamide is derived from the thermal values of $Me{\cdot}CO{\cdot}NH_2+NaOH=Me{\cdot}CO_2Na+NH_3+x$ cal., and $Me{\cdot}CO_2Na+NH_3+H_2O=Me{\cdot}CO_2NH_4+NaOH+y$ cal. J. GRANT.

Inner friction of electrolytic solutions and its interpretation according to the Debye theory. H. FALKENHAGEN and M. DOLE (Physikal. Z., 1929, **30**, 611—622).—Theoretical. The relation $\eta_\mu=\eta_0(1+A\sqrt{\mu})$ (η_μ being the viscosity coefficient at a

concentration μ expressed in equivalents per litre of solution, η_0 that obtained when $\mu=0$) applies to solutions of strong electrolytes. The mathematical development of Debye's theory is considered for the simplest case of binary electrolytes with ions of the same mobility, discussion of the general case for simple electrolytes being deferred. The square root relationship is placed on a firm theoretical basis.

R. A. MORTON.

Conductivity measurements in liquid ammonia. L. SCHMID and M. K. ZACHERL (Monatsh., 1929, **53** and **54**, 498—507).—Solutions of glycogen or inulin in liquid ammonia have the same conductivity as the solvent, thus showing that neither compound undergoes molecular change. Mannitol and dextrose show practically no change. H. BURTON.

Conductivity measurements in acetonitrile. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1929, **144**, 269—315; cf. A., 1926, 1104; this vol., 401).—Conductivities of solutions in acetonitrile of 11 salts of quaternary ammonium bases, 15 salts of primary, secondary, and tertiary amines, and 9 inorganic salts have been determined at 25° and at dilutions up to 5×10^4 litres/mol. A comparison of the measured and calculated values of Λ_∞ for tetraethylammonium picrate confirms the square root law. The influence of the nature of both solvent and salt on the strength of the salt solution is discussed. The behaviour of the solvent depends much more on its chemical character than on such physical quantities as dielectric constant or electric moment. The salts investigated fall into three classes: (1) strong salts, including those of quaternary ammonium bases, silver picrate and perchlorate, and potassium picrate and iodide, for which the Kohlrausch square root law holds even in concentrated solution; (2) a group of very weak salts consisting of the chlorides of incompletely substituted amines, where Λ increases greatly with dilution, and (3) an intermediate group consisting of picrates, bromides, and iodides of incompletely substituted ammonium bases. Kohlrausch's law of the additivity of conductivities holds good for several quaternary ammonium bases, and Stokes' law for tetraethylammonium picrate. $\Lambda_\infty\eta$ has the value 0·563 for the last-named salt, as in other solvents. Ionic mobilities and solvation numbers for alkali and halogen ions in acetonitrile have been calculated. F. L. USHER.

Electrical conductivity of organic acids in water, alcohols, and acetone, and the electronic structures of the acids. H. HUNT and H. T. BRISCOE (J. Physical Chem., 1929, **33**, 1495—1513; cf. this vol., 401).—The molecular conductances of mono-, di-, and tri-chloro- and cyano-acetic acid and of glycollic acid in methyl, ethyl, and butyl alcohols and in acetone have been determined at 30°. The solution of an acid in acetone has a conductance between that in ethyl and propyl alcohols, except in the case of trichloroacetic acid, which falls between those in propyl and butyl alcohols at most dilutions. The CH_3 radical attached to hydroxyl forms molecules of a solvent weaker in ionising power than water, and the separation of CH_3 from OH by CH_2 does not greatly alter the ionising power of the medium. The addition of a second CH_2 group, however, is accompanied by a pronounced decrease in ionising power. The presence of the methyl, ethyl, and other radicals appears to affect the basicity or hydrogen-accepting properties of the solvent.

The molecular conductances and dissociation constants of 26 organic acids, chiefly derivatives of benzoic acid, have been calculated from the limiting conductivities of hydrochloric acid, sodium chloride, and the sodium salts of the acids at 30°. The results are interpreted in terms of the electronic theory of valency and current views on molecular structure.

L. S. THEOBALD.

Transport numbers and ionic mobilities in mixed solutions of electrolytes and their interpretation in terms of the Debye–Hückel–Onsager theories. K. BENNEWITZ, C. WAGNER, and K. KUCHLER (Physikal. Z., 1929, **30**, 623—634).—Onsager's formulæ derived from the Debye–Hückel theory and applied to the ionic mobilities of strong electrolytes have been extended to solutions containing two electrolytes, one ion of which is present in very small amount in a ternary mixture of ions. In order to test the theory, conductivities, transport numbers, and ionic mobilities have been determined for mixtures of barium chloride and potassium chloride, barium chloride and hydrochloric acid, and potassium chloride and hydrochloric acid, the total concentration in each case being 0·01*N*. The mobility of the hydrogen ion in the mixtures was found to be considerably smaller than that observed in pure hydrochloric acid containing the same concentration of chlorine ions. On the other hand, the mobilities of barium and potassium ions in the acid solutions were somewhat greater than in the pure salt solutions. The results are qualitatively in accord with the theory. It must be remembered, however, that the data refer to solutions which are too concentrated for the Onsager theory to be applied quantitatively, and moreover that the components are present in definite amounts, so that the condition of a vanishingly small concentration for one ion is not fulfilled. The experimental results are, however, at variance with the classical theory. The conductivity of mixtures is discussed with special reference to the non-additivity of potassium chloride–hydrogen chloride mixtures. R. A. MORTON.

Conductivity and transport number of the chloride ion in mixtures of sodium and potassium chlorides. D. A. MACINNES, I. A. COWPERTHWAITE, and T. SHEDLOVSKY (J. Amer. Chem. Soc., 1929, **51**, 2671—2676).—The transport number of the anion in mixtures of sodium and potassium chloride at a total volume concentration of 0·1*N* at 25° has been determined by the moving boundary method, the initial formation of the boundary being produced by an automatic device. The conductivity of the solutions was also determined. There is no evidence of complex ion formation (cf. Braley and Rippie, A., 1927, 733). S. K. TWEEDY.

Transport numbers of cadmium chloride and bromide. W. W. LUCASSE (J. Amer. Chem. Soc., 1929, **51**, 2605—2608).—From *E.M.F.* measurements at 25° on the cell $Ag|AgX|CdX_2(0{\cdot}1M)|CdX_2(xM)|AgX|Ag$, with $x=0{\cdot}01$—6 when X=Cl and 0·01—3 when X=Br, and with the aid of results from a pre

vious paper, the transport numbers of the cadmium ion have been calculated (A., 1925, ii, 399). The values pass through zero at about 1·5*M* for the bromide and 4·25*M* for the chloride; in the case of the chloride there is also a minimum at about 0·03*M*.

S. K. TWEEDY.

Thermolysis of solids (Ludwig–Soret effect). H. REINHOLD (Z. Elektrochem., 1929, **35**, 627—631).—A wandering of ions through mixed crystals of the iodides, bromides, and sulphides of silver and univalent copper, when these are compressed into cylinders, and the two ends subjected to a difference in temperature, has been found to occur; the phenomenon appears to be similar to the Ludwig–Soret effect in solutions. The ends of compressed cylinders, 3 cm. long, of the mixed crystals were placed in electric furnaces at various temperatures such that the temperature fall in each case was 100° and allowed to remain for 8 days. The hotter end increased and the cooler end decreased in weight, due to the migration of silver to the former and copper to the latter. The thermolytic equilibrium bears no relation to the temperature difference, but rather to the temperatures employed. Previous work by the author (A., 1928, 846) on thermoelectric cells is discussed in the light of the results obtained.

H. T. S. BRITTON.

Potential difference: metal–solution. A. E. BRODSKY (Physikal. Z., 1929, **30**, 665—669).—The idea that electrode potentials can be resolved into a summation of two terms, one depending only on the nature of the electrode and the second on the properties of the solution, has been placed on a thermodynamic basis with the aid of the Debye–Hückel theory. For the second term a linear relationship with the reciprocal of the dielectric constant of the solvent is found to be in agreement with experimental data. Neutral salt effect and concentration effects are discussed in relation to the theoretical considerations.

R. A. MORTON.

Measurement of *E.M.F.* in dilute aqueous solutions. I. Lead electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1929, **51**, 2905—2909).—A small electrode cell is described which can be operated so as to yield reproducible potential results for solutions below 0·001*M*. From *E.M.F.* measurements with the cell $Pb(Hg)|PbCl_2|AgCl|Ag$ the normal potential of lead is found to be 0·1263 volt (? at 25°). The activity coefficients of lead chloride in solution are calculated.

S. K. TWEEDY.

Silver chloride electrode. W. R. CARMODY (J. Amer. Chem. Soc., 1929, **51**, 2901—2904).—Directions are given for preparing a silver chloride electrode having a constant potential and perfect reproducibility. To ensure the latter desiderata the electrode must be free from cyanide and protected from light, both of which increase the potential. The electrode described, when the prescribed precautions are observed, exhibits no ageing phenomena.

S. K. TWEEDY.

Electromotive properties of rare-earth metals and their amalgams. I. Lanthanum. R. MÜLLER (Monatsh., 1929, **53** and **54**, 215—223).—Lanthanum amalgams are prepared from the metal turnings and mercury at 800—900°; those containing 20—50 at.-% of the metal are obtained only with difficulty. The amalgams rich in lanthanum undergo oxidation readily in air forming the hydroxide.

[With F. KREINER and H. J. SCHMIDT.]—The potentials of lanthanum and its amalgams have been determined at 25°, using a Dolezalek electrometer. A silver electrode in a 0·1*N*-solution of silver nitrate in pyridine was used for the reference electrode and the lanthanum electrode was in a saturated solution of lanthanum bromide in pyridine. The potentials of the pure metal and the 5% amalgam are —0·71 and —0·932 volt, respectively. In an aqueous solution of the bromide the values for the metal and its 1·5% amalgam are —0·71 and —0·932 volt, respectively. The potential–temperature curve for lanthanum shows three maxima (at 19°, 26—29°, and 0°), being analogous to the curve for aluminium (A., 1926, 1105). The potentials of amalgams containing 5—96% of the metal are of the same order (limits, —0·908 and —0·944) at 25°.

H. BURTON.

Electromotive properties of rare-earth metals and their amalgams. II. Cerium. R. MÜLLER and H. J. SCHMIDT (Monatsh., 1929, **53** and **54**, 224—230).—Cerium amalgams (prepared by heating the metal at 600° in an atmosphere of mercury vapour) are very sensitive to air and moisture. Amalgams containing 15—75% of the metal could not be obtained. The amalgams are stored under paraffin, connexions for potential measurements being made with copper wire. The potentials of the metal and its 5% amalgam in a saturated solution of cerium bromide in pyridine are —0·721 and —0·965 volt, respectively, at 25°. In aqueous cerium bromide the values for the metal and its 1·5% amalgam are —0·739 and —0·946 volt, respectively. The potential–temperature curve shows chief maxima at 26° and 34°. The 0·25—8 and 75—99% amalgams show variations in potential of less than 0·1 volt at 25°.

H. BURTON.

Amount of hydrogen and oxygen present on the surface of a metallic electrode. F. P. BOWDEN (Proc. Roy. Soc., 1929, **A**, **125**, 446—462).—With the apparatus previously described (Bowden and Rideal, A., 1928, 1088), a quantitative investigation has been made of the potential changes which occur during the discharge of small quantities of electricity at a bright platinum electrode in air-free 0·2*N*-sulphuric acid saturated with either hydrogen or oxygen. The quantity of electricity required to change the potential from that of oxygen to that of hydrogen, or *vice versa*, is 9×10^{-4} coulomb per sq. cm. of accessible area, *i.e.*, 9×10^{-9} g.-ion per sq. cm. At high current densities, when the rate of deposition is so rapid that natural loss from the surface by dissolution and evaporation is inappreciable, this quantity is independent of the current density and the direction of the change, and is in agreement with that calculated on the assumption that the potential change involves the removal of a surface layer of one gas adsorbed on or between the accessible metal atoms and its replacement by the other gas. It is not sufficient to form a complete gas envelope (cf. Johnson, this vol., 639). The quantities of electricity required to establish hydrogen and oxygen overvoltage, in solutions saturated with hydrogen and oxygen, respectively,

are 6×10^{-7} and 11×10^{-6} coulomb per 100 millivolts. It is suggested that the adsorbed gas on the electrode surface is deformed with formation of oriented dipoles (which might be ions, atoms, or molecules), and that the *P.D.* across the interface is controlled by the number and electric moment of these dipoles. Further changes in the potential, with the establishment of hydrogen or oxygen over-potential, are due to an increased deformation of the dipoles with consequent increase in electric moment. There is considerable evidence, supported by experiments with oxidised platinum foil, for the formation of a layer of platinum oxide on the surface of a platinum anode on which oxygen is being deposited. The catalytic activity of the platinum surface may be markedly enhanced by the alternate oxidation and reduction of even a unimolecular layer, although this treatment causes little increase in the accessible area.

L. L. BIRCUMSHAW.

Evidence of protons in metals. A. COEHN (Z. Elektrochem., 1929, **35**, 676—680).—Three methods are described to show that electrolytically generated hydrogen diffuses through a palladium cathode, and thereby imparts to the various points on the electrode the potential which would be assumed by a hydrogen electrode. In the first experiment 0·1*N*-sulphuric acid solution was electrolysed between a platinum and a bent palladium cathode, and after stopping electrolysis the potential at different points on the latter was compared with that of the calomel electrode. At first certain points on the wire showed the oxygen electrode potential as a result of exposure to air, but after 80 hrs. the potential became equal to that of the hydrogen electrode. The second method was to observe the variation in electrical resistance of the palladium wire electrode as a result of the diffusion through it of hydrogen. In the third method advantage was taken of the ready oxidation of hydrogen contained in palladium by oxygen to form hydrogen peroxide.

H. T. S. BRITTON.

Crystalline mercurous sulphate and the Weston normal standard cell. D. B. SUMMERS and W. C. GARDINER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 19 pp.).—In view of conflicting reports as to the effect of the size of the mercurous sulphate crystals on the *E.M.F.* of the Weston element, cells with crystals of various sizes produced under different conditions have been examined over a period of several months. The crystals were prepared by recrystallisation of electrolytic mercurous sulphate from solutions of sulphuric acid, potassium hydrogen sulphate, or cadmium sulphate, and several forms of apparatus were devised to make the recrystallisation process continuous. The size of the crystals varied from 30 to 1000 μ as against an average value of 1 μ for the original electrolytic product. Photographs of typical crystals are given. It is found that the larger the crystals the higher is the initial value of the *E.M.F.* above the normal, but the more rapid is the decrease of the *E.M.F.* with time. Crystals prepared by recrystallisation from cadmium sulphate solution show exceptionally high initial values of the *E.M.F.* which decrease comparatively slowly with time. The explanation of the results is that with large crystals the surface exposed to the solution is relatively small, so that this surface is readily coated with basic salt produced by hydrolysis, whilst the acid produced by hydrolysis readily diffuses away through the loosely granular mass and thus permits further hydrolysis to occur (cf. following abstract).

H. J. T. ELLINGHAM.

Hydrolysis of mercurous sulphate by cadmium sulphate solution in the Weston normal cell. W. C. GARDINER and G. A. HULETT (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 18 pp.; cf. preceding abstract).—The extent to which mercurous sulphate in contact with mercury can be hydrolysed by means of a saturated solution of cadmium sulphate has been examined by rotating the cathode limb of a Weston cadmium cell and measuring the change in *E.M.F.* and determining the mercury content of the solid phase. When the *E.M.F.* measurements indicate that the solution contains only the basic salt, analysis shows only a comparatively slight hydrolysis of the solid mercurous sulphate, proving that a coating of basic salt forms around the crystals and prevents further action. Experiments using large crystals of mercurous sulphate confirm this view and indicate that the hydrolysis is a very slow process. It is shown that the p_H value of a saturated cadmium sulphate solution is reduced from 4·5 to 4·2—4·0 by rotating with mercury and mercurous sulphate, whereas water rotated with these substances assumes a value of 2·2, which is increased to 4·1 when cadmium sulphate is dissolved in it, so that the resulting solution can still hydrolyse mercurous sulphate. As a result of the observations made, a method of preparing the depolariser for standard cells so as to avoid hydrolysis and increase the constancy of the *E.M.F.* is suggested.

H. J. T. ELLINGHAM.

Oxidation of the depolariser in preparing standard cells. W. C. GARDINER and G. A. HULETT (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 12 pp.).—An investigation has been made of the effect of variations in the method of preparation and washing of the mercurous sulphate, of the composition of the electrolyte, and of the conditions of setting up, on the *E.M.F.* of the Weston cadmium cell over periods of several months. It is confirmed that cells with a neutral cadmium sulphate electrolyte show a gradual decrease of *E.M.F.* On the other hand, the setting up of the cell in an atmosphere containing oxygen has no apparent effect on the *E.M.F.* of neutral or acid cells (cf. A., 1925, ii, 672; B., 1928, 528). The use of solutions saturated with oxygen gave high initial values which decreased to normal values in about a month and continued to decrease, but some cells prepared in an atmosphere of an inert gas showed decreases of a similar magnitude. It would seem that cells show a greater tendency to decrease in *E.M.F.* when the mercurous sulphate is washed with a large volume of cadmium sulphate solution in an inert atmosphere. This effect is attributed to the formation of a basic mercurous sulphate. The presence of a small amount of sulphurous acid in the electrolyte has a beneficial effect owing to its preventing this hydrolysis.

H. J. T. ELLINGHAM.

Potential of solutions of sugars. II. R. WURMSER and J. GELOSO (J. Chim. phys., 1929, **26**, 424—434; cf. A., 1928, 846).—When the concentration of the sugars used (dextrose and lævulose) is varied between 0·55*M* and 0·0055*M* the limiting potential is not affected. The temperature coefficient valid between 40° and 90° also holds down to 10°. It is further concluded that the limiting potential attained by an electrode in a sugar solution, when air is excluded, depends only on the temperature and is independent of the nature of the sugar, nature of the electrode (platinum, gold, or mercury), and the nature and concentration of the buffer.

F. L. USHER.

Tyrosinase. I. Oxidation and reduction potentials of the tyrosinase system. D. OKUYAMA (J. Biochem. Japan, 1929, **10**, 463—479).—Tyrosinase gives a high reduction potential with *p*-cresol and glycine in nitrogen. The high reduction potential of tyrosine is not increased by tyrosinase even in presence of glycine. The reduction potential of pyrocatechol or quinol, but not that of resorcinol, is increased by tyrosinase in presence of glycine.

CHEMICAL ABSTRACTS.

Polarographic studies with the dropping mercury cathode. VI. Influence of fatty acids on the maximum of current due to atmospheric oxygen. J. RASCH (Coll. Czech. Chem. Comm., 1929, **1**, 560—570).—A study has been made by the dropping mercury cathode method of the influence of formic, propionic, *n*-butyric, *n*-valeric, *iso*valeric, palmitic, and stearic acids on the development and the suppression of the maximum, assumed to be due to atmospheric oxygen, in the current–voltage curves. The maximum is greatest when the ionic concentration is about $0{\cdot}5\times10^{-3}N$, as is the case for strong electrolytes; the undissociated molecules exhibit a suppressive effect on the maximum which is greater the higher the acid is in the homologous series. Experiments in alkaline solutions show that the anions of the lower fatty acids have little suppressive action, whilst the palmitate and stearate ions possess a very large suppressive activity. The suppressive activity is assumed to be due to the adsorption of the acids at the mercury cathode interface; the following concentrations represent the values for half suppression of the maximum: formic, 0·5*N*; propionic, 0·24*N*; *n*-butyric, 0·06*N*; *n*-valeric, 0·016*N*; *iso*valeric, 0·03*N*; palmitic and stearic acids, $<10^{-5}N$. A. I. VOGEL.

Overvoltage on metals. P. SEDERHOLM and C. BENEDICKS (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 15 pp.).—The potential of a platinised platinum electrode fully saturated with hydrogen and half immersed in dilute sulphuric acid changes only very slightly and in a practically linear manner with the strength of current, up to 0·4 milliamp./cm.^{2}, which is passed through it in either direction. If the electrode is completely immersed in the solution, anodic treatment with much smaller current densities causes considerable polarisation and the potential remains at relatively positive values during step-wise decrease of the anodic current density. With increasing cathodic current density, however, the potential soon returns to more negative values. A totally immersed platinum gauze electrode was subjected to several cycles of step-wise increase and decrease in cathodic current density, and increase and decrease in anodic current density. It was found that after anodic oxygen evolution, subsequent cathodic treatment caused practically reversible hydrogen evolution and on reducing the cathodic current density this reversibility could persist up to small anodic current densities. Similarly, after cathodic hydrogen evolution, subsequent anodic treatment led to oxygen evolution at a potential which changed little with current density over a certain range extending somewhat into the cathodic region. It is claimed that this nearly constant potential represents the true equilibrium value for an oxygen electrode. The difference between this value and that of the hydrogen electrode in the same solution is 1·48 volts, which represents, according to the above view, the reversible *E.M.F.* of the hydrogen–oxygen cell. The significance of these results and their bearing on the nature of overvoltage are discussed. H. J. T. ELLINGHAM.

Kinetics of passivity phenomena. W. J. MÜLLER (Z. Elektrochem., 1929, **35**, 656—670).—From a discussion of current–time and –potential curves, it appears that whether passivation is due to the formation of a surface film or to a chemical process, the passivation of an electrode depends on the attainment of a certain effective current density which always accompanies the formation of a surface film. H. T. S. BRITTON.

Effect of addition agents on the conductivity, cathodic polarisation, and grain size of deposits obtained from the cell: $Cu|CuSO_4,H_2SO_4|Cu$. B. CLARK and E. O. JONES (Trans. Faraday Soc., 1929, **25**, 583—590).—The cathodic polarisation of a cell containing as electrolyte 0·5*M*-copper sulphate and 0·1*N*-sulphuric acid and one of the following substances: gelatin, dimethylaniline, dextrose, starch, lactic acid, peptone, camphor, was measured by Haring's method at current densities ranging up to 2·5 amp./dm.^{2} The added substances increase the cathodic polarisation and decrease the conductivity of the electrolyte. From a series of electro-depositions using 2 amp./dm.^{2}, it was found that the added substances give rise to a smaller grain size of the deposits, except in the case of peptone, which causes the formation of an unsatisfactory powdery deposit.

H. T. S. BRITTON.

Action of atmospheric oxygen on photoelectric cells containing a coloured liquid. A. GRUMBACH and S. SCHLIVITCH (Compt. rend., 1929, **189**, 753—754).—Two platinum electrodes were immersed in a solution of sodium fluorescein and one of them was exposed to light from a mercury arc, with arrangements for working in air or in a vacuum. With a solution of 5 g. of fluorescein and 0·1 g. of sodium hydroxide per litre, an *E.M.F.* of 5 millivolts was obtained in air, but in a vacuum the *E.M.F.* was zero; the effect is attributed to partial oxidation of the fluorescein in air. With a solution containing 3 g. per litre of sodium fluorescein in 40% glycerol, the Becquerel effect in air is negative and the absorption effect positive; in a vacuum both effects are negative and much greater (−50·2 millivolts after

20 min. compared with +8·7 in air). The essential difference between the two effects is thus emphasised.
C. A. SILBERRAD.

Reaction velocities. J. J. VAN LAAR (Chem. Weekblad, 1929, 26, 506—510).—A mathematical exposition of the errors involved by considering total energies instead of free energies in various systems.
S. I. LEVY.

Relative critical energy of isokinetic reactions. H. DAMIANOVICH (Gazzetta, 1929, 59, 568—570).—The author's deduction that the critical energy in isokinetic reactions is proportional to the absolute temperature of the reaction holds satisfactorily for the decomposition of nitrous oxide, hydrogen iodide, and chlorine monoxide, and the relation is most rigidly satisfied when the values of the critical energy are calculated from the ratio of effective to total molecular collisions.
F. G. TRYHORN.

Effects of magnetic field on certain chemical reactions. S. S. BHATNAGAR, R. N. MATHUR, and R. N. KAPUR (Phil. Mag., 1929, [vii], 8, 457—473).—The influence on chemical reactions to be expected from a magnetic field is discussed theoretically. An investigation was made for a number of inorganic reactions and one organic reaction having very small reaction velocities and large changes in the susceptibilities of the initial and final products. It is concluded that the rate of reaction is accelerated, retarded, or uninfluenced by the field according as the sum of the molecular susceptibilities of the final products is greater, less than, or equal to those of the initial products. Weigle's mathematical relation (cf. A., 1928, 577) for the concentration of the solution within and without the field is applied to the reduction reaction of chromic acid by phosphorous acid; it indicates that the concentration of the more paramagnetic ions will be greater in the stronger field near the poles.
N. M. BLIGH.

Explosions with parahydrogen. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 305—306).—After explosion of a mixture of hydrogen and air rich in hydrogen and containing parahydrogen, the whole of the residual hydrogen is present in the normal state. This phenomenon furnishes a characteristic example of the rapid establishment of equilibrium in the explosion zone, and is ascribed to the impulse of particles of high energy content produced during the combustion.
H. F. GILLBE.

Ignition of intersecting streams of oxygen and combustible gas. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 316—326).—The minimum temperature of a stream of oxygen which when intersecting a similar stream of hydrogen, carbon monoxide, ethylene, methane, or ether vapour will cause ignition has been determined as a function of the temperature of the combustible gas, and curves constructed showing the variation of the ignition temperature T_i with the composition of the gaseous mixture. Dilution of the hydrogen or oxygen with nitrogen does not influence the ignition temperature, but in presence of carbon dioxide T_i is markedly increased. The ignition curve of oxygen–carbon monoxide mixtures exhibits a minimum at which T_i is 200° and 130° below the values for 100% oxygen and 100% carbon dioxide, respectively.
H. F. GILLBE.

Diffusion phenomena at the lower explosion limit of hydrogen–oxygen mixtures. F. GOLDMANN (Z. physikal. Chem., 1929, B, 5, 307—315).—The variation of the lower explosion limit of hydrogen–oxygen mixtures according to whether the ignition takes place at the upper or lower end of the explosion tube is due to diffusion phenomena, which have been studied by introducing into the mixture finely-divided platinum or palladium particles, formed by sparking between two electrodes placed at the end of the tube.
H. F. GILLBE.

Influence of water vapour on the heat radiation of exploding gas mixtures. Specific heat of water vapour at high temperatures. K. WOHL and G. VON ELBE (Z. physikal. Chem., 1929, B, 5, 241—271; cf. this vol., 973).—The maximum pressures attained by exploding mixtures of hydrogen and oxygen diluted with varying quantities of hydrogen, water vapour, or argon have been measured and used to calculate the loss of heat by radiation. Although in dry mixtures the loss amounts to several parts % of the heat of combustion, in the presence of water vapour it is reduced to considerably less than 1%. It is concluded that the loss in "dry" explosion is due to emission of light by freshly-activated reaction products (probably OH), and that water vapour absorbs this radiation and converts it into heat in the reaction vessel. The authors consider that the occurrence of a similar effect in the carbon monoxide–oxygen mixtures studied by Garner and Johnson is to be attributed to catalytic action shortening the time of explosion, and consequently the loss by radiation, rather than to chemi-luminescence; in the present experiments the time of explosion was unaffected by the introduction of water vapour. Values of the specific heat of water vapour between 1760° and 2400° are deduced, which are in good agreement with those calculated by means of Einstein functions from optically-determined atomic vibration-frequencies.
F. L. USHER.

Thermal reaction between chlorine and ozone. M. BODENSTEIN, E. PADELT, and H. J. SCHUMACHER (Z. physikal. Chem., 1929, B, 5, 209—232).—The velocity of decomposition of ozone in the presence of chlorine has been measured at 35° and at 50° and found to be proportional to $[Cl_2]^{1/2}[O_3]^{3/2}$, after the completion of a period of induction which varies inversely with the concentration of ozone. Although under the conditions of the experiments no intermediate product could be detected, when moist chlorine was used crystals of perchloric acid monohydrate were found, indicating the production of an oxide of chlorine; on mixing ozonised oxygen with diluted chlorine dioxide, chlorine hexoxide (Cl_2O_6) was obtained. In the light of these observations the following scheme is proposed for the mechanism of the reaction: (1) $Cl_2+O_3=ClO+ClO_2$; (2) $ClO_2+O_3=ClO_3+O_2$; (3) $ClO_3+O_3=ClO_2+2O_2$; (4) $ClO_3+ClO_3=Cl_2+3O_2$; (5) $ClO+ClO=Cl_2+O_2$. The velocity coefficients and heats of activation of reactions (1), (3), and (4) are calculated. From the ratio of the

velocity coefficients of reaction (1) and of the whole reaction, the length of the "chain" is shown to be of the order 10^4 units. The absolute velocities deduced for the partial reactions account satisfactorily for the periods of induction observed. F. L. USHER.

Thermal reaction between bromine and ozone. B. LEWIS and H. J. SCHUMACHER (Z. Elektrochem., 1929, **35**, 648—652).—The decomposition of ozone, at pressures ranging from 56·5 to 102·2 mm., by means of bromine vapour, at 0·30—9·0 mm. pressure, was studied at 7° by following the variations in pressure. The rate of decomposition was unaffected by additions of oxygen and the temperature coefficient at 0° was 3·05 for 10°, corresponding with a heat of activation of 16·5 kg.-cal. The reaction, after an induction period, in the presence of a definite amount of bromine becomes one of zero order. The material of the reaction vessel, viz., glass, quartz, had no measurable effect on the reaction. This type of decomposition probably depends on the intermediate formation of an oxide of bromine, which the authors prepared in two modifications, both of which catalyse the decomposition of ozone with equal intensity. It was prepared at −5° to +10° by allowing 3—15 mm. of bromine and 5—10 times the amount of ozone to react, when after the elapse of about 1 hr. at −5°, or 5—20 min. at 10°, a white, flocculent substance separated on the walls. At −80° the oxide can be kept for a day. It is essential that the reactants should be employed in the above amounts, otherwise no oxide may form, and also should the temperature be too high there is a risk of a severe explosion. Prolonged cooling of the oxide at −40° causes the formation of fine white needles, the transition temperature of which is 35±3°. Its formula is $(Br_3O_8)_n$.
H. T. S. BRITTON.

Inflammability of mixed gases. G. W. JONES. —See B., 1929, 930.

Nitryl chloride: formation and thermal decomposition. H. J. SCHUMACHER and G. SPRENGER (Z. Elektrochem., 1929, **35**, 653—655).—By passing ozone through nitrosyl chloride until the yellow colour is destroyed and then by lowering the temperature to −115° nitryl chloride can be separated. Its composition corresponds with the formula NO_2Cl. Its m. p. is below −115° and b. p. −15° (cf. this vol., 1155). Its decomposition into nitrogen tetroxide and chlorine was investigated at 130°, 140°, and 150°. Up to about 90% decomposition the reaction appears to be unimolecular, but afterwards becomes bimolecular. The rate is appreciably affected by additions of the products of decomposition.
H. T. S. BRITTON.

Homogeneous oxidation of acetylene. G. B. KISTIAKOWSKY and S. LENHER (Nature, 1929, **124**, 761).—The oxidation of acetylene by oxygen at 250—315° proceeds by way of glyoxal, formaldehyde, formic acid, carbon dioxide, and water; all the reaction products have been isolated. The rate of reaction is proportional to the square of the acetylene concentration and is almost independent of that of the oxygen. In packed vessels a heterogeneous oxidation direct to carbon dioxide and water takes place, the rate being proportional to the product of the acetylene and oxygen concentrations (cf. also Thompson and Hinshelwood, this vol., 1243).
A. A. ELDRIDGE.

Inflammability of mixtures of ethyl alcohol, benzene, furfuraldehyde, and acetone. G. W. JONES and J. R. KLICK.—See B., 1929, 930.

Physical chemistry of "knock" and "anti-knocks." P. LAFFITTE (J. Chim. phys., 1929, **26**, 391—423).—A general discussion of the phenomenon of "pinking" in internal-combustion engines and an examination of theories put forward in explanation of it. F. L. USHER.

Effects of knock-suppressing and knock-inducing substances on the ignition and partial combustion of certain fuels. R. E. SCHAAD and C. E. BOORD.—See B., 1929, 930.

Flame characteristics in "pinking" and "non-pinking" fuels. II. G. B. MAXWELL and R. V. WHEELER.—See B., 1929, 878.

Autoxidation of hydrazine. E. C. GILBERT (J. Amer. Chem. Soc., 1929, **51**, 2744—2751).—When oxygen is bubbled through an alkaline solution of hydrazine, hydrogen peroxide is formed but no nitrate, nitrite, or azoimide. The rate of oxidation passes through a maximum with increasing concentration of alkali hydroxide, the optimum concentration of the latter corresponding with that for the maximum rate of decomposition of hydrogen peroxide by colloidal materials. This fact, and the temperature coefficient of 1·75, indicate that the reaction is micro-heterogeneous; the reaction is governed by the rate of adsorption of hydrazine on the active surface available (possibly dust particles). The maximum rate of oxidation is accompanied by the minimum formation of peroxide. The amount of the latter appears to be the resultant of two reactions, a formation and a decomposition. Ammonia and azoimide when added to the solution have no effect, but, as in the case of other autoxidations, acetanilide, aniline, etc. influence the reaction.
S. K. TWEEDY.

Period of induction in chemical reactions: action of hypophosphorous acid on copper salts. P. NEOGI and S. MUKHERJI (J. Indian Chem. Soc., 1929, **6**, 529—545).—A study of the action of hypophosphorous acid on copper sulphate and cupric chloride, producing copper hydride and cuprous chloride, respectively, shows that the period of induction observed is increased by increasing the dilution, and also by adding alcohols, glycerol, chlorides, sulphates, nitrates, oxalates, citrates, tartrates, some sugars, etc. It is, however, decreased by rise in temperature, and by the presence of acids. The period of induction is probably due to the following successive intermediate reactions: (1) formation of copper hypophosphite, $Cu(H_2PO_2)_2$; (2) decomposition of this salt into a compound, $CuH(H_2PO_2)$, and phosphorous acid, as deduced from a study of the p_H values; (3) decomposition of the copper compound by water in the first case and cupric chloride in the second to form the hydride and cuprous chloride, respectively. The reactions are not influenced by light. The influence of added

substances is probably catalytic. The preparation of pure copper hypophosphite solution is described. It has not been found possible to prepare the pure solid. Hypophosphorous acid is a stronger acid than has generally been supposed. M. S. BURR.

Induced reactions. W. G. VANNOY (J. Physical Chem., 1929, **33**, 1593—1624; cf. Bancroft, this vol., 1019).—The induced reaction, chromic, arsenious, and tartaric acids, has been investigated. A reaction of an autocatalytic nature occurs between tartaric and chromic acids, whilst the extent and velocity of the direct oxidation of sodium tartrate are dependent on time, temperature, concentration of acid and of oxidising agent. The induction factor for this reaction, after correcting for the oxidation of the tartrate by the chromic acid, is found to be 4 and not 2·8 as determined by Schilow (A., 1903, ii, 276). The mechanism is explained on Bancroft's theory (*loc. cit.*), by the formation of Cr_2O_5 as the lower stage of the actor, but alternative views are possible. The reaction between permanganic, arsenious, and tartaric acids has also been studied. The induction factor increases with concentration of the tartrate and acid present in the solution and could not be followed beyond a value 3 owing to oxidation of the tartrate by the permanganate at higher concentrations. Indications of complex formation between arsenious acid and undissociated sodium tartrate were obtained. L. S. THEOBALD.

Kinetics of the reaction between bromic and hydrobromic acids. F. POLLAK (Monatsh., 1929, **53** and **54**, 914—925).—The reaction between bromic and hydrobromic acids in aqueous solution in the presence of phenol proceeds according to the scheme $-d[BrO_3']/dt=k[BrO_3'][Phenol][H^+]^2$ and k has the value $3{\cdot}2\times10^{-2}$ at $25\pm0{\cdot}04°$. Bromous acid is an intermediate product. In the presence of phenol the reaction $BrO_3'+2Br'+3H^+\longrightarrow3HBrO$ takes place with a measurable velocity, and it is a stage of the chief reaction $BrO_3'+5Br'+6H^+\longrightarrow3Br_2+3H_2O$ which occurs in the absence of phenol. In both cases, however, the actual velocity is determined by the reaction $BrO_3'+Br'+2H^+\longrightarrow HBrO_2+HBrO$. L. S. THEOBALD.

Hydrolysis of methyl acetate with alkali carbonates. A. MUSIL (Monatsh., 1929, **53** and **54**, 367—406).—The hydrolysis of methyl acetate with varying concentrations (0·001—1M) of rubidium, cæsium, lithium, sodium, and potassium carbonates has been studied at 25°. The reaction mixtures are fixed by the addition of barium chloride solution, boiled to expel carbon dioxide, the barium carbonate is collected, dissolved in standard hydrochloric acid, and titrated back. The calculated velocity coefficients are not always constant, and are generally smaller with M-alkali carbonate than with more dilute (0·01—0·1M) solutions. For 0·01—0·1M-solutions the coefficients increase in the order Li, Na, K, Rb, Cs. H. BURTON.

Water hydrolysis of ethyl acetate. A. SKRABAL and A. ZAHORKA (Monatsh., 1929, **53** and **54**, 562—576).—The rate of hydrolysis of ethyl acetate has been studied in acetate buffers at 25°. When the observed minimum reaction velocity is corrected for the effects due to the hydrogen and hydroxyl ions it is assumed that the residual velocity represents the effect of the uncatalysed reaction or the catalytic effect of the water molecule. This residual velocity ($k_w=1{\cdot}48\times10^{-8}$ mol./litre/min.) agrees with the value derived from similar measurements by Karlsson (A., 1925, ii, 877). The result is said to show that 36% of the ester is hydrolysed spontaneously or by the action of undissociated water when the total reaction velocity is a minimum. The relative importance of k_w in its dependence on the nature of the hydrolyte is discussed in reference to available data. H. BURTON.

Rates of saponification of commercial oils, fats, and waxes and pure triglycerides by aqueous alkali. J. W. MCBAIN, C. W. HUMPHREYS, and Y. KAWAKAMI (J.C.S., 1929, 2185—2197).—The rates of saponification by aqueous alkali of 25 oils and triglycerides have been determined under comparable conditions at 25°, the rate of change of the hydroxyl-ion concentration being followed by means of a hydrogen electrode. The rates differ considerably for the different oils and are explained as being determined mainly by their varying degrees of emulsification. Small quantities of acid in the oil have no effect, but larger quantities have a very marked effect on the rate. The ease of emulsification of the oils is not related to the emulsifying powers of the corresponding soaps. There is no relation between mol. wt. and rate of saponification, but the time required for saponification increases with the degree of unsaturation. J. A. V. BUTLER.

[Physico-chemical] study of bromosuccinic acid. II. Decomposition of bromosuccinic and acetoacetic acids in aqueous solution. III. Bimolecular reactions in dilute solution. A. ÖLANDER (Z. physikal. Chem., 1929, **144**, 73—133; see this vol., 1384).—II. The rate of decomposition of bromosuccinic acid in alkaline solution has been measured at various ionic strengths. The decomposition is shown to take place only in two ways, represented by the equations: (1) $CO_2'{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2'=\overline{O{\cdot}CO{\cdot}CH_2{\cdot}CH{\cdot}CO_2'}+Br'$; $OH'+\overline{O{\cdot}CO{\cdot}CH_2{\cdot}CH{\cdot}CO_2'}=CO'{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2'$, and (2) $CO'{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2'+OH'=CO_2'{\cdot}CH{:}CH{\cdot}CO_2'+Br'+H_2O$. The first reaction is not appreciably influenced by salts, whereas the second shows a marked positive primary salt effect which, at low ionic strengths, is in accordance with Brönsted's formula, and at greater ionic strengths is due mainly to cations. The acid decomposition of acetoacetic acid is completely analogous to the foregoing, the bimolecular reaction $Me{\cdot}C(O)'{:}CH{\cdot}CO_2'+H_2O=2Me{\cdot}CO_2'$ being catalysed by hydroxyl ions, and showing a similar positive salt effect. The decomposition of bromosuccinic acid in neutral and acid solution in the presence of buffers has also been investigated, and the velocity coefficients of the decomposition of both the primary and secondary ions have been determined. The undissociated acid is relatively stable. From these measurements the second dissociation constant of bromosuccinic acid has been found, viz., $pk_2=4{\cdot}69$ at 50°. Experiments on the decomposition in concentrated solutions in the

absence of buffers indicate that fumaric acid is formed from lactone-maleic acid or one of its condensation products, and not directly from bromosuccinic acid.

III. Theoretical. For the velocity coefficient of a bimolecular reaction in dilute solution the following expression is derived: $k=\pi RT(r_1+r_2)^2(\alpha/kT+1)^{m/2-1}e^{-\alpha/KT}/100\eta r_1 r_2 . \Gamma(m/2)$, where r_1, r_2 are the radii of the two molecules considered, m is the sum of their degrees of freedom, α the total energy of activation, η the coefficient of viscosity of the solution, and k the Boltzmann constant. The coefficient calculated by means of this expression is greatly in excess of that observed in a number of reactions, indicating that actually only a small fraction of the fully-activated molecules reacts on collision. The non-reactivity of a large proportion of the molecules may be explained on the ground that only a small part of the surface of a large molecule may be reactive, and that attached molecules of the solvent may exercise a protective action. F. L. USHER.

Hydrolysis of organic compounds in neutral and acid solutions. S. C. J. OLIVIER (Chem. Weekblad, 1929, **26**, 518—523).—A review of the influence of the position and nature of substituent groups on the rates of hydrolysis of substituted benzyl chlorides and acid chlorides. S. I. LEVY.

Autoxidation of quinol. R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1929, **189**, 694—696).—The solutions examined contained 25 g. of quinol per litre together with either varying amounts of an alkali or alkaline earth or a buffer solution prepared according to Sörensen's formulæ. The amount of oxidation of the quinol being at first proportional to time, the rate thereof has been taken as measuring the catalytic activity of the various solutions. The results indicate that for alkalis and alkaline earths the activity is proportional to the hydroxyl-ion concentration with an approximately uniform coefficient of proportionality. With buffer solutions the activity varies in the same direction as the ionic concentration, but with very varying coefficients of proportionality. C. A. SILBERRAD.

Kinetics of cell fermentation treated from the point of view of a reaction in a closed space. V. Mechanism of enzyme action. F. F. NORD and J. WEICHHERZ (Z. Elektrochem., 1929, **35**, 612—618).—The rate of fermentation of dextrose by yeast has been investigated under various experimental conditions. When the reaction vessel was revolved at higher rates the rate of fermentation increased, the outer liquid being enabled to pass more rapidly through the cell membrane. With more concentrated solutions of dextrose the rate of fermentation attained a maximum value in a longer time, and afterwards diminished more slowly (cf. Slator, J.C.S., 1906, **89**, 133; 1910, **97**, 922). Photomicrographs of yeast cells before and after immersion in 30% dextrose solution for 20 min. show that they undergo appreciable shrinking, which thereby leads to the compression of the cell pores and a reduction in the active membrane surface. H. T. S. BRITTON.

Corrosion of metals. II. General theory. W. PALMAER and others.—See B., 1929, 921.

Effect of anions on the rate of dissolution of aluminium. M. CENTNERSZWER and W. WITTAND (Z. Elektrochem., 1929, **35**, 695—701).—The anions F′, Cl′, Br′, and ClO_4' accelerate the dissolution of aluminium in hydrochloric acid solution, whilst I′, SO_4'', and NO_3' retard it. The action of the anions appears to be independent of the cations present. The accelerating effect of anions is greater at low concentrations of hydrogen ions. The accelerating action of chloride ions, and probably of other anions, increases with concentration, reaching a maximum at about 3N. Passivity in nitric and sulphuric acid solutions is reduced by those anions which accelerate the rate of dissolution, and those anions which retard dissolution increase the passivity of aluminium. H. T. S. BRITTON.

Topochemical reactions showing adlineation. E. PIETSCH, A. KOTOVSKI, and [FRL.] G. BEHREND (Z. Elektrochem., 1929, **35**, 582—586).—The following reactions between a solid and a solution visibly exhibit adlineation, in that the attack on the crystal begins along the edges and at the corners: potassium dichromate crystals and concentrated sulphuric acid solution, crystals of either copper or nickel sulphate and an alcoholic or alcohol–ethereal solution of hydrogen sulphide, the dissolution of copper sulphate crystals in alcohol, copper sulphate crystals and an alcoholic or alcohol–ethereal solution of potassium thiocyanate, copper sulphate crystals and an aqueous-alcoholic solution of potassium cyanide, potassium dichromate crystals and an ethereal solution of hydrogen peroxide, bismuth nitrate crystals and an ether–alcohol mixture, crystalline sodium thiosulphate and an ethereal solution of ferric chloride, decomposition of manganic alum, dehydration of crystalline copper sulphate with concentrated sulphuric acid, sodium acetate crystals and an ethereal ferric chloride solution, crystalline nickel sulphate and dimethylglyoxime in alcohol, potassium ferrocyanide crystals and ferric chloride in hydrochloric acid and ether. H. T. S. BRITTON.

Chemical equilibrium in autoxidation. A. GILLET and D. GUIRCHFELD (Compt. rend., 1929, **189**, 691—694).—Anthracene oil (free from products volatile below 350°) in which 25% of its weight of coal dust had been dispersed was submitted to the action of oxygen or of oxygen and nitrogen in varying proportions, at varying rates at 350°, and (*a*) the amount of oxygen absorbed and (*b*) the concentration thereof in the issuing gases determined; (*a*) is practically nil for this temperature when the concentration is below 75%, whilst (*b*) is independent of the rate at which the gas is passed into the mixture. Similar results were obtained for the oil and coal separately, and for alizarin. It is hence concluded that for any substance liable to autoxidation for each temperature there is an equilibrium pressure of oxygen below which it is not absorbed. C. A. SILBERRAD.

Quantum-mechanical explanation of activation. F. LONDON (Z. Elektrochem., 1929, **35**, 552—555).—Theoretical. H. T. S. BRITTON.

Decomposition of ozone catalysed by chlorine. M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss.

Berlin, 1929, **23**, 367—369).—The velocity of the thermal decomposition of ozone in the presence of chlorine is given by the equation $-d[O_3]/dt = k[Cl_2]^{1/2}[O_3]^{3/2}$. The following reaction chain is proposed: (1) $Cl_2+O_3=ClO+ClO_2$, (2) $ClO_2+O_3=ClO_3+O_2$, (3) $ClO_3+O_3=ClO_2+2O_2$, (4) $ClO_3+ClO_2=Cl_2+3O_2$, (5) $ClO+ClO=Cl_2+O_2$. The velocity coefficients of the individual reactions are estimated to be $k_1=1\cdot83\times10^{-7}$, $k_3=9\cdot2\times10^2$, $k_4=1\cdot70\times10^3$ at 50°. That of reaction 2 is much greater.

J. A. V. BUTLER.

Mechanism of the catalytic action of molybdic acid on the reduction of nitric acid by ferrous chloride in a hydrochloric acid medium. R. HAC and V. NETUKA (Coll. Czech. Chem. Comm., 1929, **1**, 521—527).—Molybdic acid acts as a powerful catalyst in the reduction of nitric acid by ferrous chloride. The catalytic action of molybdic acid in the presence of a large excess of ferrous chloride can be suppressed by adding the appropriate quantity of ferric chloride (about 3·0 g. $FeCl_3$ per 0·1—0·2 g. MoO_3). Molybdenum pentachloride in 6*N*-hydrochloric acid rapidly reduces nitric acid to nitric oxide even at the ordinary temperature; with molybdenum trichloride the reduction is also very rapid, but the two main products are ammonia and nitric oxide. The catalytic behaviour of molybdic acid in the reduction of nitrates in the presence of hydrochloric acid with ferrous chloride is attributed to the molybdenum pentachloride produced by the partial reduction of the molybdic acid by the ferrous chloride.

A. I. VOGEL.

Reactivity of iodine in organic solutions. II. F. FEIGL and A. BONDI (Monatsh., 1929, **53** and **54**, 508—549; cf. A., 1928, 1131).—The effect of addition of various activators to the inactive violet solution of iodine in carbon disulphide (cf. *loc. cit.*) and the reactivity of the resulting solutions towards silver saccharin have been studied. Thus, addition of benzyl sulphide causes increased production of silver iodide, provided the added sulphide is above a certain concentration; with a relatively large amount of activator quantitative formation of silver iodide is observed. Similar activation of the inactive solutions of iodine in carbon tetrachloride, tetrachloroethylene, and trichloroethylene occurs with benzyl sulphide. Benzyl sulphide also increases the activity of the partly active solutions of iodine in dichloroethylene, chloroform, and toluene (the results with toluene alone vary greatly with the specimen; in pure toluene silver iodide is formed quantitatively). The brown solution of iodine in ether is not so reactive as the activated carbon disulphide solution; benzyl sulphide increases the activity of the ethereal solution. Phenyl sulphide has practically no activating effect on carbon disulphide solutions. Phenyl benzyl sulphide is intermediate in its activating effect. The following substances are all activators (to varying extents) for carbon disulphide solutions: phenyl triphenylmethyl sulphide, methyl and ethyl sulphides, tetramethyltetrathiolethylene, the isomeric methyl dithiooxalates, pyridine, quinoline, tetramethyldiaminobenzophenone, and *N*-phenylbenzaldoxime. Little or no activating effect is given by thiophen, dibenzyl ether, dimethylpyrone, diphenyl and dibenzyl disulphides, acetophenone, benzophenone, diphenyl ether, and azobenzene.

The above activators are all known to form polyiodides; *benzyl sulphide tetraiodide* and *phenyl triphenylmethyl sulphide tetraiodide* are new. The iodine in these polyiodides is determined directly by titration. The activators are considered to serve as co-ordination centres for the iodine to take part in the reaction.

The compound formed during the action of iodine on silver saccharin is N-*iodosaccharin*. This has not been obtained in the pure state, but it is shown that no reaction occurs between the silver and *N*-iodo-derivatives in presence of benzene. With silver phthalimide and the inactive carbon disulphide solution of iodine, little silver iodide is formed; silver succinimide gives a larger amount of the iodide. Benzyl sulphide has an activating influence with both metallic derivatives.

H. BURTON.

Mechanism of oxidation processes. XVIII. Activation of hydrogen peroxide by iron. H. WIELAND and W. FRANKE (Annalen, 1929, **475**, 1—19; cf. A., 1927, 944).—The oxidising action of hydrogen peroxide on arsenious, phosphorous, and hypophosphorous acids in presence of bivalent and tervalent iron has been studied with results similar to those previously observed with organic acids (*loc. cit.*). In the presence of ferrous ions there is a primary oxidation impulse, after which the rate of oxidation is much the same whether ferrous or ferric ion is present. Variation of concentration of hydrogen peroxide does not appreciably influence the primary effect until high concentrations are reached, when a slight diminution of the primary oxidation impulse is observed. Cupric salts have an inhibiting effect on the oxidation of hypophosphorous acid in presence of ferrous salts. Cuprous salts have no activating action similar to ferrous salts. It is probable, therefore, that the effect of the cupric salt is to oxidise ferrous salt to ferric with formation of a cuprous salt. The influence of a change in the p_H value of the hypophosphite solution was also examined. The primary oxidation at p_H 0·6 was greater than at p_H 7·0, but both were less than that at p_H 4·6. The presence of dihydroxymaleic acid increases the activation by ferrous salts, and, at lower concentrations, the increase in effect is approximately proportional to the amount added, but becomes much less as the concentration increases. This behaviour is comparable with that observed in the activation of oxygen by ferrous ions (A., 1928, 965). Dihydroxytartaric acid also catalyses the activation by ferrous salts, but not to the same extent as dihydroxymaleic acid, so that activation by the latter cannot be attributed to the dihydroxytartaric acid formed. Thioglycollic acid also causes marked acceleration of the primary oxidation impulse. The action of hydrogen peroxide on linolenic acid, in presence of ferrous and ferric salts, is similar to that previously observed for other organic acids (A., 1927, 944). The extent of activation obtained supports the conclusion that, contrary to the opinion of Manchot and Lehmann (A., 1928, 261), the effect is not due to the formation of a peroxide of iron, but to the formation of a complex between the ferrous ion and the compound to be oxidised. The latter becomes more readily oxidisable,

whilst oxidation of the iron is delayed. The extent of the primary oxidation impulse will depend on the rate of formation of the complex, its degree of dissociation, and the rate of oxidation of the acid in the complex. M. S. BURR.

Mechanism of oxidation processes. XIX. Combined autoxidation systems. H. WIELAND and W. FRANKE (Annalen, 1929, **475**, 19—37).—The accelerating influence of small quantities of certain organic acids on the autoxidation of hypophosphite in presence of iron, previously observed (A., 1928, 965), has been further investigated. The following acids have been found to be active: acetoacetic, oxalacetic, acetonedicarboxylic, benzoylacetic, dihydroxytartaric, and thioglycollic acids. Salicylic and malonic acids are without action, and, although in the case of mesoxalic and benzoylformic acids there is a catalytic increase of oxygen consumption in the system iron–hypophosphite, the effect is due to oxidation of the acid. The organic acid catalysis at first increases with increasing quantity of acid, but ultimately diminishes again. Substitution of the corresponding ethyl ester for the acid reduces the effect very considerably. It is probable that even the small effect that is observed is due to very small quantities of acid set free by hydrolysis of the ester. By measuring the carbon dioxide evolution in presence and absence of hypophosphite, it has been shown that a considerable amount of oxidation of the organic acid takes place in the presence of the hypophosphite. The behaviour of mesoxalic and benzoylformic acids mentioned above, and also of pyruvic acid previously observed, represents an extreme case of this catalysis of the oxidation of the organic acid by the hypophosphite. These experiments were all carried out in solutions of p_H 4·7 buffered by sodium acetate and acetic acid. The influence of copper salts has been studied in solutions of p_H 0·6, 4·7, and 7·3, respectively. Copper sulphate alone causes practically no autoxidation of hypophosphite. In strongly acid solution it exercises a decelerating action on the catalytic effect of ferrous sulphate at first, but after about 15 min. the behaviour of the solution is not appreciably different from that of the solution containing ferrous sulphate alone. In the slightly alkaline solution copper sulphate definitely inhibits the action of ferrous sulphate. In the solution of p_H 4·7 the influence of copper sulphate is very slight. In the presence of the enolic carboxylic acids previously employed both cuprous and cupric ions are practically as active, catalytically, as the ferrous ion, but do not bring about the primary oxidation impulse characteristic of the latter. If ferrous sulphate and copper salts are added to the same solution, the combined effect is greater than the sum of the separate effects, and is greater for the cuprous ion than for the cupric. Experiments employing acetonedicarboxylic acid in presence of iron, and a substrate other than hypophosphite, namely, formic acid, alanine, thioglycollic acid, acetylenedicarboxylic acid, pyrogallol, lævulose, or dextrose, indicated no acceleration of the autoxidation process. In the most favourable cases the total effect scarcely reached that to be expected from the sum of the separate reactions. The different behaviour of hypophosphorous acid is no doubt due to its ability to form complexes. M. S. BURR.

Catalytic decomposition of ammonia. G. M. SCHWAB and (FRL.) H. SCHMIDT (Z. Elektrochem., 1929, **35**, 605—607).—See this vol., 890. H. T. S. BRITTON.

Heterogeneous catalysis. F. HABER (Z. Elektrochem., 1929, **35**, 533—535).—A discussion. H. T. S. BRITTON.

Rôle of walls of vessels in gas reactions. M. BODENSTEIN (Z. Elektrochem., 1929, **35**, 535—539).—A discussion. H. T. S. BRITTON.

Topochemistry of contact catalysis. III. Localisation of catalytic activity. G. M. SCHWAB and E. PIETSCH (Z. Elektrochem., 1929, **35**, 573—582).—Arguments are adduced to show that increased catalytic activity arises from an increase in field and reactivity, through the existence of crystal edges, boundary lines in a grain surface, and surface derangements. H. T. S. BRITTON.

Particle formation and particle action as a special case of heterogeneous catalysis. M. VOLMER (Z. Elektrochem., 1929, **35**, 555—561).—The reactions occurring at phase boundaries in giving rise to new phases are considered to be autocatalytic, and use is made of this view to account for the separation and aggregation of particles. H. T. S. BRITTON.

Orientation of molecules in the adsorption layer and heterogeneous catalysis. H. R. KRUYT (Z. Elektrochem., 1929, **35**, 539—549).—Adsorption alone does not account for the catalysis of organic reactions between large molecules, but instead a definite orientation of the reacting molecules at the surface of the catalyst must be postulated. H. T. S. BRITTON.

Influence of catalysts and of heating the silicon on solubility of silicon in hydrofluoric acid. C. BEDEL (Compt. rend., 1929, **189**, 643—644; cf. this vol., 756, 997).—The solubility of silicon (96%) in hydrofluoric acid is very markedly increased by a small addition of copper to the acid, markedly so by additions of silver or iron, but is practically unaffected by zinc, lead, or aluminium. Heating the silicon to 300° or 550° and suddenly chilling it [which should according to Koenigsberger and Schilling (A., 1910, ii, 481) have transformed it into allotropic modifications] had no effect on the solubility. C. A. SILBERRAD.

Uniform distribution of catalysts throughout porous solids. H. N. HOLMES and R. C. WILLIAMS (Coll. Symp. Mon., 1928, **6**, 283—285).—Porous silica gel was soaked in a salt solution and dried; a water-soluble gas was then admitted to the gel, which was subsequently immersed in water to allow reaction within the capillary pores to take place. CHEMICAL ABSTRACTS.

Behaviour of gaseous hydrogen halides and unsaturated hydrocarbons in the presence of contact substances. J. P. WIBAUT (Z. Elektrochem., 1929, **35**, 602—605).—Reactions between ethylene and propylene, respectively, and hydrogen chloride and hydrogen bromide are described. Of the two hydrocarbons propylene is the more reactive. No

reaction took place between propylene and hydrogen chloride when passed over asbestos at 18°, but on impregnating the asbestos with bismuth chloride a vigorous reaction ensued with the evolution of heat and the formation of *iso*propyl chloride. Antimony trichloride may be used in place of the bismuth salt, but not in the case of the reaction of hydrogen chloride with ethylene. Bismuth chloride in the dissolved state, either in water or in benzene, has no catalytic properties. If ethylene and hydrogen chloride are passed over anhydrous aluminium chloride a complicated reaction occurs. Propylene and hydrogen bromide react in presence of asbestos alone, but for ethylene an addition agent is necessary (cf. Tilman, Diss., Amsterdam, 1928). Brief reference is also made to the reactions with acetylene, an account of which is about to be published.

H. T. S. Britton.

Oxidation of physiological substances by animal charcoal. O. Fürth and H. Kaunitz (Monatsh., 1929, **53** and **54**, 127—145; cf. Warburg and others, A., 1921, i, 230; 1924, ii, 466).—Various substances have been treated with an active charcoal (Carbo medicinalis, Merck) in boiling aqueous solution. With amino-acids up to 70% of the nitrogen may be eliminated as ammonia. The decomposition of alanine is studied in detail; the effects of concentration, time of heating, and presence of oxygen are considered. The change occurring is the formation of ammonium lactate (cf. Baur, A., 1923, i, 97; Wunderly, A., 1924, ii, 841). The charcoal adsorbs some amino-acid but no ammonium salt. Inactivation of the charcoal occurs during the process; addition of fresh charcoal to the filtrate causes renewed decomposition. Amino-acids of high mol. wt. (tyrosine, leucine) are hydrolysed more readily than alanine, but histidine and proline are only slowly attacked. Amides are not affected and proteins only slightly so. Phenols are decomposed readily, but dextrose is not affected (adsorption occurs). Dihydroxyacetone, acetone, and lactic acid are partly decomposed, but β-hydroxybutyric acid is destroyed almost completely. Sugar charcoal is almost as active towards alanine as is an iron-rich animal charcoal (cf. Warburg, *loc. cit.*); addition of iron, copper, manganese, or vanadium salts diminishes the formation of ammonia nitrogen.

H. Burton.

Catalytic power of active carbons, before and after exhaustion, towards hydrogen peroxide. G. Mezzadroli and E. Vareton (Annali Chim. Appl., 1929, **19**, 415—420).—Activated carbons act as physical catalysts towards hydrogen peroxide, the decomposition of which is most rapid with appula, this being followed in order by animal charcoal, norit supra neutral, norit supra acid, industrial norit, suchar, nuchar W, antichromos, and carboraffin. After being exhausted by mixing with raw sugar solution and filtering, appula, bone-black, norit supra, and industrial norit lose, but suchar, antichromos, and carboraffin gain, in catalytic activity, a mean value for which is approached with all the materials.

T. H. Pope.

Oxidation of ammonia to calcium nitrate at a calcium oxide surface. K. Leschewski and K. A. Hofmann [with H. Galotti] (Ber., 1929, **62**, [*B*], 2509—2514; cf. A., 1926, 370; B., 1927, 600).—In the oxidation of ammonia to nitrate at an alkaline surface, fluctuations in the yield are observed owing to conversion of ammonia into nitrogen. The last-named change occurs exclusively in the gaseous phase and on the walls of the furnace and can be eliminated by causing intimate contact between the gas and alkaline surface and maintaining the temperature of the entering and emergent gas below 300°. The reacting ammonia is then converted exclusively into nitrate, and nitrogen oxides are not produced provided that the temperature is below that of the decomposition of the alkaline nitrate. As alkaline surface, slaked lime containing a small proportion of the activating heavy metal oxide (*loc. cit.*) is very suitable. The maximum yield of nitrate, calculated on ammonia oxidised, is obtained at 300°, but under these conditions there is a partial dehydration of the calcium hydroxide to oxide, which acts adversely, but can be overcome by suitable addition of water vapour to the gas mixture when the yield attains 93·9%; addition of excessive moisture diminishes the yield. The absorption of ammonia by the lime and its immediately following dehydrogenation to imide are influenced greatly by the activator, whereas the union of imide with oxygen to nitrite and nitrate is conditioned essentially by the alkaline medium. To obtain maximal yield it is necessary, owing to the lower alkalinity of the material, to use smaller concentrations of ammonia with calcium hydroxide than with soda-lime. With a rapid current of gas, a portion of the imide appears to be removed from the contact before oxidation to nitrite can occur and subsequently to be decomposed in the gas phase into nitrogen and hydrogen.

H. Wren.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. IV. Decomposition and synthesis of methyl alcohol by catalysts composed of zinc and chromium oxides. D. S. Cryder and P. K. Frolich.—See B., 1929, 934.

Catalytic decomposition of carbon monoxide. III. Is the so-called X-carbide really formed in the iron catalyst? H. Tutiya (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 609—613).—The *X*-ray spectrograms of specimens of iron, iron carbide, and ferric oxide used as catalysts in the decomposition of carbon monoxide gave no evidence of the formation of new compounds. The photograms of samples of ferric oxide taken at suitable stages of the reaction showed evidence of the successive reduction to the oxides Fe_3O_4 and FeO, and later to Fe_3C. It was found that almost all the lines of strong intensity which Hofmann (A., 1928, 853) ascribed to the X-carbide agreed with those of Fe_3O_4, not only in position, but also in order of intensity; one of the weak lines which was not common to Fe_3O_4 was due to FeO, and two were shown by Fe_2O_3.

F. G. Tryhorn.

Catalysis of hydrogen peroxide by tungstic oxide. A. Lottermoser [with W. Eichler] (Z. Elektrochem., 1929, **35**, 610—612).—The decomposition of hydrogen peroxide in the presence of tungstic oxide satisfies the expression: $dx/dt=Kx(a-x)$, and is due to the formation of the autocatalyst, WO_3,H_2O_2,

which afterwards decomposes. The rate of the reaction depends on (1) the mass of catalyst used and its size of grain—the greater the mass and the finer the particles, the greater is the catalysis; (2) the presence of foreign substances, *e.g.*, a trace of oil has a strong retarding action. Gelatin, if in sufficient quantity, can arrest action; salts and especially acids also hinder, and the effect of sodium hydroxide depends on its concentration. H. T. S. BRITTON.

Catalytic oxidising action of platinum. J. DALIETOS and K. MAKRIS (Prakt. Acad. Athenes, 1928, **3**, 569; Chem. Zentr., 1929, i, 3063).—Alcohol vapour is readily oxidised by sodium chloroplatinate, but not, under the conditions employed, by the potassium compound. A. A. ELDRIDGE.

Catalytic decomposition of hydrogen peroxide by metallic compounds. H. VON EULER and B. JANSSON (Monatsh., 1929, **53** and **54**, 1014—1022).—The velocity coefficient ($k \times 10^3$) (for the first quarter of the reaction) for the decomposition of 0·004*N*-hydrogen peroxide by a mixture of 0·01*N*-sodium hydroxide and 0·00001*N*-copper sulphate solutions is 47 at 17°; k decreases if more dilute copper solutions are used with the same concentration of alkali. Addition of glycine to a mixture of 0·002*N*-copper and -sodium hydroxide solutions (stabilisation of the copper) decreases the value of k from 34 (mean) to $<0·2$. Addition of pyridine, however, causes an increase in the velocity coefficient; with pyridine in absence of copper there is no measurable decomposition of the peroxide. Silver salts in presence of ammonia or pyridine have a more powerful action than copper salts. H. BURTON.

Catalytic decomposition of aqueous solutions of formic acid by platinum metals. IV. E. MÜLLER and W. LOERPABEL (Monatsh., 1929, **53** and **54**, 825—851).—The effect of addition of potassium osmate, sodium chloroiridate, chloroplatinic acid, ruthenium, rhodium, and palladous chlorides to aqueous formic acid solutions (containing a little sodium formate) at 100° has been studied. The rate of gas evolution varies greatly with the metal used, but osmium and ruthenium show similarities (induction period, then rapidly increasing gas evolution to a maximum, and then decrease). The induction period is not observed if finely-divided osmium metal is used in place of the salt; those metal salts not showing induction periods are readily reduced to the metal. The time necessary for the formic acid–potassium osmate mixture to reach the hydrogen potential decreases with rise of temperature. Addition of titanous chloride to the mixture at 60° causes a rapid alteration in the potential (a similar change is observed at 70° when active osmium is added); this is ascribed to partial reduction of the osmate to metal, which then catalyses the reduction of the rest of the salt by formic acid. The time necessary for the formic acid–salt mixture to attain the hydrogen potential at 100° varies from 0·5 min. (Pd) to 22 min. (Ru). The effect of addition of various salts on the acid–osmate mixture is studied. The induction period at 100° is lowered by large amounts of sodium formate and acetate, but is increased by sodium and potassium chlorides. The addition of a protective colloid (gelatin) to the acid–osmate mixture causes a marked diminution in the rate of evolution of gas; with the other metallic salts used, an increased gas evolution occurs, varying from 7% (Pd, Ru) to 730% (Rh). Palladous and platinum hydroxides on barium sulphate are more active than when used alone.

The mechanism of the decomposition, namely, adsorption of hydrogen by the metal whereby carbon dioxide is first liberated, and subsequent liberation of hydrogen, is discussed electronically. H. BURTON.

Gaseous combustion in electric discharges. IV. Effect of moisture on the cathodic combustion of carbon monoxide detonating gas. G. I. FINCH and D. L. HODGE (Proc. Roy. Soc., 1929, A, **125**, 532—542).—By using the apparatus previously described (this vol., 890), a study has been made of the combustion of moist detonating gas (a mixture of carbon monoxide and oxygen in equivalent proportions) in the cathode zone of a direct-current discharge. Platinum, silver, gold, palladium, tantalum, and tungsten were employed as cathodes. Other conditions remaining unchanged, the rate of cathodic combustion, c, is determined solely by the current, i, passed by the discharge. At freely sputtering cathodes the rate is practically independent of the total gas pressure and is retarded by the presence of moisture, the maximum retarding effect being attained when the partial pressure of moisture is about 3 mm. Higher concentrations of moisture, up to 15 mm., have no additional effect. Combustion at non-sputtering cathodes, on the other hand, is accelerated by moisture, and for any given partial pressure of moisture the ratio c/i is hyperbolically related to the total gas pressure, combustion increasing with decrease of pressure. It is inferred from the above facts that combustion of moist "detonating gas" mixtures is determined by a prior ionisation of both constituent gases, that at freely sputtering cathodes steam molecules form clusters on sputtered metal atoms, and that such clusters promote combustion by neutralising the electrostatic forces of repulsion existing between similarly charged ions. At non-sputtering cathodes combustion is proportional to the number of separate moisture clusters in the cathode zone, and is effected by the neutralising of electrostatic forces of repulsion between positively-charged ions by negatively-charged water. L. L. BIRCUMSHAW.

Active form of oxygen. L. C. COPELAND (Physical Rev., 1928, [ii], **31**, 1113).—An active form of oxygen is produced by the passage of oxygen, saturated with water vapour, through a discharge tube. Density measurements indicate the presence of a dissociated gas and association to a heavier molecule. Platinum and nickel wires glow in this gas, but copper and tungsten appear to be unaffected. Luminescence results when iodine or sulphur vapour is mixed with the gas. L. S. THEOBALD.

Decomposition of carbon monoxide in the silent electric discharge. E. OTT (J.C.S., 1929, 2422—2423; cf. Lunt and Mumford, this vol., 1150).—Malonic anhydride forms different polymerides under different conditions, and the evidence that the product of the discharge is a mixture is not conclusive.

J. A. V. BUTLER.

Effect of electric discharges on chemical reactions. R. SCHWARZ and W. KUNZER (Z. anorg. Chem., 1929, **183**, 376—383).—The combination of sulphur dioxide and chlorine is accelerated by the passage of electric discharges. The observation of Odling that sulphur dioxide and bromine unite in sunlight was not confirmed by irradiation by a mercury arc. The action of the Tesla discharge on certain reactions has been studied. No union of bromine with nitrogen or oxygen was observed. The union of silver and bromine was hindered owing to the passivation of the silver or to the removal of traces of water by the electric discharge.

The influence of electric discharges in various gases on the catalytic activity of contact platinum has been investigated. Activated oxygen and hydrogen reduce the activity of the platinum owing to the formation of oxides and hydrides at its surface.

J. A. V. BUTLER.

Gas absorption during electric discharges. M. PAWLOW (Sprawoz. Prace Polsk. Towarz. Fizycz., 1927, **3**, 101—116; Chem. Zentr., 1929, i, 2859).—When an electric discharge is passed between iron or mercury electrodes at a *P.D.* greater than 600 volts in nitrogen at a low pressure the gas pressure is diminished and nitrides are formed; when the discharge is passed between iron electrodes in nitrogen admixed with mercury vapour only iron nitride is produced. The formation of metallic nitrides is associated with cathodic sputtering. A. A. ELDRIDGE.

Electrolytic production of fluorine from fused potassium fluoride. K. FREDENHAGEN and O. T. KREFFT (Z. Elektrochem., 1929, **35**, 670—676).—The attack of graphite electrodes by a solution of potassium fluoride in hydrofluoric acid or a fused mass of potassium fluoride containing an excess of the acid is not a chemical process, but one of mechanical disintegration which occurs during electrolysis. If the amount of hydrofluoric acid is about 1·8 mols. to 1 mol. of potassium fluoride, moistened anodes of graphite or carbon could be used. Details of the apparatus used are given. The current–potential curves show that the electrolysis depends largely on the water content of the fused mass. Employing a dry fused mass fluorine could be obtained with a current density of 0·3 amp./cm.^{2} at 10 volts, whilst with 1% of water and using a current density of 0·1 amp./cm.^{2} and 4 volts the water alone undergoes decomposition. With a water content less than 0·7% the potential increases rapidly. Water causes the cell to become polarised even at 250° and destroys the anode, and the fluorine obtained is contaminated with oxygen. The behaviour of platinum and nickel anodes is discussed. The *E.M.F.* of the cell $H_2|HF,(KF)|F_2$, using platinised platinum electrodes at 0°, is 2·768 volts (Krefft, Diss., Greifswald, 1928), from which the heat of formation of hydrogen fluoride, 62·630 kg.-cal., is calculated. H. T. S. BRITTON.

Formation of zinc nitride in the electric arc. K. MASLOWSKI and H. REGULSKI (Sprawoz. Prace Polsk. Towarz. Fizycz., 1927, **3**, 87—89; Chem. Zentr., 1929, i, 2865).—Zinc nitride is formed by the electric discharge between zinc electrodes in nitrogen at a pressure below 25 mm. The substance, which probably has the formula Zn_3N_2, is decomposed in a vacuum at 500°. A. A. ELDRIDGE.

Separation of chromium from solutions of chromic acid. E. LIEBREICH and V. DUFFEK (Ber., 1929, **62**, [*B*], 2527—2538).—The processes of reduction which occur during the deposition of metallic chromium from chromic acid have been investigated by a U-tube method which permits the elucidation of the individual stages in a sharply-defined cathode space without the use of a diaphragm. Bivalent chromium is certainly produced and it appears probable that deposition of the metal occurs by discharge of the chromous ions. During electrolysis in ordinary vessels a similar cathode zone is formed around the cathode within which the reduction processes occur. H. WREN.

Effect of current density on the hardness of electro-deposited chromium. R. J. PIERSOL.—See B., 1929, 944.

Electrolytic deposition of molybdenum at a mercury cathode. J. L. MERRILL and A. S. RUSSELL (J.C.S., 1929, 2389—2393).—The conditions for the electrolytic deposition of molybdenum have been investigated. The most suitable cathode is mercury and the optimum conditions are: current density 0·6—1·0 amp. per cm.^{2}; acidity, 1·2—1·4*N*-sulphuric acid. Under these conditions 0·1 g. of molybdenum is completely deposited in about 50 min. and the use of a rotating anode does not shorten this time. In sulphuric acid solutions complete deposition is obtained at very low current densities, whereas in hydrochloric acid no deposition occurs at current densities below 2·84 amp. per cm.^{2}

J. A. V. BUTLER.

Electrolytic deposition of tungsten at a mercury cathode. K. S. JACKSON, A. S. RUSSELL, and J. L. MERRILL (J.C.S., 1929, 2394—2398).—The conditions for the electrolytic deposition of tungsten from hydrofluoric acid solutions, at a mercury cathode, have been investigated. The optimum conditions are: temperature 95°; acid concentration about 4·6*N*; current density 0·65—1·0 amp. per cm.^{2} Hydrochloric or sulphuric acid must not be present.

J. A. V. BUTLER.

Order of removal of metals from amalgams. A. S. RUSSELL (J.C.S., 1929, 2398—2401).—The order of removal of molybdenum, tungsten, and bismuth from mercury by oxidising agents has been redetermined with respect to other metals the positions of which are known (A., 1926, 911). The revised order is: zinc, cadmium, manganese, thallium, tin, lead, bismuth, copper, chromium, iron, molybdenum, cobalt, mercury, nickel, tungsten. Molybdenum and cobalt, and also mercury and nickel, lie close together in this series. J. A. V. BUTLER.

Electrolysis of molten ternary alloys. R. KREMANN [with B. KORTH, E. I. SCHWARZ, and W. PIVETZ] (Monatsh., 1929, **53** and **54**, 203—214).—Using a modified form of the apparatus described by Kremann and Gruber-Rehenburg (A., 1925, ii, 678) the effect of current density on a copper–tin alloy (29 : 71) has been investigated. With increasing current density the "relative effects" (maximal

differences in the concentration of the metals at the anode and cathode) and "absolute effects" (the values of the relative effects referred to 100 parts of the metals) increase up to a limiting value of about 6 amp./mm.^{2} The addition of small amounts of a third metal causes an increased electrolysis effect; this does not increase with larger amounts of added metal. With silver–copper–tin alloys an increase in current density again causes an increase in the relative effect. A limiting value (at 3·6 amp./mm.^{2}) is reached with 10·84% Ag (31·7% Cu; 57·4% Sn); this does not occur with lower concentrations of silver. Similar results are obtained with lead–copper–tin alloys, a limit in the absolute effect for lead being shown at 6 amp./mm.^{2} and 2·9% Pb (28% Cu; 69·2% Sn). The absolute effects at maximal current density decrease with increase of silver and lead in bronze or lead and tin in brass, and limiting values are again reached. Metallographic examinations of various lead–copper–tin anodes and cathodes show that lead and tin move to the anode (silver and copper move to the cathode). H. BURTON.

Electrochemical behaviour of gold and platinum in hydrochloric acid solution. G. GRUBE [with J. HELFER and G. LUZ] (Z. Elektrochem., 1929, **35**, 703—709).—The following reduction potentials have been determined: ${}_0E_h$ of Au|$AuCl_2'$ at 40° is 1·13±0·02 volt; at 60°, 1·04±0·03 volt: ${}_0E_h$ of $AuCl_4'$|$AuCl_2'$ at 40°, 0·95±0·01 volt, at 60°, 0·96±0·02 volt: ${}_0E_h$ of Au|$AuCl_4'$ at 40°, 1·01±0·01 volts, at 60°, 0·99±0·01 volt. Curves are given connecting the anode potentials with increasing current densities of gold and platinum anodes, for temperatures ranging between 20° and 80°, the former in solutions containing auric chloride and hydrochloric acid and the latter in hydrochloric acid solution. Similar curves are given for gold cathodes. Gold undergoes anodic dissolution at ε_h=+1·1 to +1·3 volts, the amount of polarisation depending on the acid content of the electrolyte and the temperature. It becomes passive at about ε_h 2·0 volts, the precise voltage again depending on the previous conditions. H. T. S. BRITTON.

Electrolytic chlorination of benzene in methyl alcohol. P. JAYLES (Compt. rend., 1929, **189**, 686—689).—A solution of 532 g. of benzene in 2 litres of methyl alcohol saturated with hydrochloric acid, electrolysed with no diaphragm at 15—20° for 28 hrs. by a current of 8 amp. (density 12 amp./dm.^{2}, total quantity 180 amp.-hrs.), gave a yield of 10·6% of chlorobenzene and 0·3% of benzene α-hexachloride, with current efficiency 10·5%. With a diaphragm, but otherwise similarly, 250 g. of benzene in 1·5 litres of a similar solution electrolysed for 38 hrs. by a current of 6 falling to 3 amp. (total quantity 141 amp.-hrs.) gave 35·3% of chlorobenzene and 0·9% of benzene α-hexachloride, with current efficiency 20%. The poor yield is due to the action of the chlorine on the methyl alcohol producing formaldehyde and carbon monoxide and dioxide. C. A. SILBERRAD.

Electrochemical oxidation of anthracene to anthraquinone. C. H. RASCH [with A. LOWY].—See B., 1929, 886.

Electrolysis of salts of organic acids. F. FICHTER (Z. Elektrochem., 1929, **35**, 710—712).—A review. H. T. S. BRITTON.

Luminescence during electrolysis. N. HARVEY (J. Physical Chem., 1929, **33**, 1456—1459; cf. Albrecht, A., 1928, 1307).—Luminescence occurs at the anode during the electrolysis of aminophthalic hydrazide, at fresh metallic surfaces of aluminium, zinc, cadmium, and tin when placed in a solution of aminophthalic hydrazide in 0·1*N*-sodium hydroxide, and at the surface of such solutions when played on by oxy-hydrogen or oxy-carbon monoxide flames. Luminescence also occurs when oxidising phosphorus is placed in a solution of aminophthalic hydrazide, and is connected with the formation and decomposition of ozone. It is suggested that this hydrazide is a test for active oxygen and that the term "galvano-luminescence" be used for luminescence associated with electrolysis. L. S. THEOBALD.

Quanta-yield and "Chemismus" in light reaction. J. PLOTNIKOV (J. Indian Chem. Soc., 1929, **6**, 635—640).—Theoretical. It is suggested that the method of representation of the primary stage of photochemical action as $M+h\nu=M'$ (activated molecule) has neither a real nor a symbolical significance. The energy $h\nu$ of the light quantum may transform itself into one or more of the following: heat radiation, kinetic energy of the molecule, chemical energy, new radiations of lower energy, photo-electric effect, etc. The percentage ratio of the different forms of light energy distribution depends, not only on the reacting wave-length, but also on the "Chemismus," *i.e.*, the combined effect of the chemical properties of each particular compound individually, the medium, the temperature, added catalysts, and other active and inactive components. In exceptional cases only, and under definite conditions of experiment, $h\nu$ may be converted approximately completely into any one of the above given forms of energy. M. S. BURR.

Mechanism of formation of chlorine hexoxide. M. BODENSTEIN and H. J. SCHUMACHER (Z. physikal. Chem., 1929, B, **5**, 233—236; cf. A., 1925, ii, 991).—When a mixture of chlorine and ozone is exposed to light of such wave-length as to be absorbed by the ozone rather than by the chlorine, it is suggested that the following reactions occur: (1) $O_3+E=O_3^*$; (2) $O_3^*+Cl_2=ClO+ClO_2$; (3) $ClO_2+O_3=ClO_3+O_2$; (4) $ClO_3+O_3=ClO_2+2O_2$; (5*a*) $ClO_3+ClO_3=Cl_2+3O_2$; (5*b*) $ClO_3+ClO_3=Cl_2O_6$; (6) $ClO+ClO=Cl_2+O_2$. Since (5*a*) has a large heat of activation, it should become less important in comparison with (5*b*) as the temperature is lowered, and it is in fact found that under these conditions more chlorine hexoxide is formed; the yield is also increased by increasing the surface of the containing vessel. The formation of the hexoxide from a mixture of the dioxide with ozone takes place in the two stages (1) $ClO_2+O_3=ClO_3+O_2$, (2) as in (5*b*) above. The mechanism of the photochemical formation of the hexoxide from the dioxide alone is less certain, the most probable sequence being (1) $ClO_2+E=ClO_2^*$; (2) $ClO_2^*=ClO+O$; (3) $ClO_2+O=ClO_3$; then as (5*a*) and (5*b*) above. This would lead to a yield of

1 mol. of hexoxide per 2 einsteins, which is compatible with the observations. F. L. USHER.

Mechanism of the photochemical decomposition of chlorine monoxide and of the chlorine-sensitised decomposition of ozone. H. J. SCHUMACHER and C. WAGNER (Z. physikal. Chem., 1929, **B**, **5**, 199—208; cf. Bodenstein and Kistiakovski, A., 1925, ii, 883).—The fact that the absorption of 1 light-quantum by a molecule of chlorine in the neighbourhood of 430 μμ gives rise to a direct dissociation into 2 atoms enables a simple mechanism of the chlorine-sensitised decomposition of chlorine monoxide by light of this wave-length to be formulated, on the assumption that ClO is formed as an intermediate product. The complete scheme is: (1) $Cl_2+E=2Cl$; (2) $Cl+Cl_2O=Cl_2+ClO$; (3) $ClO+ClO=Cl_2+O_2$. If it is further assumed that recombination of chlorine atoms takes place only at the surface of the containing vessel, but that reaction between the ClO molecules occurs at each collision; this mechanism leads to a quantum yield of 2, in agreement with observation. A minimum value of 58 kg.-cal. for the reaction $Cl+O=ClO$ is deduced. It is considered probable that ClO is also an intermediate product in the non-sensitised decomposition of chlorine monoxide by light. The lower quantum yield (1) observed when the decomposition takes place in carbon tetrachloride solution (cf. Bowen, J.C.S., 1923, **123**, 1199) is attributed to the presence in the solvent of impurities which use up the chlorine atoms, which are then no longer available for reaction (2) above. The intermediate formation of ClO is further shown to explain the chlorine-sensitised photochemical decomposition of ozone. F. L. USHER.

Photochemical formation of carbonyl chloride. V. Reaction between intensively dried gases. G. SCHULTZE (Z. physikal. Chem., 1929, **B**, **5**, 368—384).—The photochemical formation of carbonyl chloride from intensively dried chlorine and carbon monoxide at 1 atm. total pressure follows the same law as when moist gases are used, no appreciable retardation of the reaction being observed; the temperature coefficient from 15° to 50° is 0·9 per 10°. Under these conditions also oxygen retards the reaction on account of carbon dioxide formation, which appears to proceed more rapidly when the gases are intensively dried. H. F. GILLBE.

Photochemical action of complex and intermittent light. A. BERTHOUD (J. Chim. phys., 1929, **26**, 435—446; cf. Padoa and Vita, A., 1928, 378, 1102).—The oxidation of potassium nitrite by iodine in aqueous solution has been studied in yellow and blue light separately and when mixed, and the effect shown to be purely additive, contrary to the statement of Padoa and Vita. It is considered that in cases where the law of additivity is not followed the causes are the same as those which give rise to departure from the Grotthus–Draper law. In the bromination of cinnamic acid and the oxidation of hydriodic acid the effect of increasing the distance of the source of light, or of interposing solutions of nickel sulphate or of ammoniacal copper sulphate, is perfectly regular. The effect of intermittent light on the oxidation of hydriodic acid previously studied (cf. A., 1928, 485) has been re-examined, and found to be in agreement with theory. The velocity maximum reported by Padoa and Vita was not observed. F. L. USHER.

Photometric and spectrophotometric studies. VIII. Measurements with the König–Marten spectrophotometer. K. SCHAUM, L. HOCK, and W. DANNEFELSER (Z. wiss. Phot., 1929, **27**, 145—168).—A method is described for calibration of the König–Marten spectrophotometer whereby the number of measurements is so far reduced that investigation of changing systems may be effected. Study of the reaction between sodium hydroxide and sodium picrate indicates the existence of a light-sensitive reaction which results in the formation of ammonia, but a similar reaction has not been observed with *o*- or *p*-nitrophenol nor with 2 : 4- or 2 : 6-dinitrophenol. H. F. GILLBE.

Photochemical studies. IX. Uranyl sulphate as sensitiser for the photochemical decomposition of oxalic and malonic acids. W. C. PIERCE (J. Amer. Chem. Soc., 1929, **51**, 2731—2738).—The temperature coefficient of the photolysis, in presence of uranyl sulphate, of oxalic acid is unity and of malonic acid 1·13. The rate of reaction is independent of the concentration of the uranyl sulphate when the latter is between 0·0025*M* and 0·01*M*, but depends on the concentration of malonic acid. In view of these results possible mechanisms for these reactions are discussed. Reaction may be due to the decomposition of an intermediate uranyl ion–acid complex, or to collisions of the second kind between activated uranyl ions and acid molecules. S. K. TWEEDY.

Influence of [light] intensity on the velocity of photochemical reaction. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, **6**, 473—487; cf. A., 1926, 1216; 1928, 378, 1198).—Experiments have been made to test the conclusion that the velocity of a true photochemical reaction, of which the dark velocity is negligible, is proportional to the square root of the intensity of the incident radiation. By the use of accelerators or retarders it has been found possible to vary the velocity of the dark reactions between the following pairs of reagents: potassium oxalate and iodine, Rochelle salt and bromine, quinine sulphate and chromic acid, sodium formate and iodine. By increasing the velocity of the dark reaction, and exposing it to radiation which is only slightly absorbed by the reacting system, a truly photochemical reaction, proportional to the square root of the intensity of the incident radiation, or to the amount of energy absorbed, becomes directly proportional to the intensity of the incident radiation. On the other hand, a photochemical reaction directly proportional to the intensity of the incident radiation, or proportional to its square, can be made proportional to the square root of the intensity by decreasing the dark reaction velocity and increasing the photochemical velocity. On the basis of these results, the divergent data relating to the photochemical reaction between hydrogen and chlorine may be explained. Other known photochemical reactions are also shown to be in agreement with the authors' results. The

mechanism of photochemical reaction is discussed. It is pointed out that those photochemical reactions which obey Einstein's law of photochemical equivalence need not follow Draper's law, and conversely.

M. S. BURR.

Relation between the intensity [of incident radiation] and the velocity of the reaction between potassium oxalate and bromine in visible and infra-red radiations. A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, **6**, 523—527; cf. preceding abstract).—By retarding the dark reaction between potassium oxalate and bromine by potassium bromide, it has been shown that the relation between the velocity of reaction and the intensity of incident radiation, or the amount of energy absorbed, can be varied approximately from the fourth root to unity as the ratio of the thermal and photochemical velocities increases. Since the reaction is markedly accelerated by wave-lengths in the region of 7304 Å., which cannot atomise bromine molecules, it is concluded that, contrary to Berthoud's conception (A., 1924, ii, 327), the halogens are not, as a general rule, atomised by the absorption of radiation, but the molecules are activated and then react.

M. S. BURR.

Photosynthetic reaction. R. B. GORDON (Ohio J. Sci., 1929, **29**, 131—132).—The scheme: $6C_{55}H_{70}O_6N_4Mg$ (chlorophyll-*b*)$+6H_2O \longrightarrow 6C_{55}H_{72}O_5N_4Mg$ (chlorophyll-*a*)$+6O_2$; $6C_{55}H_{72}O_5N_4Mg+6CO_2 \longrightarrow 6C_{55}H_{70}O_6N_4Mg+C_6H_{12}O_6$ does not require the assumption of the intermediate formation of formaldehyde.

CHEMICAL ABSTRACTS.

Irradiated proteins. III. Velocity of coagulation by light of various proteins. M. SPIEGEL-ADOLF [in part with O. KRUMPEL and FERNAU] (Strahlenther., 1928, **29**, 367—374; Chem. Zentr., 1929, i, 2898—2899).—The velocity of coagulation of proteins in the light of the mercury lamp is markedly affected by the presence of traces of electrolytes and by the age of the solution after electro-dialysis. The ultra-spectrograms of the freshly-dialysed and the aged serum-albumin solutions showed no difference. The effect of previous history is also observed in the denaturation of proteins by radium, and may depend on the autolytic production of traces of electrolytes, *e.g.*, ammonia. Below a certain concentration the exposure necessary for visible change increases with the dilution; in more concentrated solutions the outer layers protect the inner. The coagulation of protein solutions by radium is arrested by salts. Salts also inhibit the appearance of turbidity when serum-albumin solutions are exposed to light. The velocity of coagulation diminishes in the order: pseudoglobulin, ovalbumin, serum-albumin.

A. A. ELDRIDGE.

Action of polarised light on photographic plates prepared from colloidal silver. A. COTTON (Compt. rend., 1929, **189**, 599—603).—The Weigert phenomenon (A., 1928, 1103) is obtainable with plates prepared by dipping a plate coated with gelatin containing collargol into a solution of cupric bromide, chloride, or iodide. Such a plate exposed for 1 hr. to polarised light from an ordinary arc lamp can be examined in the green light of mercury without fixing, or (especially an iodide plate) with shorter exposure after development. A chloride plate can also be rendered dichroic by exposure for 18 hrs. to polarised monochromatic light (366 mμ from a mercury arc with nickel oxide screen). The author prefers to attribute the phenomenon to anisotropy of distribution, rather than (Weigert's theory) to anisotropy of shape of the ultra-microscopic silver grains. The dichroism is, however, not affected by a magnetic field. This, whilst not negativing the preferred explanation, does not support a suggested mechanism thereof.

C. A. SILBERRAD.

Asymmetric synthesis and the combined action of polarised light and a magnetic field on certain photographic plates. A. COTTON (Compt. rend., 1929, **189**, 657—660).—The effect of circularly polarised light on plates prepared as previously described (*supra*) is nil, as it is also on plates prepared as described by Zocher and Coper (A., 1928, 573) if formaldehyde be the reducing agent. The effect described was, however, obtained equally whether reduction was effected by lævo- or dextro-tartrate of potassium and sodium, and is thus shown to be due to the incident light, which must in some way modify the micelles of silver according to the character of its polarisation. Further, the resultant rotatory power being the same if the plate be turned over, the arrangement assumed must resemble that of a screw which progresses as it turns. Lastly, it is pointed out that there has been no synthesis of active molecules, but merely production of an active arrangement of molecules in a medium. The action of a magnetic field previously described (*loc. cit.*) should produce double refraction in a sensitive layer of appreciable thickness, but even so there would be no production of active molecules. C. A. SILBERRAD.

Weak points in the crystal lattice and the speck concentration theory of photographic sensitivity. A. STEIGMANN (Z. wiss. Phot., 1929, **27**, 76—78).—The close connexion between these two theories of photographic sensitivity is discussed.

J. W. GLASSETT.

Blackening surfaces of two slightly sensitive emulsions. H. ARENS and J. EGGERT (Z. wiss. Phot., 1929, **27**, 79—84).—The blackening surfaces, obtained from the three-dimensional figure formed by plotting the blackening against the logarithms of the intensity and the time of exposure, have been determined for the Agfa diapositive and kine-positive emulsions. Over normal ranges of times of exposure the Schwarzschild exponent p remains approximately equal to unity, but at very low intensities and long times of exposure, as was previously noted with desensitised rapid emulsions, the value of p falls considerably and approaches zero. J. W. GLASSETT.

Photochemistry of the silver halides. VIII. Silver values and the process of fixation with sodium sulphite. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1929, **27**, 173—176).—Sodium sulphite does not dissolve the silver particles to any appreciable extent, and complexes formed in solution with the silver halides are very stable; the fixing solution may thus be readily washed out of the

gelatin film. About 85% of the silver in a silver chloride–gelatin emulsion may be extracted by 10% sodium sulphite solution, whilst the remainder is present possibly as atomic silver or as silver sulphide. Sodium sulphite appears to be the most satisfactory fixing agent yet studied. H. F. GILLBE.

Function of gelatin in photographic emulsions. S. E. SHEPPARD.—See B., 1929, 959.

Photographic sensitivity of photographic layers. F. WEIGERT.—See B., 1929, 959.

Theory of photographic light sensitivity. A. STEIGMANN.—See B., 1929, 959.

Mechanism of latent image formation. F. C. TOY.—See B., 1929, 960.

Oxidation of ferrous sulphate in aqueous solution by *X*-rays of different wave-lengths. Determination of Compton absorption. H. FRICKE (Physical Rev., 1928, [ii], **31**, 1117; cf. this vol., 408).—The amount of ferrous sulphate oxidised by *X*-rays is independent of concentration (0·01—0·00004*N*). The change is considered to be due to a primary production of activated water molecules and it is calculated that for each activated water molecule approximately 8 ferrous ions are oxidised and 2·05 oxygen molecules are reduced; in gas-free solutions, 4·1 ferrous ions are oxidised. With solutions containing added salts of light elements, the amount of ferrous sulphate transformed is independent of wave-length when the mass coefficient of photoelectric absorption of the solution is equal to that of air, but when this coefficient is larger the effect of the shorter wave-lengths becomes increasingly smaller. This is due to the Compton effect, and for λ equal to 0·204 the mass coefficient of absorption due to the production of Compton electrons equals 0·0158, in agreement with Compton's theoretical value of 0·0156. L. S. THEOBALD.

Ozonisation and interaction of oxygen with nitrogen under α-radiation. S. C. LIND and D. C. BARDWELL (J. Amer. Chem. Soc., 1929, **51**, 2751—2758).—Ozonisation in oxygen flowing past an α-ray bulb is higher per ion pair the faster is the rate of flow and the lower is the intensity of ionisation (cf. D'Olieslager, Bull. Acad. Roy. Belg., 1925, **12**, 719). The yield per ion pair is between 1·5 and 2—2·6 and probably could never exceed 3—4. The yield is controlled by secondary deozonisation caused, not by direct collision of α-particles and ozone molecules, but by a deozonising action of activated oxygen, either as ions or as atoms. Ozone, acidic nitrogen oxides, and nitrous oxide are formed when mixtures of nitrogen and oxygen flow past an α-ray bulb, and the amount of acidic oxides formed diminishes with decrease in the proportion of nitrogen in the mixture, although the total oxidising power towards potassium iodide is practically uninfluenced. This is explained on the basis of ionisation by collision of the second kind proceeding only in the direction $N_2^+ + O_2 = N_2 + O_2^+$. S. K. TWEEDY.

Chemical effects of penetrating radium radiation. XVIII. Action on acetyl and benzoyl chlorides. A. KAILAN (Monatsh., 1929, **53** and **54**, 153—164).—Prolonged action of penetrating radiation from radium on acetyl chloride causes no change in the density, but the specific conductivity increases. The number of mols. of acetyl chloride undergoing chemical change (m) is of the same order as the number of ion pairs (n) formed, and $m/n = 0·5$. In benzene or toluene solution the density increases only slightly, but the conductivity is unaltered; m/n varies from 0·3 to 0·9. Acetophenone or benzyl methyl ketone is not formed. The specific conductivity of benzoyl chloride is 30 times as high after irradiation, whilst the density is decreased slightly. Benzoic acid is produced and the ratio m/n varies from 0·4 to 1·6. H. BURTON.

Chemical inertia of the rare gases. I. Action of helium on platinum. H. DAMIANOVICH (Gazzetta, 1929, **59**, 571—577).—By passing an electrical discharge through helium at low pressures between platinum electrodes a diminution of pressure corresponding with an absorption of helium was obtained. Simultaneously a loss in weight of the electrodes corresponded with the deposition in small vessels shielding the electrodes of traces of a substance notably different from platinum. This product contained helium in a fairly stable condition and in considerable amounts. The ratio of the amount of helium absorbed to the amount of platinum lost tended asymptotically to a maximum in the different experiments. F. G. TRYHORN.

Preparation of dithiophosphates and some new dithiophosphates. P. NEOGI and M. G. GHOSH (J. Indian Chem. Soc., 1929, **6**, 599—605).—Magnesium dithiophosphate, $Mg_3P_2S_4O_4,2H_2O$, has been obtained by the action of powdered phosphorus pentasulphide on magnesium oxide suspended in ice-cold water. The soluble dithiophosphates, sodium, $Na_3PS_2O_2,11H_2O$, *potassium*, $K_3PS_2O_2,4H_2O$, ammonium, $(NH_4)_3PS_2O_2,2H_2O$, and calcium, $Ca_3P_2S_4O_4,H_2O$, have been prepared by double decomposition of the corresponding hydroxides with the magnesium salt. The insoluble dithiophosphates of *barium*, $Ba_3P_2S_4O_4,10H_2O$, *zinc*, $Zn_3P_2S_4O_4,H_2O$, *thallous*, $Tl_3P_2S_4O_4$ [?], and *lead*, $Pb_3P_2S_4O_4,4H_2O$, have been prepared by precipitation of a soluble salt of the corresponding metal with sodium dithiophosphate. Manganese, mercuric, *thorium*, and *lanthanum* dithiophosphates were also obtained, but were decomposed on washing with ice-cold water. Dithiophosphates of bismuth, mercurous mercury, copper, silver, cobalt, nickel, cadmium, and ferrous iron were probably obtained, but decomposed within a few seconds of precipitation. Attempts to obtain the dithiophosphates of aluminium, zirconium, and molybdenum were unsuccessful. M. S. BURR.

Formation of amminothiocyanates in aqueous solution. I. Simple ammines with hexamethylenetetramine. R. RIPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1929, **4**, 413—430; Chem. Zentr., 1929, i, 2993—2994).—Treatment of a solution of a metallic nitrate with alkali thiocyanate and aqueous hexamethylenetetramine (X) leads to the formation of two types of salt, $[MX_2(H_2O)_4](SCN)_2$ and $[MX_2(H_2O)_2](SCN)_2,2H_2O$, respectively. The following *compounds* were prepared:

$[CoX(H_2O)_4](SCN)_2,H_2O$; $[ZX(H_2O)_4](SCN)_2$, where Z=Zn or Co; $[CuX_2](SCN)_2,H_2O$; $[CdX(H_2O)_2](SCN)_2$; $[NiX_2(C_5H_5N)_2](SCN)_2,7H_2O$; $[NiX(H_2O)_2](SCN)_2,2H_2O$; $[MnX_2(C_5H_5N)_2](SCN)_2,3H_2O$; $Mn(SCN)_2,2X,4H_2O$; $[ZnX(C_5H_5N)_4](SCN)_2,3H_2O$; $[ZnX(C_5H_5N)_2](SCN)_2,7H_2O$; $[FeX(C_5H_5N)_3H_2O](SCN)_2,2H_2O$; $[FeX_2(H_2O)_4](SCN)_2$; $[CuX_2(C_5H_5N)_2](SCN)_2,5H_2O$; $[CdX(C_5H_5N)_4](SCN)_2,2H_2O$. A. A. ELDRIDGE.

Influence of cations of the alkali metals on the precipitation of zinc ferricyanide. F. ČŮTA (Coll. Czech. Chem. Comm., 1929, **1**, 538—550).—A study has been made of the precipitation of zinc ferricyanide under various experimental conditions with especial reference to its precipitation in the presence of alkali halides. Brown zinc ferricyanide, when precipitated from slightly acid (hydrochloric) solution of zinc chloride with potassium ferricyanide in the cold, has the composition $Zn_3[Fe(CN)_6]_2,12H_2O$, whilst the yellow substance precipitated and washed in boiling solution is anhydrous. The transition point, determined dilatometrically, is 69—70°. The solubility of zinc ferricyanide at the ordinary temperature, determined iodometrically, is $1{\cdot}24\times10^{-4}$ mol. per litre. Precipitation from zinc chloride solution by lithium, sodium, potassium, and rubidium ferricyanides in the cold and in hot solution led to the conclusion that less of the alkali ferricyanide is occluded from the hot solution than in the cold and that the proportion of occluded alkali ferricyanide increases with the rise in the atomic weight of the alkali metal. With rubidium the precipitate formed has approximately the composition $Rb_3Fe(CN)_6,4Zn_3[Fe(CN)_6]$. Zinc ferricyanide is very soluble in alkali chloride solutions, especially on warming. These solutions deposit crystalline compounds, which, for rubidium and potassium chlorides, have the composition $Rb_3[Fe(CN)_6],Zn_3[Fe(CN)_6]$ and $K_3Fe(CN)_6,4Zn_3[Fe(CN)_6]$ (hydrated) respectively. The substance obtained from lithium chloride solutions consists of zinc ferricyanide containing a little lithium ferricyanide; the compounds deposited from sodium and ammonium chloride solutions have no simple composition. Warm water decomposes these double salts into the alkali ferricyanide and zinc ferricyanide, the reaction being reversible. Cadmium and zinc ferricyanides also dissolve in alkali halide solutions. A. I. VOGEL.

Additive compounds of mercuric cyanide and hydrated metallic azides. B. RICCA and F. PIRRONE (Gazzetta, 1929, **59**, 564—568).—The *compound* $Hg(CN)_2,NaN_3,2H_2O$ was obtained as colourless crystals by mixing solutions of mercuric cyanide and sodium azide. By the action of suitable metallic salt solutions on a solution of this compound, the following products were obtained: $Hg(CN)_2,AgN_3$; $Hg(CN)_2,Cu(N_3)_2$; $Hg(CN)_2,Zn(N_3)_2$; $Hg(CN)_2,Co(N_3)_2$; and $Hg(CN)_2,Ni(N_3)_2$. When heated these compounds decompose with ignition but without explosion. F. G. TRYHORN.

X-Ray examination of the effect of heat on aluminium hydroxide, $Al_2O_3,3H_2O$. H. P. ROOKSBY (Trans. Ceram. Soc., 1929, **28**, 399—404).—The composition of precipitated aluminium hydroxide and the changes occurring when crystalline $Al_2O_3,3H_2O$ is heated were studied by the *X*-ray powder method. The crystalline hydrate of alumina, prepared from sodium aluminate, has the composition $Al_2O_3,3H_2O$, and its *X*-ray pattern differs from that of the natural hydrate, gibbsite. Alumina precipitated from aluminium chloride solution with ammonia solution varies in composition and consists of a mixture of $Al_2O_3,3H_2O$ and Al_2O_3,H_2O, the latter being usually in excess. Crystalline $Al_2O_3,3H_2O$ loses water when heated at 200°, and at 250° a definite hydrate, Al_2O_3,H_2O, is formed; its *X*-ray pattern differs from that of diaspore, but is the same as those of certain bauxites. Between 250° and 500° the hydrate Al_2O_3,H_2O loses water and γ-alumina is formed. At 1000° γ-alumina begins to change to corundum and at 1150° the change is complete. F. SALT.

Rhythmic crystallisation of alum in a metastable system. C. HRYNAKOVSKI (Bull. Soc. Amis Sci. Poznań, 1927, **B**, 49—52; Chem. Zentr., 1929, i, 2854).—The isothermal crystallisation of alum at the surface of separation of saturated and supersaturated solutions is described. A. A. ELDRIDGE.

Europium halides. G. JANTSCH, H. ALBER, and H. GRUBITSCH (Monatsh., 1929, **53** and **54**, 305—311).—Anhydrous europium chloride, m. p. 623±1°, is obtained by passing dry hydrogen chloride over the hydrated salt at 320°; it is not necessary to carry out the process under diminished pressure (cf. Kleinheksel and Kremers, A., 1928, 603). Reduction to europous chloride occurs readily in a current of hydrogen at about 500° (cf. Urbain and Bourion, A., 1912, ii, 162). Reduction of europium iodide (hydrated), alone or mixed with ammonium iodide, occurs with hydrogen iodide. Reduction of europium chloride with a mixture of hydrogen and hydrogen iodide gives mainly europous iodide. A cold solution of europous iodide is stable; the oxyiodide separates only after a long time. The electrical conductivity of the solution gradually diminishes on keeping. H. BURTON.

Order of fractionation of rare-earth bromates, and a search for illinium. J. K. MARSH (J.C.S., 1929, 2387—2389).—Discrepancies in the order of separation of the rare-earth bromates recorded by previous workers are ascribed to variations in the final temperatures of the cooled fractions. Below 20° the order of increasing solubility is found to be: samarium and europium, gadolinium, neodymium, terbium, praseodymium, dysprosium, holmium, yttrium. The possibility that illinium might be present in unusual abundance in Joachimsthal pitchblende has been disproved. J. A. V. BUTLER.

Germanium. I. R. SCHWARZ (Ber., 1929, **62**, [*B*], 2477—2483).—Dehydration of germanium dioxide, obtained by hydrolysis of germanium tetrachloride, proceeds continuously at 10° until at tension 0 mm. a product remains containing 3·2% of water, corresponding with a compound, $5GeO_2,H_2O$. The product is not further dehydrated when preserved over phosphoric oxide. The water is regarded as firmly adsorbed and not chemically united, since more water is attracted when it is exposed to moist air.

Desiccation by the acetone method yields a similar product containing 3·3% of water. Topochemical decomposition of crystalline sodium germanate by acids does not afford a suitable method of examining the system GeO_2–H_2O, since the dioxide is appreciably soluble in water and dilute acids.

Thermal analysis of the system Li_2O–GeO_2 discloses the existence of *lithium metagermanate*, Li_2GeO_3, m. p. 1239°, d_4^{21} 3·53, *n* 1·70, and *lithium orthogermanate*, Li_4GeO_4, m. p. 1298°. *Sodium metagermanate*, m. p. 1078°, d_4^{22} 3·31, *n* 1·59, is similarly identified in the system Na_2O–GeO_2, but there is no evidence of the existence of the compound $Na_2Ge_2O_5$. Measurement of the degree of hydrolysis of sodium metagermanate in dilute aqueous solution shows that germanic is appreciably stronger than silicic acid. *Barium metagermanate*, obtained by precipitation from sodium metagermanate, has the composition $BaGeO_3,5H_2O$ after remaining for some hours in contact with the solution. A basic *copper* salt, $2CuO,GeO_2,H_2O$, is described. H. WREN.

Various modifications of ammonia. L. TRONSTAD (Z. physikal. Chem., 1929, **B**, **5**, 365—367).—The differences of behaviour exhibited by the two modifications of ammonia postulated by Baly and Duncan (J.C.S., 1922, **121**, 1008) are, by analogy with recent observations on ortho- and para-hydrogen, not necessarily due to variations of reactivity, but to differences of specific heat and heat conductivity. H. F. GILLBE.

Double sulphates of bismuth with alkali metals. II. Double sulphates of bismuth and ammonium. V. CAGLIOTI and L. MALOSSI (Atti R. Accad. Lincei, 1929, [vi], **10**, 97—100; cf. A., 1927, 951).—When ammonium sulphate solution is added to a concentrated solution of bismuth nitrate containing nitric acid in the proportions required to give the 1 : 1 and 1 : 3 bismuth ammonium double sulphates the compound $Bi_2(SO_4)_3,(NH_4)_2SO_4$ slowly crystallises out. In a study of the system $Bi_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 25°, however, this compound was not found. Only one perfectly anhydrous compound is formed, viz., $(NH_4)_3Bi(SO_4)_3$. O. J. WALKER.

Action of certain dioxides on very dilute aqueous solutions of [potassium] permanganate. G. RAPIN (Compt. rend., 1929, **189**, 699—701).—The powdered dioxides of manganese, lead, or tin decompose dilute solutions (of the order of 1 g. per litre) of potassium permanganate in mutually similar fashion, very rapidly at first, and then much more slowly. The rate is proportional to the weight of dioxide added, and is increased by rise in temperature; addition of acid increases, or of alkali decreases it. It further varies with the physical and chemical nature of the dioxide. As no evolution of gas occurs, the action is attributed to the oxide passing into colloidal solution. Calcined alumina, being completely insoluble, is without action. C. A. SILBERRAD.

Preparation of a gram of rhenium. J. NODDACK and W. NODDACK (Z. anorg. Chem., 1929, **183**, 353—375).—A gram of pure rhenium has been prepared from 660 kg. of Norwegian molybdenite having a rhenium content of $2—4\times10^{-6}$. Eight methods of separating rhenium from molybdenum were tested. In the method adopted the greater part of the molybdenum was removed by five successive treatments with disodium hydrogen phosphate in nitric acid solution, whereby molybdenum is precipitated as ammonium phosphomolybdate and the whole of the rhenium remains in the solution. After each treatment the molybdenum and rhenium remaining in the solution were precipitated as sulphides by the addition of yellow ammonium sulphide, followed by acidification with sulphuric acid, and the sulphides dissolved in nitric acid. The final product was reduced in hydrogen at 1000°, and nickel, copper, cobalt, and iron were eliminated by fusion of the reduced substance with sodium hydroxide and sodium nitrate, followed by washing with water. The sulphide precipitated from the filtrate now contained 1·9% of rhenium. It was reduced by hydrogen and the easily volatile oxide Re_2O_8 was distilled by heating in a stream of oxygen at 150°. The rhenium content in the reduced product was 93·5%. The final purification was effected by repeated reductions of the sulphide with hydrogen at 1000° followed by distillation in oxygen at 150°. The total impurities in the metallic rhenium finally obtained are estimated to be less than 10^{-4}. J. A. V. BUTLER.

Finely-divided iron of atomic dimensions. W. FRANKENBURGER and K. MAYRHOFER (Z. Elektrochem., 1929, **35**, 590—600; cf. Mittasch and Frankenburger, this vol., 282).—Extremely fine particles of iron may be deposited on the walls of a vessel, cooled by immersion in either liquid nitrogen or a pentane cold bath, by condensation of iron vapour obtained from an iron spiral, which is heated by means of an electric current, in an atmosphere of nitrogen the pressure of which is of the order of 0·1—0·01 mm. No evidence could be obtained of any combination occurring between the nitrogen and the iron under the conditions of experiment, but it occurred with hydrogen, when that gas in either the perfectly dry or wet state was substituted for the nitrogen. The effect of the presence of water was to tend to lower the hydrogen content of the particles to that required by the formula FeH_2. H. T. S. BRITTON.

Stability of iron-complexes. W. FRANKE (Annalen, 1929, **475**, 37—42).—An attempt has been made to obtain experimental evidence of the existence of the ferrous iron complexes regarded by Wieland and Franke (cf. this vol., 1398) as the cause of the iron activation phenomena in oxidation. Pyruvic acid and ferrous sulphate form a brown solution which has been examined colorimetrically under conditions of varying p_H value. The relative complex formation apparently diminishes with increasing p_H. Under the conditions of optimum acidity for autoxidation, p_H 4, about 70% of the complex present at p_H 6·5 remains, whilst at the p_H of a *M*/4 solution of the acid alone, *i.e.*, 1·5, nearly 20% is left. In the same way the stability of ferric iron–acetic acid and ferric iron–glycollic acid complexes was also examined. The stability of the former decreases with increasing acidity, and more rapidly than that of the ferrous iron–pyruvic acid complex. The maximum colour

effect in the ferric iron–glycollic acid solution is at p_H 1·5 and decreases with both increasing and decreasing acidity. This behaviour is probably to be ascribed to the existence of a complex acid.

M. S. BURR.

Formation of a carbide, Fe_2C, by reduction of iron oxide with carbon monoxide at a lower temperature. W. GLUUD, K. V. OTTO, and H. RITTER (Ber., 1929, **62**, [*B*], 2483—2485).—If ferric oxide is heated in a current of carbon monoxide at 275°, reduction to triferric tetroxide rapidly occurs followed by simultaneous deposition of carbon and formation of carbide. If the percentage of carbon is plotted against the time, a graph is obtained of which the latter portions are rectilinear, showing that deposition of carbon is proportional to the time and independent of the nature and amount of substrate. Extrapolation of the curve indicates the existence of a *carbide*, Fe_2C. Confirmation is found by study of the volatilisation of carbide carbon in hydrogen at 275°, which is arrested at a point when the loss of carbon corresponds exactly with the formula Fe_2C. If a decarbonised product is again treated with carbon monoxide for a shorter period than is required for the production of the carbide, Fe_2C, and then with hydrogen, almost exactly only the newly-added carbon is removed. If, however, more carbon is deposited than corresponds with the compound Fe_2C, only so much of it is volatilised as corresponds with Fe_2C.

The experimental results of Fischer and Bahr (Ges. Abhand. Kenntn. Kohle, **8**, 265) coincide with those of the authors, and, if their graphs are treated as indicated above, the existence of the carbide Fe_2C (instead of Fe_3C_4) is demonstrated.

H. WREN.

Oxidation and reduction of silicates of iron by gases. B. BOGITCH (Compt. rend., 1929, **189**, 581—583).—The method previously employed (this vol., 400) has been used to investigate the oxidising or reducing effects at 1300° of oxygen, nitrogen, carbon dioxide, carbon dioxide–monoxide mixtures, hydrogen, and illuminating gas (containing methane) on iron silicates. The colours of the silicates were found to vary in intensity with the percentage of iron (0·1—10%), but it is considered that they are made up of combinations in varying proportions of the two yellow and two blue silicates. There are no silicates corresponding with the oxides Fe_2O_3 or Fe_3O_4, but one of the blue compounds corresponds with a suboxide.

J. GRANT.

Aquopentammino- and diaquotetrammino-cobaltic sulphates. F. JOB and L. O. TAO (Compt. rend., 1929, **189**, 641—642).—Examination by Schreinemakers' method of a solution of aquopentamminocobaltic sulphate to which sulphuric acid has been added shows that for concentrations of 0—0·5 mol. of acid per litre the solid phase is the salt itself, and for 2—4·5 mols. of acid per litre it is $[Co(NH_3)_5H_2O](SO_4),HSO_4,H_2O$ in the cold and at 56° $[CO(NH_3)_5SO_4]HSO_4,2H_2O$. For other concentrations the tie-lines are not concurrent, although nearly so for concentrations of 4·5—8·5 mols. of acid per litre. A similar method applied to diaquotetrammino-cobaltic sulphate indicates the formation at the ordinary temperature of the salts

$$[Co(NH_3)_5(H_2O)_2]_2(SO_4)_3,2{\cdot}5H_2O,$$
$$[Co(NH_3)_4(H_2O)_2]_7(SO_4)_{10}HSO_4, \text{ and}$$
$$[Co(NH_3)_4(H_2O)_2](SO_4)HSO_4.$$

C. A. SILBERRAD.

New cobaltites of the spinel type. S. HOLGERSSON and A. KARLSSON (Z. anorg. Chem., 1929, **183**, 384—394).—A series of cobaltites of the type RO,Co_2O_3 (where R is Cu, Mg, Zn, Mn, Ni) has been prepared by mixing solutions of cobalt nitrate and the nitrate of the metal, evaporating to dryness, and heating the product to 800—850°. The *X*-ray spectra of the products, examined by the Debye–Scherrer method, were all of the spinel type. The unit cell contains eight molecules. The oxide Co_3O_4 prepared in three different ways gave similar spectra and is therefore CoO,Co_2O_3. It is possible that some mixed crystal formation occurs; *e.g.*, in manganese cobaltite the bivalent manganese may be partly replaced by bivalent cobalt and tervalent cobalt by tervalent manganese, giving $(Mn,Co)O,(Mn,Co)_2O_3$.

J. A. V. BUTLER.

Double salts. XVIII. Ammino-oxalates. G. SPACU and O. VOICU (Bul. Soc. Stiinte Cluj, 1928, **4**, 154—164; Chem. Zentr., 1929, i, 3080).—The following complex salts are described:

$$K_2[Ni(C_2O_4)_2(H_2O)_2],H_2O;$$
$$K_2[Ni(C_2O_4)_2(C_6H_5{\cdot}CH_2{\cdot}NH_2)_2],2H_2O;$$
$$K_2Ni(C_2O_4)_2\ en_3,3H_2O;\quad K_2[Co(C_2O_4)_2(H_2O)_2],4H_2O;$$
$$K_2[Co(C_2O_4)_2(C_6H_5{\cdot}CH_2{\cdot}NH_2)_2],2H_2O.$$

A. A. ELDRIDGE.

Double salts. XIX. Ammines of double bromides. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1928, **4**, 187—210; Chem. Zentr., 1929, i, 3080—3081).—Three groups of *compounds* were differentiated according to the solvents used in their preparation: (1) The compounds (Bzd=benzidine) $[MnBzd_6][SnBr_6],2H_2O$; $[NiBzd_6][SnBr_6],8$ or $4H_2O$; $[CoBzd_6][SnBr_6],4H_2O$; (2) the compounds

$$[MnBzd_5(COMe_2)][SnBr_6],2H_2O;$$
$$[NiBzd_5(COMe_2)][SnBr_6],8H_2O;$$
$$[CoBzd_5(COMe_2)],6H_2O;$$

(3) $[NiBzd_5(C_5H_5N)][SnBr_6],8H_2O$;

$$[MnBzd_5(C_5H_5N)][SnBr_5(OH)];$$
$$[CoBzd_5(C_5H_5N)][SnBr_5(OH)],5H_2O;$$
$$[NiBzd_5(C_5H_5N)][SnBr_5(OH)],4H_2O.$$

A. A. ELDRIDGE.

Applications and limits of emission spectrographic analysis. G. SCHEIBE (Z. angew. Chem., 1929, **42**, 1017—1022).—The principles and practice of the quantitative spectrographic analysis of alloys are discussed, and the special value of this method for ascertaining the purity of metallic copper, lead, zinc, aluminium, and magnesium is emphasised.

H. F. HARWOOD.

Segregation of analysed samples. G. F. SMITH, L. V. HARDY, and E. L. GARD (Ind. Eng. Chem. [Anal.], 1929, **1**, 228—230).—Mixtures of arsenic trioxide with mercuric oxide or potassium sulphate, ferric oxide and silica, and ferrosoferric oxide and magnesia were filled into a brass column and subjected to mechanical jarring for 90 hrs.; in the last case the difference in density was artificially augmented by means of an electromagnet. Samples

taken from different parts of the column were then analysed. The results indicate that mixtures of materials of different densities if once mixed to uniformity following grinding to pass a 200-mesh sieve cannot be segregated by jarring or storage under vibration, irrespective of the actual densities of the components. Hence in referee analyses of supposedly identical samples if different analysts disagree the fault cannot be ascribed to segregation of the samples, provided that these have been ground to pass a 200-mesh sieve. H. F. HARWOOD.

Extension of methods of gravimetric analysis. L. MOSER (Monatsh., 1929, 53 and 54, 39—47).—A *résumé* of the following methods, which have been applied by the author and his co-workers to the determination of metals during the past 10 years. (1) Temporary hydrolysis (cf. A., 1923, ii, 438), (2) repression of hydrolysis (A., 1922, ii, 315), (3) formation of sparingly soluble adsorption compounds with tannic acid, (4) formation of complexes with sulphosalicylic acid (A., 1925, ii, 329), and (5) thermal dissociation of ammonium halides (A., 1926, 814; 1927, 435). H. BURTON.

Determination of dilute aqueous solutions of "argyrol" by photographic nephelometry. F. RIMATTEI (J. Pharm. Chim., 1929, [viii], 10, 349—363).—An apparatus for the nephelometric determination by photographic means of very dilute colloidal solutions, *e.g.*, "argyrol," is described. Monochromatic light is used and is usually produced by passing a beam from an electric arc through a green filter (Wratten 74 E), exposures being made on Lumière orthochromatic plates. The determinations may be made either by the nephelometry of absorption or of diffusion, the latter being the more sensitive; both methods are considerably more accurate than visual nephelometry. The difference in the density of the deposit on the photographic plate, produced by light passing through solutions of different titre, can be easily seen by the unassisted eye, whereas no difference can be detected in the solutions themselves. A "metoquinone" developer is used, the time of development varying from 10 to 15 min. The results obtained by the more accurate nephelometric diffusion method agree with those obtained by weight to within 4%, using aqueous solutions of argyrol containing between 1 and 2 mg. per litre. P. G. MARSHALL.

Measurement of hydrogen-ion concentration in unbuffered solutions. I. Adsorbent properties of platinised platinum. I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1929, 51, 2888—2900).—The adsorption capabilities of platinised platinum in various salt solutions were investigated. In a hydrogen atmosphere the cation is adsorbed from a neutral salt solution and an equivalent amount of free acid is formed in the solution (cf. Frumkin and Donde, A., 1927, 1021). Zinc sulphate solutions, in an atmosphere of hydrogen, increased in acidity to an extent equivalent to the amount of zinc adsorbed by the platinum. Ammonium chloride likewise became slightly acid, but in oxygen such solutions became very distinctly acid, and the acidity increased the longer the oxygen was passed. This is attributed to the formation of hexa-aquoplatinic acid, which reacts with the ammonium ions present: $H_2Pt(OH)_6+2NH_4^{\cdot}\longrightarrow(NH_4)_2Pt(OH)_6+2H^{\cdot}$. Similar results were obtained with trimethylammonium and potassium chlorides. No acid adsorption from hydrochloric acid occurs in a hydrogen atmosphere, but in an oxygen atmosphere there is equivalent adsorption of hydrogen and chlorine ions. Sodium hydroxide is strongly adsorbed in a hydrogen atmosphere; maximum adsorption occurs at a concentration of 0·0007*N*. This adsorption is increased by addition of sodium chloride and in presence of large amounts of the latter the maximum disappears. In the presence of oxygen the hexa-aquoplatinic acid formed neutralises some of the alkali and only apparent adsorption of the latter, therefore, takes place. S. K. TWEEDY.

Application of differential potentiometric titration to the determination of weak acids in dilute solution. B. L. CLARKE and L. A. WOOTEN (J. Physical Chem., 1929, 33, 1468—1480).—An apparatus and method for the differential potentiometric titration of weak acids in concentrations of the order 0·0004*N* are described. The theory of the method is developed and methods for determining the end-point are deduced. Data for 0·0004*N*-acetic acid titrated with 0·001*N*-barium hydroxide are given. No indication of a second end-point in the presence of quinhydrone such as that observed by MacInnes and Jones (A., 1927, 35) has been observed. L. S. THEOBALD.

Indicators. XVI. Sensitivity and stability of phthaleins and sulphonephthaleins to alkali. A. THIEL (Monatsh., 1929, 53 and 54, 1008—1013).—Comparison of a series of analogous phthaleins and sulphonephthaleins shows that the latter are the more stable at 18—20°; the velocity coefficients for decolorisation (cf. this vol., 445) are in the ratio of about 1000 : 1. In general, the sulpho-derivatives are also more sensitive; this is probably due to the existence of a secondary lactonic ion (cf. *loc. cit.*). The absorption maxima (lower limiting curve) of the sulphonephthaleins are about 5—10 mμ greater than for the analogous phthaleins. H. BURTON.

Determination of hydroxide and carbonate in solutions. J. LINDER.—See B., 1929, 895.

Determination of chlorine and carbonyl chloride in mixtures. S. PLETNEV (Lab. Praktika, 1928, 4, No. 2).—The free chlorine is determined in one sample with potassium iodide solution, and the total chlorine is determined in another sample which is collected in sodium hydroxide solution and treated with arsenious oxide and sodium carbonate. CHEMICAL ABSTRACTS.

Micro-determination of iodine in organic material. J. F. REITH (Pharm. Weekblad, 1929, 66, 829—845; cf. this vol., 337).—The limits of sensitiveness in micro-determinations of free iodine in aqueous solutions are indicated for various conditions, and the effects of foreign ions are examined. The benzene method is not sufficiently sensitive for general use. Very good results are obtained by oxidation to iodate by means of bromine, and subsequent titration with thiosulphate of iodine liberated by the iodate;

the presence of bromides interferes seriously. Nitrites must first be destroyed by means of sodium azide. The colorimetric determination of a chloroform extract is very suitable for small quantities, but laborious, and much affected by foreign ions. A colorimetric method based on oxidation to iodate, liberation of iodine by this, and addition of starch is also very accurate. For determination of iodine in potable and other waters, 0·5—3 litres after addition of about 2 c.c. of saturated potassium hydroxide solution are evaporated to 50 c.c., filtered, and the solution evaporated to dryness with potassium nitrate. The residue is ignited, taken up in water, and the filtration, evaporation, and ignition are repeated. The white residue is extracted with alcohol, the extract evaporated, and iodine determined in the residue by the bromine oxidation method. The necessary precautions are described in detail. Methods of determination for soils are discussed. For urine, it is recommended to ignite the evaporation residue with a mixture of potassium nitrate and carbonate; nitrite is destroyed before the determination of iodine in the final mass. S. I. LEVY.

Stabilised starch indicator. M. S. NICHOLS (Ind. Eng. Chem. [Anal.], 1929, **1**, 215).—50 G. of potato starch, mixed to a thin paste with 250 c.c. of cold water, are added gradually to 20 litres of boiling water, and the solution is boiled with continual stirring for a further 15 min. After partial cooling, 25 g. of salicylic acid are added, and dissolved by stirring. The reagent thus prepared keeps almost indefinitely, even although exposed to air, and is very sensitive. 2 C.c. are required for a 200 c.c. titration. H. F. HARWOOD.

Titration of soluble iodides in colloidal silver iodide. R. B. SMITH and W. G. CHRISTIANSEN.—See B., 1929, 909.

Reduction reactions with calcium hydride. I. Rapid determination of sulphur in insoluble sulphates. W. F. CALDWELL with F. C. KRAUSKOPF (J. Amer. Chem. Soc., 1929, **51**, 2936—2942).—Heating with calcium carbide will not quantitatively reduce sulphates to sulphides. By observing certain precautions non-volatile sulphur compounds free from metals which form acid-insoluble sulphides may be quantitatively reduced to sulphides by fusion with calcium hydride; the sulphur may be determined in the fused mass by iodometric titration: $MSO_4+2CaH_2=MS+2CaO+2H_2O$; $MSO_4+4CaH_2=MS+4CaO+4H_2$; $CaH_2 \rightleftharpoons Ca+2H$; $MS+Ca=CaS+M$. With regard to the last two of these equations it was found that fusion of sodium thiosulphate with calcium hydride yields some metallic sodium. S. K. TWEEDY.

Potentiometric titration of sulphuric acid. S. LINDA and J. ETTINGER (Rocz. Chem., 1929, **9**, 504—522).—Sodium hydroxide solution and not acid should be used in the burette in the potentiometric titration of sulphuric acid, as the error due to carbon dioxide is thereby minimised, and the solution should be strongly agitated in order to reduce the time necessary for supervention of equilibrium. The disturbing influence of carbon dioxide is considerably less than in using calorimetric methods of titration, and the potentiometric method has the further advantage of permitting the accurate titration of 0·01*N*-solutions. Identical results are obtained using calomel or zero electrodes. It is of importance that the alkali solution be standardised under the same temperature conditions as are applied during titration. R. TRUSZKOWSKI.

New isomorphous series of fluorine compounds. H. CARON and L. VANBOCKSTAEL (J. Pharm. Chim., 1929, [viii], **10**, 301—308).—A more detailed account of work already reviewed (this vol., 526). Micro-methods for the detection of small quantities of sulphuric acid in hydrofluoric acid and of sulphuric acid and aluminium in hydrofluosilicic acid are given. A. A. GOLDBERG.

Turbidimetric determination of sulphate in chromium-plating baths. L. E. STOUT and A. W. PETCHAFT.—See B., 1929, 901.

Determination of sulphate in chromic acid and in chromium-plating baths. H. H. WILLARD and R. SCHNEIDEWIND.—See B., 1929, 895.

Determination of small quantities of selenium in ores. E. T. ERICKSON.—See B., 1929, 899.

Rapid determination of nitrogen. F. M. WIENINGER and M. LINDEMANN.—See B., 1929, 939.

Micro-determination of nitrates and nitrites. K. WOIDICH (Oesterr. Chem.-Ztg., 1929, **32**, 183).—Devarda's reduction method has been adapted for micro-chemical purposes, a determination requiring only 20 min. A special form of apparatus used for the reduction and distillation is described, the ammonia formed being collected in 0·02*N*-sulphuric acid, and titrated with 0·02*N*-sodium hydroxide. In the determination of nitrates and nitrites in water, the total ammonia formed by reduction is collected in water and determined colorimetrically in the usual way, the nitrite being subsequently determined colorimetrically in a separate sample. H. F. HARWOOD.

Molybdenum-blue method for micro-determination of phosphate and arsenate ions. G. DENIGÈS.—See B., 1929, 939.

Determination of carbon dioxide in gases containing acetylene. H. FRIEDRICH.—See B., 1929, 877.

Determination of alkalis in minerals by the interferometer. G. BURGER (Monatsh., 1929, **53** and **54**, 985—988).—Using Löwe's interferometer with distilled water as a comparison liquid the curve for the system 4% sodium chloride–4% potassium chloride has been determined. The minerals studied (potash felspar, sanidine, natrolite, deep-sea earth, and kainite) are ignited with ammonium chloride and calcium carbonate, the calcium is removed as carbonate or oxalate, and the residue ignited repeatedly with small amounts of hydrochloric acid (if sulphate is present this is removed as barium sulphate). The dry residue is dissolved in water to a 4% solution and its composition determined gravimetrically and interferometrically. The two sets of values are in good agreement. H. BURTON.

Determination of true sodium content of calcium carbonate intended for use in the Lawrence Smith method for alkalis. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1929, **1**, 191—192).—The usual method of weighing the residue obtained by extracting the calcium carbonate with water gives untrustworthy results. It is preferable to dissolve 2 g. of the material in hydrochloric acid, evaporate the solution to dryness, take up the residue with 2 to 3 c.c. of water, and determine the sodium directly by precipitation with magnesium uranyl acetate solution (this vol., 900). H. F. HARWOOD.

Determination of calcium and magnesium in aluminium containing other alloying elements. K. STEINHÄUSER.—See B., 1929, 899.

Rapid detection of the metals of group II: arsenic, antimony, tin, mercury, bismuth, lead, copper, and cadmium, by means of organic reagents. G. SENSI and S. SEGHEZZO (Annali Chim. Appl., 1929, **19**, 392—396).—For separating the sulphides of the metals of group II, a reagent prepared by adding 10 g. of sodium hydroxide to 100 c.c. of 20% sodium sulphide solution free from sulphates is recommended. The separate metals may then be detected by organic reagents. T. H. POPE.

Use of phenolic acids in the detection, separation, and determination of metals. I. Separation of 2A group (analytical) metals. P. N. DAS-GUPTA (J. Indian Chem. Soc., 1929, **6**, 627—633).—The action of tannic, gallic, and 2 : 4-dihydroxybenzoic acids on the nitrates, chlorides, acetates, and sulphates of the metals of group 2A has been studied, and, as a result, alternative methods for the qualitative separation of the metals, using gallic acid when the metals are first precipitated as sulphides, and 2 : 4-dihydroxybenzoic acid when precipitation of sulphides is unnecessary, have been devised. These methods are based on the following experimental data: (1) in dilute nitric acid solution gallic acid completely precipitates bismuth, whilst lead, copper, and cadmium are unaffected; (2) in neutral or faintly acid (nitric) solution gallic acid and sodium acetate precipitate lead and copper completely; (3) in neutral or dilute nitric acid solution hydrogen peroxide and ammonia precipitate lead completely, whilst copper remains in solution; (4) in dilute nitric acid solution of the metals 2 : 4-dihydroxybenzoic acid precipitates completely mercury alone of all the group, the remaining metals then being separable by (1), (2), and (3). M. S. BURR.

[Use of hexamethylenetetramine in] micro-chemical analysis. I. M. KORENMAN (Pharm. Zentr., 1929, **70**, 709—714; cf. this vol., 286).—A 10% solution of hexamethylenetetramine yields crystalline precipitates with many phenols, such as resorcinol and pyrogallol; 0·0003 mg. of the latter may thus be detected under the microscope. A mixture of hexamethylenetetramine with an equimolecular amount of ammonium thiocyanate, potassium bromide, or potassium iodide forms a more sensitive reagent for the micro-chemical detection of the heavy metals than hexamethylenetetramine alone, the iodide mixture giving the best results. This reagent is especially sensitive for antimony and bismuth, somewhat less so for mercury, lead, copper, cadmium, and tin. Oxidising agents must be absent, as these cause precipitation of periodides of hexamethylenetetramine. H. F. HARWOOD.

Detection of heavy metals by means of "dithizone" (diphenylthiocarbazone). H. FISCHER (Z. angew. Chem., 1929, **42**, 1025—1027).—Dithizone forms coloured complex compounds with many metals, all of which, except manganese and the metals of the eighth group, belong to the sub-groups of the periodic classification. These compounds are characterised by insolubility in water and ammonia solution, and ready solubility in many organic solvents such as carbon tetrachloride and carbon disulphide (except in the case of the silver and gold compounds). Dithizone is soluble in carbon tetrachloride or disulphide to a bright green solution, and if a very dilute solution of the reagent be shaken with an almost neutral aqueous solution of one of the above metals a sharp change of colour in the non-aqueous layer results; 0·001 mg. of metal per c.c. of solution can thus be detected. The metal may be identified by comparison of the colour produced with that of known standards. Owing to the varying affinities of the metals for the reagent, it is possible to detect certain metals in the presence of others, *e.g.*, silver in presence of all other metals except gold, mercury, and the platinum metals, and zinc in presence of iron, cobalt, and nickel. Addition of an excess of potassium cyanide to the aqueous solutions of the metals prevents the reaction with dithizone except in the case of lead and tin. Traces of cobalt in presence of nickel may be detected by the addition of a very dilute ammoniacal solution of the reagent to a similar solution of the two metals; if cobalt be present an intense reddish-violet coloration results. H. F. HARWOOD.

Determination of zinc. G. SPACU and J. DICK (Bul. Soc. Stiinte Cluj, 1928, **4**, 177—181; Chem. Zentr., 1929, i, 2905).—A modification (cf. A., 1928, 608) consists in weighing the complex salt $[Zn(C_5H_5N)_2](SCN)_2$ after washing it with alcohol or ether and drying it in a vacuum. A. A. ELDRIDGE.

Rapid gravimetric determination of cadmium as oxalate. J. DICK (Z. anal. Chem., 1929, **78**, 414—417).—The cadmium is precipitated by the addition of a slight excess of ammonium oxalate to the cold, neutral solution of the sulphate or nitrate, followed by one third the volume of 95% alcohol. After 15 min. the precipitate is filtered, and washed successively with 50% alcohol, 95% alcohol, and ether. It is then dried for 2 to 3 min. in a vacuum and weighed as $CdC_2O_4,3H_2O$. The method is not available in the presence of alkalis, chlorides, or large amounts of ammonium salts. H. F. HARWOOD.

Cadmium as reducing agent in chemical analysis. H. EGNÉR (Svensk Kem. Tidskr., 1929, **41**, 240—243).—The use of electrolytically prepared cadmium as a reducing agent in quantitative analysis is advocated, and a suitable form of reductor is described. Cadmium offers the advantages over zinc that reduction takes place readily in the cold and is complete after a few minutes, and the quantity

of reducing agent required is much less than when zinc is used. The following procedure is recommended for the determination of phosphoric acid. The phosphoric acid is precipitated by Lorenz' method (A., 1901, ii, 278), filtered through a glass filter crucible, washed with a sulphuric acid solution of ammonium sulphate, and redissolved in ammonia. An excess of sulphuric acid is added, and the solution passed through the reductor and received in a solution containing iron alum and sulphuric and phosphoric acids which prevents reoxidation of the reduced molybdenum. The liquid is then titrated with permanganate solution which has been standardised against a pure phosphate. H. F. HARWOOD.

Micro-chemical reactions of salts of certain heavy metals. I. M. KORENMAN (Pharm. Zentr., 1929, **70**, 693—695).—Meurice's test for cadmium with potassium bromide and brucine sulphate (A., 1926, 703) has been applied to the micro-chemical detection of that element, and the action of the reagents on other heavy metals investigated. Cadmium, mercury, bismuth, and antimony salts all yield characteristic crystalline precipitates under the microscope, and 0·0003—0·0005 mg. of these metals may thus be detected; metals which form insoluble sulphates or bromides and substances which react with brucine sulphate, such as nitrous acid or potassium hydroxide, must be absent. H. F. HARWOOD.

Rapid determination of lead. P. F. THOMPSON. —See B., 1929, 943.

Gravimetric macro- and micro-chemical determination of copper. G. SPACU and G. SUCIU (Z. anal. Chem., 1929, **78**, 329—334).—The complex compound $[HgI_4](Cu\ en_2)$ which has been previously utilised for the determination of mercury (cf. this vol., 901) may also be employed in the determination of copper. The copper solution is neutralised with ethylenediamine, and a slight excess is added, together with 2 g. of ammonium thiocyanate and 2 g. of potassium iodide. The solution is heated to boiling and the copper precipitated with a hot, concentrated solution of potassium mercuric iodide. The whole is kept until cold, being frequently stirred meanwhile, the precipitate transferred to a Gooch crucible with a dilute solution of the precipitants, washed with alcohol and ether, and dried for 10 min. in a vacuum. The method gives excellent results in the micro-chemical determination of copper, as the final precipitate contains only 7·127% of the metal.

H. F. HARWOOD.

Potentiometric titration of mercurous ion with ammonium oxalate and its application to the determination of chromate. C. MAYR and G. BURGER (Monatsh., 1929, **53** and **54**, 493—497).—Electrometric titration of mercurous nitrate with ammonium oxalate in presence of metallic mercury gives values which are in good agreement with the electrolytic measurements. The titration is not sharp if the acid or salt (*e.g.*, sodium nitrate) concentrations are too large. For the determination of chromate the neutral chromate solution is treated with an excess of slightly acid mercurous nitrate solution, whereby the basic salt, $HgO,6Hg_2CrO_4$, is precipitated (cf. Fichter and Oesterheld, A., 1912, ii, 766). The mercurous ions remaining in the filtrate are titrated potentiometrically. The results agree well with those determined gravimetrically. The application of the method to the determination of chromium in a chrome-iron mineral is described. H. BURTON.

Determination of mercuric iodide by iodate reactions. F. G. BROCKMAN.—See B., 1929, 909.

Titration of mercurial preparations used in pharmacy. A. WØHLK.—See B., 1929, 957.

Determination of aluminium in plants. I. Use of aurintricarboxylic acid for the colorimetric determination of aluminium. O. B. WINTER, W. E. THRUN, and O. D. BIRD (J. Amer. Chem. Soc., 1929, **51**, 2721—2731).—The colorimetric determination of aluminium by means of aurintricarboxylic acid has been modified so that samples containing 0·005—0·07 mg. of aluminium may be compared against the same standard, the amount of aluminium present being read directly from a curve. The maximum colour intensity is attained when the p_H of the solution is 4; the p_H is advantageously controlled by the use of ammonium acetate and chloride as buffers. The excess of the dye is preferably decolorised by addition of ammonium carbonate.

S. K. TWEEDY.

Detection of aluminium, iron, chromium, manganese, zinc, nickel, and cobalt with organic reagents. Application to systematic qualitative analysis. G. SENSI and R. TESTORI (Annali Chim. Appl., 1929, **19**, 383—391).—The reactions of the following metals with organic reagents are summarised: Iron. Chromium: the salt is oxidised to chromate, which, in presence of free hydrochloric acid, gives a violet-red coloration with a reagent made by dissolving 2 g. of diphenylcarbazide in 10 g. of glacial acetic acid and making up to 200 c.c. with 90% alcohol. Aluminium: the solution is treated with one fifth of its volume of 1% alcoholic commercial alizarin solution, then made alkaline with ammonia, heated, and allowed to cool; formation of a red lake, insoluble in dilute acetic acid, indicates aluminium. Manganese: the very dilute solution is treated with alkali and a few drops of a solution of benzidine in 50% acetic acid; a deep blue coloration, disappearing on shaking and reappearing on addition of further reagent, and so on, indicates manganese. Cobalt gives a similar colour, but only in very concentrated solutions. Zinc: addition of alcoholic resorcinol solution to a slightly ammoniacal zinc solution gives a straw-yellow coloration, changing in turn to golden yellow, brownish-yellow, olive-green, and deep opaque blue, slowly in the cold, but rapidly on heating. Addition of a zinc salt solution to alkaline uric acid solution (5 g. of potassium hydroxide and 2 g. of uric acid in 100 c.c. of water) gives a gelatinous white precipitate which, after separation, turns greenish-blue in the air and light or when dusted with potassium persulphate. Nickel: Feigl's modification (Z. anal. Chem., 1925, **66**, 176) of Tschugaev's reaction is recommended. Cobalt: the acid solution, mixed with ammonium thiocyanate solution, is treated with a few c.c. of concentrated aqueous ammonium acetate solution and then, drop by drop, with 5% tartaric acid solution, which destroys the red coloration of ferric

thiocyanate; when the liquid is then shaken with amyl alcohol, the latter becomes blue if cobalt is present. Nickel, cobalt, and zinc together may be detected by Feigl and Tustanowska's procedure (Z. anal. Chem., 1925, **66**, 177). T. H. POPE.

Volumetric determination of manganese as dioxide. I. M. KOLTHOFF and E. B. SANDELL (Ind. Eng. Chem. [Anal.], 1929, **1**, 181—185).—Von Knorre's persulphate method for the determination of manganese has been examined, and the following procedure is recommended. To 50 c.c. of solution containing 20—100 mg. of manganese, and from 1 to 30 times this quantity of iron, sufficient sulphuric acid is added to make the acid concentration 0·5—1*N*. After addition of 3—4 g. of potassium persulphate the whole is boiled for 10 min.; if much iron is present a further quantity of persulphate must be added, and the boiling prolonged for 15 min. more. The liquid is filtered, the precipitate washed free from persulphate, and the manganese dioxide present determined either iodometrically or with ferrous sulphate and permanganate. To obtain correct results the figures obtained must be multiplied by an empirical factor, 1·024. A better method consists in substituting potassium bromate for the persulphate. In the absence of zinc or iron the results are from 3 to 5% low, but in the presence of an amount of iron from 1 to 70 times that of the manganese correct results are afforded by multiplying the percentages obtained by 1·01. Chromium, cobalt and small amounts of nickel, lead, and bismuth do not affect the method, but molybdenum, tungsten, and large quantities of phosphoric acid interfere. The method is not suitable for the determination of small amounts of manganese in presence of a large excess of iron, hence if a steel is under examination the iron should be previously removed by means of zinc oxide.

H. F. HARWOOD.

Di*iso*nitrosoacetone as a sensitive reagent for ferrous iron. J. DUBSKÝ and M. KURAŠ (Chem. Listy, 1929, **23**, 496).—1 C.c. of a 1% alcoholic solution of di*iso*nitrosoacetone added to 5 c.c. of a ferrous salt solution gives an intense blue coloration with more concentrated solutions of iron, and a violet-rose coloration with very dilute ferrous salt solutions. The colour develops 2 hrs. after addition of the reagent to $N/10^5$ solutions, and 3 hrs. after addition to $N/10^6$ solutions. This reagent may also be used for the detection of ferric iron, which should previously be reduced by alkaline hydrazine. The reaction is weakened by the presence of manganese, and inhibited in the presence of nickel or cobalt. The reagent is more sensitive than those of Slavikov [Slawik] (A., 1912, ii, 299) or of Tschugaev and Orelkin (A., 1915, ii, 489), which are not sensitive to concentrations of less than $N/10^4$ of ferrous iron.

R. TRUSZKOWSKI.

Sensitivity of some colorimetric reactions as determined by an electrochemical method. H. FRITZ (Z. anal. Chem., 1929, **78**, 418—427).—The sensitivity of various colorimetric reactions of iron, nickel, copper, and silver has been determined by an electrochemical method. A wire of the metal under examination was employed as anode in contact with a revolving cylinder of paper soaked in a solution of the reagent; a thermionic valve and suitable circuit served to regulate the current. The method may be utilised conversely for the colorimetric determination of the strength of weak currents (0·01—5 milliamp.) and for the determination of the periodicity of alternating currents of low frequencies.

H. F. HARWOOD.

Determination of cobalt by titration of [the precipitate of] potassium cobaltinitrite. A. A. VASSILIEV (Z. anal. Chem., 1929, **78**, 439—442).—The glass filter crucible containing the washed precipitate is placed in a 600-c.c. flask, and 250 c.c. of water, 50 c.c. of 0·1*N*-permanganate, and 35 c.c. of 50% sulphuric acid are added in the order named. The whole is heated at 50° for 30—40 min. until the precipitate is completely decomposed. The solution is cooled, 2—3 g. of potassium iodide are added, and the flask is stoppered and shaken until all the manganese dioxide has redissolved, when the liberated iodine is titrated with 0·1*N*-thiosulphate. The cobalt present may be calculated from the formula Co=(c.c. of 0·1*N*-permanganate−c.c. of 0·1*N*-thiosulphate)× 0·0005361. H. F. HARWOOD.

Colorimetric determination of cobalt. W. HEINZ (Z. anal. Chem., 1929, **78**, 427—439).—The various methods for the colorimetric determination of cobalt have been studied, a Duboscq colorimeter being employed for the purpose, and the results obtained are tabulated. H. F. HARWOOD.

Phenylthiohydantoic acid for determination and separation of cobalt. V. CUVELIER (Natuurwetensch. Tijds., 1929, **11**, 131—150).—In order to test the accuracy of the determination, electrolytic cobalt, containing less than 0·02% of lead, was employed in a series of tests, which showed errors of the order of 0·1—0·2% on quantities of 1—200 mg. The precipitate is ignited at a temperature not exceeding 650°, the residue taken up in the minimum quantity of concentrated hydrochloric acid, sulphuric acid added, the whole dried carefully and then ignited, the temperature being raised gradually to 550°; the anhydrous sulphate is cooled and weighed with precautions to prevent access of moisture. The conclusion of Willard and Hall (A., 1922, ii, 874, 875) that in the presence of iron small quantities of that metal are carried down in the precipitate is confirmed, but the amount may be reduced by boiling the finely divided precipitate with concentrated hydrochloric acid. A procedure is described whereby in the precipitation of 25 mg. of cobalt in presence of 1 g. of iron, only 1·4 mg. of the latter is left with the cobalt. Nickel if present is best separated by means of dimethylglyoxime before precipitation of cobalt; no other metals interfere if the procedure is suitably modified. S. I. LEVY.

Cyanates. VI. Detection of cobalt. Test for cobalt in presence of iron. R. RIPAN (Bul. Soc. Stiinte Cluj, 1928, **4**, 144—154; Chem. Zentr., 1929, i, 2905).—The following salts have been prepared:

$[Ni(C_5H_5N)_4](NCO)_2$, $K_2[Co(NCO)_4]$,
$[Zn(C_5H_5N)_2](NCO)_2$, $[Cu(C_6H_7N)_2](NCO)_2$,
$[Cu(C_{14}H_{15}N)_2](NCO)_2$, $K[Cd(NCO)_3]$,
$[Cd(C_5H_5N)_2](NCO)_2$. The formation of the blue salt $K_2Co(NCO)_4$ from a solution of a cobalt salt,

potassium cyanate, and a drop of acetic acid in presence of acetone permits the detection of 0·02 mg. of cobalt. Iron is precipitated by hot potassium cyanate solution, whilst cobalt remains dissolved if ammonium salts are present. A. A. ELDRIDGE.

Rapid potentiometric determination of nickel. T. HECZKO (Z. anal. Chem., 1929, **78**, 325—329).—4 G. of citric or tartaric acid are added to the nickel solution, followed by an excess of ammonia and a little ammonium nitrate or chloride. The solution is then titrated with 0·4*N*-potassium cyanide, a silver wire immersed in a mixture of potassium iodide and silver nitrate solutions in an Emich filter tube being employed as comparison electrode. The solution must be kept well stirred during the titration. Iron and manganese do not influence the results, but tervalent chromium must be absent.

H. F. HARWOOD.

Determination of uranium and thorium with 8-hydroxyquinoline. F. HECHT and W. REICH-ROHRWIG (Monatsh., 1929, **53** and **54**, 596—606).—When soluble uranyl salts are treated with 8-hydroxyquinoline in approximately neutral media the sparingly soluble, non-hygroscopic *compound* $UO_2(C_9H_6ON)_2,C_9H_7ON$ is precipitated. The hydroxyquinoline content of this is determined by bromide–bromate titration and the metal as U_3O_8 by igniting with oxalic acid. In presence of acetic acid (5—10%) an excess of 8-hydroxyquinoline must be used to ensure complete precipitation of the complex. Any mineral acid present is removed by ammonium (not sodium) acetate. The method can be used for the determination of small amounts of uranium. The compound $Th(C_9H_6ON)_4$ exists in hydrated and anhydrous forms. Dehydration is best carried out at 160—170°. Precipitation of the thorium complex is quantitative only in dilute acetic acid solution. The thorium solution is treated with sodium or ammonium acetate, neutralised to phenol-red, and treated at 50° with twice the calculated amount of 8-hydroxyquinoline in dilute acetic acid to give a concentration of 2—4% of acetic acid. The mixture is heated to 70° and then treated with 2*N*-sodium hydroxide to give an acetic acid concentration of 0·3%. The complex is filtered and washed with alcohol (water causes hydrolysis); the anhydrous form is obtained. The method can be used for the determination of small amounts. H. BURTON.

Thermoelectric temperature scales. W. F. ROESER (Bur. Stand. J. Res., 1929, **3**, 343—358).—The differences between four thermoelectric temperature scales based on the m. p. of (*a*) antimony, silver, and gold, (*b*) zinc, antimony, silver, and gold, (*c*) zinc, aluminium, and copper, and (*d*) zinc, antimony, and copper as calibration points have been determined. The maximum difference between (*a*) and (*b*) was 0·1°, between (*a*) and (*c*) 0·2°, and between (*a*) and (*d*) 0·3°. Any one of these temperature scales is reproducible to within 0·1°. The f. p. of the copper-silver eutectic alloy (71·9% Ag) was found to be 779·4°±0·1° and the difference between the m. p. of gold and copper 20°±0·1°. For calibrating thermocouples the following m. p. temperatures are recommended: copper 1083°, gold 1063°, silver 960·5°, aluminium (99·81%) 659·23°, antimony 630·52°, zinc 419·57°.

A. R. POWELL.

Laboratory apparatus for continuous circulation of liquids and vapours. R. S. HUGHES-DON, G. J. ROBERTSON, and J. READ (J.S.C.I., 1929, **48**, 263—264T).—Descriptions are given, with figures, of two types of circulatory apparatus which have been used in work on the catalytic hydrogenation and dehydrogenation of piperitone, menthone, *iso*-menthone, etc. (cf. J.C.S., 1923, **123**, 2924). The substance, in a thin liquid film or as vapour, is brought repeatedly into contact with the catalyst at a known temperature and in the presence of any desired gaseous medium. The action is continuous and automatic.

Dropping bottle for reagents. P. FUCHS (Z. anal. Chem., 1929, **78**, 411—414).—A simple form of dropping bottle, constructed on the siphon principle, is described. H. F. HARWOOD.

Accurate drop recorder. O. S. GIBBS (Science, 1929, **69**, 649—650).—An apparatus giving an accuracy of 600 drops per c.c. is described (cf. J. Lab. Clin. Med., 1927, **12**, 686). L. S. THEOBALD.

Simple method of providing a burette with an automatic zero adjustment. J. FISCH (Chem.-Ztg., 1929, **53**, 799).—The lower part of the burette is clamped to the neck of a stock bottle provided with a stopper bored with three holes into which pass the stem of a stoppered funnel for filling, a soda-lime tube, and a long tube passing from the bottom of the bottle above the top of the burette and bent in the shape of an inverted U so that the other limb passes through a stopper in the top of the burette. This stopper also carries a short tube terminating in a length of rubber tubing; by applying gentle suction to the latter the liquid is drawn up from the bottle into the burette. A. R. POWELL.

Burette clamp and holder. M. HOLLINGSWORTH (Ind. Eng. Chem. [Anal.], 1929, **1**, 233).—A new form of burette holder for use with burettes connected to stock bottles of volumetric solutions is described. H. F. HARWOOD.

Filtering vessel. J. MIKA (Z. anal. Chem., 1929, **78**, 334—340).—The special flask described is provided with a narrow side tube containing an asbestos filtering mat, resting on a platinum spiral. After carrying out a precipitation in the flask the precipitate may be collected and washed by connecting the side tube to a filter-pump; the flask and precipitate are finally weighed together after being dried.

H. F. HARWOOD.

Thermostat to work off A.C. mains. J. HUME (J. Opt. Soc. Amer., 1929, **19**, 158—161).—The thermostat and relay are figured and described. To expose a larger surface for heating or cooling the toluene tube is made zigzag; there is an improved method of adjustment to give the desired temperature. To reduce sparking in the thermoregulator a condenser of capacity 0·002 microfarad is inserted in parallel therewith. A thermostat thus constructed has worked continuously for 5 months with maximum variation of 0·001°. To construct a glass-fronted

metal tank pressure tubing is employed as a seal between the glass and the metal.

C. A. SILBERRAD.

Automatic regulation of temperatures up to 600° by means of a platinum resistance regulator. E. A. COOKE and J. C. SWALLOW (J. Sci. Instr., 1929, **6**, 287—293).—The change in temperature of the windings of a 15-ohm platinum wire, wound in the form of a resistance thermometer and forming one arm of a Wheatstone bridge in balance at the required temperature, destroys the balance and allows a current to operate a moving-coil relay which controls an additional heating current. A device to avoid sticking contacts is described. The accuracy is $\pm 0{\cdot}1$ at 350°, and $\pm 0{\cdot}2$ at 600°. J. GRANT.

Simple air thermometer. J. E. SHRADER (J. Opt. Soc. Amer., 1929, **19**, 162—163).—The instrument employs a short scale. The bulb is protected by being placed inside a metal reservoir which may be filled with steam or ice-packed; the reservoir has also an opening into which a constant-pressure thermometer may be placed for a simultaneous experiment therewith. C. A. SILBERRAD.

High vacuum technique. Effect of ionisation on pump speeds. C. T. KNIPP and P. C. LUDOLPH (J. Opt. Soc. Amer., 1929, **19**, 152—157).—Two new designs of mercury-vapour pumps with internal water cooling are figured and described, with details of their performance. It is also shown that the effect of ionisation of the air pumped is to increase the speed if the direction of flow of the electrons is with the air stream, or to decrease it if opposed thereto.

C. A. SILBERRAD.

Vacuum arc. V. M. ALBERS (J. Opt. Soc. Amer., 1929, **19**, 146—147).—The essential points of the apparatus are: (i) a rack and pinion inside the vacuum chamber, worked from outside, to move one electrode so as to strike the arc; (ii) a water-cooling arrangement for each electrode so as to prevent the material used to make the joints air-tight from melting, and (iii) the placing of the window through which the light of the arc passes at the end of a side tube so as to prevent its being affected by vapours from the arc. The apparatus was used to examine the spectrum of a beryllium arc in hydrogen.

C. A. SILBERRAD.

[Extractor.] JALADE.—See B., 1929, 909.

Simple micro-mol. wt. determination. K. SCHWARZ (Monatsh., 1929, **53** and **54**, 926—930).—The apparatus consists of two bulbs in series joined in ∩-formation to one bulb which can be evacuated at the top of the ∩. A substance of known mol. wt. (0·05 g.) is placed in the two-bulb arm and the substance (1—5 mg.) the mol. wt. of which is to be determined in the other. A solvent (benzene, carbon tetrachloride, or acetone) is added to both substances (5 and 0·5 c.c., respectively), the apparatus evacuated and sealed. After keeping for 24—48 hrs. at 15° (whereby solutions of equal vapour pressure result) the bulbs are cut off and the weights of solvent in each arm determined. The mol. wts. calculated from these weights of substances and solvents are in good agreement with the calculated values.

H. BURTON.

Study of hydration changes by a volume change method. H. A. NEVILLE and H. C. JONES (Coll. Symp. Mon., 1928, **6**, 309—318).—The dilatometer consists of a petrolatum mould enclosed in a bottle and covered with a layer of oil which can rise in a capillary tube. The method was applied to a study of the course of hydration of plaster of Paris, Portland cement, and gelatin. After elimination of thermal effects the curves obtained with the first two substances closely resemble that for the third, indicating that adsorption of water in hydration occurs in the gel structure, rather than by the formation of definite hydrates. CHEMICAL ABSTRACTS.

Laboratory rectifying columns with non-syphoning bubbling-cap plates. J. H. BRUNN (Ind. Eng. Chem. [Anal.], 1929, **1**, 212—213).—Five types of laboratory rectifying columns for fractional distillation are described. Their construction obviates the possibility of liquid in the column siphoning back into the still when cold liquid is added to the latter, or if the distillation is interrupted. Test distillations using a 1 : 1 mixture of benzene and chloroform showed that the bulk of the latter could be recovered with a purity of 98—99%. H. F. HARWOOD.

Device for maintaining a constant rate of flow of liquids [for leaching purposes]. J. D. SULLIVAN (Ind. Eng. Chem. [Anal.], 1929, **1**, 233).—A wooden float in the vessel containing the liquid carries a glass siphon which can be adjusted with reference to the liquid surface to any desired hydrostatic head; if a very small outflow be desired the end of the siphon under the liquid may be constricted. This device ensures delivery of a constant stream of solution at a uniform rate so long as any liquid remains in the container. H. F. HARWOOD.

Crucibles with handles for use in ignitions and fusions. KÖNIG (Chem.-Ztg., 1929, **53**, 851).—The crucible is provided with a handle at one side for lifting with crucible tongs. H. F. HARWOOD.

Combination electrochemical switchboard. W. F. MUNN (Ind. Eng. Chem. [Anal.], 1929, **1**, 208—209).—A type of laboratory switchboard adapted for use in a number of different fields of work is described. H. F. HARWOOD.

Electrolytic [switch]board for determination of lead. O. W. HOLMES and D. P. MORGAN (Ind. Eng. Chem. [Anal.], 1929, **1**, 210—212).—A form of switchboard for use in the electrolytic determination of lead in low-grade tailings is described, and the procedure for carrying out the analysis is discussed. The same apparatus may also be employed for copper.

H. F. HARWOOD.

Simple thermionic valve (audion) potentiometer for p_H determinations. G. LJUNGGREN and R. ELMQVIST (Svensk Kem. Tidskr., 1929, **41**, 213—216; cf. A., 1922, ii, 307; 1925, ii, 1196).—A portable apparatus constructed entirely from standard "wireless" components is described. A compensation method is employed in making the determinations, the grid being first of all given zero potential by connexion with the cathode, and the strength of the anode current measured. The unknown *E.M.F.* is then introduced between grid and cathode, and by

means of a variable resistance the anode current is brought back to its former value, when the desired potential can be read directly on a millivoltmeter. An accuracy of ±1 millivolt is attainable.

H. F. HARWOOD.

Simple thermionic valve apparatus for carrying out electrometric titrations. V. EHRHARDT (Chem. Fabr., 1929, 443—445, 455—457, 463—465).—A convenient form of apparatus for electrometric titrations is described in detail. The solution to be titrated forms one of a pair of half elements, the other being a calomel electrode. The latter is connected to the negative end of the valve filament circuit, the former to the grid. A milliammeter, reading from 0 to 0·5 milliamp., is inserted in the anode circuit, and shows a sudden deflexion when the end-point is reached. In order to increase the sensitivity, a constant current is passed through the instrument in the reverse direction by means of a 4-volt accumulator in series with an 800-ohm resistance, a 60-volt accumulator being used in the main anode circuit. A difference of only 0·2 volt in the titration potential at the end-point will then cause a difference of 0·44 milliamp. in the anode current. An efficient mechanical stirrer is employed in the solution under titration. Electrometric titrations of ferrous salts in presence of hydrochloric acid invariably show an end-point several tenths of a c.c. before that obtained by titration in the ordinary way, and in the former case the end-point is perfectly sharp, even with 0·01*N*-permanganate. An advantage of the apparatus described above is that it permits the determination of one oxidising or reducing substance in the presence of another, *e.g.*, chromic acid can be titrated in the presence of nitric acid or chlorates, which is not possible when the compensation method is employed. The presence of minute amounts of oxidising or reducing constituents in gases can also be detected if these latter are allowed to bubble through the liquid in the titration vessel. By employing a second electrode and suitable modification of the circuit the apparatus may also be employed for titrations where the end-point is denoted by the change in conductivity of the solution; examples of a number of typical curves obtained in this way are given.

H. F. HARWOOD.

Geochemistry.

Ions and electric currents in the upper atmosphere of the earth. E. O. HULBURT (Physical Rev., 1929, [ii], **34**, 1167—1183).

Diurnal and nocturnal measurements of the quantity of ozone in the upper atmosphere. D. CHALONGE and F. W. P. GÖTZ (Compt. rend., 1929, **189**, 704—706).—Measurements were made by day at Arosa (1856 m.), where the clearness of the sky allows of this all the year round, with the Chalonge spectrograph (A., 1928, 389), and also with that of Dobson (A., 1926, 493), and a constant difference in their indications was determined, those of the latter being uniformly lower. Measurements were also made with the former instrument on a series of consecutive days and nights. Coupling these results with those previously obtained it is concluded that in these latitudes the presence or absence of the sun has no effect on the thickness of the layer of ozone.

C. A. SILBERRAD.

Reaction-regulating power of sea-water. R. MARGARIA (Atti R. Accad. Lincei, 1929, [vi], **10**, 123—128).—Titration curves show that, when acid or slightly alkaline, sea-water changes its reaction appreciably on addition of comparatively small proportions of acid or alkali. When, however, the p_H value reaches 10 or 11, the opposite is the case, but the buffering influence thus exhibited is only apparent, being due to the gradual precipitation of magnesium hydroxide. At p_H 7·4, this buffering power is only 0·0016, whereas that of blood-serum is 0·0206.

T. H. POPE.

Characteristics of the Red Sea with regard to the nitrogen cycle. G. BINI (Atti R. Accad. Lincei, 1929, [vi], **9**, 1128—1133).—Determinations of nitrogen compounds in samples of water from various localities in the Red Sea have been made, and the bearing of the analyses on the nitrogen cycle is discussed. The absence of nitrates is probably due to the large numbers of denitrifying bacteria in these waters and to the scarcity of inflowing fresh-water. The scanty vegetation in the Red Sea is a consequence of the absence of nitrates.

F. G. TRYHORN.

Phthalein reaction of certain mineral waters. O. BAUDISCH and H. VON EULER (Biochem. Z., 1929, **212**, 149—157).—A discussion of the possible relationships between the geological sources of certain mineral waters and the state of combination of the iron which they contain.

W. MCCARTNEY.

Occurrence of silicates in natural waters. O. W. REES (Ind. Eng. Chem. [Anal.], 1929, **1**, 200—201).—The silica obtained in the analysis of natural waters should be expressed as SiO_3 and reckoned with the acidic radicals, especially where the alkalis are not determined directly, but are calculated from the difference between the sum of the positive and negative ions present.

H. F. HARWOOD.

Spectrochemistry of Portuguese mineral waters. The water of Cambres. A. P. FORJAS (Compt. rend., 1929, **189**, 703—704; cf. A., 1928, 730).—Spectrochemical examination of the mineral waters of Cambres (Corredoura) shows the presence of radium, lead, uranium, vanadium, zinc, copper, germanium, and probably thallium, in addition to sodium, potassium, lithium, calcium, strontium, barium, magnesium, aluminium, manganese, titanium, and iron also detected chemically.

C. A. SILBERRAD.

Iodine survey of Nebraska. W. H. ADOLPH and F. J. PROCHASKA (J. Amer. Med. Assoc., 1929, **92**, 2158—2160).

CHEMICAL ABSTRACTS.

Iodine in S. Carolina. J. H. MITCHELL (Science, 1929, **69**, 650—651).—The iodine content at depths of soil up to 18 in. from six different localities in S. Carolina has been determined together with that of 8 rivers and 36 foodstuffs and vegetables. A marked increase in iodine content from the surface to a depth of 18 in. is reported. L. S. THEOBALD.

Petrography of the Alpi Aurine and Vedrette Giganti regions. A. BIANCHI (Atti R. Accad. Lincei, 1929, [vi], **9**, 1145—1150).

Petrographic studies on the zone of Canavese. Granite of Belmonte. H. FENOGLIO (Atti R. Accad. Lincei, 1929, [vi], **9**, 1141—1145).—A microscopical and chemical examination has been made of granite from Belmonte. An analysis gave as the percentages of the main constituents: SiO_2 69·91, TiO_2 0·51, Al_2O_3 15·20, Fe_2O_3 3·24, CaO 1·21, Na_2O, 2·77, K_2O 4·79; the percentages of TiO_2 ZrO_2, FeO, MnO, MgO, SrO, BaO, H_2O, F, and S (in all cases less than 1%) were determined. F. G. TRYHORN.

Nontronite from Chenlo, Pontevedra. I. P. PONDAL (Arq. Seminario Est. Galegos, 1929, **2**, 9—14).—The composition of the nontronite of Pontevedra corresponds with the formula $Fe_2O_3,3SiO_2,2H_2O$. The material readily absorbs and loses water as the atmospheric temperature and humidity vary, and the large number of varieties of the material described in the literature is ascribed to this phenomenon. H. F. GILLBE.

Tungsten-bearing minerals of Galicia. I. Analysis of wolframites from La Brea, Corpiño, and Carboeiro, Pontevedra. I. P. PONDAL and J. VÁZQUEZ-GARRIGA (Arq. Seminario Est. Galegos, 1929, **3**, 1—5).—Various tungsten ores from the neighbourhood of Lalin have been analysed; *X*-ray analysis indicates the presence of about 6% of tantalum pentoxide in the residue insoluble in hydrochloric acid. H. F. GILLBE.

Pyrites of Galicia. Pyrites from La Mañoca, Santiago. I. P. PONDAL (Arg. Seminario Est. Galegos, 1929, **2**, 3—5).—The iron pyrites from La Mañoca contains Fe 46·25, S 30·83, Cu 0·28, Ni 0·02, As 0·08, residue insoluble in hydrochloric acid 21·91%. H. F. GILLBE.

Elastic properties of certain basic rocks and of their constituent minerals. L. H. ADAMS and R. E. GIBSON (Proc. Nat. Acad. Sci., 1929, **15**, 713—724).—Determinations of the compressibility of labradorite, jadeite, grossularite, and almandite, and of diabase rocks, combined with others previously known, enable a list of compressibilities at various pressures of all important constituents of basic rocks to be given. The maximum velocity at which longitudinal elastic waves can travel through basaltic rocks is 7·4 km. per sec. It is concluded that the possible components of the earth below 60 km. and above the core are in the following ascending order of probability: holocrystalline basalt, eclogite, peridotite. A. J. MEE.

Geologic relations of the diaspore and flint fire clays of Missouri. H. S. MCQUEEN (J. Amer. Ceram. Soc., 1929, **12**, 687—697).—The general geology of the north-central Ozark region of Missouri is described. In this area, diaspore, flint clay, "burley" clay (a high-alumina clay containing oolites or "burls"), and plastic clay are found in inverted, cone-shaped, sink-hole type deposits in the Pennsylvanian sandstone. The diaspore clay is characterised by the presence of oolites composed of the mineral diaspore, which occur in a porous groundmass of fine-grained clay. The origin and mode of occurrence of the clays are briefly discussed. F. SALT.

Origin of nickel silicates at Webster, N.C. C. S. ROSS. E. V. SHANNON, and F. A. GONYER (Econ. Geol., 1928, **23**, 528—552). CHEMICAL ABSTRACTS.

Mineralogical composition of tripoli of Kaluga district, U.S.S.R. E. M. YANISHEVSKI (Trans. Inst. Econ. Min. Met., Moscow, 1929, No. 42, 32—50).—The diatomaceous earth contains SiO_2 75·59—78·76, TiO_2 0·27—0·94, Al_2O_3 9·67—10·57, Fe_2O_3 3·15—3·74, CaO 0·69—1·05, MgO 1·46—1·72, K_2O 0·56—0·78, Na_2O 0·27—0·54, SO_3 0·11—0·29, loss on ignition 4·41—4·70%. CHEMICAL ABSTRACTS.

Orthites of certain massive rocks of the Transbaïkal region. B. Z. KOLENKO (Bull. Acad. Sci. Leningrad, 1929, 243—260).—Although in small quantities, orthite is of widespread occurrence in the massive rocks of the Transbaïkal region. It is found mostly in rocks of acid character, particularly the granite-gneisses, but occasionally in basic rocks such as diorite and gabbro. T. H. POPE.

Radioactive mineral deposits, and the present output of radium. R. THORŒUS (Svensk Kem. Tidskr., 1929, **41**, 216—222).—The principal commercially exploitable deposits of radioactive minerals are briefly described, and statistics of radium production given. H. F. HARWOOD.

Analysis of a peat profile. R. THIESSEN and R. C. JOHNSON (Ind. Eng. Chem. [Anal.], 1929, **1**, 216—220).—The changes occurring in peat after deposition have been studied by carrying out a series of analyses of samples taken at intervals from a peat bed 10 ft. thick. The results show that the lignin and cellulose decrease with depth, and hence with age, whilst the humus and insoluble matter increase. Owing to the varying nature of the plants which gave rise to the peat at different periods it cannot be decided from the analyses whether the humus is mainly derived from lignin or from cellulose, but the former is probably the principal source. Details are given of the methods of analytical investigation employed. H. F. HARWOOD.

Composition of peculiar clinkers found in snags after forest fires. D. T. ENGLIS and W. N. DAY (Science, 1929, **69**, 605—606).—Analyses of samples from various localities show close agreement in composition and the view of their meteoritic origin is disproved. L. S. THEOBALD.

Meteoric stone of Hinojo, Buenos Aires. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, **5**, [2], 1—7).—The material, *d* 3·407—3·411, contained: (magnetic fraction) insol. 41·525, $(Al,Fe)_2O_3$ 23·885, CaO 0·266, MgO 9·000, NiO 1·489, Fe 21·482, Ni 0·908, Co 0·046, S 1·766—1·853, P

0·104%, Cr and Mn traces; (stony fraction) SiO_2 37·320, Al_2O_3 2·410—2·425, FeO 13·360, Fe_2O_3 17·975, MnO 0·652, Cr_2O_3 trace, NiO 1·516—1·614, CoO 0·046, CaO 2·475, MgO 21·787, K_2O 0·207, Na_2O 1·653, P_2O_5 0·480, H_2O and loss 0·119%.

CHEMICAL ABSTRACTS.

El Mocovi meteorite. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, **5**, [2], 9—12).—The meteorite, *d* 7·632—7·716, contained: siliceous material 0·210, Fe 93·135, Ni 5·680, Co 0·304, graphite 0·239, S 0·141, P 0·166, Cr trace, Mn 0·010, (Ir, Ru, Os) 0·035—0·087%. CHEMICAL ABSTRACTS.

Cachari meteoric stone. E. H. DUCLOUX (Rev. fac. cienc. quim. La Plata, 1929, **5**, [2], 13—23).—Average analytical results for the meteorite, *d* 3·13 (values for portions soluble or insoluble in hydrochloric acid are also recorded), are: loss on ignition 0·196, SiO_2 48·475, Al_2O_3 13·945, Fe_2O_3 0·237, FeO 19·803, MnO 0·783, Cr_2O_3 0·062, CoO none, TiO_2 0·072, CaO 8·617, MgO 6·840, K_2O 0·127, Na_2O 0·919, P_2O_5 0·058, SO_3 0·056%, NiO and S traces.

CHEMICAL ABSTRACTS.

Renca (San Luis) meteorite. E. H. DUCLOUX and F. PASTORE (Rev. fac. cienc. quim. La Plata, 1929, **5**, [2], 111—120).—The meteorite, *d* 3·410, contained: SiO_2 38·392, Al_2O_3 3·030, FeO 20·802, MnO 0·778, Cr_2O_3 0·464, CaO 1·441, MgO 20·047, NiO 1·128, K_2O 0·577, Na_2O 2·367, SO_3 0·062, S 2·588, Fe 7·788, Ni 0·787, Co 0·048, P 0·008%. Analytical results for the magnetic and stony fractions, respectively, are also recorded. CHEMICAL ABSTRACTS.

Elements in the sun. C. E. ST. JOHN (Proc. Nat. Acad. Sci., 1929, **15**, 789—793).—The principles underlying the identification of lines in the solar spectrum are outlined. Fifty-eight elements have been found in the sun. C. W. GIBBY.

Organic Chemistry.

Application of the Abbé number to the refractometric determination of the constitution of organic liquids. W. BIELENBERG (Z. angew. Chem., 1929, **42**, 972—975).—Calculations of the Abbé number $\nu=(n_D-1)/(n_F-n_C)$ for a large number of organic compounds show that, for all the different members of each type of compound, the Abbé numbers fall within a certain range which is specific for that type. Ethylenic linkings, especially when conjugated, depress the value of the Abbé number in a manner strictly parallel to the exaltation of the molecular refractivity. The Abbé number is therefore a function which throws considerable light on the constitution, state of unsaturation, relative position of double linkings, and the presence of conjugation in liquid organic compounds. It is particularly valuable, since it does not require knowledge of the mol. wt. In cases where the Abbé number assigns a compound to one of two or more classes then the values of n_D and (n_F-n_C) are decisive. A. A. GOLDBERG.

Oxidation mechanisms of the paraffin hydrocarbons. G. EGLOFF, R. E. SCHAAD, and C. D. LOWRY, jun.—See B., 1929, 930.

Action of aluminium chloride on certain saturated aliphatic hydrocarbons. J. JURKIEWICZ and K. KLING (Przemysł Chem., 1929, **13**, 481—492).—Above 370—390° anhydrous aluminium chloride has an exclusively disintegrating action on ethane, propane, and *n*- and *iso*-butane, the percentage decomposition increasing with the mol. wt. of the hydrocarbon. In the case of *iso*butane, an unidentified higher hydrocarbon was obtained at 245° in the presence of this catalyst.

R. TRUSZKOWSKI.

Action of carbonyl chloride on ethylenic linkings. I. Hydrocarbons and alcohols. E. PACE (Gazzetta, 1929, **59**, 578—590).—Carbonyl chloride reacts in presence of aluminium chloride with ethylenic hydrocarbons or alcohols in toluene solution to give, respectively, β-chloro-acid chlorides, and β-chlorolactones. The reaction is carried out by passing carbonyl chloride into the solution, kept generally at 35—40°, for 2—20 hrs. until the mixture is dark brown and no more gas is absorbed, and the product is isolated by fractional distillation or evaporation of the toluene after brief treatment with water. Ethylene yields β-chloropropionyl chloride, b. p. 144·5°, hydrolysed to the acid by boiling dilute hydrochloric acid. *iso*Amylene yields *β-chloro-γ-methylvaleryl chloride*, b. p. 168° (*acid*, m. p. 72—73°, yielding *γ-methyl-Δ^{α}-pentenoic acid*, b. p. 212° in boiling alkaline solution, and *β-hydroxy-γ-methylvaleric acid*, m. p. 127°, with silver oxide). Styrene yields *β-chloro-β-phenylpropionyl chloride*, m. p. 139° (decomp.). Allyl alcohol yields *β-chloro-γ-butyrolactone*, m. p. 45°, which yields the *β-hydroxy-γ-butyrolactone*, m. p. 68°, converted into *βγ-dihydroxybutyric acid*, a syrup. Cinnamyl alcohol yields *β-chloro-α-phenyl-γ-butyrolactone*, m. p. 105°, whence *β-hydroxy-α-phenyl-γ-butyrolactone*, m. p. 86°, and *βγ-dihydroxy-α-phenylbutyric acid* ($+H_2O$), m. p. 125°, are obtained. α-Terpineol yields a *chlorolactone*, m. p. 51°, which yields a *hydroxylactone*, m. p. 112°, converted into an unstable *dihydroxy-acid* which readily loses carbon dioxide and water to give α-terpineol.

R. K. CALLOW.

Isomerides of Δ^{β}-pentene. I. Δ^{β}-Pentene from γ-bromopentane and γ-pentanol. M. L. SHERRILL, B. OTTO, and L. W. PICKETT. **II. Δ^{β}-Pentene from β-bromopentane and β-pentanol.** M. L. SHERRILL, C. BALDWIN, and D. HAAS (J. Amer. Chem. Soc., 1929, **51**, 3023—3033, 3034—3041).—I. Diethylcarbinol is saturated with hydrogen bromide at −10° and then heated at 60° until reaction is complete. Repetition of this process until absorption is complete gives γ-bromopentane (I), b. p. 118·2—118·5°/760 mm., d_4^{20} 1·2170, n_D^{20} 1·44431. If phosphorus tribromide or hydrogen bromide under pressure is used during the preparation of I some β-bromopentane is also formed. Δ^{β}-Pentene (II), b. p. 36·40±0·05°/760 mm., d_4^{20} 0·6503, n_D^{20} 1·37965, is

obtained from I by the action of methyl-alcoholic potassium hydroxide at 110—115°, and purified by distillation of its azeotropic mixture, b. p. 31·4± 0·05°/760 mm., with methyl alcohol (corresponding mixture with ethyl alcohol, b. p. 34·7±0·05°), and subsequent removal of the alcohol by washing. Dehydration of diethylcarbinol with 60% sulphuric acid gives II and polymerised (?) material. Addition of hydrogen bromide to II in carbon tetrachloride solution affords 98% of I, but in acetic acid solution 22% of β-bromopentane (III) is formed in addition to 78% of I (cf. Lucas and Moyse, A., 1925, i, 770; Kharasch, Chem. Rev., 1928, 5, 571). Addition of bromine to II gives βγ-dibromopentane. Exposure of II to sunlight or ultra-violet light causes transformation into an isomeric pentene, which differed slightly from II in physical properties; a specimen with n_D^{20} 1·37934 when treated with hydrogen bromide yielded a mixture of 15% of I and 85% of III (cf. Kharasch, *loc. cit.*). With bromine, βγ-dibromopentane is formed.

II. β-Bromopentane is converted as above into a mixture of Δ^{α}- and Δ^{β}-pentenes, separable by fractional distillation of the azeotropic mixtures with methyl alcohol. The purest Δ^{β}-pentene (IV) obtained had b. p. 35·85±0·05°/760 mm., d_4^{20} 0·6481, n_D^{20} 1·37849 (azeotropic mixtures with methyl and ethyl alcohols, b. p. 30·85±0·05° and 33·7±0·2°/760 mm.; bromine additive product, βγ-dibromopentane). Addition of hydrogen bromide to IV in absence of solvent gives 93—95% of β-bromopentane, but in acetic acid only 85% is formed. Exposure of IV to ultra-violet light causes a slight increase in the value of *n*, but the hydrogen bromide addition is the same as with IV. The results indicate that II and IV are electronic and not geometrical isomerides (cf. Kharasch, *loc. cit.*), IV being the more stable. H. BURTON.

Isomerides of Δ^{β}-pentene. III. Ultra-violet absorption spectra of isomeric Δ^{β}-pentenes. E. P. CARR (J. Amer. Chem. Soc., 1929, **51**, 3041—3053).—Absorption spectra measurements have been made of the isomeric Δ^{β}-pentenes described by Sherrill and others (preceding abstract), and it is found that they show marked differences, particularly in the region of the shallow absorption band in the near ultra-violet. The curve for the stable Δ^{β}-pentene (from β-bromopentane) is similar in form to that of trimethylethylene (Lüthy, A., 1924, ii, 80), but differs widely from that of the Δ^{β}-pentene obtained from γ-bromopentane. This difference indicates that the pentenes are not *cis–trans* isomerides (cf. Errera and Henri, A., 1925, ii, 1137). The effect of a polar solvent (acetic acid) on the spectra of the isomerides is to cause a shift in the absorption of one towards the other; hexane (non-polar) has no effect. After prolonged exposure of the unstable Δ^{β}-pentene to diffused light there is a shift in the absorption towards that of the stable isomeride; a more absorptive polymeride is also produced (cf. *loc. cit.*). After exposure to ultra-violet light the absorption spectrum of the unstable pentene shows a decided shift to the visible, whilst under identical conditions the stable form shows only a slight shift towards the curve of its isomeride. The more absorptive isomeride is the stable form. The results agree with the interpretation of electronic isomerism as proposed by Kharasch (Chem. Rev., 1928, 5, 571). H. BURTON.

***n*-Hentriacontene.** R. PUMMERER and H. KRANZ (Ber., 1929, **62**, [*B*], 2620—2628).—In relationship to the constitution of caoutchouc and guttapercha, the examination has been made of a long-chain hydrocarbon with an isolated terminal ethylenic linking.

Myricyl alcohol, m. p. 88°, is prepared by hydrolysis of carnauba wax by alcoholic potassium hydroxide in presence of benzene. It appears to have the composition $C_{31}H_{63}\cdot OH$ and to be identical with melissyl alcohol from beeswax. The compound is converted by palmityl chloride at 130—180° into myricyl palmitate, m. p. 75°, which, when boiled under 13 mm. pressure and then distilled, yields palmitic acid and *hentriacontene*, b. p. 295°/15 mm., m. p. 64° (yield 70—80%). Analyses and determinations of mol. wt. in camphor and naphthalene indicate the composition $C_{31}H_{62}$, the somewhat high values in naphthalene giving no certain criterion of association. One % solutions in warm benzene after long preservation solidify to jellies which contain no macroscopic crystals, but show bright and dark zones between crossed Nicols. Gel formation, such as is observed with azo-dyes and soap solutions, can therefore take place in the absence of charged particles (ions) which have a directive action. The relative viscosity of hentriacontene is very small. The sudden increase in solubility in benzene and chloroform for a rise of 10° is comparable with that observed for guttapercha in ether. Catalytic hydrogenation of the unsaturated hydrocarbon in presence of *cyclo*hexane and spongy platinum affords hentriacontane, m. p. 68°, also obtained from palmitone by Clemmensen's method. When titrated with bromine in chloroform or treated with iodine chloride, hentriacontene gives the expected analytical results. The *dibromide*, m. p. 62°, prepared in carbon disulphide, loses part of its bromine (as hydrogen bromide) when treated with alcohol under mild conditions, yielding a product which is stable towards boiling alcohol and does not contain ethoxyl, and hence probably has a different arrangement of the carbon skeleton. Alkaline permanganate is slowly decolorised by hentriacontene in benzene; ozone converts the hydrocarbon into formic acid and an acid, m. p. 88°. H. WREN.

Homogeneous oxidation of acetylene. G. B. KISTIAKOWSKY and S. LENHER.—See this vol., 1395.

Induced chlorination of ethylene dichloride. Effect of oxygen on the reaction between ethylene and chlorine. T. D. STEWART and D. M. SMITH (J. Amer. Chem. Soc., 1929, **51**, 3082—3095).—When ethylene and chlorine are allowed to react in a darkened glass vessel (previously heated at 500° and evacuated at 1×10^{-6} mm.) there is a short inhibition period followed by an autocatalytic reaction. The rate of reaction becomes relatively high as soon as the liquid reaction products begin to separate on the walls of the vessel. The following reactions occur: (*a*) $C_2H_4+Cl_2=C_2H_4Cl_2$; (*b*) $C_2H_4Cl_2+Cl_2=C_2H_3Cl_3+HCl$: reaction *b* is not independent of reaction *a*. In presence of oxygen the total reaction rate decreases and reaction *b* tends to be eliminated; a small amount of oxygen is

almost as effective as a large amount. Nitrogen and water have no apparent effect on the induced substitution reaction. On an evacuated surface trichloroethane vapour is a more powerful catalyst than ethylene dichloride vapour for the reaction between ethylene and chlorine. On an unevacuated surface neither of the vapours is an effective catalyst. In presence of oxygen, liquid ethylene dichloride is a better catalyst than liquid trichloroethane; both liquids are more effective in absence of oxygen. The evacuated surface is not a catalyst, but as evacuation of the walls progresses more hydrogen chloride appears in the reaction mixture. Oxygen and excess of chlorine reduce the specific reaction rate to the same minimum value. It is suggested that there is an induced additive reaction as well as an induced substitution reaction; the latter is induced by the former, the heat of reaction of ethylene dichloride being utilised to promote the formation of trichloroethane.

H. BURTON.

Catalysts for the formation of alcohols from carbon monoxide and hydrogen. IV. Decomposition and synthesis of methyl alcohol by catalysts composed of zinc and chromium oxides. D. S. CRYDER and P. K. FROLICH.—See B., 1929, 934.

Tests for methyl alcohol. H. LEFFMANN and C. C. PINES.—See B., 1929, 886.

Synthesis of phytol. F. G. FISCHER and K. LÖWENBERG (Annalen, 1929, **475**, 183—204; cf. A., 1928, 989).—Condensation of βζ-dimethylundecan-κ-one (obtained by reduction of ψ-ionone with hydrogen and palladised calcium carbonate in alcohol under pressure) with sodamide and acetylene gives *γηλ-trimethyl-Δ$^{\alpha}$-dodecinen-γ-ol* (I), b. p. 135·5—136·5°/10 mm., d_4^{25} 0·8464, n_D^{25} 1·4488 (*acetate*, b. p. 152—152·5°/11 mm.; *silver* salt). Reduction of this with either sodium and moist ether or a zinc–copper couple in aqueous alcohol does not give satisfactory results, but with hydrogen and palladised calcium carbonate it is smoothly converted into *γηλ-trimethyl-Δ$^{\alpha}$-dodecen-γ-ol*, b. p. 140·5°/10 mm. This is converted by heating with acetic anhydride for 90 hrs. at 100° into the *acetate*, b. p. 146—153°/11 mm. (at higher temperatures loss of water occurs with the formation of a *hydrocarbon*, b. p. 120—121°/10 mm., which is probably tetrahydrofarnesene), which undergoes amonotropic change and is separated by fractionation after hydrolysis into tetrahydrofarnesene, the original carbinol, and *γηλ-trimethyl-Δ$^{\beta}$-dodecen-α-ol* (tetrahydrofarnesol), b. p. 152—156°/10 mm. (*acetate*, b. p. 164—167°/11 mm.). The last is converted by the action of phosphorus tribromide in light petroleum at −10° into its *bromide*, b. p. 153—159°/10 mm. (slight decomp.), which is condensed in the crude state with ethyl acetoacetate in the presence of alcoholic sodium ethoxide at −10°. Ketonic hydrolysis of the condensation product yields *methyl δθμ-trimethyl-Δ$^{\gamma}$-tridecenyl ketone*, b. p. 173·5—175°/10 mm. This is reduced by hydrogen and palladised calcium carbonate to methyl δθμ-trimethyltridecyl ketone, b. p. 173·5—174°/10 mm., d_0^{25} 0·8337, n_D^{25} 1·4434, identical with the ketone $C_{18}H_{36}O$ obtained by chromic acid oxidation of phytol (*loc. cit.*; cf. Heilbron and Thompson, this vol., 790). Further condensation of this ketone with acetylene gives *γηλπ-tetramethyl-Δ$^{\alpha}$-hexadecinen-γ-ol*, b. p. 183—185°/11 mm., which undergoes similar rearrangement with acetic anhydride to yield γηλπ-tetramethyl-Δ$^{\beta}$-hexadecen-α-ol (*silver* salt of *hydrogen phthalate*, m. p. 117—119°; *semicarbazone* of the *pyruvate*, m. p. 72—75°), identical in all respects with natural phytol, together with phytadiene, identical with a specimen obtained by the action of phthalic anhydride on natural phytol. Investigation of the action of 98% formic acid on the various acetylenic tertiary carbinols prepared above shows that with the reagent, contrary to Rupe and his collaborators (cf. A., 1926, 821), αβ-unsaturated methyl ketones are the main products of this rearrangement. Thus I gives mainly (90% of product, 55—60% yield) *methyl αει-trimethyl-Δ$^{\alpha}$-decenyl ketone*, b. p. 148—149°/10 mm., isolated as its *semicarbazone*, m. p. 133—134°, and reduced by hydrogen and palladised calcium carbonate to *methyl αει-trimethyldecyl ketone*, b. p. 139—140°/10 mm. (*semicarbazone*, m. p. 45·5—46·5°), which is further reduced by sodium and alcohol to *γηλ-trimethyldodecan-β-ol*, b. p. 146·8—147·2°/11 mm. By means of its hydrogen sulphite derivative a small yield of *βζκ-trimethyl-Δ$^{\alpha}$-dodecenaldehyde*, b. p. 156—157°/11 mm., is isolated from the products of the rearrangement. Similarly, the main product of the rearrangement of *α-cyclo*hexylethin-α-ol with formic acid is not *cyclo*hexylideneacetaldehyde (Rupe, Messner, and Kambli, A., 1928, 640), but Δ^{1}-*cyclo*hexenyl methyl ketone (reduced to *cyclo*hexyl methyl ketone). *iso*Phytane, $C_{20}H_{42}$, b. p. 171·8—172·6°/11 mm., d_4^{25} 0·7853, n_D^{25} 1·4382, obtained by heating tetrahydrogeranyl bromide with potassium in benzene, is identical with phytan (βζλπ-tetramethylhexadecane). Acid hydrolysis of ethyl tetrahydrogeranylacetoacetate yields *δε-dimethyldecoic acid*, b. p. 159·5—160·5°/10 mm., d_4^{25} 0·8862, which may be identical with the acid, $C_{10}H_{20}O_2$, obtained by oxidation of the ketone obtained by degradation of phytol (Willstätter, Mayer, and Hüni, A., 1911, i, 144). J. W. BAKER.

Reactions relating to carbohydrates and polysaccharides. XXIII. Synthesis and properties of hydroxyalkylidene-glycols and -glycerols. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, **51**, 3115—3123).—Condensation of acraldehyde with ethylene glycol containing one third of its weight of hydrogen chloride gives *ethylene γ-chloropropylidene ether*, b. p. 70—72°/18 mm., which when heated with powdered potassium hydroxide affords *ethylene acrylidene ether*, b. p. 115—116°. Oxidation of this with dilute potassium permanganate yields 41% of *ethylene βγ-dihydroxypropylidene ether* (I), b. p. 136—138°/5 mm., n_D^{17} 1·4695. Acraldehyde and glycerol condense after several weeks at 50—60°, forming αβ-acrylideneglycerol, b. p. 204—215°, n_D^{17} 1·4638 (cf. Nef, A., 1905, i, 3), methylated to the corresponding *γ-methyl ether*, b. p. 70°/13 mm., n_D^{17} 1·4408. This methyl ether is hydrolysed by 75% alcohol containing 0·5% hydrochloric acid to glycerol α-methyl ether, and is oxidised by dilute permanganate, yielding *αβ-(β′γ′-dihydroxypropylidene)glycerol γ-methyl ether*, b. p. 146°/1—2 mm., n_D^{17} 1·4680. Similar oxidation of αβ-acrylideneglycerol gives only a small amount of

αβ-(β′γ′-dihydroxypropylidene)glycerol (II), b. p. 146°/0·15 mm., n_D^{17} 1·4888. When I or II is heated at 110° in absence or presence of potassium hydroxide, sodium or aluminium ethoxide, or exposed to sunlight, polymerisation does not occur. H. BURTON.

Action of the oxides of nitrogen on ethers. I. O. I. EGOROVA (Ukraine Chem. J., 1929, 4, 193—198).—The action of nitrogen oxides on *iso*amyl ether yielded a mixture of *iso*amyl nitrite, *iso*amyl nitrate, and a small quantity of nitro*iso*pentane. With diphenyl ether a mixture of *o*- and *p*-nitrodiphenyl ethers was obtained, identified by reduction to the amino-compounds (m. p. 42·7°—44·7° and 83°, respectively) with tin and hydrochloric acid.

M. ZVEGINTZOV.

"Ring contraction" during the formation of internal ethers (oxides) from glycols. A. FRANKE (Monatsh., 1929, 53 and 54, 577—587).—Hückel's criticism of the author's previous results (A., 1923, i, 530) on the formation of αε-oxides from ωω′-diols has led to an examination of the oxide obtained from decane-ακ-diol (I).

[With H. GOMOLKA.]—Reduction of ethyl sebacate with sodium and alcohol gives a 66·5% yield of I, b. p. 179°/11 mm., m. p. 71°, which on treatment with 50% sulphuric acid and distillation with superheated steam yields *αε-oxidodecane* (II), b. p. 198—202°, 84°/14 mm. Oxidation of II with dilute potassium permanganate gives mainly succinic and hexoic acids, together with small amounts of glutaric and valeric acids. When II is heated with fuming hydrobromic acid at 100° in a sealed tube *αε-dibromodecane*, b. p. 155°/13 mm., is formed. This is converted by way of the *diacetate*, b. p. 153°/9 mm. (37—42% yield), into *decane-αε-diol*, b. p. 157°/9 mm., readily convertible into II. H. BURTON.

Reactions of the α-oxides with amino-acid esters. III. Aromatic amino-acids. IV. Aliphatic and homologous aromatic acids. A. I. KIPRIANOV (Ukraine Chem. J., 1929, 4, 215—229).—III. Trimethylethylene oxide and *iso*butylethylene oxide react with aromatic amino-acids much less readily than ethylene oxide; in the case of trimethylethylene oxide no reaction takes place, whilst *iso*butylethylene oxide gave the normal additive products of the oxide molecule to the amino-group. With methyl anthranilate, *iso*butylethylene oxide gave methyl alcohol as a by-product, thus indicating the probable formation and decomposition of the ε-lactone, which, however, could not be isolated.

IV. Two mols. of *iso*butylene oxide reacted with glycine ester to give the *compound*

$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}N{<}\begin{matrix}CH_2{-}CO\\CH_2{\cdot}CMe_2\end{matrix}{>}O$, b. p. 162—167°/5 mm. If molar proportions of the reacting substances were used, *ethyl N-hydroxy*iso*butylaminoacetate*, b. p. 155—160°/4 mm., was obtained.

With excess of ethylene oxide ethyl phenylaminoacetate also gave the corresponding *lactone*,

$OH{\cdot}CH_2{\cdot}CH_2{\cdot}N{<}\begin{matrix}CHPh{\cdot}CO\\CH_2{-}CH\end{matrix}{>}O$, b. p. 239—240°/7 mm. With equimolecular amounts, no product could be isolated. *iso*Butylene oxide and methyl phenylaminoacetate in equimolecular proportions yielded *methyl phenyl-β-hydroxy*iso*butylaminoacetate*, b. p. 170—173°/7 mm. Under the same conditions, ethyl phenylaminoacetate did not react.

M. ZVEGINTZOV.

Synthesis and properties of phenyl-β-hydroxyethylaminoacetic acid. A. I. KIPRIANOV (Ukraine Chem. J., 1929, 4, 231—240; cf. preceding abstract).—The action of α-oxides on the esters of amino-acids decreases with increase of mol. wt., so that amino-carbinol acids cannot be obtained by this method from secondary amines.

Phenyl-β-hydroxyethylaminoacetolactone,

$NPh{<}\begin{matrix}CH_2{-}CH\\CH_2{\cdot}CO\end{matrix}{>}O$, m. p. 75°, was obtained by the action of ethylene chlorohydrin on sodium phenylaminoacetate when boiled under reflux condenser for 9 hrs. or by the action of phenyl-β-hydroxyethylamine on sodium chloroacetate; a third method was to act on phenyl-β-hydroxyethylamine with ethyl chloroacetate. If bromoacetic acid was used, some hydroxyethyliminodiacetic acid, m. p. 167—169°, was obtained. The lactone on keeping in air for 2 months became transformed into a violet *substance* very similar in appearance and properties to dyes of the triphenylmethane series, such as crystal-violet.

M. ZVEGINTZOV.

Partial esterification of polyhydric alcohols. IX. True β-ether of glycerol. A. FAIRBOURNE (J.C.S., 1929, 2232—2235).—The author questions the structure of the "α"-monomethyl and "αβ"-dimethyl ethers of glycerol, given by Gilchrist and Purves (A., 1926, 153), and shows that migration of the methoxyl radical does not take place as assumed by these workers. *βγ-Dichloro-α-methoxypropane*, b. p. 158°, *d* 1·162, *n* 1·443, was prepared by the chlorination of methyl allyl ether in ethereal solution, and found to differ from αγ-dichloro-β-methoxypropane, which was assumed by Gilchrist and Purves to be identical with the ether described. *Glycerol β-monomethyl ether* was prepared by hydrolysis of αγ-dichloro-β-methoxypropane and its structure confirmed by converting it into its di-*p*-nitrobenzoate, m. p. 155°, as compared with m. p. 108° for the corresponding α-ether derivative. J. W. PORTER.

Alkyl peroxides. IV. Ultra-violet absorption of hydrogen peroxide and of the simple mono- and di-alkyl peroxides in solution. E. LEDERLE and A. RIECHE (Ber., 1929, 62, [*B*], 2573—2585; cf. Rieche and Hitz, this vol., 1268).—Very marked analogy in refraction and absorption is found between ketones and peroxides. Replacement of hydrogen by methyl in the chromophore itself causes a stabilisation, whereas loosening of the electron sheath of the chromophore is induced by the stabilisation of directly vicinal octets. The "deformation energy" caused by the replacement of hydrogen by methyl amounts to about 2 kg.-cal. per mol. for the CO group. The following absorption graphs are recorded: hydrogen peroxide, methyl and ethyl hydrogen peroxides in water; dimethyl, methyl ethyl, and diethyl peroxides in hexane; hydrogen peroxide and methyl hydrogen peroxide in 1% sodium or potassium hydroxide; methyl hydrogen peroxide in heptane. The graphs are closely similar to one another and disclose the

existence of the ions $O_2^{=}$, MeO_2^{-}, and EtO_2^{-}. The polarity of peroxides is discussed and a constitutional formula is proposed in which the two oxygen nuclei are placed in a common electron sheath and the valency directions to the hydrogen atoms or alkyl groups deviate by about 70° from the O—O axis.

H. WREN.

Influence of poles and polar linkings on the course pursued by elimination reactions. IV. Olefinic degradation of sulphones. G. W. FENTON and C. K. INGOLD (J.C.S., 1929, 2338—2341; cf. A., 1927, 650; 1928, 1126).—The decomposition of a series of complex sulphones by means of potassium hydroxide has been studied, and the ease with which the different alkyl groups are eliminated as olefines compared with a corresponding series of quaternary ammonium hydroxides, in which the order of ease of elimination is as follows: β-phenylethyl>ethyl, *iso*propyl, *sec.*-butyl>*n*-propyl >*n*-amyl >*n*-hexyl, *n*-heptyl, *n*-octyl>*iso*amyl>*iso*butyl. In the case of phenyl-β-phenylethyl-, diethyl-, di*iso*propyl-, and di-*n*-propyl-sulphones the decomposition proceeds smoothly, the last-named compound decomposing with less ease than the first two. With di-*n*-butylsulphone the reaction is exceedingly slow, whilst no decomposition takes place with di-*n*-octyl-, di*iso*amyl-, and di*iso*butyl-sulphones. Ethyl*iso*amyl- and ethyl-*n*-octyl-sulphone decompose normally. It is concluded that there is some point between diethyl- and di-*n*-octyl-sulphones such that all sulphones R'_2SO_2 containing radicals, R′, occurring to the left of this point undergo the degradation whilst all sulphones R''_2SO_2, containing radicals, R″, occurring to the right of it do so only slightly or not at all. The same is assumed to be true also for unsymmetrical sulphones containing a group such as phenyl, incapable of elimination as an olefine. The reactions are also discussed in terms of the electronic theory of valency. *Ethyl*-n-*propyl-sulphone*, m. p. 25°, b. p. 142—143°/23 mm., and *silver propane-α-sulphinate* are described. J. W. PORTER.

New petroleum by-product: octanesultone [lactone of γ-hydroxy-*n*-octanesulphonic acid]. E. L. BALDESCHWIELDER and H. A. CASSAR (J. Amer. Chem. Soc., 1929, **51**, 2969—2978).—During the manufacture of higher secondary and tertiary alcohols, the permanent gases from the stills are scrubbed with sulphuric acid. Dilution of the acid extract affords a liquid of high sulphur content which on cooling and storing deposits a dark-coloured solid, from which, by extraction with benzene and precipitation with petroleum, is isolated *γ-hydroxy*-n-*octanesulphono-lactone* (I) $C_5H_{11}\cdot\overset{\overline{\quad O \quad}}{CH\cdot CH_2\cdot CH_2\cdot SO_2}$, m. p. 129°. This is readily volatile in steam, does not react with bromine, acetyl chloride, or phosphorus pentachloride, and when heated with dilute sulphuric acid under pressure or distilled over potassium hydroxide yields isomeric octanes and octenes. Treatment of I with hot barium or potassium hydroxide solution affords the *barium*, $C_{16}H_{32}O_7S_2Ba$ (II), or *potassium* (III) salts (corresponding *silver* salt) [designated type *A*]. Acidification of II regenerates I, whilst bromination of II or III in aqueous solution gives a *bromo-octanesultone* (type *A*) (IV), $C_8H_{15}O_3BrS$, m. p. 112° (corresponding *chloro*-derivative, m. p. 122·5°) also formed by bromination of the solutions of salts obtained from I and 20% solutions of sodium hydroxide, or sodium and potassium carbonates. Hydrolysis of IV with barium or potassium hydroxide solution and purification through the lead salt affords a *bromohydroxyoctanesulphonic acid*, m. p. 90° (*barium* and *potassium* salts). The bromine atom in IV is not removed by fusion with sodium hydroxide. When I is hydrolysed with an aqueous suspension of barium carbonate a mixture of barium salts (type *B*, syrupy, and type *C*, crystalline) is obtained. Bromination of type *B* in aqueous solution yields a *bromo-octanesultone* (type *B*), $C_8H_{15}O_3BrS$, m. p. 139° [corresponding *chloro*-derivative (V), m. p. 118·5°]. Hydrolysis of V first with barium hydroxide solution and then with dilute sulphuric acid gives an *octenesultone*, $C_8H_{14}O_3S$, m. p. 92·5°, brominated in aqueous alkaline solution to a *bromo-octenesultone*, $C_8H_{13}O_3BrS$, m. p. 117°. Bromination of the *calcium* salt of type *C* (isomeric with type *A*) gives bromo- and dibromo-octanes, whilst steam distillation of the acidified salt yields a mixture of octenes, b. p. mainly 113—115°.

H. BURTON.

Helicoidal configuration in long-chain compounds. W. B. LEE and P. J. VAN RYSSELBERGE (J. Physical Chem., 1929, **33**, 1543—1557; cf. A., 1928, 107).—On the assumption of Baeyer's strain theory, in so far as the αε and αζ positions favour ring formation, a new helicoidal configuration for long-chain compounds is derived and briefly discussed. The carbon atoms of a straight chain are assumed to lie on a helix drawn on a cylinder which has the dimensions calculated by Langmuir from Adam's measurements on unimolecular films and are regularly spaced round a helix the pitch of which brings the odd and even carbon atoms in two perpendicular planes. This model is shown to account for many physical and chemical properties, which are discussed in relation to it, especially the C_5, C_{10}, C_{15} periodicity exhibited by many organic acids. L. S. THEOBALD.

Racemisation. I. Racemisation of halogen-substituted esters. T. WAGNER-JAUREGG (Monatsh., 1929, **53** and **54**, 791—812).—A more detailed account of work previously reviewed (this vol., 425). H. BURTON.

Crotonic acid. F. KAUFLER. **I. By-products in the preparation** [with P. HALBIG]. **II. Addition of water to crotonic acid** [with G. BASEL] (Monatsh., 1929, **53** and **54**, 119—126).—I. Oxidation of crotonaldehyde with oxygen (cf. Duchesne and Delépine, A., 1924, i, 1281), subsequent conversion of the product into sodium salts, and extraction with alcohol gives about 6% of sodium *iso*crotonate. When oxidation is carried out in presence of sodium carbonate at 25°, and the reaction mixture is acidified with hydrochloric acid, acetic and 8% of β-chloro-α-hydroxybutyric acid, m. p. 85—86° [*sodium* salt, $C_8H_{13}O_6Cl_2Na$, m. p. 172° (decomp.)] (separated through the insoluble zinc salt), are formed as by-products. The last-named acid is formed by the action of hydrochloric acid on αβ-oxidobutyric acid.

II. When crotonic acid is heated with 20% hydrochloric acid about 80% is converted into a mixture of

β-hydroxy- and -chloro-butyric acids. With boiling 5, 10, or 20% sulphuric acid hydration to β-hydroxybutyric acid occurs to the extent of 53—70% after 4—5 days. H. BURTON.

Conductivity titration of solutions of the sodium salts of the lower fatty acids. M. GEHRKE and H. H. WILLRATH (Z. angew. Chem., 1929, **42**, 988—990).—Excess of 0·1*N*-hydrochloric acid is added to the solution and the acidified mixture titrated with 0·1*N*-sodium hydroxide. Two discontinuities are shown by the conductivity curves corresponding with the beginning and end of the neutralisation of the fatty acid. Formic acid is exceptional in that one angle is flattened and the position is obtained by extrapolation. The method is general for acids having dissociation constants for 0·1*N*-solution greater than 5×10^{-4} and also to phenols. C. IRWIN.

Tetramethylmargaric acid and tetramethylstearic acid. R. KUHN and H. SUGINOMÉ (Helv. Chim. Acta, 1929, **12**, 915—921).—*Phytyl iodide* [*α-iodo-γηλο-tetramethylhexadecane*], b. p. 152—154°/0·12—0·22 mm., d_4^{20} 1·0791, n_D^{20} 1·4799, is prepared by saturating dihydrophytol (Willstätter and Mayer, A., 1908, i, 383) at −20° with hydrogen iodide and heating at 70—80° in a sealed tube. The bromide, b. p. 147°/13 mm., 161°/0·8 mm. (cf. Karrer, Helfenstein, and Widmer, this vol., 49), is obtained by heating dihydrophytol with hydrobromic acid at 210—220°. Condensation of the bromide, or, preferably, the iodide, with ethyl potassiomalonate yields *ethyl phytylmalonate*, b. p. 191—192°/0·34 mm., converted into *ειvρ-tetramethylstearic acid*, b. p. 182°/0·22 mm. (*tribromoanilide*, m. p. 63·5—64·5°). Treatment of the Grignard compound of phytyl bromide with carbon dioxide yields *δ0μπ-tetramethylmargaric acid*, b. p. 169°/0·21 mm. (*tribromoanilide*, m. p. 62—63°). R. K. CALLOW.

Sulphonated oils. V. Preparation of ricinoleic acid sulphuric ester from ricinoleic and sulphuric acids. K. NISHIZAWA and M. SINOZAKI (J. Soc. Chem. Ind. Japan, 1929, **32**, 779—783; cf. Grün and Woldenberg, A., 1909, i, 284).—Sulphuric acid (100 g.) is gradually added during 3 hrs. to a mixture of 100 g. of ricinoleic acid (prepared from castor oil) and 100 g. of ether with vigorous agitation at 25°, the mixture is preserved for 2 hrs.; when 150 g. of ether are used, the mixture is preserved for 2—17 hrs. The product is colourless and almost pure and is isolated by acidification or as potassium hydrogen salt. K. KASHIMA.

Photochemical decomposition of lactic acid. G. R. BURNS (J. Amer. Chem. Soc., 1929, **51**, 3165—3171).—Aqueous solutions of lactic acid are decomposed by radiations of wave-lengths shorter than 2500 Å. in absence of oxygen. The main products of the decomposition are carbon dioxide and alcohol; the alcohol formed is, however, 19% in excess of the amount required by the change $CHMe(OH)\cdot CO_2H \longrightarrow EtOH+CO_2$. Other products of the decomposition are carbon monoxide (3·82%; the percentages are of the total gaseous products), methane (2·18%), ethane (2·18%), and unsaturated hydrocarbons (probably ethylene, 0·89%). Acetaldehyde or hydrogen peroxide could not be detected. The ratio between the energy absorbed and the carbon dioxide produced corresponds with a quantum yield of approximately 0·65. The results agree in the main with those of von Euler (A., 1911, ii, 452; 1912, ii, 407; 1913, ii, 544; cf. Scharz, Arch. ges. Physiol., 1918, **170**, 650) but not with those of Neuberg (A., 1912, i, 314) and Baudisch (A., 1920, ii, 461). H. BURTON.

Acetoacetic ester condensation. S. M. MCELVAIN (J. Amer. Chem. Soc., 1929, **51**, 3124—3130).—An excess of ethyl acetate, propionate, butyrate, or *iso*butyrate is treated with dry sodium ethoxide (0·5 mol.) and the reaction mixture distilled periodically to remove excess of ester and the alcohol formed during the reaction (the distillate is replaced with ester until no more alcohol distils). Refractometric determinations of the alcohol in the distillate, formed according to the reaction $2CH_2R\cdot CO_2Et+NaOEt \longrightarrow CH_2R\cdot C(ONa){:}CR\cdot CO_2Et+2EtOH$, give values of 0·83, 0·97, 1·03, and 0·03 mol., respectively. The yields of isolated keto-esters are 0·34, 0·405, 0·38, and 0 mol., respectively. The results support Claisen's mechanism (A., 1887, 583), which is reversible (cf. Higley, A., 1907, i, 461). Scheibler and Marhenkel's postulate of an intermediate enolate as an essential step in the reaction (A., 1927, 1167) is not upheld by the results with ethyl *iso*butyrate. It is suggested that the ethyl acetate–sodium ethoxide additive product may undergo decomposition either into the original components or sodium hydroxide and keten acetal (cf. Scheibler and Marhenkel, *loc. cit.*). H. BURTON.

Determination of configuration in the terpene series. IV. Optically active *iso*propylsuccinic acids. J. VON BRAUN and W. REINHARDT (Ber., 1929, **62**, [*B*], 2585—2587; cf. this vol., 679).—*dl-iso*Propylsuccinic acid, b. p. 130°/15 mm. with considerable conversion into the anhydride, readily obtained from ethyl α-bromo*iso*valerate and ethyl sodiomalonate, is resolved with some difficulty into its optical antipodes by treatment with strychnine in aqueous solution. The more sparingly soluble alkaloidal salt affords (+)-iso*propylsuccinic acid*, m. p. 87—88°, $[\alpha]_D$ +24·01° in water (*anilide*, m. p. 200°, $[\alpha]_D^{20}$ −36·5° in alcohol). The mother-liquors from the salt of the (+)-acid yield (−)-iso*propylsuccinic acid*, which, after purification through the *ethyl* ester, b. p. 119—120°, d^{20} 0·9896, $[\alpha]_D^{20}$ −15·05°, had m. p. 85—90°, $[\alpha]_D$ >21° in water. H. WREN.

Reduction of methyl esters of polymethylenedicarboxylic acids with fifteen to twenty-one carbon atoms by sodium and alcohol. P. CHUIT and J. HAUSSER (Helv. Chim. Acta, 1929, **12**, 850—859).—Glycols, $OH\cdot[CH_2]_n\cdot OH$ (n=15—21), have been prepared by reduction of the methyl esters of the corresponding acids (A., 1926, 499) by sodium and alcohol. Certain of the related compounds (cf. this vol., 677) have been prepared in a greater state of purity by improved methods. αν-Dicyanotridecane, m. p. 31—31·5°, b. p. 215—216° (from αν-dibromotridecane), yields tridecane-αν-dicarboxylic acid, the methyl ester of which is reduced to pentadecane αο-diol, m. p. 87°, which yields with hydrobromic acid αο-dibromopentadecane, m. p. 27·2—27·5°, b. p.

197°/2 mm. Hexadecane-απ-diol yields απ-dibromohexadecane, m. p. 56·2—56·7°. *α-Bromohexadecan-π-ol*, m. p. 53—54° (*acetate*, m. p. 31°, b. p. 192—194°/1 mm.), is obtained in poor yield from hexadecane-απ-diol monoacetate and hydrogen bromide. *Heptadecane-αρ-diol*, m. p. 96—96·5°, yields αρ-dibromoheptadecane, m. p. 38—38·4°, b. p. 208—210°/3 mm. Octadecane-ασ-diol, m. p. 98·6—99° (lit. 92°), b. p. 210—211°/2 mm., yields *ασ-dibromoheptadecane*, m. p. 63·5—64°, b. p. 205—207°, from which *heptadecane-ααρρ-tetracarboxylic acid*, m. p. 89—90°, may be obtained by condensation with malonic acid. *Nonadecane-ατ-diol*, m. p. 101°, b. p. 212—214°/1·5 mm., yields *ατ-dibromononadecane*, m. p. 46·2—46·5°, b. p. 210—211°/1·5 mm. Octadecane-ασ-dicarboxylic acid, m. p. 123° (lit. 124—125°) (*methyl* ester, m. p. 65·5—66°, b. p. 223—224°/2 mm.; *ethyl* ester, m. p. 54·5—55°, b. p. 230—232°/2 mm.), is obtained by the malonic ester method. *Eicosane-αν-diol*, m. p. 103°, b. p. 215—217°/1·5 mm., yields *αν-dibromoeicosane*, m. p. 67·4—68°, b. p. 220—222°/2 mm. Nonadecane-ατ-dicarboxylic acid, m. p. 123° (lit. 111°, 117°) [methyl ester, m. p. 65·3—65·8° (lit. 56—57°), b. p. 225—228°/3 mm.; *ethyl* ester, m. p. 57°, b. p. 238—239°/3 mm.], is obtained by the malonic ester method. *Heneicosane-αφ-diol*, m. p. 105—105·5°, b. p. 223—224°/1·5 mm. (*acetate*, m. p. 60°, b. p. 240°/3 mm.), yields *αφ-dibromoheneicosane*, m. p. 52·5—53°, b. p. 226—228°/2·5 mm. The ascending curves of the m. p. of the series of odd- and even-numbered glycols cross after the fifteen-atom member and then rejoin at the eighteen-atom member to give a single curve. The ascending curves of the m. p. of the dibromo-compounds, at first roughly parallel, afterwards converge slightly. The even-numbered compounds in each case have the higher m.-p. curve. R. K. CALLOW.

Constitution of anhydrotricarballylic acid. R. MALACHOWSKI (Bull. Acad. Polonaise, 1929, A, 265—273).—The structure $\begin{matrix} O & CO \\ | & \\ CO\cdot CH_2 & \end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$ for anhydrotricarballylic acid, prepared in 87—91% yield by the action of acetic anhydride below 45° on tricarballylic acid, is supported by the following experiments. α-Methyl *trans*-aconitate is reduced by platinum-black and hydrogen to *α-methyl tricarballylate*, m. p. 111—112°, and is identical with the ester obtained by the alcoholysis of anhydrotricarballylic acid with methyl alcohol or by the treatment of the anhydro-acid with diazomethane in ether with the formation of the *α-methyl* ester of the anhydro-acid, m. p. 59—60°, followed by ring fission of the latter by water. Tricarballylic acid, m. p. 160—161°, is produced in 87% yield from *trans*-aconitic acid, platinum-black, and hydrogen, and, in a less pure form, by the reduction of *cis*-aconitic acid. Attempts to reduce the anhydrides of *cis*- and *trans*-aconitic acid dissolved in glacial acetic acid with platinum-black and hydrogen were unsuccessful. A. I. VOGEL.

Tests for acetone and aldehyde. H. LEFFMANN and C. C. PINES (Bull. Wagner Free Inst., 1929, 4, 39—41).—For the detection of formaldehyde in the presence of acetaldehyde the most satisfactory results are obtained with a solution of 1 g. of potassium guaiacolsulphonate in 10 c.c. of concentrated sulphuric acid. Acetone can be readily detected in the presence of formaldehyde by adding a concentrated aqueous or preferably glycerol solution of sodium nitroprusside containing ethylamine to a dilute aqueous solution of the mixture; a red ring is formed at the contact zone. A. I. VOGEL.

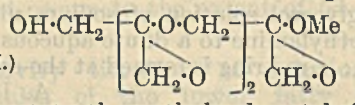
Manufacture of chloroacetaldehyde. I. G. FARBENIND. A.-G.—See B., 1929, 887.

Bromination products of *iso*butaldehyde. R. DWORZAK and W. PRODINGER (Monatsh., 1929, 53 and 54, 588—595).—Bromination of *iso*butaldehyde (I) at about −10° and treatment of the product with alcohol affords α-bromo*iso*butaldehyde (II), its ethyl acetal (III), and *bromoparaisobutaldehyde* (IV) $C_{12}H_{23}O_3Br$, b. p. 128·5°/10 mm. Attempted depolymerisation of IV at 160° gives I, but II could not be isolated. Bromination of I at about 30° and treatment with alcohol gives small amounts of II, III, and IV; the main product is the compound (V), m. p. 82·5°, previously described (this vol., 1166). The stability of V towards various acidic reagents is noted, but hydrolysis with sodium hydrogen carbonate or alcoholic potassium hydroxide solution gives α-hydroxy*iso*butaldehyde. The substance is now considered to be *αα'ββ'-tetrabromodiisobutyl ether* (cf. Stepanov, A., 1927, 42; Hibbert, Perry, and Taylor, this vol., 791). H. BURTON.

Thermal decomposition of acetone in the gaseous state. F. O. RICE and R. E. VOLLRATH (Proc. Nat. Acad. Sci., 1929, 15, 702—705; cf. Hinshelwood and Hutchison, A., 1926, 691).—When vaporised acetone was passed with nitrogen at a known rate through a quartz tube heated in an electric furnace, for every 100 mols. of acetone decomposed approximately 60 mols. of keten were recovered. Hence the primary reaction in the unimolecular decomposition of acetone is probably the separation of a molecule of methane and the formation of keten, which, at the high temperature, undergoes a bimolecular decomposition into ethylene and carbon monoxide. If this is the correct explanation, 100 mols. of decomposed acetone should give 100 mols. of methane, 30 mols. of ethylene, and 60 mols. of carbon monoxide. This result agrees fairly closely with that of Hinshelwood and Hutchison (*loc. cit.*) as far as the gases are concerned. A. J. MEE.

Polymerisation and condensation. V. Condensation products of methyl*cyclo*dihydroxyacetone. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1929, 84, 39—47).—The action of methyl alcohol containing 0·5% of hydrogen chloride on commercial dihydroxyacetone led principally to the methyl*cyclo*acetal of dihydroxyacetone (cf. Fischer and Taube, A., 1927, 857). The mother-liquor was treated with ethyl acetate and the precipitated oil, after removal of solvents, was acetylated with acetic anhydride and pyridine, the product consisting of diacetoxyacetone and the *acetate* of the *methyl*cyclo*acetal* of *dihydroxyacetone*, m. p. 135°. The residue from the ethyl acetate mother-liquor was similarly acetylated, yielding *acetyldihydroxyacetonylmethylcyclodihydroxyacetone*, m. p. 184°. When heated at or slightly above its m. p., methyl*cyclo*dihydroxyacetone formed [*di*(*dihydroxyacetonyl*)]*methyldihydr-*

oxyacetone (I), m. p. 300° (decomp.), methyl alcohol being eliminated. On treatment with *p*-nitrophenyl-



(I.)

hydrazine acetate, the methyl*cyclo*acetal of dihydroxyacetone gave the *p*-nitrophenylosazone of dihydroxyacetone. The glucosidic linking in the acetal is thus so unstable as scarcely to modify the reactions of the compound in comparison with those of dihydroxyacetone itself. C. R. HARINGTON.

Detection and isolation of biochemically formed methylglyoxal as its dioxime. C. NEUBERG and M. SCHEUER (Monatsh., 1929, **53** and **54**, 1031—1035).—A preparation of *B. lactis aërogenes* is washed successively with physiological saline and water, then dried, the dry material triturated with acetone, filtered, and washed with acetone and ether. The residual product produces methylglyoxal from magnesium hexosediphosphate solution (cf. this vol., 354, 722), which is isolated as the dioxime or the dioxime nickel salt. H. BURTON.

Bial's reagent and various colour reactions of carbohydrates. H. SZANCER (Pharm. Zentr., 1929, **70**, 663—665).—When 1 c.c. of a pentose solution is mixed with a few drops of alcoholic thymol solution, and an equal volume of concentrated sulphuric acid is poured down the side of the tube, a red ring is formed which gives its colour to the whole liquid on mixing; with dextrose or lactose a less intense red ring is obtained, but the colour disappears on mixing. With α-naphthol in place of thymol, pentoses, dextrose, and lactose give a dark blue ring with a lower brown ring, which is due to the α-naphthol alone; mixing yields a dark blue, turbid liquid, which deposits blue flocks on dilution with water. With β-naphthol, pentoses yield a deep violet ring, and, on mixing, a dirty grey, turbid liquid; dextrose or lactose gives an indistinct violet ring, disappearing on mixing. With vanillin, pentoses give a bright red ring and a deep red solution on mixing; dextrose yields a yellow ring and a red solution, gradually deepening, on mixing; lactose gives a bright yellow ring and a yellow mixed solution; eugenol gives a multicoloured ring due, not to furfuraldehyde, but to the eugenol itself. T. H. POPE.

Bial's pentose reaction. H. SZANCER (Pharm. Zentr., 1929, **70**, 645—646).—In its original form Bial's reaction for pentoses is characteristic of these sugars, hexo-aldoses and the corresponding polysaccharides requiring a more protracted action of the hydrochloric acid present before giving the reaction. The lævulic acid formed in the latter case retards the reaction of orcinol with furfuraldehyde, but not that with hydroxymethylfurfuraldehyde. Mixtures of pentoses with other sugars sometimes fail to give the characteristic coloration. Thus, the presence of lævulose determines the production of a brown coloration, but aldoses cause no interference. T. H. POPE.

Trinitrophenol as a sugar reagent. H. SZANCER (Pharm. Zentr., 1929, **70**, 665—666).—Addition of ammonium sulphide to aqueous picric acid solution results in the change, gradual in the cold but rapidly on heating, of the yellow colour to deep red, the picric acid being reduced to ammonium picramate. A similar reduction is effected by sugars with a free aldehydic or ketonic group when 2 c.c. of 0·5% aqueous picric acid solution is treated with 20—25 drops of 5% sodium or potassium hydroxide and 2 c.c. of the sugar solution of at least 0·20% concentration. The reaction is not applicable to the detection of sugar in urine, since normal urine is coloured deep red by neutral or faintly alkaline picric acid solutions owing to the presence of creatinine. T. H. POPE.

Determination of reducing sugars with potassium mercuric iodide. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], **10**, 292—301).—The process of Baudouin and Lewin (A., 1927, 476) for the microdetermination of dextrose has been improved by the addition of barium sulphate, which greatly facilitates dissolution of the mercury, and the conditions under which it is specific have been determined. Under these conditions the presence of 2—3 parts of mannitol or 10 parts of sucrose with each part of dextrose does not appreciably affect the results. The method has been extended for the approximate determination of dextrose and mannitol in their mixtures. A. A. GOLDBERG.

Oxidative decomposition of sugars. VI. Degradation of dextrose into C_3 chains by alkaline-earth carbonates. K. BERNHAUER and H. WOLF. VII. Transformation of methylglyoxal. K. BERNHAUER and B. GÖRLICH (Biochem. Z., 1929, **212**, 443—451, 452—465).—VI. When dextrose is boiled with alkaline-earth carbonates, 12—13% is obtained as triose (methylglyoxal and glycerol) and the rest is present chiefly as a mixture of saccharic acids. Lactic acid is not formed.

VII. Methylglyoxal when treated with magnesium or calcium carbonates in aqueous suspension at the ordinary temperature is converted into a triose (probably glyceraldehyde) and is then partly condensed into hexose. The formation of lactic acid from methylglyoxal is discussed (cf. this vol., 297, 543). P. W. CLUTTERBUCK.

Formation of glucosazone. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, **51**, 3161—3165).—When dextrose is treated with an equimolecular quantity of phenylhydrazine in presence of alcohol and 75% acetic acid, and the mixture kept for some days, a 63% yield (on phenylhydrazine used) of glucosazone is obtained instead of the phenylhydrazone described by Behrend and Lohr (A., 1908, i, 765). In dilute acetic acid solution a 62·5% yield of the osazone results. Similar results are given by lævulose. The phenylhydrazones of dextrose (Fischer, A., 1887, 567; Skraup, A., 1889, 1130) and lævulose (Landrieu, A., 1906, ii, 270) undergo conversion into glucosazone when solutions in dilute acetic acid are kept for some days. The change probably involves intramolecular oxidation and reduction. Mannosephenylhydrazone is stable under the same conditions. H. BURTON.

Glucosazone reaction. N. TAKETOMI and K. MIURA (J. Soc. Chem. Ind. Japan, 1929, **32**, 776—779).

—For obtaining a maximum yield of glucosazone by Fischer's method, the ratio of phenylhydrazine hydrochloride and crystallised sodium acetate should be 1 : 2·7—2·8. The yield of osazone increases with increasing amount of the reagents up to about 3·2 g. of the hydrochloride in 20 c.c. of water. The duration of heating influences greatly the yield of osazone. The reaction is not completed within less than 3 hrs., but beyond this decomposition takes place.

K. KASHIMA.

Fluorine derivatives of carbohydrates. B. HELFERICH and R. GOOTZ (Ber., 1929, **62**, [*B*], 2505—2507).—α-Acetobromoglucose is converted by technical silver fluoride in acetonitrile at the atmospheric temperature into β-*acetofluoroglucose*, m. p. up to 98° after very frequent crystallisations, $[\alpha]_D^{18}$ +21·9° in chloroform. The product is considerably more stable than the corresponding chloro-compound, but de-acetylation by ammonia or sodium methoxide does not yield uniform products. Hepta-acetylfluorolactose is hydrolysed by sodium methoxide to the very stable α-*fluorolactose*, decomp. 180—195°, $[\alpha]_D^{16}$ +83·2° in water.

H. WREN.

Modifications of galactose. C. N. RIBER, J. MINSAAS, and R. T. LYCHE (J.C.S., 1929, 2173—2185; cf. A., 1926, 1228).—A study of the change of volume of an aqueous solution of ordinary galactose (α-galactose) leads to the conclusion that more than two modifications of the sugar must be present. The presence of a third modification *B* together with α-galactose *A* and β-galactose *C* is postulated. A repetition of earlier work using β-galactose prepared by a new method, and also a study of the alteration in optical rotation, leads to the conclusion that each of the modifications is convertible into both the others (cf. Smith and Lowry, A., 1928, 510). This result does not preclude the existence of a fourth modification, the existence of which is suspected from a theoretical study of the optical rotations of the four penta-acetates of galactose and the three methylgalactosides.

The following constants are given for pure β-galactose, prepared by evaporation of an aqueous solution of ordinary galactose at the ordinary temperature under aseptic conditions over calcium chloride in a vacuum: monoclinic prisms, β 106° 25′; $a : b : c$ = 0·827 : 1 : 0·775; $[\alpha]_D^{20}$ +54·2° in water, $[R_G]_D$ 62·62°; V_m 108·94 c.c.

J. W. PORTER.

Melezitose in honey-dew honey from the lime. F. E. NOTTBOHM and F. LUCIUS.—See B., 1929, 955.

Synthesis of glucosides. III. Glucosides of hydroxyxanthones. A. ROBERTSON and R. B. WATERS (J.C.S., 1929, 2239—2243).—2-O-*Tetra-acetyl*-β-*glucosidoxyxanthone*, m. p. 173°, $[\alpha]_D^{20}$ −36·4° in acetone, was prepared by the action of *O*-tetra-acetyl-α-glucosidyl bromide on 2-hydroxyxanthone, and gave 2-β-*glucosidoxyxanthone*, m. p. 237°, on hydrolysis. The latter is hydrolysed by warm 15% hydrochloric acid and by emulsin to 2-hydroxyxanthone and dextrose. 4-O-*Tetra-acetyl*-β-*glucosidoxyxanthone*, m. p. 199—200°, $[\alpha]_D^{20}$ −31·8° in acetone, was prepared similarly to the 2-isomeride, and gave 4-β-*glucosidoxyxanthone*, m. p. 274° (decomp.), with similar properties to the 2-isomeride. 7-O-*Tetra-acetyl*-β-*glucosidoxy*-1-*hydroxyxanthone*, m. p. 176—177°, $[\alpha]_D^{20}$ −33·4° in acetone, was prepared in a similar manner from euxanthone, and gave on acetylation 7-O-*tetra-acetyl*-β-*glucosidoxy*-1-*acetoxanthone*, m. p. 211°, $[\alpha]_D^{20}$ −34·2° in acetone. On de-acetylation 7-β-*glucosidoxy*-1-*hydroxyxanthone* (I), m. p. 218—219°, was formed. 1-*Hydroxy*-7-*acetoxyxanthone diacetoborate* is produced when euxanthone and boroacetic anhydride are refluxed and is decomposed by water to give 1-*hydroxy*-7-*acetoxyxanthone*, m. p. 160°, which on methylation yields 7-*acetoxy*-1-*methoxyxanthone*, m. p. 176°. Hydrolysis of the latter furnishes 7-*hydroxy*-1-*methoxyxanthone*, m. p. 235°. 7-O-*Tetra-acetyl*-β-*glucosidoxy*-1-*methoxyxanthone*, m. p. 166—168°, was prepared by methylation of the corresponding hydroxy-compound, and hydrolyses readily to 7-hydroxy-1-methoxyxanthone. These reactions show conclusively that natural glycuronate euxanthic acid corresponds in structure with I.

J. W. PORTER.

Plant colouring matters. XV. The sugar of α-crocin. P. KARRER and K. MIKI (Helv. Chim. Acta, 1929, **12**, 985—986).—α-Crocin (A., 1928, 644) is hydrolysed by alcoholic ammonia at the ordinary temperature. The sugar formed in solution is acetylated and isolated as the acetate, which is identical with gentiobiose octa-acetate.

R. K. CALLOW.

Sulphurylation of starch. M. SAMEC (Monatsh., 1929, **53** and **54**, 852—854).—A suspension of potato-starch in water is made into a paste with an equal volume of 0·8*N*-sodium hydroxide solution, and then treated with a chloroform solution of sulphuryl chloride at 5—7°. Dialysis and subsequent electro-dialysis of the reaction mixture affords mobile and viscous phases. These show widely differing physical properties; the mobile phase contains nearly four times as much SO_3 as the viscous.

H. BURTON.

Inulin phosphate. M. LÜDTKE (Biochem. Z., 1929, **212**, 475—476).—The preparation of inulin monophosphate by the action of phosphoryl chloride on inulin in pyridine and pouring into water is described. The ester reacts acid to litmus and liberates carbon dioxide from sodium carbonate, but is insoluble in water, aniline, ammonia, or sodium hydroxide.

P. W. CLUTTERBUCK.

Fractional precipitation of cellulose acetate and properties of the fractions. J. G. MCNALLY and A. P. GODBOUT (J. Amer. Chem. Soc., 1929, **51**, 3095—3101).—A sample of a commercial acetone-soluble cellulose acetate when fractionally precipitated by the addition of varying amounts of water or aqueous acetone (3 : 1) to a 10% solution in acetone, gives various fractions (removed by centrifuging) which have almost identical acetyl values and specific rotations, but differ widely in m. p., viscosity, and solubility in various organic solvents. The results indicate that the original acetate contains a series of micelles; these differ either in the number of glucose anhydride units they contain or in the manner in which they are joined together to form the micelle.

H. BURTON.

Cellulose methylene ether. F. C. WOOD (Nature, 1929, **124**, 762).—*s*-Dichlorodimethyl sulphate reacts with soda-cellulose giving monomethylenecellulose,

$C_6H_7O_2(OH)(CH_2O_2)$. Other methylene inorganic and organic esters give somewhat similar results. Monochlorodimethyl sulphate forms a mixed methyl methylenecellulose ether. A. A. ELDRIDGE.

Pine lignin. IX. P. KLASON (Ber., 1929, 62, [*B*], 2523—2526).—An alternative method of calculation leads to the formula $C_{120}H_{132}O_{42}$ for lignin, identical with that deduced by Freudenberg and others (this vol., 1046). Freudenberg's conception is founded on the presence in lignin of an aliphatic hydroxyl group which can be methylated, but no phenolic hydroxyl group. Vanillin cannot be methylated by methyl sulphate. Irregular results in the methylation of α-lignosulphonic acid are thus explained, since the process affects only aliphatic hydroxyl groups, if present, whereas the *para*-phenolic hydroxyl is not affected. Freudenberg's assumption of the absence of a free phenolic hydroxyl group in lignin appears premature. Since Tiemann has shown that vanillin can be methylated by methyl bromide and alkali, this process has been extended to lignin. Dry lignin, containing 14% OMe, had 15·5% OMe after treatment with methyl sulphate, showing that the bulk of the water of the aliphatic part had been removed by desiccation. After treatment with alkali and methyl bromide the methoxyl content was 20·5%, or 20% after successive treatment with methyl sulphate and methyl bromide. The increase corresponds with the presence of one third of the phenolic hydroxyls in lignin in the free form; this assumption is confirmed by the behaviour of lignin towards *N*-potassium hydroxide. In lignin and in the α-sulphonic acid a trimeric form of lignin is present. The formula $(3C_{10}H_{10}O_3+2H_2O)+H_2SO_3+C_{10}H_9N-H_2O$ is now advanced for naphthylamine α-lignosulphonate. The constitution of lignin is discussed. H. WREN.

Lignin. XII. Acetylated hydrochloric acid lignin. W. FUCHS and O. HORN (Ber., 1929, 62, [*B*], 2647—2653; cf. this vol., 1282).—Treatment of Willstätter lignin with acetic anhydride containing sulphuric acid yields almost quantitatively an acetyl-lignin with 19·2% of acetyl. Elementary analysis, coupled with determinations of methoxyl and acetyl, indicate in a compound, $C_{50}H_{52}O_{20}$, the presence of four methoxyl, four acetoxy-, and very probably an ethylene oxide group in a mixed aromatic–heterocyclic system. Lignin in wood can be so acetylated that the product appears to contain three acetyl groups in excess of those present in acetylated Willstätter lignin. It appears, therefore, that the mixed aromatic–heterocyclic nucleus which must be considered present in wood and isolated lignin must be so altered by hydrochloric acid that its activity towards acetylation is diminished. The action of bromine on acetyl-lignin is so greatly influenced by small amounts of water that little information is afforded by a study of the products of the change. Ozone converts acetyl-lignin suspended in acetic acid into about 10% of products resembling those derived from other complex natural materials. Hydrogen peroxide in pyridine does not greatly affect lignin in 48 hrs. at the ordinary temperature, but, under more drastic conditions the acetyl groups are largely removed; after re-acetylation a product with a very slightly increased oxygen content is obtained. Treatment of lignin, acetyl-lignin, and oxidised acetyl-lignin with hydrochloric acid gives very varying amounts of formaldehyde. It is considered doubtful if formaldehyde is a product of the fission of lignin, and the assumed presence of a piperonyl component in lignin is regarded as unjustified (cf. Freudenberg and Harder, A., 1927, 342). The possibility of characterising lignin in its various forms by quantitative study of its swelling in pyridine is indicated. H. WREN.

Lignin. I. Acetylation and preparation of degradation products soluble in water. H. FRIESE (Ber., 1929, 62, [*B*], 2538—2550).—Treatment of spruce wood with a mixture of acetic acid, acetic anhydride, and zinc chloride leaves a residue (yield about 150%) retaining the original structure and containing 54·67% of acetic acid and 3·88% OMe. Extraction of the residue with acetone removes about 8% of the material, which does not differ appreciably in constitution from the remainder, which is insoluble in all media. The precipitate obtained by pouring the acid liquor (see above) into water contains considerable amounts of lignin; a separation of the components is not effected by fractionation. If zinc chloride is replaced by sulphuric acid, about half the wood can be brought into solution, but the residue still contains carbohydrates even after the treatment has been repeated until nothing further is dissolved. Treatment of spruce and pine meal with sulphuric acid and acetic anhydride in differing concentrations at a relatively very low temperature leads to the isolation of a methoxyl-free fraction (*A*), soluble in chloroform but insoluble in water, and an unsaccharifiable component (*B*) rich in methoxyl and soluble in water. The portion *B*, provisionally regarded as lignin acetates (about 17% of the wood), is not homogeneous and is divided by hydrolysis into a portion very freely soluble in methyl alcohol and water and a part soluble in water only. The methoxyl content for different preparations varies between wide limits. A slight reducing power towards Fehling's solution is probably due to the presence of traces of sugars. The preparations are soluble in ammonia, alkali hydroxide, and sodium carbonate. Concentrated hydrochloric acid causes resinification. With pyridine and acetic anhydride an acetic acid content of 26—36% is reached, according to the richness in methoxyl. The portion insoluble in methyl alcohol is a brown powder which does not absorb moisture from the air, whereas the soluble portion is extraordinarily hygroscopic (also as acetate). The mol. wts. in freezing water are about 600 and 172, respectively. The first-named product has 51% C and the last-named only 38%. Products containing 62% C, as usually assumed for lignin, have not been isolated. Since oxidation during the course of the reaction is improbable, it is likely that the original lignin is in ether- or ester-like union with a portion of the polysaccharides of the wood. The union is easily disrupted by hydrolysis, but, if drastic conditions are employed, condensation and elimination of water occur simultaneously, thereby explaining the high carbon content of lignin.

H. WREN.

Lignin. V. Relation of lignin and resin. A. FRIEDRICH and A. SALZBERGER (Monatsh., 1929, **53** and **54**, 989—1001).—The resin extracted from pine wood by an alcohol–benzene (1 : 1) mixture differs from the sap resin. The former resin (5·21% OMe) is separated into (*a*) benzene-soluble and (*b*) benzene-insoluble fractions; extraction of (*a*) with light petroleum gives a soluble part (60% of *a*) containing only 1·45% OMe. Dissolution of *b* in alcohol and precipitation with acidulated water affords a lignin-like substance, m. p. 129—134° with darkening (12·85% OMe); treatment of the alcoholic solution with light petroleum yields a product, decomp. above 300° (13·7% OMe), similar to pinewood lignin. Chloroform–ether extraction and precipitation affords a product (about 14·5% OMe) which can be methylated or benzoylated. Its reactions with bromine, ferric chloride, and phenylhydrazine are similar to those of soluble pinewood lignin (B., 1926, 151; A., 1927, 861). Zinc dust distillation yields a product similar to that obtained by Karrer and Bodding-Wiger (A., 1923, i, 1183) from lignin.

A similar lignin-like substance is also isolated from beechwood resin. A relationship between the lignin found in the resin and that in the cellulose appears probable. H. BURTON.

Acetylated wood, the combination of the incrustation, and a method of separation of the constituents of wood. H. SUIDA and H. TITSCH (Monatsh., 1929, **53** and **54**, 687—706).—Acetylation of resin-free, degummed, powdered beech and pine woods and of cotton with acetic anhydride in presence of pyridine and/or dimethylaniline for 15—35 days at 100°, gives products containing 30·1—35·2% OAc (cf. A., 1928, 1227). Using Fuchs' method (A., 1928, 743) and not degummed beech and pine woods the acetyl content is of the order 36—38% and not 41% (cf. Fuchs, *loc. cit.*; Horn, this vol., 175).

The separation of the resin-free, degummed beech wood into lignin and cellulose is carried out as follows. The acetylated wood (acetic anhydride, acetic acid, and sulphuric acid at 32—35°) is separated into (*a*) chloroform-soluble (86—91% of acetylated wood) and (*b*) chloroform-insoluble parts. Extraction of *a* with acetone gives soluble (22—26%) and insoluble fractions (69—74%), which on hydrolysis with sodium hydroxide solution afford lignin and cellulose, respectively. The above chloroform-soluble material is soluble in warm phenol and can be precipitated unchanged by the addition of alcohol.

Native cellulose (the wood skeleton) is regarded as a heteromicellar structure, whilst "purified" cellulose fibres are homomicellar (cf. Meyer and Mark, A., 1928, 621). H. BURTON.

Three compounds extracted from Steyrian lignite. A. SOLTYS (Monatsh., 1929, **53** and **54**, 185—186).—The concentrated light petroleum extract of the lignite deposit a sterol-like *substance*, probably $C_{30}H_{50}O$, m. p. 265°, $[\alpha]_D^{22}$ −19·1° in benzene. Distillation of the residue yields 0·5—1% of a hydrocarbon $C_{15}H_{28}$ (probably a fully hydrogenated sesquiterpene), b. p. 265°, d^{22} 0·8994, $[\alpha]^{22}$ +5·62°, and about 1% of iosene (cf. following abstract). H. BURTON.

Iosene, a new hydrocarbon from Steyrian lignite. A. SOLTYS (Monatsh., 1929, **53** and **54**, 175—184).—The lignite crust is extracted with light petroleum and the residue from the extract distilled in a vacuum. The fraction, b. p. 195—220°/12 mm., contains the hydrocarbon iosene, $C_{20}H_{34}$, m. p. 74°, $[\alpha]_D^{22}$ +23·81° in alcohol. This is identical with hartite, bombiccite, and hofmannite (cf. Ciusa and others, A., 1921, ii, 343; 1922, ii, 385), and probably with the hydrocarbon isolated from Piberstein–Lankovitz lignite by Dolch and Strebinger (Mikrochem., 1924, 94). Individual substances could not be isolated when iosene is oxidised with nitric acid or potassium permanganate; iosene is saturated (to bromine; hydrogenation; ozone). Attempted dehydrogenation of iosene with sulphur at 260° affords a *compound*, $C_{20}H_{28}S_3$, m. p. 198°, $[\alpha]_D^{19}$ −436·6° in benzene. Prolonged treatment with selenium at 360—380° yields retene (*quinone*, m. p. 198°); iosene is, therefore, related to abietic acid. It is presumed that it contains four rings and alternative structures are indicated. H. BURTON.

Preparation of dihalogenated mixed secondary aliphatic amines. I. M. DE MONTMOLLIN and P. MATILE. **II.** M. DE MONTMOLLIN and F. ACHERMANN (Helv. Chim. Acta, 1929, **12**, 870—873, 873—881).—I. An investigation of possible methods of preparing amines of the type of β-bromoethyl-β-bromobutylamine has been made. 2-*Naphthyl* β-p-*toluenesulphonamidoethyl ether*, m. p. 116°, is obtained in 45% yield by the condensation of *p*-toluenesulphonamide with 2-naphthyl β-bromoethyl ether in boiling alcoholic potassium hydroxide, and is then condensed with α-chloro-β-ethoxybutane by heating with the theoretical amount of alcoholic potassium hydroxide under pressure at 110°, whereby p-*toluenesulphon*-β-*naphthoxyethyl*-β-*ethoxybutylamide* (I), m. p. 137°, is obtained in 45% yield. The condensation of β-aminoethyl alcohol with α-chloro-β-ethoxybutane in alcoholic solution at 200° yields a mixture from which the secondary amine may be partly separated by distillation and converted into β-*hydroxyethyl*-β′-*ethoxybutylnitrosoamine*, b. p. 168—171°/15 mm., which yielded on hydrolysis a mixture (II) of the dihydroxy- and hydroxyethoxy-amines, b. p. 170—210°/15 mm. Finally, β-*hydroxyethyl*-β-*hydroxybutylamine* (III) (see below) was prepared by condensation of α-amino-β-hydroxybutane with ethylene oxide. Treatment of I, II, or III with hydrobromic acid (cf. this vol., 916) yielded the *hydrobromide*, m. p. 190° (decomp.), of β-*bromoethyl*-β-*bromobutylamine* (*picrate*, m. p. 139°).

II. A detailed investigation has been made of the best methods of preparing β-bromoethyl-β-bromobutylamine in quantity by the last of the methods outlined in the previous paper. α-Nitro-β-hydroxybutane (*picrolonate*, m. p. 154°), is prepared by condensation of propaldehyde with nitromethane, and is best reduced (yield 50%) to α-amino-β-hydroxybutane by aluminium amalgam (cf. Tordoir, A., 1902, i, 265). The interaction of α-butylene oxide (A., 1924, i, 360) and concentrated ammonia gives α-amino-β-hydroxybutane in 33% yield. α-Amino-β-ethoxybutane (picrate, m. p. 152—154°; *picrolonate*,

m. p. 169—170°), has been prepared by a modification of Bookman's method (A., 1896, i, 199) by the interaction of α-chloro-β-ethoxybutane and alcoholic ammonia at 140°. The condensation of α-amino-β-hydroxybutane with ethylene oxide (cf. Knorr, A., 1899, i, 461) is effected in the cold, and yields a mixture of the syrupy primary, secondary, and tertiary amines, which are separated only with difficulty by fractional distillation. No crystalline product is obtained by treatment with nitrous acid, but when the mixture is ethylated by treatment with potassium and ethyl bromide, β-*ethoxyethyl*-β-*ethoxybutylamine*, b. p. 105—107°/9 mm., 210—212°/720 mm. (*nitroso*-derivative, b. p. 150—152°), and *di*-(β-*ethoxyethyl*)-β-*ethoxybutylamine*, b. p. 140—142°/12 mm., are readily separated by fractional distillation. The condensation of α-amino-β-ethoxybutane with ethylene oxide yields similarly β-*hydroxyethyl*-β-*ethoxybutylamine*, b. p. 115—117°/10 mm. (*nitroso*-derivative, b. p. 165—166°; *picrolonate*, m. p. 125—126°), which is readily ethylated. *Di*-(β-*hydroxyethyl*)-β-*ethoxybutylamine*, b. p. 162°/11 mm., is obtained with excess of ethylene oxide. By heating the non-ethylated, partly ethylated, or completely ethylated bases with hydrobromic acid in sealed tubes there are obtained β-bromoethyl-β-bromobutylamine hydrobromide, m. p. above 300° (free *base*, an unstable oil; *picrolonate*, m. p. 148—150°), and *di*-(β-*bromoethyl*)-β-*bromobutylamine hydrobromide*, m. p. above 300° (*base*, an oil; *picrate*, decomp. 260°). R. K. Callow.

Hydrochlorides of α-amino-alcohols. K. A. Krasuski and K. G. Kosenko (Ukraine Chem. J., 1929, **4**, 199—209).—By passing dry hydrogen chloride through a cooled ethereal solution of α-amino-alcohols, the hydrochlorides were obtained as crystalline non-hygroscopic precipitates. With excess of hydrogen chloride the salts first became highly hygroscopic, and finally liquefied, forming liquid additive compounds with several molecules of hydrogen chloride which on keeping at the ordinary temperature, gave off hydrogen chloride and reprecipitated the solid salts.

If dry solid hydrochlorides were further treated with hydrogen chloride, they liquefied with evolution of heat, but the resulting compounds were very unstable, and decomposed into the original salts with evolution of hydrogen chloride. Tertiary amines were found to add hydrogen chloride most readily to form additive compounds with two extra molecules; the secondary were less reactive and added only one extra molecule, whilst the primary reacted only to a very slight extent. In general, it was found that the less basic are the properties of the amino-alcohol, the more readily it absorbs excess of hydrogen chloride, and the more actively the hydrochloride reacts with the gas to form the unstable additive compounds. M. Zvegintzov.

Action of *iso*amylamine on *iso*propylethylene oxide. K. A. Krasuski and F. F. Krivonos (Ukraine Chem. J., 1929, **4**, 211—213).—*iso*Propylethylene oxide in 33% aqueous or benzene solution reacts with *iso*amylamine less readily than with ammonia (which reacts at the ordinary temperature), heating for 10 hrs. on the water-bath being necessary. A 50% yield of iso*amylaminomethyl*iso*propylcarbinol*, $CHPr^{\beta}(OH)\cdot CH_2\cdot NH\cdot[CH_2]_2\cdot Pr^{\beta}$, b. p. 125—127°/25 mm. (*hydrochloride*, m. p. 263°; *picrate*, m. p. 130—132°), is obtained. M. Zvegintzov.

Polysaccharides. XL. Enzymic degradation of chitin. II. P. Karrer and G. von François (Helv. Chim. Acta, 1929, **12**, 986—988; cf. this vol., 915).—Chitin from mushrooms is decomposed by snail chitinase in the same way as chitin from lobster shells (*loc. cit.*) with the formation of *N*-acetylglucosamine in 80% yield, suggesting that plant and animal chitins are identical. When chitosan is acetylated by boiling with acetic anhydride and sodium acetate the product is decomposed by chitinase to yield *N*-acetylglucosamine, indicating that an acetyl group is necessary for this degradation and supporting the assumption that chitosan is simply de-acetylated chitin. R. K. Callow.

Preparation and properties of xanthhydrol as a reagent for carbamide. F. G. Kny-Jones and A. M. Ward (Analyst, 1929, **54**, 574—575).—Xanthhydrol is very unstable; it has m. p. about 120—123° according to mode of heating, and decomposes above this temperature. For use in the determination of carbamide it should be freshly prepared by reducing xanthone by means of alcoholic sodium amalgam. The alkaline alcoholic solution is poured into excess of water, and the product collected and redissolved in methyl or ethyl alcohol, as the alcoholic solution is much more stable than the solid. D. G. Hewer.

Complex metallic cyanides. III. Compounds of iron and cobalticyanic acids with bivalent heavy metals. H. Reihlen and W. Zimmermann (Annalen, 1929, **475**, 101—119).—A systematic investigation of the complex salts formed by the action of cadmium sulphate on potassium ferro- and ferri-cyanide. When a hot solution of potassium ferricyanide is treated with an excess of cadmium sulphate solution the *potassium* salt $[\{(H_2O)_2Fe^{\cdot\cdot\cdot}(CN)_6Cd\}_3Cd][K(H_2O)],12H_2O$ (I) is formed. If the precipitate obtained with cold solutions is treated at 100° with cadmium sulphate solution it is converted into the *cadmium* salt, $[\{(H_2O)_2Fe^{\cdot\cdot\cdot}(CN)_6Cd\}_3Fe^{\cdot\cdot\cdot}(?Cd)][Cd(H_2O)_4]_{0\cdot5},22H_2O$. In the presence of 3·5*N*-ammonia solution I is not stable, the precipitate then consisting of the basic *salt* $[\{(HO)_2Fe^{\cdot\cdot\cdot}(CN)_6Cd\}_3Cd][Cd(NH_3)_4]_3NH_4$ (II), providing the ratio Cd : Fe in the solution is $>2:1$. If this ratio is less than this value initial crystallisation of II is followed by separation of the *compound* $[\{Cd(CN)_6Fe^{\cdot\cdot\cdot}(OH)_2\}_3Cd][Cd(NH_3)_4]_2(NH_4)_3,3H_2O$. With potassium cobalticyanide a *basic cobalt* salt similar to II is obtained. When I is dissolved in 2*N*-ammonia and the solution is saturated with ammonia at −15° the complex *ammonium* salt $[\{(HO)_2Fe^{\cdot\cdot\cdot}(CN)_6Cd\}_3Cd](NH_4)_7$ crystallises, contaminated with the *compound* $[\{Fe(CN)_6Cd(OH)_2\}_3Cd][Cd(NH_3)_6]_{0\cdot3}(NH_4)_{6\cdot35},14H_2O$. By similar methods the corresponding complex *zinc* and *nickel* salts, $[\{(OH)_2FeZn(CN)_6\}_3Zn](NH_4)_6K,8H_2O$ and $[\{(OH)_2Fe(CN)_6Ni\}_3Ni][Ni(NH_3)_6](NH_4)_{4\cdot5}K_{0\cdot5},27H_2O$, are obtained. Degradation of the complex heptabasic anion $[Fe_3Cd_4(CN)_{18}(OH)_6]$ to derivatives of the simple anion $[FeCd(CN)_6]$ may be effected in

two ways. First by dissolving any salt of type I in ammonia, adding ammonium sulphate to depress the hydroxyl-ion concentration, and removing the excess of ammonia over sulphuric acid in a vacuum, and thus is obtained the *hexammine cadmium* salt, $[Fe(CN)_6Cd]_2[Cd(NH_3)_6],2H_2O$. Fission of the co-ordination complex to yield the corresponding ferricyanide, $[Fe(CN)_6][Cd(NH_3)_6]_3$, is not possible in solution. The second method consists in the addition of cadmium sulphate solution to a hot solution of potassium chloride and ferricyanide, no precipitation occurring, but on cooling the *potassium* salt, $[Fe(CN)Cd]K$, slowly crystallises. The chief differences between the complex cadmicyanides of bi- and ter-valent iron is that the polymerised (polynuclear) co-ordination complex which the former are also presumed to form is much more readily broken down to the simple anion $[Fe^{\cdot\cdot}Cd(CN)_6]''$ (which is stable to 6*N*-ammonia), and the salts contain no water molecules combined in the co-ordination complex. The *sodium* salt, $[Fe^{\cdot\cdot}(CN)_6Cd][NaH_2O]_2\,H_2O$, is obtained either by heating cadmium sulphate solution with an excess of sodium ferrocyanide solution (Fe : Cd=2·5 : 1), or by shaking the precipitate obtained when an excess of cadmium su phate is used for a long period with concentrated sodium chloride solution. The corresponding *potassium* ($+4H_2O$) and *ammonium* ($+6H_2O$) salts are similarly prepared. In the presence of a high concentration of ammonia the *hexammine cadmium* salt $[Fe^{\cdot\cdot}(CN)_6Cd][Cd(NH_3)_6],H_2O$, and with lower concentrations the *tetrammine cadmium* salt $[Fe^{\cdot\cdot}(CN)_6Cd][Cd(NH_3)_4]+H_2O$ and $+6H_2O$, are obtained. That the precipitate obtained by heating together solutions of sodium ferrocyanide and cadmium sulphate is a mixture of the *compounds* $[FeCd(CN)_6]Na_2$ and $[FeCd(CN)_6]Cd,H_2O$ and not the complex $[\{Fe^{\cdot\cdot\cdot}Cd(CN)_6\}_3Cd]Na_4$ is proved by the fact that the ratio Cd : Fe in the precipitate remains the same as that in the mother-liquor when its value in the latter is altered. The structure of these complex salts and their bearing on the constitution of insoluble Prussian blue are discussed. J. W. BAKER.

Alkylation of hexacyanocobaltic acid. F. HÖLZL, T. MEIER-MOHAR, and F. VIDITZ (Monatsh., 1929, **53** and **54**, 237—255).—When hexacyanocobaltic acid or its alkoxonium derivatives (this vol., 898) are heated with alcohols in a sealed tube at 100°, alkylation occurs. Thus the acid and alcohol give the *compound* $[(CN)_5{\cdot}Co{\cdot}CNEt]H_2$, isolated as its *dipyridine* salt. Treatment of the reaction product from methyl alcohol and the methoxonium derivative of the acid with pyridine affords a *substance*, $[(CN)_5{\cdot}Co{\cdot}CNMe]H_2(C_5H_5N)_3$ or $[(CN)_4{\cdot}Co{\cdot}(CNMe)_2]H(C_5H_5N)_3$. Propylation is similar to ethylation, but proceeds more slowly. Carbylamine is formed during the reactions. The relation between time of reaction and corrected amount of 0·1*N*-alkali hydroxide necessary for neutralisation of the reaction mixture is studied. The mechanism of the formation of the alkylated products is discussed; the production of an intermediate imino-compound is postulated. H. BURTON.

Photosensitiveness of nitroprussides. H. LEFFMANN and C. C. PINES (Bull. Wagner Free Inst., 1929, **4**, 41—42).—When a concentrated aqueous solution of sodium nitroprusside is mixed with aqueous solutions of uranium acetate, silver nitrate, mercuric nitrate, ferrous sulphate, or ferric chloride, precipitates, presumably of the corresponding nitroprussides, are formed in all cases except with ferric chloride. All the precipitates, except that of uranium, were notably changed after exposure to sunlight for 10 min.

A. I. VOGEL.

Possibility of formation of tetrazomethane, CN_4. H. HOLTER and H. BRETSCHNEIDER (Monatsh., 1929, **53** and **54**, 963—984).—Treatment of methylenebisurethane (I) with nitrous fumes in ethereal suspension affords impure *dinitrosomethylenebisurethane* (II), a yellow oil, which decomposes readily when heated; II does not give Liebermann's reaction. Decomposition of II with dilute alkali hydroxide (whereby tetrazomethane might be produced) causes evolution of nitrogen; with concentrated aqueous or methyl-alcoholic alkali hydroxide in the cold, a sodium salt is first formed and decomposes on warming or diluting with water. Decomposition of an ethereal solution of II with water gives a trace of formaldehyde (isolated as the "dimedon" compound); the amount of formaldehyde is increased when aqueous sodium hydroxide is used. With sodium propoxide in ethereal propyl-alcoholic solution, II gives a small amount of a substance, probably formaldehyde dipropylacetal, b. p. 134—142°, hydrolysed by 50% sulphuric acid to formaldehyde.

Treatment of pyrocatechol with an ethereal solution of II in presence of 25% methyl-alcoholic potassium hydroxide solution affords a small amount of methylenedioxybenzene. Similarly, 3 : 4-dihydroxyaniline, methyl protocatechuate, and the phenolic base from *dl*-tetrahydroberberine (Späth and Mosettig, A., 1926, 965) all furnish varying amounts of the corresponding methylenedioxy-derivatives. The above reactions are to be expected with tetrazomethane. It is suggested that the tetrazomethane reacts only with free phenols and not with phenoxides; it is shown that an ethereal solution of diazomethane does not react with sodium β-naphthoxide until methyl alcohol is added.

The by-reactions occurring during the decomposition of II by alkali hydroxide have been studied. With methyl-alcoholic potassium hydroxide, I and *ethylmethoxymethylurethane* (III), b. p. 103—104°/9 mm. [obtained from methoxyacetamide by Blaise's method (A., 1926, 943)], were isolated. Hydrolysis of III with 10% sulphuric acid gives methyl alcohol and formaldehyde; benzylamine and III at 200° yield dibenzylcarbamide. When II is decomposed with sodium benzyloxide in benzyl alcohol–ether solution, *ethylbenzyloxymethylurethane*, b. p. 185—190°/10 mm., is produced. The formation of these alkyloxy-derivatives probably occurs thus: $[CO_2Et{\cdot}N(NO){\cdot}]_2CH_2 \xrightarrow[-HNO_2]{+H_2O} CO_2Et{\cdot}N(NO){\cdot}CH_2{\cdot}NH{\cdot}CO_2Et \xrightarrow{KOH} N_2CH{\cdot}NH{\cdot}CO_2Et \xrightarrow{R{\cdot}OH} OR{\cdot}CH_2{\cdot}NH{\cdot}CO_2Et$. An ethereal solution of II gradually decomposes to I and nitrogen oxides. H. BURTON.

Influence of poles and polar linkings on the course pursued by elimination reactions. V. Thermal decomposition of quaternary phosphon-

ium hydroxides. G. W. FENTON and C. K. INGOLD (J.C.S., 1929, 2342—2357).—The decomposition of quaternary ammonium hydroxides results in the production of olefines, whilst the simpler phosphonium hydroxides yield paraffins. It is suggested that in the latter case, paraffinic degradation takes place at a lower temperature than that required for olefinic degradation. The facility of olefinic degradation depends largely on the extent to which the β-hydrogen atom eliminated from the cation is activated or deactivated by the β-substituents of the group forming the olefine. Electron-repelling alkyl groups deactivate, and consequently phosphonium hydroxides which should be capable of forming simple aliphatic olefines are not favourable cases for observation of olefinic degradation. For this reason the decomposition of the following complex phosphonium hydroxides was studied. The β-phenylethyl-triethyl compound gave some styrene and triethylphosphine at the temperature of paraffinic decomposition, which was still the main reaction, whilst ββ-diphenylethyl-tri-*n*-butylphosphonium hydroxide yielded *as*-diphenylethylene and tri-*n*-butylphosphine as the main products. The presence of paraffinic degradation products was just discernible. Olefinic degradation of phosphonium hydroxides is thus possible and the conditions for its facilitation are similar to those established for the ammonium series. A table is given showing quantitatively the hydrocarbon products of the decomposition of a number of phosphonium hydroxides.

The phosphonium hydroxides were prepared by interaction of the corresponding phosphines and alkyl halides followed by treatment with moist silver oxide under suitable conditions. The following compounds are described: *tetramethylphosphonium picrate*, m. p. >290°. The residue after decomposition of the hydroxide was trimethylphosphine oxide, b. p. 210—212°, m. p. 140—141° (*hydroxytrimethylphosphonium trichloroacetate*, m. p. 64°); *trimethylethylphosphonium picrate*, m. p. 290°; *dimethylethylphosphine oxide*, b. p. 223—225°, m. p. 73—75°; *methyltriethylphosphonium picrate*, m. p. 239°, triethylphosphine oxide, b. p. 238—240°, m. p. about 46° (chromate, 99—100°); *triethyl*-n-*propylphosphonium picrate*, m. p. 91°; *ethyltri*-n-*propylphosphonium iodide* and *picrate*, m. p. 64°; *tri*-n-*propyl*-n-*butylphosphonium iodide*, m. p. 239—240°, and *picrate*, m. p. 67°; *tri*-n-*propyl*-n-*octylphosphonium chloroaurate*, m. p. 38°; phenyltrimethylphosphonium iodide, m. p. 236°; *benzyltrimethylphosphonium bromide*, m. p. 222°; *triphenylbenzylphosphonium bromide*, m. p. 288°; β-*phenylethyltriethylphosphonium picrate*, m. p. 70°. ββ-*Diphenylethyltri*-n-*butylphosphonium hydroxide*, no salts described. n-*Propyltri*-n-*butylphosphonium hydroxide*, no salts described. ω-*Carbethoxytetramethylphosphonium chloride*, m. p. 160° (decomp.), and *picrate*, m. p. 124—125°. Full details are given of the thermal decomposition products of the above phosphonium hydroxides. J. W. PORTER.

Constitution and dissociation of the Grignard reagent. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1929, 51, 3149—3157).—Magnesium alkyl, aralkyl, and aryl halides have been treated with an equivalent of magnesium and benzophenone in ether–benzene solution, and the amounts of benzpinacol formed determined. With magnesium ethyl and benzyl chlorides and phenyl bromide no pinacol results. Amounts varying from 0·057 to 17·3% (on benzophenone used) are formed with magnesium methyl and *n*-butyl iodides and benzyl bromide. With magnesium *n*-butyl iodide, *tert.*-butyl chloride, and benzyl bromide and no added magnesium no pinacol is formed, but magnesium triphenylmethyl chloride and bromide give, under the same conditions, 22·0 and 31·6% of the pinacol respectively; at the same time triphenylmethyl peroxide (55·3 and 57·9%) is also formed. This is explained by a dissociation of the Grignard reagent, $CPh_3{\cdot}MgX \longrightarrow CPh_3{\cdot} + {\cdot}MgX$; the pinacol formation is a function of the ·MgX. A mixture of magnesium diethyl, magnesium iodide, magnesium, and benzophenone in ether–benzene solution and an atmosphere of hydrogen yields after prolonged stirring benzpinacol (12·83%) and diphenylethylcarbinol. When the reaction is carried out in an atmosphere of nitrogen for a short time, only diphenylethylcarbinol (18%) is isolated. The following change occurs: $MgEt_2 + MgI_2 \longrightarrow 2Et{\cdot}MgI$. It is concluded that the equilibrium $2R{\cdot}MgX \rightleftharpoons R_2Mg + MgX_2$ and the dissociation $R{\cdot}MgX \longrightarrow R{\cdot} + {\cdot}MgX$ probably occur to some extent with all Grignard reagents. H. BURTON.

Sterol group. V. Constitution of cholesterilene. A. C. BOSE and W. DORAN (J.C.S., 1929, 2244—2248).—The action of heat on methyl cholesterylxanthate, m. p. 127°, $[\alpha]_D^{25}$ −51·1° in toluene (best prepared by the action of carbon disulphide and methyl iodide on potassium cholesteryl oxide obtained by the action of emulsified potassium on a dry benzene solution of cholesterol) (Tschugaev and Fomin, A., 1910, i, 734), forms only one hydrocarbon, cholesterilene, m. p. 79°, identical with the product obtained by the dehydration of cholesterol with anhydrous copper sulphate (Mauthner and Suida, A., 1896, i, 425; a cleaner product being obtained by heating the reactants at 200°/5 mm.), since either product is reduced by hydrogen and palladium-black to the same mixture of cholestane and ψ-cholestane. The supposed isomeride "β-cholesterylene" described by Tschugaev and Fomin (*loc. cit.*) is an impure form of cholesterilene containing sulphur which is removed only by repeated treatment with concentrated alcoholic potassium hydroxide or by liquid sodium–potassium amalgam. J. W. BAKER.

☞ **Quantitative evidence of the structure of the benzene ring and the orientation of its six hydrogen atoms.** R. REINICKE (Z. Elektrochem., 1929, 35, 780—789).—A theory of the structure of benzene, based on the tetrahedral quadrivalency of carbon and the value of the space-lattice of the diamond obtained by Ehrenberg (Z. Krist., 1926, 63, 320), is advanced, in support of which various physical data, *e.g.*, dielectric constants, of some benzene derivatives are quoted. H. T. S. BRITTON.

Catalytic hydrogenation of halogenated organic compounds. M. BUSCH and W. SCHMIDT (Ber., 1929, 62, [*B*], 2612—2620; cf. A., 1925, ii, 823).—

During the quantitative removal of bromine from bromobenzene, by means of hydrogen, diphenyl is produced in considerable amount in addition to benzene. Hydrogen derived from hydrazine does not act more advantageously, although more rapidly, than that derived from other sources. Apparently the proportion of diphenyl produced is connected with the dielectric constant of the solvent. In methyl alcohol the yield is 60%, whilst in ethyl alcohol it is 30% (depressed by addition of water) and reaches a minimum in *iso*propyl alcohol. Hydrogenation of the nucleus is not observed. Partial poisoning of the catalyst by benzene, phenol, or dimethylaniline depresses the yield of diphenyl, which attains its maximum when the halogen is removed from the nucleus as rapidly as possible. Other reducing agents (zinc dust and potassium hydroxide or ammonia) do not affect bromobenzene, which, however, affords about 10% of diphenyl when treated with methyl-alcoholic potassium hydroxide and palladised calcium carbonate at 140°. The presence of substituents in halogenobenzenes influences the production of diaryls in proportion as it affects the mobility of the halogen atoms, but, in general, the yield of diaryl is somewhat lower than with the unsubstituted compounds. 1-Bromonaphthalene does not yield dinaphthyl. *o*-Dibromobenzene behaves as a normal disubstituted product, either remaining intact or being reduced to benzene. *p*-Dibromobenzene gives diphenyl, *p*-diphenylbenzene, and *p*-diphenyldiphenyl containing halogen. *p*-Di-iodobenzene behaves similarly. Bromo- and iodo-diphenyl yield homogeneous *p*-diphenyldiphenyl. The tendency towards the production of long ring chains finds its limitation in the physical properties of the complex compounds which cause their immediate separation from the alcoholic solution, thus preventing further action. Benzyl halides afford dibenzyls in appreciable amount. If palladium as catalyst is replaced by platinum or nickel, diaryls are not produced or are formed only in minor amount; this may be connected with their much slower rate of reaction. H. WREN.

Polymethylbenzenes. I. Jacobsen reaction with pentamethylbenzene, and preparation of prehnitene [1 : 2 : 3 : 4-tetramethylbenzene]. L. I. SMITH and A. R. LUX (J. Amer. Chem. Soc., 1929, **51**, 2994—3000).—The formation of hexamethylbenzene (I) and prehnitenesulphonic acid (II) from pentamethylbenzene, by treatment with sulphuric acid at the ordinary temperature (cf. Jacobsen, A., 1887, 660), has been studied in detail. Reaction occurs essentially in the manner described by Jacobsen (*loc. cit.*). The initial reaction mixture is decomposed by a specific amount of ice; this precipitates I and II. These are separated by extraction with water. Prehnitene is obtained conveniently from sodium prehnitenesulphonate by slow addition of a saturated solution of the sodium salt to sulphuric acid at 140—155°, and removing the hydrocarbon formed in a current of steam. The yield is 80—90%. When pentamethylbenzenesulphonic acid is kept in a desiccator over sulphuric acid for 8 weeks small amounts of I and II appear to be formed. This indicates that the first stage of the Jacobsen reaction is sulphonation with subsequent rearrangement of the sulphonic acid produced. H. BURTON.

Polymethylbenzenes. II. M. p. of tetra-, penta-, and hexa-methylbenzenes, and f.-p. diagram of mixtures of durene [1 : 2 : 4 : 5-tetramethylbenzene] and *iso*durene [1 : 2 : 3 : 5-tetramethylbenzene]. L. I. SMITH and F. H. MACDOUGALL (J. Amer. Chem. Soc., 1929, **51**, 3001—3008).—Bromination of mesitylene in carbon tetrachloride solution and treatment of the product formed with alcoholic sodium ethoxide (to remove bromomethyl derivatives) affords bromomesitylene, b. p. 102·5—103·5°/14 mm., m. p. −1 to 1°. Conversion of this into the Grignard reagent and treatment with methyl sulphate gives a 60% yield of *iso*durene, b. p. 86·5°/18 mm. When bromoprehnitene, m. p. 26·2—26·4° (lit. 30°), is converted into the Grignard reagent and this is decomposed by dilute acid, a 61% yield of prehnitene is obtained. The f. p. of this is identical with that prepared by the Jacobsen method (preceding abstract). The f. p. (corr.) of the hydrocarbons prepared are: durene, 79·28±0·05°; *iso*durene, −24·0±0·1°; prehnitene, −6·40±0·05°; pentamethylbenzene, 54·0±0·1°; hexamethylbenzene, 164·8±0·1°. The f.-p. diagram for the system durene–*iso*durene is given, and the molar latent heats of fusion of durene and *iso*durene are calculated to be 5022 and 2550 g.-cal., respectively. H. BURTON.

Synthesis of propyl- and propenyl-benzene and their homologues. L. BERT and M. ANGLADE (Compt. rend., 1929, **189**, 645—646).—Reduction of cinnamyl *n*-butyl ether (prepared by the action of alcoholic potassium hydroxide on α-chloro-γ-phenyl-Δ^{α}-propene; cf. A., 1925, i, 803) with sodium and alcohol gives a mixture of *n*-propyl- and propenylbenzene. Similarly, from 2 : 4-dimethylcinnamyl *n*-butyl ether are obtained 2 : 4-*dimethyl*-n-*propylbenzene*, b. p. 92°/18 mm., 206—207° (corr.)/735 mm., d_4^{19} 0·8786, n_D^{19} 1·501, and 2 : 4-*dimethyl*-Δ^{α}-*propenylbenzene*, b. p. 100°/20 mm., 213—215° (corr.)/735 mm., $d_4^{17\cdot5}$ 0·9096, $n_D^{17\cdot5}$ 1·540, which is separated from the saturated hydrocarbon as its *dibromide*, b. p. 178°/22 mm., $d_4^{17\cdot5}$ 1·5435, $n_D^{17\cdot5}$ 1·586, or its *hydrobromide*, b. p. 138°/19 mm., $d_4^{19\cdot5}$ 1·233, $n_D^{19\cdot5}$ 1·545. J. W. BAKER.

Action of iodine on the alkali derivatives of *aci*nitro-compounds. C. D. NENITZESCU (Ber., 1929, **62**, [*B*], 2669—2672).—A solution of the potassium salt of 9-*iso*nitrofluorene is converted by iodine in potassium iodide or by electrolysis at a platinum anode and copper cathode into αβ-dinitro-αβ-ditriphenylene-ethane, m. p. 184°. αβ-Dinitro-αβ-diphenylethane, m. p. 150—151°, is obtained from iodine and the sodium derivative of phenyl*iso*nitromethane at 0°, whereas if cooling is not adopted or if the solution is electrolysed a dark brown oil is obtained which is converted by hot, 50% potassium hydroxide into 3 : 4 : 5-triphenyl*iso*oxazole, m. p. 212°. When phenylnitromethane is dissolved in a large excess of alkali hydroxide and treated with iodine in boiling solution, stilbene is formed in 80% yield. H. WREN.

Chloronitrotoluenes. L. GINDRAUX (Helv. Chim. Acta, 1929, **12**, 921—934).—A comparative study of the chlorination of benzene, toluene, and

o-nitrotoluene in presence of various catalysts shows that a mixture of iron and iodine is exceptionally active. A 90% yield of monochlorotoluenes (60% *o*-, 40% *p*-) is obtained from toluene at 50°. *o*-Chlorotoluene has d^{21} 1·077, n^{19} 1·5275, and *p*-chlorotoluene has d^{21} 1·031, n^{19} 1·5223. The proportions of the isomerides in a mixture are readily determined from the refractive index, the variation of which with composition is practically linear. Chlorination of *o*-nitrotoluene at 50—60° yields 6-chloro-*o*-nitrotoluene, m. p. 37° (65·9%), and 4-chloro-*o*-nitrotoluene, m. p. 37° (34·1%) (crystallographic data) (cf. G.P. 107,505; Fierz, "Operationen der Farbenchemie," p. 100; G.P. 434,402). Separation is achieved by a combination of fractional distillation, when the 6-chloro-compound, b. p. 114·6°/11 mm., distils first, and freezing out, the eutectic being at 3·5°, 45% of 6-chloro-*o*-nitrotoluene. 6-Chloro-*o*-nitrotoluene is best converted into 6-chloro-*o*-nitrobenzaldehyde, m. p. 70·5°, by Janson's method (G.P. 107,501) of bromination to the benzyl bromide, m. p. 58°, and oxidation of the latter. 4 : 4′-Dichloroindigotin (crystallographic data) and 4 : 4′-dichloro-5 : 5′-dibromoindigotin (G.P. 193,438) have absorption maxima in xylene at $\lambda = 599·5$ and 614·3, respectively. 6-Chloro-*o*-toluidine is converted by the method of G.P. 241,910 into *3-chloro-2-methylphenylthiolacetic acid*, m. p. 104°; this yields *6 : 6′-dichloro-7 : 7′-dimethylthioindigotin*, which dyes cotton in bright red and wool in brownish-red shades and has an absorption maximum in xylene at $\lambda = 544·8$. *5-Chloro-2-methylphenylthiolacetic acid*, m. p. 101°, and *4 : 4′-dichloro-7 : 7-dimethylthioindigo* (browner shades, absorption maximum in xylene at $\lambda = 553·6$) are obtained similarly. Nitration of *p*-chlorotoluene in sulphuric acid under different conditions yields slightly varying proportions of the 2- and 3-nitro-compounds (53—62·5% and 37·5—47%, respectively). 4-Chloro-*m*-nitrotoluene reacts with ammonia at 175° under pressure to give 3-nitro-*p*-toluidine, m. p. 114°, in 82% yield. 3-Nitro-*p*-cresol cannot be prepared from the chloro-compound, but is obtained in 90% yield by the action of 10% sodium hydroxide solution on 3-nitro-*p*-toluidine. The preparation of 4-methoxy-*m*-toluidine, m. p. 50°, from 3-nitro-*p*-chlorotoluene by heating with potassium hydroxide and methyl alcohol and reduction of the product is described. The "eriochromazurole" dyes obtained by condensing *o*-cresotic acid with 2 : 4- and 2 : 6-dichlorobenzaldehyde and oxidation of the products have absorption maxima at $\lambda = 593·0$ and 597·8, respectively, in sodium hydroxide, and at $\lambda = 521·5$ and 536·3, respectively, in sulphuric acid solution.

R. K. Callow.

Organo-alkali compounds containing sulphur. K. Fuchs (Monatsh., 1929, **53** and **54**, 438—444).—Various sulphoxides have been treated with sodium phenyl or benzyl in the hope of obtaining sulphonium compounds. The products isolated are highly coloured, air-sensitive organo-alkali compounds (formed from equimolecular amounts of the reactants in benzene or toluene solution at the ordinary temperature). Thus diphenyl sulphoxide (I) and sodium benzyl (II) in benzene afford a red product, decomposed by hydrogen chloride to I and a small amount of phenyl benzyl sulphoxide (III). When the reaction is carried out in toluene, the hydrogen chloride decomposition products are III (35%) and a small amount of I. *pp′*-Ditolyl sulphoxide and II react similarly in toluene and after treatment with hydrogen chloride, 30—35% of *p*-tolyl benzyl sulphoxide and some unchanged material are obtained. Similar decomposition of the product from III and II gives only III. Decomposition of the reaction product from I and II with carbon dioxide gives a small amount (benzene) or 35—40% (toluene) of the acid $Ph·SO·CHPh·CO_2H$ (IV), decomp. 142—143°, according to the solvent. This acid is synthesised from sodium α-chlorophenylacetate and sodium phenyl sulphide in methyl alcohol, whereby α-phenylthiolphenylacetic acid, $SPh·CHPh·CO_2H$, m. p. 102—103°, results. Oxidation of this with hydrogen peroxide in acetone or acetic acid solution gives IV. Thermal decomposition of IV yields thiophenol and benzoylformic acid whilst oxidation of IV with an excess of hydrogen peroxide gives benzenesulphonylphenylacetic acid, decomp. 142—143° into carbon dioxide and phenyl benzyl sulphone.

When I is treated with sodium phenyl at 80—90° in benzene and an atmosphere of nitrogen, a 50% yield of diphenylene sulphide is obtained; *pp′*-ditolyl sulphoxide gives dimethyldiphenylene sulphide. Similarly, I and II yield a small amount of diphenylene sulphide. Diphenyl sulphide does not react with sodium aryls at the ordinary temperature; at 70—80° some fission occurs. Diphenyl sulphone and II react in toluene solution forming a red solution; decomposition of this with hydrogen chloride at −60° gives the original sulphone, oily products, and a compound, m. p. 178·5°, of composition corresponding with $Ph·SO_2·CHPh_2$.

H. Burton.

Reactions of vinyl chloride and benzene in presence of aluminium chloride. J. M. Davidson [with A. Lowy] (J. Amer. Chem. Soc., 1929, **51**, 2978—2982).—When benzene is treated with vinyl chloride in presence of aluminium chloride at 0—5°, the main products are *as*-diphenylethane and an anthracene-type resin; small amounts of ethylbenzene and 9 : 10-dimethyl-9 : 10-dihydroanthracene are also formed (cf. Böeseken and Bastet, A., 1914, i, 156). Very small amounts of aluminium chloride give small yields of the products, whilst relatively large amounts cause a diminution in the amount of *as*-diphenylethane formed. When the reaction is carried out at 60—70° an increased amount of the anthracene derivative is produced; this is not the case when the initial reaction mixture (0—5°) is heated. The presence of a trace of iodine accelerates the reaction at 0—5°, and relatively large amounts of the anthracene are formed; the amounts of *as*-diphenylethane and resin are diminished. In presence of a small amount of mercury increased production of ethylbenzene occurs, probably owing to reduction of α-chloro-α-phenylethane, which is considered to be the intermediate product. Styrene or metastyrene is not produced during the reaction (cf. Böeseken and Bastet, *loc. cit.*). The resin formed during the reaction melts at 50—65°, decomposes when heated to 300°, affords small amounts of 9 : 10-dimethyl-9 : 10-dihydroanthracene

at 220°/0·5 mm., and on oxidation with chromic oxide in acetic acid–benzene solution gives anthraquinone. H. BURTON.

Mechanism of formation of compounds of the dibenzyl series from the nitrotoluenes and their derivatives by the action of alcoholic alkali hydroxides. A. K. PLISOV (Ukraine Chem. J., 1929, 4, 241—279).—A *résumé* of former work on the formation of stilbene derivatives from chlorinated aromatic nitro-compounds, and the investigation of the action of alcoholic alkali hydroxides on toluene derivatives. Sodium or potassium alkoxides were allowed to react with benzyl chloride, benzyl bromide, benzylidene chloride, *o*- and *p*-nitrotoluene, *p*-nitrotoluene-*o*-sulphonic acid, *o*- and *p*-dinitrotoluene, *p*-nitrobenzyl bromide, *o*- and *p*-nitrobenzylidene chloride, the following conclusions being reached. The *o*- and *p*-nitrotoluenes and most of their derivatives form products of the dibenzyl series, the reaction taking place even below 0°, whilst the *m*-compounds do not react in this way. With halogen derivatives of the nitrotoluenes which have the halogen in the side-chain ethers are obtained in the case of the *m*-compounds, and dibenzyl derivatives (with ethers as by-products) in the case of the *o*- and *p*-compounds. Coloured intermediate compounds are also formed; these, however, cannot be isolated. The dibenzyl derivatives can be produced only from the *o*- and *p*-compounds if in the alcoholic radical a hydroxyl can take up a position adjacent to the "tautomeric" hydrogen atom (*i.e.*, from the side-chain); this does not take place in the case of *m*-compounds. All the nitrotoluenes, and most of their derivatives, react in the tautomeric form, giving first unstable quinonoid salts, which are rapidly decomposed. The formation of stilbene derivatives is effected by the nitroso-compounds, but at high temperatures the formation of stilbenes may not take place at all, whilst azo-compounds can be formed. The rates of the various reactions depend on the presence of other groups. A series of mechanisms for the various reactions is discussed. M. ZVEGINTZOV.

Stereochemistry of aromatic compounds. IX. Tetraphenylene and the mobility of benzene rings. R. KUHN (Annalen, 1929, 475, 131—136).—The hydrocarbon, m. p. 318° (corr.), obtained by heating dry 4 : 4′-di-iododiphenyl with copper at 300° is not a cyclic tetraphenylene as stated by Sircar and Majumdar (A., 1928, 1235), but is *pp*′-diphenyldiphenyl identical with a specimen prepared by Gerngross and Dunkel's method (A., 1924, i, 720). The other products of the reaction are fractions containing iodide, that subliming at 450—500°/15 mm. being reduced by zinc and acetic acid to a hydrocarbon, m. p. 465°, probably hexaphenyl. The stereochemistry of compounds containing aromatic ring systems is discussed. J. W. BAKER.

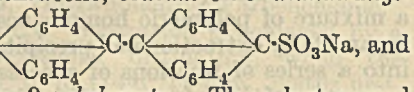
Highly polymerised compounds. XXII. Constitution of polyindene. H. STAUDINGER, A. A. ASHDOWN, M. BRUNNER, H. A. BRUSON, and S. WEHRLI. **XXIII. Behaviour of polyindenes when heated.** H. STAUDINGER, H. JOHNER, and V. WIEDERSHEIM. **XXIV. Hydropolyindenes.** H. STAUDINGER, H. JOHNER, G. SCHIEMANN, and V. WIEDERSHEIM (Helv. Chim. Acta, 1929, 12, 934—957, 958—961, 962—972).—XXII. The polymerisation of indene takes place rapidly under the influence of catalysts, the best of which are, in order of efficacy, stannic chloride, titanic chloride, boron trichloride, antimony pentachloride, and antimony trichloride. The reaction is carried out in benzene or chloroform solution, and the product is isolated by pouring the coloured solution into alcohol. The product is a white powder, mean mol. wt. 2000—5000. Polyindenes are hemicolloidal; no eucolloidal products can be obtained (cf. this vol., 305). The product is a mixture of polymeric homologues which are partly separable by extraction and precipitation with solvents into a series of fractions of successively higher temperatures of liquefaction (180—185° to 230—240°), increasing mol. wts. (1600—6000), and increasing viscosities in solution, corresponding with a variation in mean degree of polymerisation from 14 to 52. The viscosities of solutions of indene and of styrene, on the one hand, and of polyindenes and of polystyrenes, on the other, are similar in magnitude, and this indicates a similar molecular structure in the two polymeric homologous series. Polyindenes, unlike polystyrenes, however, do not undergo ozonolysis. The product of the action of ozone is a white powder, charring at 200°, the composition of which corresponds with a mixture of polymerised monoxide and dioxide. Polystyrenes and polyindenes are probably, like polymerised α-methylstyrenes, formed from long chains, the terminal valencies of which become saturated by forming rings. The fact that the mol. wt. is the greater the lower is the temperature and the higher the concentration at which polymerisation is carried out is probably due to the easier formation of rings in the one case, and the tendency to form longer chains in the other. No polyindenes showing evidence of crystalline structure with *X*-rays can be isolated.

XXIII. The behaviour of polyindenes when heated shows that they are true polymerides, in which the original indene molecules are bound by covalencies, and not merely associated. Polyindene mixtures of mean mol. wt. 1500, 3000, and 6000, and correspondingly different viscosities in solution, show no change in the viscosities when heated dry or in solution at 200° in nitrogen. In air or oxygen the products of highest mol. wt. show signs of breaking down and darken. At 270—280° there is evidence of partial cracking.

XXIV. Polyindenes are reduced by hydrogen in presence of nickel at 270° under the same conditions as polystyrenes (this vol., 306) to yield hydropolyindenes; these are white powders of lower m. p. (100—200°) which are unattacked by concentrated sulphuric acid and give no coloration with tetranitromethane. When heated above 300° cracking takes place and products of paraffin-like odour are formed. It is not possible to prove strictly that complete hydrogenation takes place in all cases without change in molecular size on account of the partial cracking of polyindenes which takes place at the elevated temperatures necessary for reduction, but incomplete hydrogenation yields products of only slightly lower viscosity, whilst the Florida earth on which the catalyst is deposited can alone cause degradation. In solution in methyl*cyclo*hexane or decahydronaphthal-

ene at 299° it is possible to hydrogenate polyindenes of low mol. wt. without decomposition. The results with polystyrene (this vol., 1287) show, however, that cryoscopic measurements indicate the size of the molecules, which can react without disruption.

R. K. CALLOW.

***meso*-Derivatives of anthracene and of 9 : 9′-dianthranyl.** M. MINAEV and B. FEDOROV (Ber., 1929, 62, [*B*], 2489—2494).—9-Nitroanthracene is converted by sodium sulphite in boiling aqueous solution into sodium nitrite and a mixture of unchanged 9-nitroanthracene, *sodium* 9 : 9′-*dianthranyl*-10-*sulphonate*,  , and *sodium anthracene*-9-*sulphonate*. The last-named compound is readily decomposed by boiling, dilute mineral acids into anthranol and sodium hydrogen sulphite, which react further to yield anthracene and sodium hydrogen sulphate. When oxidised by alkaline permanganate it gives anthraquinone almost quantitatively. With aqueous ammonia at 200° it affords 9-aminoanthracene, m. p. 115—116° (decomp.) (cf. Meisenheimer and Connerade, A., 1904, i, 391). Sodium 9 : 9′-dianthranyl-10-sulphonate (also *monohydrate*) may be prepared in poor yield by the action of warm, very dilute sodium hydroxide on sodium anthracene-9-sulphonate; it is oxidised in alkaline solution to anthraquinone and transformed by dilute acids into 9 : 9′-dianthranyl. 10-Hydroxy-9 : 9′-dianthranyl appears to be produced in poor yield by the action of sodium hydroxide, whereas aqueous ammonia at 190—200° yields 10-*amino*-9 : 9′-*dianthranyl*, m. p. above 305° (decomp.). Unlike 9-aminoanthracene, 10-amino-9 : 9′-dianthryl suffers normal diazotisation and the products couple with β-naphthol and other hydroxynaphthalenes and their sulphonic acids.

H. WREN.

Synthesis of anthracene homologues. I. 2 : 6- and 2 : 7-Dimethylanthracenes. G. T. MORGAN and E. A. COULSON (J.C.S., 1929, 2203—2214).—The presence of the above homologues of anthracene in the distillate from low-temperature tar has been confirmed by comparison with the synthetic products, and doubts concerning the constitution of other homologues have been cleared up. Three methods are given for the preparation of 2 : 4 : 4′-trimethylbenzophenone, and the structure of the ketone is made clear by one of them, viz., the interaction of the Grignard compound of 4-bromo-*m*-xylene with *p*-toluonitrile. The ketimine thus formed is hydrolysed to the ketone, which when maintained at its b. p. for some time slowly passes into 2 : 7-dimethylanthracene, identical with the 1 : 6- or 1 : 7-compound described by Lavaux (A., 1910, i, 548). In a similar manner 2 : 5 : 4′-trimethylbenzophenone can be prepared from 2-iodo-*p*-xylene and *p*-toluonitrile, and converted into 2 : 6-dimethylanthracene, which corresponds with the homologue described by Lavaux as the 2 : 7-derivative (cf. Flumiani, A., 1924, i, 1327).

2 : 7-*Dimethylanthracene*, m. p. 241° (corr.), yields on oxidation 2 : 7-*dimethylanthraquinone*, m. p. 170° (corr.), which is further oxidised to 2-*methylanthraquinone*-7-*carboxylic acid*, m. p. 283° (corr.) (described by Lavaux as 6-methylanthraquinone-1-carboxylic acid). *Anthraquinone*-2 : 7-*dicarboxylic acid*, m. p. above 360°, is produced when 2-methylanthraquinone-7-carboxylic acid is boiled with an excess of chromic anhydride in acetic acid.

J. W. PORTER.

Phenanthrene derivatives. R. K. CALLOW and J. M. GULLAND (J.C.S., 1929, 2424—2425).—Details are given of an improved method for the preparation of 9-bromo-10-nitrophenanthrene based on that of Austin (*ibid.*, 1908, **93**, 1760). The preparation of a dinitrophenanthrene, m. p. 255—260°, is also described. 9-*Phenanthrylaminoacetonitrile*, m. p. 231—235°, was prepared by the action of potassium cyanide in formaldehyde solution on 9-aminophenanthrene, and on alkaline hydrolysis furnished 9-*phenanthrylglycine*, m. p. 199—201°. This when boiled with acetic acid yielded a substance, m. p. 203—206° (decomp.), probably 2 : 5-diketo-1 : 4-di-(9′-phenanthryl)piperazine. Diphenanthracridine or a complex acridine derivative, m. p. above 320°, is stated to be formed by the action of formaldehyde on 9-aminophenanthrene in acetic acid solution.

J. W. PORTER.

Linear pentacene series. XIII. Nomenclature. Questions of structure. E. PHILIPPI (Monatsh., 1929, **53** and **54**, 638—642).—Dinaphthanthracene (Philippi, A., 1914, i, 826) is renamed *lin.*-pentacene; the numbering is as before. Re-investigation of the hydrocarbon (*loc. cit.*) confirms its instability. Energetic reduction of a dinitropentacenequinone has given *tetradecahydropentacene*, m. p. 227°. The author considers that the dihydroxypentacenediquinone of Hernler and Sommer (this vol., 1453) has each of the hydroxyl hydrogen atoms related to three oxygen atoms.

H. BURTON.

Formation of tertiary amines in the reduction of nitriles and carbonyl compounds in basic solution. A. SKITA and F. KEIL (Monatsh., 1929, **53** and **54**, 753—763).—The formation of tertiary (and in some cases secondary) amines has been observed during the reduction of nitriles, alone or in presence of other compounds. Tertiary amines are also produced during the reduction of ketones in presence of amines (cf. A., 1928, 1120, 1228).

[In part with H. HAVEMANN and W. FAUST.]—Hydrogenation of acetonitrile in aqueous solution and in presence of colloidal platinum at the ordinary temperature affords 85% of triethylamine. When a mixture of the nitrile and *cyclo*hexanone is used, 5% of *N*-ethyl*cyclo*hexylamine is isolated in addition to 45% of triethylamine. Tripropylamine is obtained similarly from propionitrile; in presence of *cyclo*hexanone, 10% of *N*-propyl*cyclo*hexylamine, b. p. 185° (*hydrochloride*, m. p. 248—250°; *phenylthiocarbimide* derivative, m. p. 122—123°), and 25% of dipropylamine result. Butyronitrile furnishes a mixture of di- [*hydrochloride*, m. p. 283—284°; picrate, m. p. 60—61° (lit. 59·5°)] and tri-butylamines [picrate, m. p. 104—105° (lit. 100·5°)]; in presence of *cyclo*hexanone, 10% of N-*butyl*cyclo*hexylamine*, b. p. 207° (*hydrochloride*, m. p. 290°), 20% of di-, and 16% of tri-butylamines result. Valeronitrile yields mainly di-*n*-amylamine [hydrogen oxalate, m. p. 212·5—213° (lit. 210—211°)]; a small amount of the tertiary

amine is also formed. Reduction of *p*-methoxybenzonitrile in presence of *cyclo*hexanone affords di-*p*-methoxybenzylamine, m. p. 34—35° (*hydrochloride*, m. p. 243—244°; *picrolonate*, m. p. 208°), and *p*-methoxybenzyl*cyclo*hexylamine (*hydrochloride*, m. p. 202°). *p*-Hydroxybenzyl*cyclo*hexylamine (*loc. cit.*) is obtained similarly from *p*-hydroxybenzonitrile.

*Dimethyl*iso*propylamine*, b. p. 67—67·5° (*hydrochloride*, m. p. 205—206°), is formed from acetone and dimethylamine. *dl-N*-Methylephedrine [β-dimethylamino-α-hydroxy-α-phenylpropane][O-*benzoate*, b. p. 212—214°/20 mm., m. p. 65° (*hydrochloride*, m. p. 185—187°)], is prepared by reduction of a mixture of phenyl methyl diketone and dimethylamine, or the diketone, formaldehyde, and methylamine.

H. BURTON.

Triphenyltriaminoethylene. I. Synthesis of triphenyltriaminoethylene and some of its derivatives. II. Action of sulphur on triphenyltriaminoethylene. R. SHIBATA (Tech. Rep. Tohoku, 1929, 8, 21—25, 27—39).—Triphenyltriaminoethylene, m. p. 147° (decomp.), is obtained in 29% yield by heating trichloroethylene (1 mol.) with aniline (3 mols.) in the presence of excess of 16% aqueous sodium hydroxide at 90—95° for 48 hrs. The following derivatives are described: *mono-*, and *tetra-sulphonic acids* (the latter with $8H_2O$), by heating with three times its weight of sulphuric acid for 4 hrs.; *acetyl* derivative, m. p. 123°; *dihydrochloride*, m. p. 167° (decomp.). *Tri*-p-*tolyltriaminoethylene*, m. p. 143° (decomp.), is produced by heating *p*-toluidine, trichloroethylene, and 20% aqueous sodium hydroxide at 100° for 48 hrs.

II. The following substances were isolated by heating together sulphur (1 part) and triphenyltriaminoethylene (5 parts) at 150° for 40 min.: diphenyldiaminoethylene, m. p. 132·5°; a *compound*, $C_{20}H_{19}N_3S$, m. p. 102—104°, probably triphenyltriaminothiolethylene, $C(NHPh)_2{\cdot}C(NHPh){\cdot}SH$; dithiooxanilide, m. p. 134·5—135°, and a *compound*, m. p. 149·5°, of unknown constitution. Similar treatment of tritolyltriaminoethylene yielded two *compounds*, m. p. 200° and 136—137°, respectively, the constitution of which was not elucidated. Oxidation of dithio-oxanilide in acetone with potassium permanganate afforded oxanilide and thio-oxanilide, whilst a *substance*, $C_{14}H_{10}N_2S_2$, m. p. 137°, and probably dehydrothio-oxanilide together with phenyl thiocarbimide were obtained by oxidation of a benzene solution with lead peroxide and glacial acetic acid.

A. I. VOGEL.

Bromination of *p*-anisidine and *p*-acetanisidide, and nitration of 3 : 5-dibromo-*p*-acetanisidide and some of its derivatives. E. BUREŠ and M. NEDĚLKOVÁ (Časopis Českoslov. Lék., 1929, 9, 23—28; Chem. Zentr., 1929, i, 2639).—The violet product of interaction of bromine and *p*-anisidine obtained by Wieland and by Fries is considered to be an additive compound. The action of dry bromine on *p*-acetanisidide or *p*-anisidine yields the 3 : 5-dibromo-compound.

A. A. ELDRIDGE.

Compounds of the nature of "germanin" (Bayer 205). H. BAUER and J. BECKER (Arb. Staatsinst. exp. Ther., Frankfurt a. M., 1928, 16 pp.; Chem. Zentr., 1929, i, 2970).—Variations in the composition of "germanin" weaken its therapeutic activity. Nitrobenzoyl chloride was allowed to react with an aminonaphthalenesulphonic acid, the product was reduced, and the resulting substance again treated with nitrobenzoyl chloride, the product being again reduced and the amino-compound condensed with carbonyl chloride. Variations consisted in the substitution of benzenesulphonic or aminobenzenearsinic for naphthalenesulphonic acids, and of thiocarbamide, oxalyl, malonyl, diethylmalonyl, phthalyl, *iso*phthalyl, and terephthalyl for the carbamide grouping. Further, methyl groups were replaced by propyl or *iso*propyl, were removed, or were increased in number. The following acid chlorides were employed: 3-*nitro*-4-*methylbenzoyl chloride*, b. p. 139—140°/2 mm., f. p. 11°, from *p*-toluonitrile by nitration, hydrolysis of the product, and treatment of the acid, m. p. 187°, with phosphorus pentachloride; 5-*nitro*-2 : 4-*dimethylbenzoyl chloride*, m. p. 58° (approx.), from *m*-xylidine by conversion through the diazo-compound into 2 : 4-dimethylbenzonitrile, hydrolysis, nitration of the acid to the 5-nitro-compound, and treatment with phosphorus pentachloride; 3-*nitro*-4-*methoxybenzoyl chloride*, m. p. 43—46° (indef.); 3-*nitro*-4-*dimethylaminobenzoyl chloride*.

A. A. ELDRIDGE.

Reduction of nitro-compounds in pyridine solution. O. L. BRADY, J. N. E. DAY, and C. V. REYNOLDS (J.C.S., 1929, 2264—2266).—Reduction of nitro-compounds which are only sparingly soluble in alcohol with hydrogen or ammonium sulphide may be effected by passing hydrogen sulphide into a solution or suspension of the nitro-compound in pyridine containing a little water with or without the addition of ammonia or piperidine, the conditions depending on the particular nitro-compound. Thus 2 : 4-dinitromethylaniline, 2 : 5-dinitroaniline, 2 : 5- and 3 : 5-dinitro-*p*-toluidine give, respectively, 4-nitro-2-aminomethylaniline (60% yield), 4-nitro-*m*-phenylenediamine, 5-nitro-2 : 4-tolylenediamine, and 5-nitro-3 : 4-tolylenediamine. 4 : 6-Dinitromethyl-*m*-toluidine gives 6-*nitro*-4-*aminomethyl*-m-*toluidine*, m. p. 180°, converted by nitrous acid into 5-*nitro*-1 : 6-*dimethyl*-1 : 2 : 3-*benztriazole*, m. p. 203°, whilst *m*-dinitrobenzene and 1-nitronaphthalene give *m*-nitroaniline (67% yield) and α-naphthylamine (76% yield). Reduction of 2 : 4 : 6-trinitrotoluene with hydrogen sulphide in hot pyridine solution in the presence of piperidine gives 6-nitro-2 : 4-tolylenediamine, whilst at 0° the product is 2 : 6-dinitro-*p*-toluidine.

J. W. BAKER.

Derivatives of 4 : 4′-diaminodiphenylmethane. H. RIVIER and A. FARINE (Helv. Chim. Acta, 1929, 12, 865—869).—4 : 4′-Diaminodiphenylmethane is prepared more conveniently by condensing aniline hydrochloride with methylal, instead of formaldehyde. Oxidation of the acetyl derivative with chromic acid in acetic acid gives a 70% yield of 4 : 4′-diaminobenzophenone, m. p. 244—245° (phenylhydrazone, m. p. 240—241°), by way of the acetyl derivative, m. p. 235° (cf. Fierz and Koechlin, A., 1918, i, 549). Partial bromination of 4 : 4′-diaminodiphenylmethane gives a poor yield of the 3 : 3′-*dibromo*-compound, m. p.

111—112°, which is best prepared by hydrolysis of the *acetyl* derivative, m. p. 230—231°, obtained by bromination of 4 : 4′-diacetamidophenylmethane in acetic acid. The 3 : 5 : 3′ : 5′-*tetrabromo*-compound, decomp. 250°, or m. p. 270° (decomp.) when rapidly heated, is prepared by bromination in acid solution. The bromo-compounds are formed in poor yield from the corresponding anilines and methylal. 3 : 3′-*Dibromo*-4 : 4′-*diaminobenzophenone*, m. p. 243—244°, is obtained by direct bromination, and the *acetyl* derivative, m. p. 237—238°, by bromination, acetylation, or oxidation from the appropriate compound.

R. K. Callow.

Fluorene series. Action of benzaldehyde on 2 : 7-diaminofluorene and the relation of fluorene to diphenyl. Action of phthalic anhydride on 2 : 7-diaminofluorene. A. Novelli (Anal. Asoc. Quím. Argentina, 1929, **17**, 25—30, 31—41, and Anal. Fís. Quím., 1929, **27**, 740—749, 750—754).—2 : 7-Diaminofluorene condenses with benzaldehyde when heated, preferably in alcoholic solution. The product is not a "Kaufler compound," analogous to that supposed to have been obtained from benzidine (Barzilowski, A., 1892, 854; cf. Dennett and Turner, A., 1926, 391), but 2 : 9-*dibenzylidene*-2 : 7-*diaminofluorene*, m. p. 247—250° (decomp.), which may be diazotised in concentrated sulphuric acid and the diazonium sulphate coupled with β-naphthol to yield a blue *azo-dye*.

2 : 7-Diaminofluorene condenses with phthalic anhydride in boiling water to yield N-*monophthalyl*-2 : 7-*diaminofluorene*, m. p. above 300°, for which a phthalide structure is suggested. The reaction is thus analogous to that of benzidine (Le Fèvre and Turner, A., 1926, 1131). The compound may be diazotised in concentrated sulphuric acid and the diazonium compound coupled with β-naphthol. When boiled with benzaldehyde or salicylaldehyde it yields the 2 : 9-*dibenzylidene* derivative, m. p. above 300°, and the 2 : 9-*disalicylidene* derivative, m. p. about 300°.

R. K. Callow.

Oxidation of 2 : 7-diaminofluorene. C. Ruiz (Anal. Asoc. Quím. Argentina, 1929, **17**, 42—48).—The formation of 4 : 4′-di-(*p*-aminophenyl)azobenzene by the transformation of 4 : 4′-diphenylquinonediimine, obtained by the oxidation of benzidine, is regarded as an argument in favour of the Kaufler formula for benzidine. 2 : 7-Diaminofluorene, similarly, is oxidised by lead dioxide in boiling chloroform to give 7 : 7′-*diamino*-2 : 2′-*azofluorene*, m. p. 273—275° (*dihydrochloride*, m. p. above 300°), in 14% yield. This compound may be diazotised in suspension in concentrated hydrochloric acid and the solution coupled with naphthionic acid. It is reduced by stannous chloride to give 2 : 7-diaminofluorene.

R. K. Callow.

***p*-Cymene. XII. 2-*p*-Cymyl-4-semicarbazide and derivatives.** A. S. Wheeler and J. G. Park (J. Amer. Chem. Soc., 1929, **51**, 3079—3082).—2-*p*-Cymylcarbamide (I), m. p. 168—169° (cf. Demonbreun and Kremers, A., 1924, i, 1002), is conveniently prepared from 2-amino-*p*-cymene and potassium cyanate in acetic acid solution. When 2-amino-*p*-cymene is heated with carbamide at 150—170°, the chief product formed is s-*di*-2-p-*cymylcarbamide*, m. p. 240° with darkening. Prolonged treatment of I with hydrazine hydrate in alcoholic solution affords 2-*p*-*cymyl*-4-*semicarbazide*, m. p. 112° [*hydrochloride*, m. p. 166—168° (decomp.)]. This condenses readily with ketones and 2-p-*cymyl*-4-*semicarbazones* of the following are described: acetone, m. p. 182° (this and the following m. p. are corr.); methyl ethyl ketone, m. p. 182—183°; αγ-dichloroacetone, m. p. 173° (decomp.); mesityl oxide, m. p. 163°; ethyl acetoacetate, m. p. 133·5°; *cyclo*hexanone, m. p. 192·5°; camphor, m. p. 217°; carvone, m. p. 97°; benzophenone, m. p. 150°; acetophenone, m. p. 212°, and benzoin, m. p. 172°.

H. Burton.

***p*-Cymene. XIII. 2-*p*-Cymylhydrazine and derivatives.** A. S. Wheeler and C. L. Thomas (J. Amer. Chem. Soc., 1929, **51**, 3135—3139).—Diazotisation of 2-amino-*p*-cymene and subsequent reduction with sodium sulphite affords 2-*p*-cymylhydrazine (I), b. p. 129—132°/5 mm., m. p. 26·5°, d_{23}^{23} 0·9863, n^{25} 1·5551 (cf. Demonbreun and Kremers, A., 1924, i, 1002) [hydrochloride, m. p. 198° (lit. 186—187°); *hydrobromide*, m. p. 174°; *sulphate*, m. p. 130°; *picrate*, decomp. suddenly at 124°; p-*nitrobenzoyl* derivative, m. p. 177°]. *Cinnamaldehyde*-, m. p. 90°; *salicylaldehyde*-, m. p. 87°, and *benzophenone*-2-p-*cymylhydrazones*, m. p. 88°, are described. Unstable derivatives were obtained by using methyl ethyl ketone, acetophenone, and benzaldehyde (cf. Demonbreun and Kremers, *loc. cit.*), whilst no condensation occurred with methyl nonyl ketone, *pp*′-tetramethyldiaminobenzophenone, or benzoylacetone. When I is treated with carbamide, 2-p-*cymyl*-1-*semicarbazide*, m. p. 171°, is formed; with potassium thiocyanate in acetic acid solution 2-p-*cymyl*-1-*thiosemicarbazide*, m. p. 184°, results. Carbon disulphide and I yield an unidentified *compound*, m. p. 177°.

H. Burton.

Relation between quinonehydrazones and *p*-hydroxyazo-compounds. VII. Aliphatic-aromatic *pp*′-dihydroxy- and -diamino-bisazo-compounds. W. Borsche, W. Müller, and C. A. Bodenstein (Annalen, 1929, **475**, 120—131).—Condensation of benzoquinone with the dihydrazides of various dibasic acids in alcoholic solution in the presence of hydrochloric acid does not yield cyclic benzoquinonehydrazones of the type

$C_6H_4 \begin{matrix} N{\cdot}NH{\cdot}CO \\ N{\cdot}NH{\cdot}CO \end{matrix} > [CH_2]_r$, but 2 mols. of benzoquinone condense with 1 mol. of the dihydrazide to yield *p*-hydroxyazo-compounds of the type $R(N{:}N{\cdot}C_6H_4{\cdot}OH)_2$. Thus with carbohydrazide is obtained *di*-p-*hydroxyphenylcarbodiazone* (R=CO) decomp. 228°, whilst by addition of sodium acetate and anisaldehyde to the filtrate the *anisylidene* derivative, m. p. 187°, of *p*-hydroxybenzeneazoformhydrazide (which cannot itself be isolated) is obtained, the same substance being obtained, together with the dianisylidene derivative, by condensation of anisaldehydecarbohydrazone with benzoquinone. Similarly, by addition of acetophenone instead of anisaldehyde is obtained *acetophenone*-p-*hydroxybenzeneazoformhydrazone*, m. p. 168—169°. Similar condensation of benzoquinone with carboxyamidocarbohydrazide (Pellizzari and Roncagliolo, A., 1907, i, 833) yields ω-*carboxyamido*-p-*hydroxybenzeneazoformhydrazide*,

$HO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 215—216° (decomp.). Toluquinone and carbohydrazide condense to give *di-4-hydroxy-3-methylphenylcarbodiazone*, m. p. 207° (decomp.). With the dihydrazides of the following dibasic acids, oxalic, m. p. 244—245° (lit. 241°); malonic; succinic; glutaric; adipic, m. p. 178° (lit. 171°); sebacic, m. p. 187—188° (lit. 184—185°), and *diphenic* acid, m. p. 216—217° (*dibenzylidene*, m. p. 186—187°; *dianisylidene*, m. p. 224—225°, derivatives; acetophenone condensation *product*, m. p. 214°), benzoquinone condenses to yield *oxalyl-* $+2H_2O$ and anhydrous, m. p. 242—243°; *malonyl-*, m. p. 242—243°; *succinyl-* [*dibenzoyl* derivative, m. p. 200° (decomp.)]; *glutaryl-*, decomp. 193—194°; *adipyl-* (*dibenzoyl* derivative, m. p. 258—259°); *sebacyl* +MeOH, m. p. 195°, and *diphenyl-2 : 2'-dicarboxyl-*, m. p. 170—171°, *-bis-4-azophenols*, whilst by the action of benzaldehyde on the appropriate mother-liquors are obtained p-*hydroxybenzeneazomalonyl-*, m. p. 238—239°, and p-*hydroxybenzeneazosebacyl-*, m. p. 135—137°, *-benzylidenehydrazone*. *Succinylbis-5-azo-o-cresol*, m. p. 204—205°, is prepared similarly from toluquinone. Condensation products of a similar type, $R(NH{\cdot}N{:}C_6H_4{:}N{\cdot}OH)_2$, are obtained with benzoquinone monoxime and thus are obtained *bisbenzoquinone - 1 : 1' - oxime - 4 : 4' - carbohydrazone* $+H_2O$, decomp. 205°, *-oxalhydrazone*, decomp. above 320°; *-malonhydrazone*, decomp. 235°; and *sebacylhydrazone*, decomp. 205°. These are reduced by hydrogen and colloidal palladium in *N*-sodium hydroxide solution to the *p*-aminobenzenehydrazo-derivatives $R(NH{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2)_2$, and thus are obtained *carbodi-*p-*aminophenylhydrazide* and *succindi-*(p-*aminophenylhydrazide*). These are oxidised by atmospheric oxygen to *di-*p-*aminophenylcarbodiazone*, m. p. 205—210° (decomp.), and *succinylbis-4-azoaniline*, decomp. 320°, respectively. Aminourazole (obtained by heating carboxyamidocarbohydrazide) condenses with benzoquinone and toluquinone to yield *substances* probably of the type

$$O{:}C_6H_4{:}N{\cdot}N{<}\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}.$$

J. W. BAKER.

Cleavage of azo-dyes by sulphites. K. H. ENGEL (J. Amer. Chem. Soc., 1929, **51**, 2986—2994).—Prolonged treatment of an azobenzene derivative with an aqueous solution of a normal sulphite (2 mols.) at 90—95° in closed vessels causes fission, usually with the formation of an aniline, salts of a sulphamic acid, $R{\cdot}NH{\cdot}SO_3H$, and compounds of the type $R{\cdot}N(O{\cdot}SO_2H)_2$. Thus, 4-hydroxyazobenzene is decomposed by ammonium sulphite to aniline (0·78 mol.), phenylsulphamic, (0·22 mol.), *p*-hydroxyphenylsulphamic (0·22 mol.), and *p*-aminophenol-*NN*-disulphonic acids (0·78 mol.). No free ammonia or *p*-aminophenol and only a small amount of sulphate are formed during the reaction; 98·8% of the sulphite used is in combination with the fission products. Treatment of the mixed sulphonic acids formed with boiling hydrochloric acid gives aniline, *p*-aminophenol-2-sulphonic acid, and the very soluble p-*aminophenol-*O-*sulphonic acid* (*α-naphthaleneazo-*derivative). The last-named compound is hydrolysed only slowly by 5*N*-hydrochloric acid at 90—93°. With sodium or potassium sulphite, reaction is carried out at 140—150°; with ammonium sulphite at 130—135°, reaction is more rapid than at 90—93°, but the products formed are essentially the same. 4-Hydroxyazobenzene-4'-sulphonic acid undergoes similar fission with ammonium sulphite; free sulphanilic acid is produced. Rearrangement of the *N*-sulphonic acids obtained gives *p*-aminophenol-2- and *-O*-sulphonic acids. It is suggested that the primary product of the change is an additive compound formed from the azobenzene and sulphite. The two nitrogen atoms of the azo-group are assumed to differ functionally from one another. H. BURTON.

Direct dibromination of *m*-bromophenol. H. H. HODGSON and J. NIXON (J.C.S., 1929, 2424).—Bromination of 3-bromo-2-nitrophenol in acetic acid yields 3 : 4 : 6-*tribromo-2-nitrophenol*, m. p. 109°. This is converted by methyl sulphate into 3 : 4 : 6-tribromo-2-nitroanisole, identical with a specimen obtained by methylation and nitration of the product of the bromination of *m*-bromophenol (Kohn and Strassmann, A., 1925, i, 1264). The product of the last-named reaction is therefore 3 : 4 : 6-tribromophenol. J. W. BAKER.

Bromophenols. XXXIV. Debromination of bromocresols with zinc dust and acetic acid. M. KOHN and A. ARON (Monatsh., 1929, **53** and **54**, 48—61; cf. A., 1927, 966).—Treatment of tetrabromo-*o*-cresol with zinc dust and acetic acid affords 3 : 5 : 6-tribromo-*o*-cresol [*methyl ether* (I), b. p. 308—311°/745 mm., m. p. 71°; *benzoate*, m. p. 133°; acetate, m. p. 77—78° (corr.)], purified by conversion into I and subsequent demethylation with 66% hydrobromic acid in acetic acid solution. Nitration of I gives the 4-*nitro*-derivative, m. p. 111°. 3 : 5-Dichloro-4 : 6-dibromo-*o*-cresol, m. p. 199° (lit. 196—197°), is debrominated similarly to 3 : 5-*dichloro-6-bromo-o-cresol*, m. p. 68° (*methyl ether*, b. p. 283—286°/745 mm., m. p. 59°; *benzoate*, m. p. 102°), whilst 2 : 3 : 5-tribromo- or tetrabromo-*p*-cresol furnishes 2 : 5-*dibromo-*p-*cresol*, m. p. 60° (*methyl ether*, b. p. 274—278°/748 mm., m. p. 78°; *benzoate*, m. p. 89°). Nitration of this in acetic acid solution yields 2 : 5-*dibromo-3-nitro-*p-*cresol*, m. p. 118°. H. BURTON.

Substitution products of 4-nitro- and 4-acetamido-diphenyl ether. H. A. SCARBOROUGH (J.C.S., 1929, 2361—2367).—Iodine monochloride in acetic acid converts 4-nitrodiphenyl ether (I) into 4-*iodo-4'-nitro-*, m. p. 71° (*iodochloride*), reduced and acetylated to give 4-*iodo-4'-acetamido-* (II), m. p. 174° [also obtained by iodination of the 4-*acetamido-*compound, (III), m. p. 127°], which is hydrolysed to 4-*iodo-4'-amino-diphenyl ether*, m. p. 91°. This is converted into 4-*bromo-4'-iodo-*, m. p. 72°, which is also obtained by bromination of 4-*iodo-*, m. p. 48°, prepared from 4-*amino-diphenyl ether* (*hydrochloride*, m. p. 238°). Chlorination and bromination of I also occurs in the 4'-position. Dry bromine converts I or 4-bromo-4'-nitro- into 2 : 4-*dibromo-4'-nitro-diphenyl ether* (IV), m. p. 81° (also prepared from potassium 2 : 4-dibromophenoxide and *p*-chloronitrobenzene). Reduction and acetylation of 4-chloro-4'-nitro- gives 4-*chloro-4'-acetamido-*, m. p. 146°, converted by nitric (*d* 1·5) and acetic acids at 80° into 4'-*chloro-3-nitro-4-acetamido-*, m. p. 98° [also obtained in small yield by

chlorination of V (below)], hydrolysed to 4′-*chloro*-3-*nitro*-4-*amino*-, m. p. 114°, which is deaminated to 4′-*chloro*-3-*nitro-diphenyl ether*, m. p. 60°. Bromination of III in acetic acid in the presence of fused sodium acetate yields 4-*bromo*-4′-*acetamido*-, m. p. 161° (also obtained by reduction and acetylation of the 4-bromo-4′-nitro-derivative), which is converted by nitric and acetic acids at 80° into 4′-*bromo*-3-*nitro*-4-*acetamido-diphenyl ether*, m. p. 107° [also obtained by bromination of V (below)]. The last is hydrolysed to 4′-*bromo*-3-*nitro*-4-*amino*-, m. p. 144°, which is deaminated to 4′-*bromo*-3-*nitro-diphenyl ether*, m. p. 64°. Nitration of II gives 4′-*iodo*-3-*nitro*-4-*acetamido*-, m. p. 123° [also, in small yield, by iodination of V (below)], hydrolysed to 4′-*iodo*-3-*nitro*-4-*amino-diphenyl ether*, m. p. 155°. Nitration of III gives 3-*nitro*-4-*acetamido*- (V), m. p. 100°, hydrolysed to 3-*nitro*-4-*amino*-, m. p. 82°, which is converted by deamination, reduction, and acetylation into 3-acetamido-diphenyl ether (Ullmann and Sponagel, A., 1907, i, 38). Reduction and acetylation of IV gives 2 : 4-*dibromo*-4′-*acetamido*-, m. p. 158°, nitrated to the 3′-*nitro*-derivative, m. p. 141°, hydrolysed to 2 : 4-*dibromo*-3′-*nitro*-4′-*amino-diphenyl ether*, m. p. 107°. This is deaminated to 2 : 4-*dibromo*-3′-*nitrodiphenyl ether*, m. p. 72°. 4 : 4′-*Di-iododiphenyl ether*, m. p. 139°, is obtained by the action of excess of iodine monochloride in acetic acid on diphenyl ether, or by the Sandmeyer reaction from the 4-iodo-4′-amino-derivative. J. W. BAKER.

Products of condensation of aminophenols with aldehydes. T. G. LEVI (Gazzetta, 1929, **59**, 544—548).—A number of compounds, some of which are applied in rubber manufacture, have been prepared by the condensation of aldehydes with aminophenols. The latter react in aqueous solution or suspension, or as the hydrochloride in presence of sodium acetate, when the hydrochloride of the product separates. With aldehydes insoluble in water the reaction is carried out in acetic acid. The following are described: derivatives of *p*-aminophenol: methylene- (G.P. 68,708) and *ethylidene*-, brown, insoluble, infusible powders, probably polymerides; *furfurylidene*-, m. p. 176·5° (*hydrochloride*); o-*nitrobenzylidene*-, m. p. 154°; *terephthalylidene*-, m. p. 256°; derivatives of *o*-aminophenol: *methylene*- and *ethylidene*- (polymerides?); *furfurylidene*-, amorphous; o-*nitrobenzylidene*-, m. p. 104°; *terephthalylidene*-, m. p. 213°; derivatives of 2 : 4-diaminophenol: *dimethylene*- and *diethylidene*- (polymerides?); *diisovalerylidene*- (*hydrochloride*, m. p. 126°); *difurfurylidene*-, tarry; *dibenzylidene*-, m. p. 106°; *disalicylidene*-, m. p. 170°; *dicannamylidene*- (*hydrochloride*); *divanillylidene*- (*hydrochloride*); *terephthalylidene*-, infusible and insoluble.

R. K. CALLOW.

Mixed aromatic hydroxysulphones. I. Hydroxyphenyl-*p*-hydroxytolylsulphone. J. ZEHENTER and F. GOSCH (J. pr. Chem., 1929, [ii], **123**, 276—283).—When a mixture of phenol and *p*-cresol is heated with concentrated or fuming sulphuric acid at 160—180° there are obtained 4 : 4′-dihydroxydiphenylsulphone, di-*p*-hydroxyditolylsulphone, and *hydroxyphenyl*-p-*hydroxytolylsulphone* $+H_2O$ (I), m. p. 175° (*diacetate*, m. p. 161°; *dibenzoate*, m. p. 165°; *sodium* salt +2EtOH, by the action of sodium carbonate; *disodium* salt +EtOH, by the action of sodium on an alcoholic solution of I). Treatment of I with nitric acid (*d* 1·1—1·26) at 100° gives a *nitro*-derivative, m. p. 181—182° (decomp.), whilst bromination in ethereal solution affords a *tribromo*-derivative, m. p. 215°. Treatment of I with sulphuric acid at the ordinary temperature furnishes a disulphonic acid (*barium* salt $+7H_2O$), together with phenol-4- and *p*-cresol-3-sulphonic acids; at higher temperature complete fission of I into the phenol- and cresol-sulphonic acids occurs. H. BURTON.

Highly polymerised compounds. XXV. Polyanethole. H. STAUDINGER and M. BRUNNER (Helv. Chim. Acta, 1929, **12**, 972—984).—The polymerisation of anethole to polyanethole is readily effected in solution by Florida earth (cf. Lebedev and Filonenko, A., 1925, i, 225) or by metallic chlorides, such as stannic chloride, which forms a deeply-coloured solution. 1 Molecule of stannic chloride can cause quantitative polymerisation of 274 molecules of anethole, *i.e.*, a much larger amount than that with which it could form a complex compound. Polyanethole is a white, amorphous powder of hemicolloidal properties. The degree of polymerisation increases with fall of temperature or increase of concentration of the reaction mixture. The product may be separated into more and less soluble fractions having mean mol. wts. rising from 950 to 9500, temperatures of liquefaction rising from 110—140° to 280—330°, and increasing viscosities in solution, corresponding with a variation in the mean degree of polymerisation from 7 to 65. The variation of the viscosity of solutions with temperature indicates that no dissociation occurs. Treatment of polyanethole with hydriodic acid yields polypropenylphenol, which, instead of showing the expected phenolic properties, is a brown powder, swelling, but not dissolving, in alcoholic potassium hydroxide, phenol, or alcohol, and may be a "three-dimensional" condensation product.

R. K. CALLOW.

α-Naphtholsulphonic acids. E. GEBAUER-FÜLNEGG and A. GLÜCKMANN (Monatsh., 1929, **53** and **54**, 100—110).—Treatment of a potassium α-naphtholsulphonate with ethyl chloroformate gives the corresponding potassium *O*-carbethoxy-α-naphtholsulphonate, converted by phosphorus pentachloride into the *O*-carbethoxy-α-naphtholsulphonyl chloride. The following are described: O-*carbethoxy*-α-*naphthol*-2-, m. p. 130°; -3-, m. p. 140°; -5-, m. p. 174°; -6-, m. p. 112°, and -7-*sulphonyl chlorides*, m. p. 105°. Instead of the -8-sulphonyl chloride the *compound* $SO_2Cl{\cdot}C_{10}H_6{\cdot}O{\cdot}POCl_2$(1 : 8), m. p. 78°, is formed. O-*Carbethoxy*-α-*naphthol*-2 : 7-*disulphonyl chloride*, m. p. 156°, is obtained similarly from the disulphonic acid formed by hydrolysis of α-naphthol-2 : 4 : 7-trisulphonyl chloride (A., 1928, 751). O-*Carbethoxy*-α-*naphthol*-5- and -6-*sulphonanilides*, m. p. 127° and 140°, respectively, are hydrolysed by alcoholic potassium hydroxide to α-*naphthol*-5- and -6-*sulphonanilides*, m. p. 201° and 181°, respectively (the -7-*sulphonanilide*, m. p. 155°, is also described). When *O*-carbethoxy-α-naphthol-3-sulphonyl chloride is treated with aniline an oxygen-free *substance*, m. p. 153°, results. Hydrolysis of this with potassium

hydroxide solution gives a *compound*, m. p. 236° with charring, which is sulphur- and nitrogen-free.

Treatment of α-naphthol-2-, -4-, or -7-sulphonic acids with an excess of chlorosulphonic acid at the ordinary temperature affords α-naphthol-2 : 4 : 7-trisulphonyl chloride, m. p. 174° (cf. *loc. cit.*). α-Naphthol-5-, -6-, and -8-sulphonic acids yield similarly *α-naphtholtrisulphonyl chlorides* with m. p. 140°, 203°, and 217°, respectively [the corresponding *trianilides* have m. p. 227°, 203°, and 240° (all with charring)]. The probable alternative orientations of these tri-derivatives are discussed. The product obtained from α-naphthol-3-sulphonic acid and chlorosulphonic acid could not be obtained crystalline; when it is treated with aniline a *chloronaphtholdisulphondianilide*, m. p. 250° with charring, results.

H. BURTON.

β-Naphtholdisulphonyl chlorides. J. POLLAK, E. GEBAUER-FÜLNEGG, and E. BLUMENSTOCK-HALWARD [with A. SCHLESINGER and H. STEHNO] (Monatsh., 1929, **53** and **54**, 83—89).—The β-naphtholdisulphonyl chloride (I), m. p. 177°, previously described (A., 1928, 751, 752) is formulated as the 1 : 5-derivative, since it is obtained by the action of chlorosulphonic acid on β-naphthol-5-sulphonic acid at the ordinary temperature. The potassium salt of *O*-carbethoxy-β-naphthol-5-sulphonic acid [*sulphonyl chloride* (II), m. p. 101°; *anilide*, m. p. 188°] is converted similarly into I. Hydrolysis of I with slightly diluted hydrochloric acid and treatment of the residue first with ethyl chloroformate and then with phosphorus pentachloride yields II (not affected by similar hydrolysis and treatment). β-*Naphthol*-1 : 7-*disulphonyl chloride*, m. p. 169° (*dianilide*, m. p. 233°), is obtained by the action of chlorosulphonic acid on β-naphthol-7-sulphonic acid. β-Naphthol-4-sulphonic acid gives an uncrystallisable product; when this is treated with aniline aβ-*naphtholdisulphondianilide*, m. p. 290°, results. *Tribarium* and *tripotassium* salts of β-naphthol-1 : 5-, -1 : 6-, and -1 : 7-disulphonic acids are described.

H. BURTON.

***N*-Hydroxyethyl derivatives of *o*-aminophenol.** I.G. FARBENIND. A.-G.—See B., 1929, 935.

Nitration of β-naphthol-6-sulphonic acid. N. N. VOROSHTZOV and N. M. KASATKIN.—See B., 1929, 934.

Halogen derivatives of *cyclo*hexane-1 : 4-diol. L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1929, **189**, 701—703).—Treatment of *cyclo*hexane-1 : 4-diol with hydrochloric acid (3 mols.; *d* 1·19) at 100° for 6 hrs. gives 1 : 4-dichloro*cyclo*hexane (principal product), 4-chloro*cyclo*hexanol, and smaller amounts of $\Delta^{1:3}$-*cyclo*hexadiene and Δ^{1}-*cyclo*hexen-4-ol. When the dichloro-compound is cooled, crystals of trans-1 : 4-*dichloro*cyclo*hexane*, m. p. 102°, b. p. 79—80°/13 mm., are precipitated, the residual liquid, b. p. 79—80°/13 mm., d_4^{15} 1·1831, n_D^{15} 1·4950, consisting mainly of cis-*isomeride*. Diminution of the amount of hydrochloric acid increases the yield of 4-chloro*cyclo*hexanol, b. p. 105°/12 mm., d_4^{17} 1·1435, n_D^{17} 1·4930, but it was impossible to separate this substance into two isomerides. The *phenylurethane*, m. p. 99°, is described. Treatment of *cyclo*hexane-1 : 4-diol with hydrobromic acid gave the corresponding dibromo-compound, which on freezing deposited crystals of trans-1 : 4-*dibromo*cyclo*hexane*, m. p. 112°, the residual liquid, b. p. 114—115°/15 mm., d_4^{20} 1·7834, n_D^{20} 1·5531, being the impure cis-*isomeride*. The use of a smaller excess of hydrobromic acid gave 4-bromo*cyclo*hexanol, which could not be separated from the dibromo-compound by distillation. The action of benzoyl chloride on the mixture gave 4-*bromo*cyclo*hexyl benzoate*, b. p. 203—204°/18 mm., d_4^{20} 1·3456, n_D^{20} 1·5520. Treatment of *cyclo*hexane-1 : 4-diol with acetyl chloride at 100° in a closed vessel yielded 4-*chloro*cyclo*hexyl acetate*, b. p. 111—112°/18 mm., $d_4^{19\cdot5}$ 1·1282, $n_D^{19\cdot5}$ 1·4659. 4-*Bromo*cyclo*hexyl acetate*, b. p. 124°/17 mm., d_4^{21} 1·3381, n_D^{21} 1·4873, is also described. The action of the requisite hydracid on these compounds gave small amounts of mixed 1 : 4-dihalogeno*cyclo*hexanes.

A. A. GOLDBERG.

Physical properties of guaiacol. T. S. CARSWELL (J. Amer. Pharm. Assoc., 1929, **18**, 995—997).—Guaiacol, purified by crystallisation of the sodium salt, precipitation as the magnesium salt, repeated fractional crystallisation, and fractionation in vacuum, had m. p. 28·2°, b. p. 204·65°/746·4 mm. A needle-shaped form, m. p. −3·2°, has been prepared by crystallisation of molten guaiacol supercooled to −10°.

E. H. SHARPLES.

Bromoguaiacol carbonate. Determination of guaiacol carbonate. L. H. CHERNOFF (J. Amer. Chem. Soc., 1929, **51**, 3072—3074).—Bromination of guaiacol carbonate (I) in warm methyl-alcoholic solution gives *bromoguaiacol carbonate*, m. p. 178°. Using 0·1—0·5 g. of I and diluting the reaction mixture with an equal volume of water gives almost quantitative yields. For the determination of guaiacol carbonate admixed with substances such as starch, it is extracted with chloroform. The chloroform is evaporated and the residue brominated as above.

H. BURTON.

Alkylation of aromatic compounds. H. MEYER and K. BERNHAUER (Monatsh., 1929, **53** and **54**, 721—752).—When a solution of an aromatic compound in an alcohol is added gradually to well-stirred 70—80% sulphuric acid at 70—80° (bath temperature), alkylation occurs. When benzyl alcohol is used, reaction is best carried out at 40°. If the compound used is insoluble in the alcohol, the latter is added drop by drop and the former either gradually or altogether. With *n*-butyl alcohol, *sec.*-butyl derivatives are formed; *n*-propyl alcohol affords *iso*propyl derivatives, and *iso*butyl alcohol furnishes *tert.*-butyl compounds. Methyl alcohol does not react and ethyl alcohol ethylates only at 170° under pressure. Benzene, benzyl alcohol, and 70% sulphuric acid at 40° give diphenylmethane and 1 : 4-dibenzylbenzene (*dinitro*-derivative, m. p. 146°) (oxidised by chromic and acetic acids to 1 : 4-dibenzoylbenzene). Benzene, *iso*propyl alcohol, and 80% sulphuric acid at 65° yield *iso*propyl- (I), 1 : 4-di*iso*propyl- (II), and 1 : 3 : 4-tri-*iso*propyl-benzenes (III). Sulphonation of I affords a disulphonic acid (*barium* salt), converted by fusion with potassium hydroxide at 330—340° into a *dihydroxy*i*sopropylbenzene*, m. p. 108—109° (*dibenzoate*, m. p. 114—115°). Oxidation of II with chromic, acetic, and sulphuric acids furnishes terephthalic acid,

whilst oxidation of III with nitric acid (*d* 1·16) gives an iso*propylbenzenedicarboxylic acid*, m. p. above 300°. Benzene and *iso*butyl alcohol afford a mixture of *tert.*-butyl- and 1 : 4-di-*tert.*-butyl-benzenes; *n*- or *sec.*-butyl alcohol yields *sec.*-butyl- and 1 : 4-di-*sec.*-butyl-benzenes (a small amount of the 1 : 2-derivative is also formed); *cyclo*hexanol furnishes mainly *cyclo*hexylbenzene. Benzylation of toluene gives phenyl-*p*-tolylmethane and anthracene; *o*-xylene yields 4-benzyl-*o*-xylene (oxidised to trimellitic acid) and 1-methylanthracene, m. p. 199° (oxidised to *anthraquinone*-1-*carboxylic acid*, m. p. 292°); *m*-xylene affords 4-benzyl-*m*-xylene (*nitro*-derivative, m. p. 115°) and 2-methylanthracene (IV) [oxidised to *anthraquinone*-2-*carboxylic acid*, m. p. 284° (*chloride*, m. p. 147°; *ethyl* ester, m. p. 147°)]; *p*-xylene furnishes IV and the corresponding benzylxylene. The above anthracenes are formed by oxidation of the intermediate 9 : 10-dihydro-derivatives. *iso*Propylation of toluene yields *p*-cymene, oxidised by potassium dichromate and sulphuric acid at 60° to a mixture of *p*-methylacetophenone (*phenylhydrazone*, m. p. 97°) and p-*acetobenzaldehyde*, b. p. 135—138°/vac. (*bis-phenylhydrazone*, m. p. 121°; *dioxime*, m. p. 177°). *p-tert.*-Butyl- and *p-sec.*-butyl-toluenes are obtained from toluene and *iso*- and *sec.*-butyl alcohols, respectively.

Benzylation of phenol gives a small amount of 2-, in addition to 4-hydroxydiphenylmethane; with *cyclo*hexanol, 4-*cyclo*hexylphenol (*benzoate*, m. p. 118·5°; *methyl ether*, m. p. 59°) is formed. Phenol and methyl*cyclo*hexanol furnish 4-*methyl*cyclo*hexylphenol*, m. p. 110—111° (*benzoate*, m. p. 87°; *methyl ether*, m. p. 41°), decomposed by treatment with silver sulphate (attempted dehydrogenation) to phenol and *tetrahydrotoluene*, b. p. 104°. Benzylation of *o*-cresol yields *phenyl*-4-*hydroxy*-m-*tolylmethane*, m. p. 35° (*oxalate*, m. p. 109°; *benzoate*, m. p. 115°); *iso*butyl alcohol and *o*-cresol give 5-*tert.*-butyl-*o*-cresol (nitro-derivative, m. p. 85—86°). *iso*Propylation of *m*-cresol affords 6-*iso*propyl-*m*-cresol [nitroso-derivative, m. p. 165—167° (decomp.); *methyl ether*, b. p. 215—220°]. *p*-Cresol could not be alkylated.

Resorcinol and *iso*propyl alcohol form 4-iso*propyl*-, m. p. 105°, and 4 : 6-*di*iso*propyl-resorcinol*, m. p. 162° (*monomethyl ether*, m. p. 123°, by alkylation of resorcinol monomethyl ether); resorcinol dimethyl ether furnishes *mono*-, b. p. 245—250°, and *di*-iso*propylresorcinol dimethyl ethers*, m. p. 41° (main product). Similarly, salicylic acid gives 5-*iso*propyl-salicylic acid (*acetyl* derivative, m. p. 63·5°; *phenyl* ester, m. p. 43°). 5-tert.-*Butylacetylsalicylic acid* has m. p. 128°. 2-*Nitro*-5-iso*propyltoluene*, b. p. 230—240°, and 4-chloro*iso*propylbenzene, b. p. 190—195°, are obtained by *iso*propylation of *o*-nitrotoluene and chlorobenzene, respectively.

*iso*Propylation of naphthalene in presence of 80% sulphuric acid at 80° gives alkylated naphthalene-sulphonic acids. Dilution of the reaction mixture and distillation with superheated steam yields the *iso*-propylnaphthalenes. The following derivatives are described: 1-*iso*propylnaphthalene, purified through the 4-sulphonic acid [*potassium* and *aniline*, m. p. 190° (decomp.), salts]; 2-*iso*propylnaphthalene, sulphonated to the 1-sulphonic acid, m. p. 137° (decomp.) [*potassium* and *aniline*, m. p. 209—210° (decomp.), salts; *sulphonyl chloride*, m. p. 61°; *sulphonamide*, m. p. 140°]; 1 : 6-*di*iso*propylnaphthalene*, m. p. 52°, oxidised by 5% nitric acid to naphthalene-1 : 6-dicarboxylic acid (*methyl* ester, m. p. 98—98·5°) and 1(or 6)-*iso*propyl-6(or 1)-naphthoic acid (*methyl* ester, b. p. 323—327°); tri*iso*propylnaphthalene (oxidation and subsequent esterification furnishes a *methyl di*-iso*propylnaphthoate*, b. p. 206°/vac., and *methyl* iso*propylnaphthalenedicarboxylates*, m. p. 192° and 132—134°, respectively); *tetra*iso*propylnaphthalene*, m. p. 127° (*nitro*-derivative, m. p. 201°), oxidised by nitric acid (*d* 1·3) to a *di*iso*propylnaphthalenedicarboxylic acid*, m. p. above 300°. A mixture of 2 : 6- and 2 : 7-di*iso*propylnaphthalenes is also obtained (from the oxidation products a *methyl* iso*propylnaphthoate*, m. p. 73—74°, is isolated after esterification). 4- and 2-iso*Propyl*-α-*naphthol* (*benzoate*, m. p. 121°; *methyl ether*, b. p. 217—222°/50—55 mm.) have m. p. 72° and 65—66°, respectively. Distillation of a mixture of potassium cyanide and 2-*iso*propylnaphthalene-1-sulphonate in a current of carbon dioxide, and hydrolysis of the resulting nitrile with 40% alcoholic alkali hydroxide, furnishes 2-iso*propyl*-α-*naphthoic acid*, m. p. 146°.

*iso*Propylation of naphthalene-2-sulphonic acid in presence of concentrated sulphuric acid at 120° gives 1 : 6-*di*iso*propylnaphthalene*-3(or 7)-*sulphonic acid* (V) [*potassium* $+H_2O$, and o-*toluidine*, m. p. 215—216°, salts; *sulphonyl chloride*, m. p. 71°; *sulphonamide*, m. p. 179—180°; *hydrazide*, m. p. 130—132° (decomp.); *methyl* ester, m. p. 77°], converted by the usual methods into 1 : 6-*di*iso*propyl*-β-*naphthol*, m. p. 90° (*methyl ether*, m. p. 59°; *benzoate*, m. p. 99°), and 1 : 6-di*iso*propylnaphthalene. The residue after removal of V is desulphonated, oxidised, and esterified, whereby methyl naphthalene-2 : 6-dicarboxylate and a methyl *iso*propylnaphthoate, m. p. 73°, are formed. *iso*Propylation of naphthalene-1-sulphonic acid at 40—45° yields a *di*iso*propylnaphthalenesulphonic acid* (o-*toluidine*, m. p. 214°, and *potassium* salts; *sulphonyl chloride*, m. p. 119°; *sulphonamide*, m. p. 151°), converted into a *di*iso*propylnaphthalene*, b. p. 317—319°, m. p. 38°. Tetra*iso*propylnaphthalene is obtained by steam-distillation of the reaction mixture. Naphthalene and *iso*butyl alcohol afford mainly a *di*-tert.-*butylnaphthalene*, m. p. 142°. H. BURTON.

Sequoyite [pentahydroxymethoxy*cyclo*hexane], a cyclose from redwood (*Sequoia sempervirens*). E. C. SHERRARD and E. F. KURTH (J. Amer. Chem. Soc., 1929, **51**, 3139—3141).—The cycloses extracted from the dry heartwood of *Sequoia sempervirens* (B., 1928, 636) are pinite and *sequoyite* (trace <0·06%), m. p. 234—235° (*penta-acetate*, m. p. 198°), separable by fractional crystallisation from aqueous alcohol. The new cyclose is decomposed by hydriodic acid, yielding methyl iodide and *i*-inositol, thus showing it to be a monomethyl ether of *i*-inositol (cf. *loc. cit.*). H. BURTON.

Sterol group. VI. Dihydroergosterol and the formation of isomerides. I. M. HEILBRON, F. JOHNSTONE, and F. S. SPRING (J.C.S., 1929, 2248—2255).—Reduction of ergosterol with sodium and boiling amyl alcohol gives mainly α-dihydroergosterol

I) (Heilbron, Sexton, and Spring; this vol., 809) together with a small quantity of the stereoisomeric *γ-dihydroergosterol* (II), m. p. 205—206° $[\alpha]^{20}_{5461}$ −10° in chloroform, saturation of the 1 : 2 (or 1 : 13) double linking having occurred, and in agreement with this neither I nor II gives a colour with antimony trichloride. Moreover, I is converted into II by heating with a solution of sodium amyloxide. Acetic anhydride converts I into an *acetate*, the m. p. and specific rotation of which depend on the duration of acetylation, which is converted by anhydrous hydrogen chloride in chloroform solution into the *acetate*, m. p. 108—109°, $[\alpha]^{20}_{5461}$ −25·2° in chloroform, of *β-dihydroergosterol* $+x H_2O$ (III), m. p. 124°, $[\alpha]^{18}_{5461}$ −7·0° in chloroform (no colour with antimony chloride), the free dihydrosterol being liberated by the action of alcoholic potassium hydroxide. It is suggested that the conversion of the α- into the β-dihydro-isomeride involves the prior addition of hydrogen chloride to the 6 : 7-double linking and subsequent elimination from the 2 : 7-positions giving rise to a new double linking at 2 : 3. Both isomerides absorb 1 mol. of hydrogen in the presence of palladium in ether to give α-ergostenol. Boiling alcoholic mercuric acetate converts I with elimination of 2 atoms of hydrogen into *ergosterol*-D (ergostatrienol-*D*), m. p. 167°, $[\alpha]^{18}_{5461}$ +17·8° (*acetate*, m. p. 172°, $[\alpha]^{20}_{5461}$ +15·9° in chloroform) (cf. Windaus and Auhagen, this vol., 1065), which is characterised by three bands in its absorption spectrum at 235, 243, and 252 μμ. A similar banded structure is shown by ergosterol-*A* and, contrary to Windaus and Linsert (A., 1928, 1372), by dehydroergosterol, which has bands at 312, 327, and 345 μμ. Similarly, III is converted by alcoholic mercuric acetate into *ergosterol*-E $+x H_2O$, m. p. 124—125°, $[\alpha]^{18}_{5461}$ −22·9° in chloroform (yellow colour with antimony trichloride) (*acetate*, m. p. 119—120°, $[\alpha]^{18}_{5461}$ −38·0° in chloroform). Oxidation of I with chromic oxide and acetic acid, or catalytically by heating with copper bronze at 250—270°/2 mm., converts it into α-ergostadienone (IV), m. p. 182—183° [*semicarbazone*, m. p. 254° (decomp.)], identical with the ketone obtained by Windaus and Auhagen (*loc. cit.*) by the action of nickel on ergosterol. The action of anhydrous hydrogen chloride on a chloroform solution of IV isomerises it to *β-ergostadienone*, m. p. 125° (*semicarbazone*, m. p. 266°), which is also obtained by chromium oxide oxidation of III. Both the α- and β-ketones are reduced by hydrogen (2 mols.) and palladium-black to α-ergostenol. J. W. BAKER.

Yeast ergosterol. IV. F. REINDEL and A. DETZEL (Annalen, 1929, **475**, 78—86).—*epi*Ergostanol, m. p. 207°, $[\alpha]_D$ +13·5°, obtained together with *allo*-α-ergostanol (I) by the catalytic reduction of *allo*-α-ergostanone, and differentiated from I by its non-precipitation by digitonin, is oxidised by chromic anhydride in glacial acetic acid at 70° to *allo*-α-ergostanone, m. p. 160—164° (ketazine, m. p. 272°), identical with the ketone obtained from I, and thus proving that it is a configurational isomeride, and a dicarboxylic acid, $C_{27}H_{46}O_4$, m. p. 219°. By the addition of warm alcohol to a warm ethereal solution of α-ergostanyl acetate (Reindel and Walter, A., 1928, 295), and repeated crystallisation from methyl alcohol followed by hydrolysis of the resulting pure acetate, m. p. 184°, $[\alpha]_D$ −20°, with sodium ethoxide, dihydroergosterol, m. p. 174—179°, $[\alpha]_D$ −19·4°, was isolated: this indicates that the previously described α-ergostanol is a mixture containing dihydroergosterol. When ergosterol, m. p. 150°, $[\alpha]_D$ −130°, is distilled under low pressure, it passes over at 248—250°/0·8 mm.; the method is therefore unsuitable for the separation of the sterols. The pale yellow distillate had m. p. 140—145°, $[\alpha]_D$ −104·5°, was almost completely precipitated by digitonin, and absorbed 1 mol. of oxygen when kept in a vacuum over calcium chloride for 14 days, the rotation increasing simultaneously. A labile moloxide together with a small quantity of a peroxide is formed; acetylation gave ergosteryl acetate, m. p. 163°. If the distilled ergosterol is recrystallised five times from alcohol, a white product, $[\alpha]_D$ −104°, is obtained which is unchanged on long keeping. A. I. VOGEL.

Sterol group. VII. Isolation of zymosterol. I. M. HEILBRON and W. A. SEXTON (J.C.S., 1929, 2255—2257).—By the action of bromine in acetic acid on the crude mixture of yeast sterols left after removal of most of the ergosterol a mixture of bromides is obtained which is separated by fractional crystallisation from chloroform and alcohol. The least soluble bromide, m. p. 168°, is converted by debromination with zinc dust into a sterol, m. p. 108—110°, $[\alpha]^{22}_{5461}$ +38·6° in chloroform, apparently identical with zymosterol isolated by Wieland and Asano (this vol., 1200) and, in agreement with these authors but contrary to Smedley-Maclean (A., 1928, 329), having the composition $C_{27}H_{44}O$ (acetate, m. p. 106—107°; Wieland and Asano, *loc. cit.*, give m. p. 104—106°). This sterol is reduced by hydrogen and palladium to *dihydrozymosterol* $+H_2O$, m. p. 115—116°, $[\alpha]^{22}_{5461}$ +28·9° in chloroform (*acetate*, m. p. 83—84°). J. W. BAKER.

Zymosterol. F. REINDEL and A. WEICKMANN (Annalen, 1929, **475**, 86—100).—Crude zymosterol, purified by fractional crystallisation from light petroleum followed by methyl alcohol, had $[\alpha]_D$ +30° to +35°; subsequent repeated boiling with animal charcoal gave a product with m. p. 107—110°, $[\alpha]_D$ +49·5° (acetyl derivative, m. p. 102—104°, $[\alpha]_D$ +32·4°), in which the presence of ergosterol could not be detected by the very sensitive Tortelli–Jaffé colour reaction or by the ultra-violet absorption spectrum. Analysis led to the formula $C_{27}H_{44}O$ (cf. Maclean, A., 1928, 329, $C_{27}H_{42}O$; Penau and Tanret, this vol., 809, $C_{27}H_{42}O_2$). Zymosterol gives the Salkowski colour reaction, the sulphuric acid becoming yellowish-red and the chloroform remaining colourless; with acetic anhydride and sulphuric acid there is a blue coloration becoming green; with arsenic trichloride, a steel-blue coloration becoming violet with a green fluorescence, and with antimony chloride, a pale red coloration becoming yellow and finally bluish-green. Titration with perbenzoic acid in chloroform solution indicated the presence of two double linkings. Reduction in glacial acetic acid or in glacial acetic acid–ether solution with platinum-black and hydrogen resulted in the absorption of 1 mol. of hydrogen and the formation of dihydrozymosterol (I), m. p. 120—

122°, $[\alpha]_D$ +20·7°, precipitated by digitonin (acetate, m. p. 81—84°, also obtained by direct hydrogenation of zymosteryl acetate; cf. preceding abstract); perbenzoic acid revealed the presence of one double linking in I. The presence of three double linkings indicated by iodine titration (Maclean, *loc. cit.*; Penau and Tanret, *loc. cit.*) is attributed to substitution by, as well as addition of, iodine. The presence of only two double linkings is supported by the small values of the absorption coefficients in the ultraviolet (cf. cholesterol).

When a vigorous stream of hydrogen chloride is passed into a dry chloroform solution of zymosterol acetate at 0° for 1 hr., two isomeric *zymosterol hydrochlorides*, m. p. 87—88° and 120—122°, respectively, are obtained. Dihydrozymosterol under similar conditions yielded an *isomeride*, m. p. 75°. Zymosteryl acetate in ether–glacial acetic acid solution containing ammonium acetate reacts with 1 mol. of bromine in glacial acetic acid to form an impure *zymosteryl acetate dibromide*, m. p. 156—157°.

A. I. VOGEL.

Determination of double linkings in sterols. F. REINDEL and K. NIEDERLÄNDER (Annalen, 1929, **475**, 147—157).—Examination of the results obtained with a large number of sterol derivatives shows that the Hübl method for the determination of the number of double linkings in the molecule is untrustworthy, the values being high if no allowance is made for the amount of hydrogen iodide evolved and very low if this is determined by addition of potassium iodate and titration of the liberated iodine, and this value deducted from the total amount of iodine absorbed. With Marshall's method (iodine chloride in carbon tetrachloride solution; A., 1900, ii, 376) trustworthy results are obtained with cholesterol derivatives but not with those of ergosterol. The large amount of hydrogen iodide liberated is probably formed in accordance with the reactions: $:CH_2+CII=:CHCl+HI$ and $\cdot CHCl\cdot CHI\cdot CH_2\cdot \rightleftharpoons \cdot CHCl\cdot CH{:}CH\cdot$ (or $\cdot CCl{:}CH\cdot CH_2\cdot$)+HI. Much more trustworthy results are obtained by Kaufmann's method (0·1*N*-solution of bromine in carbon tetrachloride) if allowance is made for the large quantity of hydrogen bromide formed, although even with this reagent somewhat low results are obtained with ergosterol derivatives.

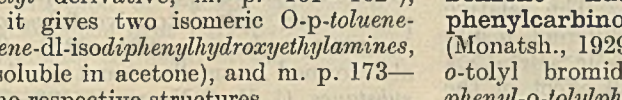
J. W. BAKER.

Substitution and addition. II. Esterification with *p*-nitrobenzoyl chloride. J. MEISENHEIMER and W. SCHMIDT (Annalen, 1929, **475**, 157—182; cf. A., 1925, i, 527).—Esterification of phenylethylcarbinol (1 mol.) with *p*-nitrobenzoyl chloride (2 mols.) in ethereal solution under reflux reaches its maximum value (20—30%) only after several days. If the reaction is carried out in a sealed tube at 100° with benzyl alcohol, 95% esterification occurs after 3 days, whilst with phenylethylcarbinol only 2% of the ester is obtained. In carbon tetrachloride (in which hydrogen chloride is much less soluble) under reflux, however, 80% esterification of phenylethylcarbinol has occurred after 20 hrs. In the sealed tube experiments the ester is first formed, but suffers fission into α-chloro-α-phenylpropane and *p*-nitrobenzoic acid during the prolonged heating at 100°, and it is shown that such fission of the pure ester is almost complete after heating with 2*N*-ethereal hydrogen chloride at 100° for 3 days. Of the six possible reactions the following must be considered: (ACl=acid chloride); (1) $R\cdot OH+ACl \xrightarrow{k_1} R\cdot OA+HCl$; (2) $R\cdot OH+HCl \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} RCl+H_2O$; (3) $R\cdot OA+HCl \xrightarrow{k_3} RCl+HOA$; (4) $ACl+H_2O \xrightarrow{k_4} HCl+HOA$, and by a kinetic analysis the reaction velocity curve for each of these reactions is plotted. Initially (1) is predominant, but its velocity rapidly decreases, whilst (2) and (4) increase rapidly to a maximum and then decrease rapidly: (3) persists throughout but is important relative to (1), (2), and (4) only after a long period, when these last reaction velocities have become very small. The reaction $R\cdot OH+HOS \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} R\cdot OS+H_2O$ is unimportant. For phenylethylcarbinol the values of the various velocity coefficients are, respectively, k_1 8×10^{-4}; k_2 1×10^{-2}; k_2' 5×10^{-3}; k_3 3×10^{-3}; k_4 3×10^{-2}; $k_5=k_5'=1\times10^{-4}$. The experimentally determined curve showing the percentage of ester formed at various times is in good agreement with the compound curve based on these reactions. Similar agreement between the theoretical and experimental curves is obtained for the esterification of ethylvinylcarbinol, for which the values of the velocity coefficients are k_1 $1\cdot0\times10^{-3}$; k_2 $3\cdot5\times10^{-3}$; k_2' $1\cdot0\times10^{-3}$, and k_3 $0\cdot17\times10^{-3}$. Thus the velocity of esterification is about 1·25 times that of phenylethylcarbinol, whilst fission of the esters occurs more slowly, and hence under similar conditions a large percentage of ester is formed with ethylvinylcarbinol. The detection of 1·4% of benzyl alcohol in the presence of 98·6% of phenylethylcarbinol depends on the very small velocity of fission of benzyl *p*-nitrobenzoate into *p*-nitrobenzoic acid and benzyl chloride. Similar esterification (in a sealed tube) of other alcohols has been investigated, and under approximately comparable conditions benzyl and allyl alcohols are esterified to the extent of 90%, methylethylcarbinol 99%, diphenylcarbinol (p-*nitrobenzoate*, m. p. 131—132°) and phenylvinylcarbinol yield very little ester, the chlorohydrocarbon being the main product, and in the last case, in confirmation of Burton (A., 1928, 880), it is the chloride or ester of cinnamyl alcohol which is formed by rearrangement. Styrylethylcarbinol (p-*nitrobenzoate*, m. p. 53°) yields mainly α-phenyl-$\Delta^{\alpha\gamma}$-pentadiene by loss of water, so that the results are not comparable, whilst very little esterification occurs with trimethylcarbinol. The results of Norris and Ashdown (A., 1925, i, 626) on the velocity of esterification of alcohols with *p*-nitrobenzoyl chloride in ether are criticised on the basis of this investigation, since a large quantity of hydrogen chloride is formed as a result of the reactions (2) and (4), thus making some of the values too high. The correctness of the structures of styrylethylcarbinol, its chloride, and of phenylvinylcarbinol is proved by ozonolysis.

J. W. BAKER.

Optically active diphenylhydroxyethylamines and *iso*hydrobenzoins. II. J. READ, I. G. M. CAMPBELL, and T. V. BARKER (J.C.S., 1929, 2305—2318).—Resolution of *dl*-*iso*diphenylhydroxyethyl-

amine (I) (Read and Steele, A., 1927, 557) is effected by successive treatment with *d*-tartaric acid and *d*-camphor-10-sulphonic acid. The hydrogen tartrate, m. p. 177°, $[\alpha]_D$ −42·6°, of the *l*-base, m. p. 115°, $[\alpha]_D$ −133° in alcohol (Erlenmeyer, A., 1897, i, 480, gives −109·7°) [d-*α-bromocamphor-π-sulphonate*, m. p. 210° (decomp.), $[\alpha]_D$ +15·9° in water], separates first, whilst from the base obtained from the mother-liquor the *d*-camphor-10-sulphonate, $[\alpha]_D$ +60·4°, of the *d*-base, m. p. 115°, $[\alpha]_D$ +134° in alcohol [d-*α-bromocamphor-π-sulphonate*, m. p. 220° (decomp.), $[\alpha]_D$ +94·0° in water], is prepared. Attempts to resolve the *dl*-base with *d*-α-bromocamphor-π-sulphonic acid give only dl-iso*diphenylhydroxyethylamine* d-*α-bromocamphor-π-sulphonate*, $[\alpha]_D$ +51·7°. *O*-Acetyl-*dl*-*iso*diphenylhydroxyethylamine (II), m. p. 152°, best prepared by the action of acetic anhydride in benzene on I, could not be made to react with benzaldehyde, but *acetylbenzylidene*-dl-iso*diphenylhydroxyethylamine*, m. p. 114°, is obtained by the action of boiling acetic anhydride on benzylidene-*dl*-*iso*diphenylhydroxyethylamine (III), and is converted into II by bromine and alcohol. O-*Acetyl*-l-iso*diphenylhydroxyethylamine* (IV) has m. p. 158°, $[\alpha]_D$ −6·3° in alcohol (*hydrochloride*, m. p. 190°, $[\alpha]_D$ −32·8° in water). Boiling acetic anhydride converts the original bases into the diacetyl-*dl*-, m. p. 118°, and *diacetyl*-l-, m. p. 127°, $[\alpha]_D$ +27·7° in alcohol (hydrolysed to IV), derivatives. Contrary to Erlenmeyer and Arnold (A., 1905, i, 193), no racemisation of the monoacetyl derivatives occurs in boiling alcohol. *p*-Toluenesulphonyl chloride and pyridine convert I into its O-p-*toluenesulphonyl* derivative, m. p. 142—145° (N-*acetyl* derivative, m. p. 161—162°), whilst with III it gives two isomeric O-p-*toluenesulphonylbenzylidene*-dl-iso*diphenylhydroxyethylamines*, m. p. 179° (less soluble in acetone), and m. p. 173—174°, for which the respective structures

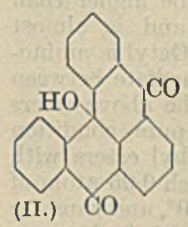


are suggested, since only the latter is hydrolysed by bromine and alcohol. d-iso*Diphenylhydroxyethylamino*-d-*methylenecamphor*, m. p. 168°, $[\alpha]_D$ +144° to 179° in alcohol, is prepared by the usual method. The following derivatives of *l*-*iso*diphenylhydroxyethylamine are described: *O*-benzoyl, m. p. 215°, $[\alpha]_D$ −38·5° in methyl alcohol (lit. −29·0°); *O*-*p*-nitrobenzoyl, m. p. 132°, $[\alpha]_D$ −48·3° in alcohol; salicylidene, m. p. 132—134°, $[\alpha]_D$ −91·5° in alcohol; anisylidene, m. p. 152°, $[\alpha]_D$ −72·4° in alcohol; piperonylidene, m. p. 144°, $[\alpha]_D$ −83·3° in alcohol; 4-hydroxy-3-methoxybenzylidene, m. p. 155°, $[\alpha]_D$ −84·4° in alcohol. By the action of nitrous acid on *l*-*iso*diphenylhydroxyethylamine is obtained *l*-*iso*hydrobenzoin, m. p. 146°, $[\alpha]_D$ −92° (*diacetyl*, m. p. 109—110°, $[\alpha]_D$ 26·9° in alcohol, and *benzylidene*, m. p. 70·5°, $[\alpha]_D$ −27·6° in alcohol, derivatives), and from the *d*-base is obtained *d*-*iso*hydrobenzoin, m. p. 146°, $[\alpha]_D$ +92° in alcohol (*acetone* derivative, m. p. 48°, $[\alpha]_D$ +65·2° in alcohol). *Benzylidene*-dl-iso*hydrobenzoin* has m. p. 84°.

A detailed crystallographic study of *d*-, *l*-, and *dl*-*iso*hydrobenzoin is described. When deposited from ethyl acetate the *d*- and *l*-forms exhibit characteristic hemihedral facets which are not developed when chloroform is the solvent. In agreement with this the *dl*-compound separates from ethyl acetate as a conglomerate of enantiomorphously related crystals composed of *d*- and *l*-components. A similar resolution into *d*- and *l*-forms occurs from chloroform, though in this case the characteristic hemihedral facets are absent; segregation is here rendered possible through the circumstance that either the right or left side of each crystal displays a marked tendency to degenerate into curved boundaries. The relationship between molecular enantiomorphism and crystalline form is discussed. J. W. BAKER.

Triphenylmethyl chloride and pyridine. [Goldschmiedt's condensation products of 2-hydroxy-3-naphthoic acid with aromatic aldehydes and their relationships to the triphenylmethane group.] M. REBEK [with G. MANDRINO] (Ber., 1929, **62**, [*B*], 2508—2509; cf. this vol., 556).—Agreement is expressed with Helferich (A., 1925, i, 790, 1269; 1926, 517) in ascribing the formula $C_{19}H_{16}O,C_5H_5N,HCl$ to the compound obtained from triphenylmethyl chloride, pyridine, and water, since it yields triphenylcarbinol after prolonged desiccation at 100°/vac. The existence of a compound, $C_{19}H_{15}Cl,C_5H_5N$, from triphenylmethyl chloride and anhydrous pyridine is, however, probable. Methyl 2-hydroxy-1-α-chlorobenzyl-3-naphthoate, pyridine, and water afford the *compound* $C_{19}H_{15}O_3Cl,C_5H_5N,H_2O$, m. p. 162—164°, whilst anhydrous pyridine appears to give a salt free from water. H. WREN.

Triphenylmethane derivatives with linked benzene nuclei. V. Diketodimethylenetriphenylcarbinol. R. WEISS and J. REICHEL (Monatsh., 1929, **53** and **54**, 187—198).—Magnesium *o*-tolyl bromide and *o*-benzoylbenzoic acid give *phenyl*-o-*tolylphthalide*, m. p. 120°, reduced by sodium amalgam and alcohol to 2-*methyltriphenylmethane*-2′-*carboxylic acid*, m. p. 197° (*methyl* ester, m. p. 94°). Oxidation of this phthalin with alkaline potassium permanganate yields *triphenylmethane*-2 : 2′-*dicarboxylic acid* (I), m. p. 214—215° (*dimethyl* ester), which when treated with sulphuric acid at 70—90° in acetic acid solution undergoes ring closure and oxidation, forming the *acetate*, m. p. 230°, of *diketodimethylenetriphenylcarbinol* (II), m. p. 232°. Formation of II occurs also when I is treated with sulphuric acid and when the chloride of I is treated with aluminium chloride in carbon disulphide solution. When I is treated with sulphuric acid in presence of aluminium filings at 50—60°, II is again formed. Reduction of II does not occur with sodium amalgam and alcohol, whilst with hydriodic acid (*d* 1·7) a *compound*, $C_{21}H_{14}O_2$ (probably dimethylenetriphenylmethaneketonol), m. p. 241—242°, is formed. This last-named compound is soluble in dilute ammonia or sodium hydroxide solution.



(II.)

Magnesium *o*-tolyl bromide and ethyl benzoate give phenyldi-*o*-tolylcarbinol (III), b. p. 210—213°/16 mm., which, contrary to the statement of Cook (A., 1928, 293), could not be oxidised by potassium permanganate solution to triphenylcarbinol-2 : 2′-dicarboxylic

acid. Treatment of III with dry hydrogen bromide at 130—140° gives unexpectedly *phenyldi-o-tolylmethane*, b. p. 180—185°/12 mm., m. p. 104°; a small amount of the hydrocarbon is obtained also by reducing III with zinc and hydrochloric acid in acetic acid solution. Chlorination of phenyldi-*o*-tolylmethane at 125—130° in sunlight gives a *dichloro*-, m. p. 57°, or a *tetrachloro*-derivative, m. p. 63—65°, according to the time of reaction. H. BURTON.

Optical activity and polarity of substituent groups. XI. *sec.*-β-Octyl esters of benzoic acids containing basic and acidic substituents. H. G. RULE, J. B. MILES, and (in part) W. E. MACGILLIVRAY (J.C.S., 1929, 2274—2281; cf. this vol., 570).—The rotatory powers, for light of various wave-lengths, of amino-, dimethylamino-, hydroxy-, and carboxy-substituted benzoates of *d*- and *l*-*sec.*-β-octyl alcohols have been determined both in the ionised and non-ionised states. In the *o*-substituted derivatives the presence of a substituent of *op*-directive type leads to a fall in rotatory power which is greatest with the amino- and dimethylamino-groups, these two basic esters exhibiting anomalous dispersion. Conversion into their hydrochlorides (formation of a positive pole) results in increased rotatory power and much less complex dispersion. The increase in rotation due to the presence of the *m*-directive carboxyl group is changed into a depression in the sodium salt, the sign of the rotation of the salt in aqueous solution becoming inverted at concentrations above $c=13$. In the presence of 1 equivalent of potassium ethoxide the rotatory power of the salicylate is depressed to such an extent that the sign is inverted. The relative changes in rotatory power due to different *o*-substituents are $NO_2>CO_2H>H, OH>Me>Br>Cl>I>OMe>NMe_2>NH_2$, the very small effect of the hydroxyl group probably being due to chelation. The *p*-dimethylamino- and *p*-amino-substituted esters possess abnormally high rotatory powers which fall to normal values in their hydrochlorides. The values for various *p*-substituents are in the order $NMe_2>NO_2>CO_2H>Br>OMe>Cl, Me>H$, which closely approximates to that of the general polar type. Contrary to this suggestion, however, the value for sodium octyl terephthalate tends to be higher than that of the hydrogen octyl ester, and is almost independent of concentration. *sec.*-β-Octyl *m*-aminobenzoate has optical properties intermediate between those of the *o*- and *p*-derivatives. The above esters are best prepared in an optically pure condition (20—40% yield) by heating the methyl esters with *d*- or *l*-β-octyl alcohol (1 mol.), in which 0·05 atom of sodium has been dissolved, at 130—140°, and thus are prepared l-sec.-β-*octyl anthranilate*, b. p. 183°/10 mm., p-*aminobenzoate*, b. p. 200°/10 mm., m. p. 69—70° (*hydrochloride*, m. p. 131—133°); d-β-*octyl* p-*dimethylaminobenzoate*, b. p. 180°/1·8 mm., *salicylate*, b. p. 170°/10 mm. l-*Octyl* m-*aminobenzoate*, b. p. 195—198°/18 mm. (slight decomp.), is prepared by reduction of the corresponding nitro-derivative with aluminium amalgam. J. W. BAKER.

Chemical effects of penetrating radium radiation. XVIII. Action on acetyl and benzoyl chlorides. A. KAILAN.—See this vol., 1406.

Benzylthiobenzamide. T. G. LEVI (Gazzetta, 1929, 59, 548—549).—*Benzylthiobenzamide*, m. p. 86°, is prepared by heating benzylamine (1 mol.) and sulphur (1 atom) at 130—140°, rising to 200°, or in a sealed tube at 180° for several hours. Thiobenzamide is not found in the product under these conditions (cf. Wallach, A., 1891, 189). The same compound is formed from benzylbenzamide and phosphorus pentasulphide. It is decomposed by fusion with solid potassium hydroxide to give benzylamine. It is insoluble in 10% sodium hydroxide solution. R. K. CALLOW.

Dioximes. LV. G. PONZIO (Gazzetta, 1929, 59, 552—555).—The statement by Gastaldi (A., 1926, 1247) that the action of hydroxylamine on benzoylurethane yields benzamidoformhydroxamic acid is erroneous, and the criticism of the author's formulation of the transformation of phenylhydroxyglyoxime into 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole (A., 1926, 850, 1159) is fallacious. In fact, the product is benzhydroxamic acid, and the transformation of acylurethanes, $R{\cdot}CO{\cdot}NH{\cdot}CO_2Et$, when treated with hydroxylamine in methyl alcohol at 40—50° for several days, into hydroxamic acids, $R{\cdot}C(:NOH){\cdot}OH$, is a general reaction. In this way acetylurethane yields acethydroxamic acid, *propionylurethane*, m. p. 83°, yields propionhydroxamic acid, m. p. 98—99°, and benzoylurethane, m. p. 112° (prepared by an improved method), yields benzhydroxamic acid, m. p. 128—129°. The reaction is analogous to that of β-ketonic esters, and further analogy is found in the reaction of benzoylurethane with phenylhydrazine to give the *phenylhydrazone*, m. p. 217°, which decomposes when melted to give 3-*hydroxy*-2 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 231—232°. This compound is also formed in small amount by dehydration of the *substance*, $C_{14}H_{13}O_2N_3$, m. p. 133—134°, obtained by the interaction of phenylhydrazine and benzoylformhydroxamic acid, or of the product obtained by the action of hydroxylamine on ethyl phenylglyoxylate. R. K. CALLOW.

Isomerism of the oximes. XXXV. Amidoximes. O. L. BRADY and F. H. PEAKIN (J.C.S., 1929, 2267—2271).—The action of alcoholic dimethylamine on *m*-nitrobenzhydroxamyl chloride at 0° affords m-*nitrobenzodimethylamidoxime* (I), m. p. 160° (together with *mm'*-dinitrodiphenylfuroxan). Although in this compound the tautomeric system $CR(:NOH){\cdot}NH_2 \rightleftharpoons CR(:NH){\cdot}NH{\cdot}OH$ is blocked, all attempts to prepare stereoisomerides were unsuccessful. This may be due to a betaine structure, and in agreement with this view it cannot be converted into an *O*-methyl ether, treatment with dry silver oxide and methyl iodide in boiling benzene causing decomposition to m-*nitrobenzodimethylamide*, m. p. 81°, and *N*-methylhydroxylamine. Methylation of *m*-nitrobenzamidoxime with methyl sulphate in sodium hydroxide gives its O-*methyl ether*, m. p. 75°, converted by sodium nitrite and concentrated hydrochloric acid into m-*nitrobenzmethoxamyl chloride*, m. p. 51°, which with dimethylamine gives only *m*-nitrobenzoic acid. Ethyl chloroformate converts a dry chloroform suspension of I into the *carbethoxy*-derivative, m. p. 94°, which is different from and not convertible under the usual conditions of betaine change into the similarly

prepared *carbomethoxy*-derivative, m. p. 87°, of m-*nitrobenzomethylethylamidoxime*, m. p. 123°, the last-named being prepared by the action of alcoholic methylethylamine on *m*-nitrobenzhydroxamyl chloride at 0°. The failure of this interconversion and the fact that it does not undergo the Beckmann change makes it impossible to assign a configuration to *m*-nitrobenzodimethylamidoxime. Thus phosphorus pentachloride in ether or concentrated sulphuric acid at 130° is without action, whilst benzenesulphonyl chloride and anhydrous sodium carbonate in chloroform and benzoyl chloride in 2*N*-sodium hydroxide convert it, respectively, into its *benzenesulphonyl*, m. p. 138°, and *benzoyl*, m. p. 152°, derivatives. J. W. BAKER.

Nature of the alternating effect in carbon chains. XXXI. Directive influence of ψ-acid systems in aromatic substitution. Nitration of ψ-acidic phenylnitromethanes and their salts. J. W. BAKER (J.C.S., 1929, 2257—2264).—The proportion of the *m*-isomeride formed in the nitration of the *lithium* salt, +EtOH, and solvent-free, m. p. 200°, of ethyl α-nitrophenylacetate at −12° to 0° increases from 29% in nitric acid, d_4^{15} 1·497, to 82·5% in nitric acid, d_4^{15} 1·529, whilst over the same range of acid concentration the proportion of *m*-isomeride produced in the nitration of free ethyl α-nitrophenylacetate remains constant at 84—85%. Similarly, over the same range of acid concentration the potassium (or sodium) salt of phenylnitromethane yields 42—67% of *meta*, whilst for free phenylnitromethane the proportion of *meta* remains constant at 67%. Thus, whilst in agreement with Baker and Ingold (A., 1926, 1131), nitration of ψ-acidic phenylnitromethane derivatives of the type $CHPhR{\cdot}NO_2$ yields mainly *m*-nitro-products, nitration of the anions of the *aci*-form, $\overline{CPhR{:}NO{\cdot}O}^{\ominus}$, occurs largely in the *op*-positions (despite the contrary influence of the more distant dipole on the nitro-group) owing to the directive effect of the anionic charge which, by tautomeric displacements, has free access to the carbon atom adjacent to the benzene nucleus. The results suggest that the speed of conversion of the liberated anion of the molecular ψ-acid is greatly increased with increasing strength of the acid medium. In the preparation of ethyl α-nitrophenylacetate by condensation of ethyl phenylacetate and ethyl nitrate with sodium in ether small quantities of *substances*, m. p. 162—163° and 133—134°, are also obtained. J. W. BAKER.

Beckmann rearrangement in presence of free radicals. E. S. WALLIS (J. Amer. Chem. Soc., 1929, **51**, 2982—2986).—When a solution of benzylmethylacetazide in benzene is mixed with triphenylmethyl in absence of oxygen and kept at 35°, rearrangement of the azide into α-benzylethylcarbimide occurs (cf. Jones and Wallis, A., 1926, 279). No other product, other than triphenylmethyl peroxide, is isolated during the analysis of the rearrangement products. The result appears to support the view that in the change $R{\cdot}CON_3 \longrightarrow R{\cdot}NCO$, the radical R during its migration from carbon to nitrogen becomes a positive ion (cf. *loc. cit.*). H. BURTON.

Tyrosines methylated in the nucleus and the formation of melanin. H. SCHMALFUSS and W. PESCHKE (Ber., 1929, **62**, [*B*], 2591—2598).—Introduction of methyl groups into *p*-tyrosine, no matter what position they occupy in the benzene nucleus, impedes the production by tyrosinase of melanin or an intermediate product leading to melanin.

Hippuric acid is converted by 4-hydroxy-*o*-tolualdehyde, acetic anhydride, and sodium acetate into α-*benzamido*-4-*acetoxy*-2-*methylcinnamlactimide*, $C_{19}H_{15}O_5N$, m. p. 157°, hydrolysed by sodium hydroxide to α-*benzamido*-4-*hydroxy*-2-*methylcinnamic acid*, decomp. 254°, converted by phosphorus and hydriodic acid into dl-α-*amino*-β-4-*hydroxy*-o-*tolylpropionic acid*, decomp. 261°. α-*Benzamido*-4-*acetoxy*-2 : 5-*dimethylcinnamlactimide*, m. p. 166°, similarly yields successively α-*benzamido*-4-*hydroxy*-2 : 5-*dimethylcinnamic acid*, decomp. 239°, and dl-α-*amino*-β-4-*hydroxy*-2 : 5-*dimethylphenylpropionic acid*, decomp. 249°. α-*Benzamido*-4-*acetoxy*-3 : 5-*dimethylcinnamlactimide*, m. p. 190°, α-*benzamido*-4-*hydroxy*-3 : 5-*dimethylcinnamic acid*, decomp. 222°, and dl-α-*amino*-β-4-*hydroxy*-3 : 5-*dimethylphenylpropionic acid*, decomp. 253°, are described, as are also α-*benzamido*-4-*acetoxy*-2 : 3-*dimethylcinnamlactimide*, m. p. 183°, α-*benzamido*-4-*hydroxy*-2 : 3-*dimethylcinnamic acid*, m. p. 236°, and dl-α-*amino*-β-4-*hydroxy*-2 : 3-*dimethylphenylpropionic acid*, decomp. 284°. H. WREN.

Comparative stability of stereoisomeric ethylene derivatives and their synthesis by ultraviolet light. (MME.) RAMART-LUCAS and J. HOCH (Compt. rend., 1929, **189**, 696—699).—The applicability of measurements of absorption spectra and of heats of combustion to the differentiation of the *cis*- and *trans*-isomerides in cases of geometrical isomerism is discussed. Measurements of the absorption curves of diethyl αα′-diphenylfumarate, diethyl αα′-diphenylmaleate: dimethyl αα′-di-*m*-tolylfumarate, dimethyl αα′-di-*m*-tolylmaleate; dimethyl αα′-di-*p*-tolylfumarate and dimethyl αα′-di-*p*-tolylmaleate show that, contrary to general rule, in all these three pairs the absorption curve of the *cis*-isomeride lies closer to the visible region than does that of the *trans*-isomeride. According to the work of Ramart-Lucas (A., 1928, 760, 1000) these facts show that, in these three pairs of isomerides, the *cis* is the more stable at low temperatures. In view of these facts, the method of differentiating *cis*- and *trans*-isomerides (Henri and Errera, A., 1925, ii, 1137) is criticised. The three fumarates were prepared from the corresponding maleates by the (irreversible) action of ultra-violet light; this reaction gave, in addition, carbalkoxyarylindones, also formed by the action of ultra-violet light on the dialkyl αα′-diarylfumarates. Irradiation of the sodium salts of the αα′-diarylmaleic acids with ultra-violet light gave the sodium salt of the arylindonecarboxylic acid. A. A. GOLDBERG.

Action of alkali hypochlorite on hemipinimide. W. M. RODIONOV, S. J. KANEVSKAJA, and G. W. KUPINSKAJA (Ber., 1929, **62**, [*B*], 2563—2567).—Hemipinic acid is prepared by oxidation of opianic acid by alkaline permanganate or by treatment of it with hot, very concentrated sodium hydroxide and separation of meconine from the product by cold, 10% sodium carbonate. Hemipinimide is treated with potassium hydroxide and potassium hypochlorite at

a temperature not exceeding 60° and, after addition of sodium hydrogen sulphite, the solution is neutralised to litmus with hydrochloric acid and then acidified with acetic acid, whereby 2-aminoveratric acid, m. p. 181—182°, is precipitated (yield 31%). Extraction of the filtrate with chloroform leads to the isolation of 2-*amino*-5 : 6-*dimethoxybenzoic acid*, m. p. 98—99° (yield about 64%), converted by deamination into 2 : 3-dimethoxybenzoic acid. 2-*Hydrazino*-5 : 6-*dimethoxybenzoic acid hydrochloride*, m. p. 195—196° after darkening at about 140—145°, is described.

H. WREN.

Derivatives of hemipinic acid. F. FALTIS and F. KLOIBER (Monatsh., 1929, **53** and **54**, 620—637). —Various derivatives of hemipinic acid have been synthesised in connexion with the constitution of an oxidative degradation product of *iso*chondodendrine (cf. this vol., 698).

[With L. GUTLOHN and A. B. G. ATTIA.]—Opianic acid is nitrated in acetic acid solution to nitroopianic acid (I) and its anhydride, m. p. 240—245° (decomp.) (cf. Wegscheider, A., 1897, i, 348). Reduction of I with stannous chloride and hydrochloric acid in boiling aqueous suspension gives 3 : 4-dimethoxyanthranil-2-carboxylic acid, which on dissolution in 20% sodium hydroxide and subsequent treatment with the theoretical amount of sulphuric acid affords 6-*aminohemipinic acid* $+H_2O$ (II), which loses water of crystallisation at 100°, and at 110—130° is transformed into the *anhydride*. When heated rapidly, II decomposes at 190—210°. Elimination of carbon dioxide occurs during the esterification of II with methyl-alcoholic hydrogen chloride, and methyl 3-amino-5 : 6-dimethoxybenzoate (*hydrochloride*) is probably formed. Diazotisation of II and subsequent treatment with potassium iodide gives 6-*iodohemipinic anhydride*, m. p. 190—191°, converted by treatment with concentrated potassium hydroxide solution and methyl sulphate into *methyl* 6-*iodohemipinate* (III), m. p. 62° (formed also by the action of diazomethane on the methyl hydrogen ester). 6-*Chlorohemipinic anhydride* has m. p. 165—166°. 6-Diazohemipinic acid decomposes in aqueous suspension at 85—90° to 6-*hydroxyhemipinic acid*, m. p. 167° (decomp.) or 194—196° after softening at 175°, according to the rate of heating (the isolation of this acid is carried out with peroxide-free ether). Treatment of this with diazomethane and subsequent hydrolysis with alcoholic potassium hydroxide furnishes 3 : 4 : 6-*trimethoxyphthalic acid* ($+H_2O$), m. p. 216—217°. When diazohemipinic acid is treated with cuprous cyanide in acid solution and the product formed hydrolysed with hydrochloric acid, about 20% of 3-*hydroxy*-5 : 6-*dimethoxybenzoic acid*, m. p. 186—188°, is obtained (cf. Faltis and Kloiber, this vol., 699). 3 : 5 : 6-*Trimethoxybenzoic acid* has m. p. 101—102°.

Condensation of III with the sodium derivative of methyl *p*-hydroxybenzoate in presence of copper powder and copper acetate gives methyl anisate instead of the expected condensation product (Faltis and Zwerina, this vol., 698). Methyl anisate is formed by the decomposition of III to a sodium salt with simultaneous methylation of the methyl *p*-hydroxybenzoate. When the sodium derivative of methyl *p*-hydroxybenzoate is treated with copper powder and copper acetate, about 27% of methyl anisate is formed thus : $2NaO{\cdot}C_6H_4{\cdot}CO_2Me \longrightarrow NaO{\cdot}C_6H_4{\cdot}CO_2Na + MeO{\cdot}C_6H_4{\cdot}CO_2Me$.

H. BURTON.

Action of nitric acid on abietic acid and certain derivatives. P. LEVY [with T. PESCH, A. CLAUBERG, and H. RAALF] (Ber., 1929, **62**, [*B*], 2497—2504). —Under the conditions adopted, trimellitic acid (cf. Ruzicka and Pfeiffer, A., 1925, i, 1419) or nitroabietic acid is never obtained by the action of nitric acid on abietic acid. It depends entirely on experimental conditions whether oxidation or nitration is observed.

Abietic acid, m. p. 170—171°, $[\alpha]_D^{15}$ $-98{\cdot}45°$, the homogeneity of which is established by its oxidation by permanganate to tetrahydroxyabietic acid as sole non-volatile product, is converted by prolonged boiling with nitric acid (*d* 1·18), which is occasionally renewed during the process, into ββ-dinitropropane, m. p. 53°, minute amounts of fatty acids volatile with steam, and an acid, $C_{11}H_{16}O_6$, m. p. 224° (decomp.), identical with that obtained by Steele (A., 1922, i, 739); occasionally it is possible to isolate an acid, $C_{12}H_{18}O_6$, m. p. 214° (decomp.), identical with that to which the author has previously assigned the composition $C_8H_{12}O_4$ (A., 1913, i, 620). Treatment of abietic acid with a mixture of 1 vol. of nitric acid (*d* 1·52) and 5 vols. of acid (*d* 1·40) at a temperature raised slowly from the atmospheric to 130° affords a mixture of the acids $C_{12}H_{18}O_6$ and $C_{11}H_{16}O_6$. Dibromodihydroabietic acid, m. p. 171°, $[\alpha]_D^{15}$ $-102{\cdot}8°$, when heated with nitric acid of gradually increased concentration affords αα-dibromo-α-nitropropane, b. p. 76°/15 mm., and the acid, $C_{11}H_{16}O_6$, m. p. 222°; this acid is also obtained when a concentrated acid is used initially, but volatile compounds do not appear to be produced. Oxidation of tetrahydroxyabietic acid with nitric acid by the "gradual process" yields the acids $C_{11}H_{16}O_6$ and (?)$C_{12}H_{18}O_6$. Abietic acid therefore contains a retene skeleton with a terminal substituted hexahydrobenzene ring.

H. WREN.

Polysulphides of aromatic carboxylic acids and esters. R. EDER.—See B., 1929, 889.

Isomerisation of hydroxyaldehydes. II. Transformation of bromodi*cyclo*hexylacetaldehyde and di*cyclo*hexylglycollaldehyde. S. DANILOV and E. VENUS-DANILOVA (Ber., 1929, **62**, [*B*], 2653—2668; cf. A., 1928, 64).—Di*cyclo*hexylacetaldehyde, b. p. 153—153·5°/10 mm., d_4^{20} 0·9621, n_D 1·49025, is converted by bromine in dry carbon disulphide at 0° into *bromodi*cyclo*hexylacetaldehyde*, m. p. 59·5° (yield about 77°). It is transformed by aqueous-alcoholic hydroxylamine or semicarbazide into the *oxime*, m. p. 143° (decomp.) after becoming yellow at 126° and softening at 138°, and *semicarbazone*, m. p. 215—218° (decomp.) after becoming yellow at 185° and brown at 210°, of *hydroxydi*cyclo*hexylacetaldehyde*. When heated with silver oxide and water at 100° it yields di*cyclo*hexylacetic acid, m. p. 134·5—135°. Treatment of the bromoaldehyde with silver acetate in aqueous alcohol affords *hydroxydi*cyclo*hexylacetaldehyde*, m. p. 74·5°, and a non-crystalline *product*, (?) $\begin{matrix}C(C_6H_{11})_2\\CH(OH)\end{matrix}>O$. Both products give the oxime and semicarbazone described above and are oxidised to *di*cyclo*hexyl ketone*, b. p. 160°/

24 mm. [*oxime*, m. p. 154—155°; *semicarbazone*, m. p. 195° (decomp.)], and *dicyclohexylglycollic acid*, m. p. 162—163° (further identified by reduction to dicyclohexylacetic acid, m. p. 134·5°). Both forms of the aldehyde are isomerised when heated with aqueous alcohol containing a little sulphuric acid at 135° to *dodecahydrobenzoin*, b. p. 140—141·5°/3 mm., d_4^{20} 1·0100, n_D 1·49170, with slight decomposition and formation of a diketone [*oxime*, m. p. 117—118°; α-*semicarbazone*, m. p. 175—176°; β-*semicarbazone*, m. p. 188° (decomp.)]. The benzoin is oxidised by Fehling's solution to *dodecahydrobenzil*, b. p. 168—169°/16 mm., d_4^{20} 1·0134, n_D 1·48453 [*dioxime*, m. p. about 213° (decomp.); *disemicarbazone*, m. p. about 116° (decomp.)]. The diketone, in contrast to benzil, is not converted into the corresponding hydroxy-acid by aqueous-alcoholic potassium hydroxide, but yields hexahydrobenzaldehyde and *cyclo*hexanecarboxylic acid with resinous products. The action of sodium on ethyl *cyclo*hexanecarboxylate in ether yields a mixture of dodecahydrobenzoin (84%) and dodecahydrobenzil (16%), from which the hydroxyketone is obtained by reduction with zinc and sulphuric or, preferably, acetic acid. It is transformed by magnesium phenyl bromide into *α-phenyl-αβ-dicyclohexylethane-αβ-diol*, m. p. 163—163·5°, oxidised by chromic acid in acetic acid to phenyl *cyclo*hexyl ketone, m. p. 53·5° (semicarbazone, m. p. 167·5—168°), and *cyclo*hexanecarboxylic acid. H. WREN.

Photochemistry of nitrated benzaldehydes. II. E. BAMBERGER and F. ELGER (Annalen, 1929, **475**, 288—308).—In continuation of previous work (A., 1910, i, 267) which led to the formulation of the transformation of *o*-nitrobenzaldehyde into alkyl *o*-nitrosobenzoate as $NO_2{\cdot}C_6H_4{\cdot}CHO \longrightarrow NO_2{\cdot}C_6H_4{\cdot}CH(OR)_2 \longrightarrow NO{\cdot}C_6H_4{\cdot}C(OH)(OR)_2 \longrightarrow NO{\cdot}C_6H_4{\cdot}CO_2R$, *o*-nitrobenzaldehyde ethyleneacetal (*o*-nitrobenzylideneglycol) has been prepared and examined independently of Tanasescu and Tanasescu (A., 1926, 726). Whilst the formulation of the product of insolation, not as $NO{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_2H_4{\cdot}OH$, but as $NO{\cdot}C_6H_4{\cdot}C(OH)<^{O\cdot CH_2}_{O\cdot CH_2}$, in accordance with the second of the above series of reactions, has some support, the evidence as a whole is ambiguous. Glycol monobenzoate, m. p. 37—38° (lit. 45°), like the product, does not react with phthalic anhydride, and the proof of the absence of a primary alcoholic group in the latter is, therefore, invalid. Again, the condensation of silver *o*-nitrosobenzoate with β-iodoethyl alcohol yields an identical product, although the isomerisation of glycol mono-*o*-nitrosobenzoate to the cyclic compound is not excluded.

The insolation of *p*-nitrobenzaldehyde in methyl alcohol yields as chief product *p*-nitrobenzaldehyde dimethylacetal, m. p. 28·2—29° (lit. 24·5—25·5°), accompanied by small amounts of an *acid*, m. p. 235—235·5°, traces of *p*-aminobenzoic acid, and a small quantity of *methyl* p-(p′-*nitrobenzylideneamino*)*benzoate*, m. p. 216—216·5°. This Schiff's base is hydrolysed by hot dilute sulphuric acid to give *p*-aminobenzoic acid and *p*-nitrobenzaldehyde, or by sodium hydroxide in aqueous acetone to give the methyl ester and the aldehyde, and it may be prepared by condensation of the two last-named compounds in acetic acid. Insolation of *m*-nitrobenzaldehyde in ethyl alcohol yields the diethylacetal, some *m*-nitrobenzoic acid, amorphous acids, traces of an amino-acid, and a *substance*, (?)$C_{16}H_{14}O_4N_2$, m. p. 242—242·5°, which is not identical with the Schiff's base, *ethyl* m-(m′-*nitrobenzylideneamino*)*benzoate*, m. p. 124—125·5°. In preliminary investigations on the insolation of heptaldehyde and benzaldehyde in alcohol the acetals have been separated, but these are also formed in control experiments in the dark. Insolation of *p*-nitrobenzaldehyde yields in ether 2 : 2′-azoxybenzaldehyde and an acid, m. p. 225—235°, in toluene, polymerised *p*-aminobenzaldehyde and an acid, m. p. 234—235°, and in benzene a similar acid.

R. K. CALLOW.

Tautomerism of *o*-nitrobenzaldehyde. I. J. POSTOVSKI (J. Russ. Phys. Chem. Soc., 1929, **61**, 719—722).—The tautomerism of *o*-nitrobenzaldehyde: (I) $C_6H_4<^{CHO}_{NO_2} \rightleftharpoons C_6H_4<^{C(OH)}_{NO}>O$, (II) alleged by Tanasescu (A., 1926, 1247; 1928, 178), was investigated by Sugden's method of parachor determination. The calculated parachor values for formulæ I and II are 312·2 and 294·0, respectively, whilst the average experimental value for molten *o*-nitrobenzaldehyde (m. p. 93—93·5°) is 308·5, thus indicating that isomeride I greatly predominates, although the existence of II, especially in solution, is not excluded.

M. ZVEGINTZOV.

[Occurrence of free, substituted methylenes in chemical reactions.] E. KLEUCKER (Ber., 1929, **62**, [*B*], 2587—2588).—The high m. p. 187—189° of the product obtained by Bergmann and Hervey (this vol., 695) from benzyl chloride and *o*-nitrobenzaldehyde excludes the possibility that it is a *p*-nitrostilbene oxide, the two forms of which have been described (m. p. 74—76° and about 122°, respectively) by Chrzescinski (Diss., Strassburg, 1911). The production of ditriphenylene-ethylene from 9-chlorofluorene does not necessarily involve the primary formation of a free methylene radical, but can be explained according to the scheme $\left[{}^{C_6H_4}_{C_6H_4}>CCl\right]Na + Cl{\cdot}CH<^{C_6H_4}_{C_6H_4} \longrightarrow {}^{C_6H_4}_{C_6H_4}>CCl{\cdot}CH<^{C_6H_4}_{C_6H_4} + NaCl$, and subsequent loss of hydrogen chloride. H. WREN.

Catalytic effect of platinum-black and platinum oxide in hydrogenation. F. SIGMUND (Monatsh., 1929, **53** and **54**, 607—619).—When phenylacetaldehyde di-*n*-propylacetal (I) is treated with hydrogen in presence of platinum oxide (6% of wt. of I) and alcohol, absorption of hydrogen ceases after a short time. Addition of acetic acid (half volume of alcohol) causes reduction to proceed and *hexahydrophenylacetaldehyde di-n-propylacetal*, b. p. 122—126°/10 mm., is obtained. Cinnamaldehyde diethylacetal is reduced readily in presence of platinum-black and alcohol to β-*phenylpropaldehyde diethylacetal*, b. p. 121—124°/9 mm. Further reduction in presence of the oxide and alcohol ceases after a time, but addition of acetic acid catalyses the reduction. With 30% of platinum-black in acetic acid or 10—12% of platinum oxide in alcohol and acetic acid (2 : 1) reduction proceeds with the same

velocity. β-*Hexahydrophenylpropaldehyde diethylacetal* has b. p. 130—132°/12 mm.

Reduction of benzaldehyde diethylacetal in presence of platinum-black gives a mixture of hexahydrotoluene, hexahydrobenzyl ethyl ether, and hexahydrobenzyl alcohol (cf. Skita, A., 1916, i, 41).

H. BURTON.

α-Hydroxydiphenylacetaldehyde. E. ZERNER and H. GOLDHAMMER (Monatsh., 1929, **53** and **54**, 485—492).—Reduction of α-*acetoxydiphenylacetyl chloride*, m. p. 91°, by Rosenmund and Zetzsche's method (A., 1918, i, 300; 1921, ii, 320) and hydrolysis of the product with 1% hydrochloric acid gives α-*hydroxydiphenylacetaldehyde*, m. p. 154—155° [the phenylhydrazone (I), m. p. 132°, is identical with the product obtained by the action of magnesium phenyl bromide on ethyl diazoacetate (Zerner, A., 1913, i, 1312, 1387); *oxime*, m. p. 127°; *semicarbazone*, m. p. 144°]. When the phenylhydrazone (I) is boiled with dilute sulphuric acid a red *substance* (II) is produced by loss of 1 mol. of water. Oxidation of II with potassium permanganate gives benzophenone, whilst reduction with zinc dust, acetic acid, and a small amount of hydrochloric acid affords phenylhydrazine and a *substance* (III) $C_{28}H_{20}O_2$ (probably a dimeric diphenylketen), m. p. 113—114°. Hydrolysis of III with alcoholic potassium hydroxide gives diphenylacetic acid. Reduction of II with hydrogen in presence of palladised charcoal and benzene gives diphenylacetaldehydephenylhydrazone, indicating that II is diphenylketenphenylhydrazone. When II is heated with acetic acid, alone or in presence of hydrochloric acid, a nitrogen-free substance, m. p. 136°, is formed in small amount. Treatment of this with zinc dust and acetic acid gives III. α-*Methoxydiphenylacetyl chloride* has m. p. 89—90°.

H. BURTON.

Displacement of the aldehyde group in piperonal and its derivatives. A. H. PARIJS (Diss., Leiden, 1928, 194 pp.).—Nitration of piperonal (25 g.) afforded 6-nitro-3 : 4-methylenedioxybenzaldehyde (I), m. p. 147° (5 g.) and 4-nitropyrocatechyl methylene ether, m. p. 95·5° (26·4 g.); on further nitration the former yielded 4 : 5-dinitropyrocatechyl methylene ether (II), m. p. 100°. The following derivatives of 4-nitropyrocatechyl methylene ether were prepared: 5-amino-, m. p. 193—197°; 5-methylamino-, m. p. 171°; 5-ethylamino-, m. p. 133°; 5-propylamino-, m. p. 115°; 5-butylamino-, m. p. 137°; 5-amylamino-, m. p. 95°; 5-heptylamino-, m. p. 79°; 5-dimethylamino-, m. p. 98°. Derivatives of I were prepared as follows: diacetate, m. p. 142°; 6 : 6′-dinitro-3 : 4 : 3′ : 4′-bismethylenedioxybenzylideneazine, m. p. 257° (decomp.); phenylhydrazone, m. p. 218·5° (decomp.); *p*-nitrophenylhydrazone, m. p. 245° (decomp.); semicarbazone, m. p. 272·5—278° (decomp.). With methyl-alcoholic sodium sulphide, II afforded 6 : 6′-dinitro-3 : 4 : 3′ : 4′-bismethylenedioxydiphenyl sulphide, m. p. 234° (transition at 215—220° to orange form); sodium disulphide gave a disulphide, m. p. 266°. On chlorination, piperonal (25 g.) gave 6-chloropiperonal (III), m. p. 115° (19 g.), and 4 : 5-dichloropyrocatechyl methylene ether, m. p. 82° (2·5 g.). Nitration of III [diacetate, m. p. 133°; benzylideneazine, m. p. 303° (decomp.); phenylhydrazone, m. p. 117—118°; *p*-nitrophenylhydrazone, m. p. 281—282° (decomp.); semicarbazone, m. p. 280° (decomp.); semioxamazone, m. p. 299° (decomp.)] gave 5-chloro-4-nitropyrocatechyl methylene ether, m. p. 70° [corresponding amino-compound, m. p. 254—255° (decomp.)]. Bromination of piperonal (50 g.) afforded 6-bromopiperonal, m. p. 129° (28·5 g.) [diacetate, m. p. 128°, benzylideneazine, m. p. 249—252° (decomp.); *p*-nitrophenylhydrazone, m. p. 253° (decomp.); semicarbazone, m. p. 230° (decomp.); semioxamazone, m. p. 278—279° (decomp.)], and 4 : 5-dibromopyrocatechyl methylene ether, m. p. 85°. Nitration of the former compound gave the 4-nitro- and 3 : 4-dinitro-derivatives; 5-bromo-3-nitro-4-methylaminopyrocatechyl methylene ether has m. p. 67° (decomp.). With nitric acid the diacetate of I affords 6-nitro-3 : 4-dihydroxybenzaldehyde, m. p. 203° (decomp.) [benzylideneazine, m. p. 278° (decomp.); semicarbazone, m. p. 254° (decomp.); phenylhydrazone, m. p. 203° (decomp.); *p*-nitrophenylhydrazone, m. p. 290° (decomp.)]; 6-bromo-3 : 4-dihydroxybenzaldehyde, m. p. 220° (from 6-bromopiperonal and nitric acid), gave a benzylideneazine, m. p. 251° (decomp.); semicarbazone, m. p. 239°; *p*-nitrophenylhydrazone, m. p. 243° (decomp.). 4-Nitro-5-amino-1 : 2-dimethoxybenzene, m. p. 175°, was obtained from 4 : 5-dinitroveratrole; the following homologues were prepared: 5-ethylamino-, m. p. 174—175°; 5-propylamino-, m. p. 141—142°; 5-butylamino-, m. p. 114°; 5-amylamino-, m. p. 90·5°; 5-heptylamino-, m. p. 84°; 5-dimethylamino-, m. p. 130—131°. 4 : 5-Dinitroveratrole and sodium sulphide afford 6 : 6′-dinitro-3 : 4 : 3′ : 4′-tetramethoxydiphenyl sulphide, m. p. 220—220·5° (corresponding disulphide, m. p. 212° (decomp.)].

CHEMICAL ABSTRACTS.

Preparation of 2 : 4 : 6-trihydroxybenzaldehyde 4-methyl ether and its tetra-acetylglucoside. P. KARRER, N. LICHTENSTEIN, and A. HELFENSTEIN (Helv. Chim. Acta, 1929, **12**, 991—993; cf. A., 1927, 564; 1928, 65).—Phloroglucinolaldehyde (2 : 4 : 6-trihydroxybenzaldehyde) in acetone is boiled with methyl sulphate and sodium hydroxide. The oil left on evaporation is dissolved in dilute sulphuric acid, and the ethereal extract of this is evaporated and extracted with hot water. The aqueous solution deposits 2 : 4-dihydroxy-6-methoxybenzaldehyde, and when the filtrate is evaporated and extracted with carbon tetrachloride, 2 : 6-dihydroxy-4-methoxybenzaldehyde is obtained. Use of excess of methyl sulphate leads to formation of the 2 : 4-dimethyl ether. 2-*Tetra-acetylglucosidophloroglucinolaldehyde 4-methyl ether*, m. p. 177° after sintering at 175°, is obtained by interaction of the 4-methyl ether with acetobromoglucose in cold, aqueous acetone in presence of potassium hydroxide, and 4-*tetra-acetylglucosidophloroglucinolaldehyde 2-methyl ether*, m. p. 151°, is prepared by a similar method from the 2-methyl ether.

R. K. CALLOW.

Isomerism of oximes. XXXVI. Methylation of aldoximes and ketoximes. O. L. BRADY and N. M. CHOKSHI (J.C.S., 1929, 2271—2274).—In agreement with previous results (Brady and Goldstein, A., 1926, 1142) methylation of various pairs of isomeric ketoximes which differ only slightly in their dissoci-

ation constants gives approximately the same proportion of *N*- to *O*-ethers with both α- and β-isomerides. Thus the ratio *N*-ether/*O*-ether for α- and β-furfuraldoximes, *p*-nitrobenzophenoneoximes, and phenyl *p*-tolyl ketoximes, determined by the method previously described (*loc. cit.*), is, respectively, 1 : 095 and 1 : 0·85, 1 : 1·15 and 1 : 2·55, 1 : 2·97 and 1 : 2·16, the corresponding values of $k_A \times 10^{11}$ for the first four named being 1·5, 1·4, 1·4, and 3·4, respectively. With α-2-methoxy-1-naphthaldoxime, acetophenoneoxime (k_A $0{\cdot}33 \times 10^{-11}$), and benzophenoneoxime (k_A $0{\cdot}50 \times 10^{-11}$) the ratio *N*-/*O*-ether is 1 : 0·96 (cf. Brady and Goldstein, A., 1927, 973), 1 : 1·43, and 1 : 1·16, respectively, the values for the amount of *N*-ether formed from ketoximes being minimum ones. When α-*p*-nitrobenzophenoneoxime is exposed in benzene to ultra-violet light some *p*-nitrobenzophenone is formed, but most of the oxime is recovered unchanged. J. W. BAKER.

Polymorphism of organic compounds. II. Prognosis of polymorphism and systems of polymorphs. C. WEYGAND (Ber., 1929, **62**, [*B*], 2603—2612; cf. this vol., 815, 1072).—Systematic examination of the relationships in the chalkone series permits the prediction of a further *modification* of phenyl styryl ketone, m. p. 48°, and indicates its actual method of isolation by seeding supercooled phenyl styryl ketone with 3 : 5-diphenyl*iso*oxazole. The second missing *form* of phenyl styryl ketone is produced initially when undercooled phenyl styryl ketone is inoculated with the stable "59" variety.

A reply is made to von Auwers and Schaum (this vol., 1082). H. WREN.

[Occurrence of free substituted methylenes in chemical reactions.] G. HAHN (Ber., 1929, **62**, [*B*], 2485—2489).—The action of phenylhydrazine on the condensation product from *p*-nitrobenzyl chloride and benzil (cf. Bergmann and Hervey, this vol., 695) gives the corresponding *phenylhydrazone*, $C_{27}H_{21}O_3N_3$, m. p. 169—170°. Bergmann's "*p*-nitrobenzylidene ether of stilbenediol" is *α-benzoyl-α-phenyl-β-p-nitrophenylethylene oxide*, reaction occurring in the manner of an aldol condensation, Ph·CO·COPh+

$$Cl{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow \begin{matrix} CPhBz \\ O\text{——} \end{matrix}\!\!>CH{\cdot}C_6H_4{\cdot}NO_2.$$

Similarly, the formation of a *phenylhydrazone*, $C_{27}H_{19}O_3N_3$, m. p. 134—135°, from the "*p*-nitrobenzylidene derivative of phenanthraquinol" (*loc. cit.*) shows the compound to be the *oxide* of 9-*keto*-10-*p-nitrobenzylidene*-9 : 10-*dihydrophenanthrene*. The synthesis of α-benzoyl-α-phenyl-β-*p*-nitrophenylethylene oxide is effected by the action of hydrogen peroxide in alkaline solution on p-*nitrobenzylidenedeoxybenzoin*, m. p. 163—164°, prepared by the condensation of *p*-nitrobenzaldehyde with deoxybenzoin under the influence of alcoholic hydrogen chloride.

The experiments of Bergmann and Hervey do not appear capable of placing the transitory existence of methylene radicals beyond doubt. H. WREN.

Organic compounds of sulphur. XV. Thermolabile thio-ethers. A. SCHÖNBERG, O. SCHÜTZ, V. BRUCKNER, and J. PETER (Ber., 1929, **62**, [*B*], 2550—2562; cf. this vol., 1300).—*s*-Tetraaryldimethyl sulphides undergo thermal decomposition according to the scheme $(Ar_2CH)_2S_2 \longrightarrow Ar_2C{:}S + Ar_2CH_2$, and very labile thio-ethers can be obtained by suitable choice of the aryl group. Purely aromatic dithiols are very unstable thermally, giving disulphides, thioketones, and non-uniform products; change appears to occur according to the scheme: $2Ar_2C(SAr')_2 \longrightarrow Ar'S{\cdot}SAr' + Ar_2C{:}S$ (and other heterogeneous stabilisation products). Aryl triarylmethyl sulphides decompose thus: $2Ar_3C{\cdot}SAr' = 2Ar_3C + Ar'S{\cdot}SAr'$. Highly arylated sulphur compounds derived from methyl sulphide, ethylene sulphide, or dithiolmethane are thermally more labile than the corresponding oxygen compounds, but more stable than the corresponding disulphides. Replacement of the substituent CPh_2R by $O\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CR$ (R is a univalent residue) increases lability as observed in the hexa-arylethane group.

Diphenylmethane is obtained from dibenzhydryl sulphide at 290°, whereas dibenzhydryl disulphide undergoes decomposition at 185°. Di-9-xanthyl sulphide at 205° yields xanthene, xanthione, and dixanthyl; the last-named substance can be prepared by heating xanthene with xanthione in an atmosphere of dry carbon dioxide at 200—210°. Diphenylthioldiphenylmethane at 200—225°/0·03 mm. affords thiobenzophenone (identified as tetraphenylethylene sulphide) and diphenyl disulphide. *Di*-p-*tolylthioldiphenylmethane*, m. p. 73°, from benzophenone chloride and *p*-tolyl mercaptan, at 210° yields thiobenzophenone and di-*p*-tolyl disulphide. *Di*-β-*naphthylthioldiphenylmethane*, m. p. 133°, decomposes at 210°. Xanthone is converted by boiling oxalyl chloride into the corresponding dichloride, which, with *p*-thiocresol, yields *di*-p-*tolylthiolxanthene*, m. p. 107°, transformed at 205° into xanthione and di-*p*-tolyl disulphide. *Diphenylthiolxanthene*, m. p. 117°, affords xanthione and diphenyl disulphide; diphenyl does not appear to be produced. Diphenyl-*p*-tolylmethyl chloride is converted by *p*-tolylmercaptan into *diphenyl*-p-*tolyl*-p-*tolylthiolmethane*, m. p. 87—88°, which yields di-*p*-tolyl disulphide, m. p. 45—46°, at 200°. Triphenylphenylthiolmethane affords a small amount of diphenyl disulphide at 220°/0·05 mm.

Since mild reduction of the "dibiphenylenethiolpinacol" of Manchot and Krische (A., 1905, i, 142) yields fluorene and hydrogen sulphide, the compound is regarded as di-9-fluorenyl disulphide (cf. Bergmann and Hervey, this vol., 695). H. WREN.

Nuclear condensation of phenols and phenolic ethers with nitriles to ketimines and ketones of phenols and phenolic ethers. IV. Syntheses with phenol, *o*-, *m*-, and *p*-cresols, and *p*-tolyl methyl ether. J. HOUBEN and W. FISCHER (J. pr. Chem., 1929, [ii], **123**, 262—275).—Trichloroacetonitrile reacts with phenol in presence of chlorobenzene and aluminium chloride at 50—60° affording a 95% yield of *ωωω-trichloro-4-hydroxyacetophenone*, b. p. 170°/0·5 mm., m. p. 99—99·5°, readily decomposed by alkali hydroxide or carbonate to chloroform and *p*-hydroxybenzoic acid. Similar condensation of *o*-cresol gives 90% of *ωωω-trichloro-4-hydroxy-3-methylacetophenone*, m. p. 90—91°; when condensation is effected in presence of benzene the yield of

ketone is 40% and some *o*-tolyl trichloroacetate is formed. *m*-Cresol yields a mixture of equal parts of *ωωω-trichloro-4-hydroxy-2-methyl-*, m. p. 84—87° [*ketimine*, m. p. 122—124° (slight decomp.)], and *ωωω-trichloro-2-hydroxy-4-methyl-acetophenone*, b. p. 162—163°/17 mm. *p*-Tolyl methyl ether furnishes ωωω-trichloro-2-methoxy-5-methylacetophenone, b. p. 168—169°/15 mm., m. p. 46—49° (cf. A., 1927, 1078); in absence of chlorobenzene the yield is improved. *p*-Cresol yields 80% of *p*-tolyl trichloroacetate and 11% of the corresponding acetophenone, hydrolysed by alkali to 6-hydroxy-*m*-toluic acid, m. p. 148—151°; when condensation is carried out in benzene some ωωω-trichloroacetophenone is produced.

H. BURTON.

Constitution of phloridzin. F. WESSELY and K. STURM (Monatsh., 1929, **53** and **54**, 554—561).—Methylation of phloridzin (I) with diazomethane in ethereal methyl-alcoholic solution gives an amorphous *trimethyl* derivative, $[\alpha]_D^{24}$ —58·69° in methyl alcohol, hydrolysed by 4% sulphuric acid to dextrose and *trimethylphloretin* (II), m. p. 110·5° (*acetate*, m. p. 58—60°). Methylation of phloretin also gives II. Treatment of II with acetic anhydride and sodium acetate at 160—170° affords 5 : 7-*dimethoxy*-4-β-p-*methoxyphenylethylcoumarin*, m. p. 168° after sintering at 166·5° (obtained also by methylation of the known 5 : 7-dihydroxy-derivative), showing that II is 2-*hydroxy*-4 : 6-*dimethoxyphenyl* β-p-*methoxyphenylethyl ketone*. This is proved by reducing 2-hydroxy-4 : 6-dimethoxyphenyl *p*-methoxystyryl ketone with hydrogen in presence of platinum and alcohol, whereby II is formed. Phloridzin is, therefore, 4 : 6-dihydroxy-2-glucosidoxyphenyl β-*p*-hydroxyphenylethyl ketone.

H. BURTON.

Manufacture of naphthalene derivatives [synthesis of naphthazarin from quinol]. BRIT. CELANESE, LTD., G. H. ELLIS, H. C. OLPIN, and E. W. KIRK.—See B., 1929, 935.

Synthesis of alizarin. V. I. MINAEV and B. P. FEDEROV.—See B., 1929, 936.

Hystazarin ethylene ether. H. RAUDNITZ [with W. BÖHM] (J. pr. Chem., 1929, [ii], **123**, 284—288).—Condensation of phthalic anhydride with dihydrobenzdioxin (Ghosh, J.C.S., 1915, **107**, 1588) in presence of a mixture of aluminium and sodium chlorides at 130—140°, and subsequent vacuum sublimation of the neutral product formed, gives *hystazarin ethylene ether* (I), m. p. 299—300°, and a small amount of alizarin ethylene ether. These are separated by treatment with hydrobromic acid (*d* 1·49) at 170—180°, whereby I is unaffected. Hydrolysis of I with sulphuric acid at 200° causes migration of a hydroxyl group and alizarin is the main product obtained. Hystazarin, not melted at 330° [diacetate, m. p. 213° (lit. 205—207°)], is purified by vacuum sublimation.

H. BURTON.

Reduction potentials of various phenanthrenequinones. L. F. FIESER (J. Amer. Chem. Soc., 1929, **51**, 3101—3111).—The normal reduction potentials of 43 phenanthrenequinones have been determined at 25° by titration with potassium ferricyanide, titanous chloride, tetrabromo-*o*-benzoquinone, or benzoquinone (?) in presence of (*a*) 0·1*N*-hydrochloric acid, (*b*) 50% alcohol, 0·1*N* in hydrochloric acid and 0·2*N* in lithium chloride, (*c*) 37% alcohol, 0·047*M* in potassium dihydrogen phosphate and 0·047*M* in disodium hydrogen phosphate, or (*d*) 95% alcohol, 0·2*N* in hydrochloric acid and 0·2*N* in lithium chloride. Comparison of the results for phenanthrene-1 : 2-, -1 : 4-, and -3 : 4-quinones (and derivatives) with the values for the corresponding naphthaquinones (and derivatives) shows that the former compounds have the higher potentials; this is attributed to the more reactive naphthalene (as compared with benzene) ring which is joined to the benzoquinone residue. The values for phenanthrene-9 : 10-quinone are abnormally high, probably because of a strain resulting from the spatial configuration of the molecule. Introduction of groups into either the 1- or 3-position of the 9 : 10-quinone causes the same change in potential, which is greater than when the substituent is in the 2- or 4-position. An increased potential occurs with introduced nitro- (most effective), cyano-, keto-, carboxy-, or sulpho- (least effective) groups, and a decreased value with methoxy-, hydroxy-, methyl, or amino-groups. Introduction of a second like substituent causes a further increase or decrease.

Oxidation of *methyl phenanthrene-3-carboxylate*, m. p. 97°, with chromic oxide in acetic acid gives *methyl phenanthrene-9 : 10-quinone-3-carboxylate*, m. p. 212°. Similar oxidation of 3-benzoylphenanthrene (from magnesium phenyl bromide and phenanthrene-3-carboxyl chloride) yields 3-*benzoylphenanthrene-9 : 10-quinone*, m. p. 205—206°.

H. BURTON.

1 : 2-Benzo-3 : 4-anthraquinone [2 : 3-benzophenanthraquinone]. L. F. FIESER and E. M. DIETZ (J. Amer. Chem. Soc., 1929, **51**, 3141—3148).—*o*-4-Methoxy-1-naphthoylbenzoic acid, m. p. 196—197° (improved method of preparation given) (cf. Scholl, Seer, and Zincke, A., 1921, i, 677), is reduced with zinc dust and sodium hydroxide solution to phenyl-4-methoxy-1-naphthylmethane-2′-carboxylic acid, m. p. 221—223° (corr.). This readily undergoes ring closure on dissolution in cold sulphuric acid, yielding 3-*methoxy*-1 : 2-*benz*-10-*anthrone* [*acetyl* derivative, m. p. 197° (corr.)], which is reduced by aluminium amalgam and ammonia in alcoholic suspension to 3-*methoxy*-1 : 2-*benzanthracene*, m. p. 167—168° (9 : 10-*quinone*, m. p. 188·5°). Demethylation of this with 40% hydrobromic acid in acetic acid affords 3-*hydroxy*-1 : 2-*benzanthracene*, m. p. 196—205° (decomp.) [*acetate*, m. p. 129° (9 : 10-*quinone*, m. p. 232°)], which with *p*-nitrobenzenediazonium sulphate in acetic acid gives the 4-p-*nitrobenzeneazo*-derivative, dark red. The moist azo-compound is reduced by stannous chloride and hydrochloric acid in boiling butyl alcohol to 4-*amino*-3-*hydroxy*-1 : 2-*benzanthracene* [*triacetyl* derivative, m. p. 203—205° (corr.); corresponding *methyloxazole*, m. p. 175·5°]. Oxidation of this amine with chromic oxide in acetic acid yields 1 : 2-*benzo*-3 : 4-*anthraquinone* (I), m. p. 262—263° (corr.; some decomp.), which with zinc dust, acetic anhydride, and sodium acetate gives 3 : 4-*diacetoxy*-1 : 2-*benzanthracene*, m. p. 201° (corr.) (9 : 10-*quinone*, m. p. 198—199°). 3 : 4-*Dihydroxy*-1 : 2-*benzanthraquinone* gives an intense green coloration with boroacetic anhydride, indicating that one hydroxyl group

is adjacent to a quinone carbonyl group. Oxidation of I with hydrogen peroxide in acetic acid solution affords *2-phenylnaphthalene-3 : 2′-dicarboxylic acid*, m. p. 252° (corr.), converted by treatment with sulphuric acid into *1 : 2(or 2 : 3)-benzofluorenone-4(or 5)-carboxylic acid*, m. p. 268° (corr.).

H. BURTON.

Perylene and its derivatives. XXVI. A. ZINKE and H. KOLMAYR (Monatsh., 1929, **53** and **54**, 361—366).—Condensation of dibromo- (I) or dichloroperylene-3 : 10-quinone (II) (Zinke and others, A., 1924, i, 1080) with *o*-thiolbenzoic acid in presence of amyl alcohol, potassium carbonate, and copper powder gives a *di-(o-carboxyphenylthiol)perylene-3 : 10-quinone* (red aqueous solution). Attempts to obtain the corresponding thioxanthone from this afforded only amorphous products. Bromination or chlorination in nitrobenzene solution at 100° regenerates I or II. Similar condensation of I or II with anthranilic acid affords an *o-carboxyanilinoperylene-3 : 10-quinone*, violet-black; one halogen atom is replaced by hydrogen during the reaction. Treatment of this acid with sulphuric acid at 100° affords the corresponding *acridone*, reddish-brown. Orientation of the halogen atoms in I and II is not possible from these results. H. BURTON.

Linear pentacene series. XIV. Pentacene-6 : 13-quinone. F. HERNLER and K. SCHNÜRCH (Monatsh., 1929, **53** and **54**, 643—645; see this vol., 1436).—Oxidation of pentacene, tetrahydropentacene, or the compound obtained by reduction of pentacenediquinone with zinc dust and ammonia (Seka and Sekora, A., 1927, 363) with ferric chloride in acetic acid solution affords varying amounts of pentacene-6 : 13-quinone, m. p. 393° (corr.; cf. Mills and Mills, J.C.S., 1912, **101**, 2194). H. BURTON.

Linear pentacene series. XV. 6 : 13-Dihydroxypentacene-5 : 7 : 12 : 14-diquinone. F. HERNLER and O. SOMMER (Monatsh., 1929, **53** and **54**, 646—650).—1 : 4-Dihydroxy-β-naphthoic acid is converted by prolonged treatment with sulphuric acid at the ordinary temperature into 6 : 13-dihydroxypentacene-5 : 7 : 12 : 14-diquinone (I), m. p. 424° (corr.) (*diacetate*, m. p. 358°) (cf. Hartenstein, Diss., Jena, 1892, 6; Russig, A., 1900, i, 601). Attempted reduction of I with zinc dust, acetic anhydride, and sodium acetate gives the above diacetate; treatment with red phosphorus and hydriodic acid has no effect. Distillation of I over copper in a current of hydrogen gives mainly unchanged material, and it is considered that Russig's tetrahydroxypentacenequinone cannot be prepared. Oxidation of I with chromic acid affords unchanged material and water-soluble products. Pentacene-5 : 6 : 7 : 12 : 13 : 14-triquinone (cf. Russig, *loc. cit.*) is unknown. H. BURTON.

Linear pentacene series. XVI. Pentacene-5 : 7 : 12 : 14-diquinonedisulphonic acid and tetrahydroxypentacene-5 : 7 : 12 : 14-diquinone. F. HERNLER and T. BRUNS (Monatsh., 1929, **53** and **54**, 651—658).—Sulphonation of pentacene-5 : 7 : 12 : 14-diquinone (cf. Philippi and Seka, A., 1925, i, 556) with fuming sulphuric acid (45—50% SO_3) at 130° in presence of a small amount of mercury affords a disulphonic acid (probably 1 : 8 or 1 : 11), darkens at 280°, sinters about 300°, softens about 390°, and is not melted at 500° (potassium and silver salts). Fusion of this acid with potassium hydroxide at 180—200° in presence or absence of potassium nitrate yields a mixture of *tetrahydroxypentacenediquinones*, not melted at 500°, partly separable by extraction with ether or alcohol. The products give a characteristic red colour in concentrated sulphuric acid, blue in alkaline solution, reduced by hyposulphite to a brown vat. H. BURTON.

Linear pentacene series. XVII. Dinitro-, diamino-, and dihydroxy-pentacene-5 : 7 : 12 : 14-quinones. G. MACHEK (Monatsh., 1929, **53** and **54**, 659—667).—Nitration of pentacene-5 : 7 : 12 : 14-diquinone with nitric (*d* 1·51) and sulphuric acids at 65° affords a mixture of isomeric dinitro-derivatives (I), decomp. above 400° (43·1%), and (II), decomp. 346—350° (45·8%) (cf. Seka and Schmidt, A., 1927, 363). Reduction of I with alkaline sodium hyposulphite or sodium hydrogen sulphide solution yields a *diaminopentacenediquinone* (III), dark violet, decomp. above 450°; II yields similarly a *diamino*-derivative (IV), reddish-violet, decomp. 389—390°. Decomposition of the diazonium salts from III and IV at 100° gives the corresponding *dihydroxypentacene-5 : 7 : 12 : 14-diquinones*, m. p. 375—380° after darkening and partial decomp. at 320°, and 304—305° after darkening and partial decomp. at 270°, respectively. All the above derivatives can be sublimed at 270—310°/0·02—0·05 mm. The positions of the substituents in these derivatives are probably 1 : 8 and 1 : 11. H. BURTON.

Constituents of kawa root. IX. Synthesis of yangonin. W. BORSCHE and C. K. BODENSTEIN (Ber., 1929, **62**, [*B*], 2515—2523; cf. this vol., 442).—Yangonic acid, m. p. 123—124° (decomp.), obtained according to Winzheimer (A., 1908, i, 805), is converted by diazomethane into its *methyl* ester, $C_{15}H_{16}O_5$, m. p. 78·5°, which loses methyl alcohol when boiled with acetic anhydride and yields acetylyangonolactone, $CO<\begin{matrix}CH{:}C(OAc)\\CH{=}{=}CR\end{matrix}>O$ ($R{=}OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}$), m. p. 133°, obtained but not investigated by Winzheimer; the compound is prepared also from yangonic acid and boiling acetic anhydride. It is converted by methyl alcohol at 100° or by methyl-alcoholic potassium hydroxide at the atmospheric temperature into yangonolactone, m. p. 238°, from which yangonin is derived by the action of ethereal diazomethane or of methyl sulphate and sodium hydroxide.

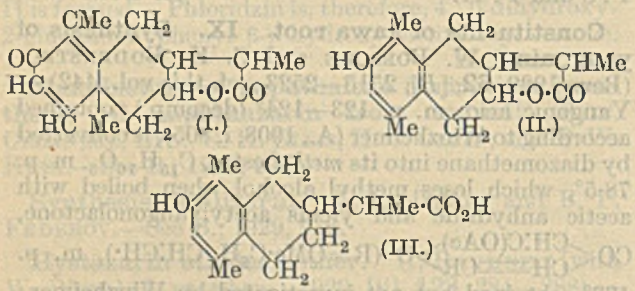
Ethyl acetonedicarboxylate, sodium, and *p*-methoxycinnamyl chloride in ether afford *ethyl α-p-methoxycinnamylacetone-αα′-dicarboxylate*, $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}CHR{\cdot}CO_2Et$, m. p. 51—52° (*copper* compound, m. p. 138—140°), which, when heated with acetic anhydride, gives a mixture of *ethyl acetylisoyangonolactone-3-carboxylate*, $OAc{\cdot}C<\begin{matrix}CH\text{———}CO\\C(CO_2Et){:}CR\end{matrix}>O$, m. p. 220°, and *ethyl acetylyangonolactone-3-carboxylate*, $CO<\begin{matrix}CH{=}C(OAc)\\C(CO_2Et){:}CR\end{matrix}>O$, m. p. 104—105°. Treatment of the mixture of acetylated esters with methyl-alcoholic sodium hydroxide affords *ethyl yangonolactone-3-carboxylate*, orange

prisms or golden-brown rhombs, m. p. 149—150°, hydrolysed to the corresponding *acid*, $C_{15}H_{12}O_6$, m. p. 212—215° (decomp.). Decarboxylation of the acid in boiling nitrobenzene gives yangonolactone, m. p. 238—239°.

On an isolated occasion, treatment of yangonic acid with boiling acetic anhydride gave *acetyl*iso*yangonolactone*, $C_{16}H_{14}O_5$, m. p. 185—186°, which is stable towards cold alkali hydroxide solution, but converted by boiling 10% sodium hydroxide into yangonolactone. In alkaline solution it is hydrogenated in presence of colloidal palladium to *acetyl*-*dihydro*iso*yangonolactone*, (?) $OAc{\cdot}C{<}^{CH-CO}_{CH:CR'}{>}O$ ($R'=OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2$), m. p. 107—108°. Hydrogenation of acetylyangonolactone suspended in methyl alcohol in presence of colloidal palladium affords *dihydroyangonolactone*, $CO{<}^{CH_2-CO}_{CH:CHR'}{>}O$, m. p. 181—182°, converted by methyl sulphate and sodium hydroxide into dihydroyangonin, m. p. 101—103°.

H. WREN.

Constitution of santonin. I. Synthesis of *dl*-santonous acid. G. R. CLEMO, R. D. HAWORTH, and E. WALTON (J.C.S., 1929, 2368—2387).—Earlier formulæ for santonin are critically discussed and a new formula (I) is advanced which conforms better with its chemical properties and with modern views of structural units (isoprene units forming a farnesene skeleton). Santanin thus falls in the selinene group of sesquiterpenes. Its conversions into *desmotropo*-santonin (II) and *dl*-santonous acid (III) are



considered to involve the migration of the methyl group attached to the quaternary carbon atom together with the wandering of a nuclear hydrogen atom. The following investigations have led to the synthesis of III: *m*-xylene, β-cyanoethyl *p*-toluenesulphonate, and powdered aluminium chloride when boiled together yielded β-2 : 4-*dimethylphenylpropionitrile*, b. p. 264—267°/760°, which by hydrolysis with methyl-alcoholic potassium hydroxide gave β-2 : 4-dimethylphenylpropionic acid, m. p. 106°. Similar experiments with *p*-xylene gave identical compounds owing to migration of a methyl group. Slow addition of aluminium chloride to *p*-xylyl methyl ether and acetyl chloride in light petroleum solution formed 4-*methoxy*-2 : 5-*dimethylacetophenone*, m. p. 78—79°. *p*-Xylenol, aluminium chloride, and liquid hydrocyanic acid reacted in dry benzene; subsequent steam-distillation gave 6-hydroxy-2 : 5-dimethylbenzaldehyde, m. p. 62°, 4-hydroxy-2 : 5-dimethylbenzaldehyde, m. p. 132—133°, and *di*-(4-*hydroxy*-2 : 5-*dimethylphenyl*)*acetonitrile*, m. p. 250° (*methyl ether*, m. p. 190°). 4-Hydroxy-2 : 5-dimethylbenzaldehyde condensed with malonic acid in hot pyridine solution containing a little piperidine to form 4-*hydroxy*-2 : 5-*dimethylcinnamic acid*, m. p. 223—225° (*acetyl* derivative, m. p. 168—169°). Methyl sulphate and methyl-alcoholic potassium hydroxide converted it into 4-*methoxy*-2 : 5-*dimethylbenzaldehyde*, b. p. 147—149°/12 mm., m. p. 34° (corresponding *acid*, m. p. 163—165°), which with malonic acid, pyridine, and piperidine at 100° gave 4-*methoxy*-2 : 5-*dimethylcinnamic acid*, m. p. 200—202°. This was reduced by sodium amalgam in 5% sodium hydroxide solution to β-4-*methoxy*-2 : 5-*dimethylphenylpropionic acid*, m. p. 120—121°, from which the corresponding *chloride*, b. p. 171°/12 mm., m. p. 34°, was obtained, using thionyl chloride. Heating the chloride with aluminium chloride and light petroleum gave 6-*methoxy*-4 : 7-*dimethyl*-α-*hydrindone*, m. p. 162—164°, whilst β-4-*methoxy*-2 : 5-*dimethylphenylpropion*-*anilide* and -*amide* (3-*bromo*-derivative, m. p. 152°), m. p. 134—135° and 127—128°, respectively, were formed normally. Treatment of the amide with sodium hypochlorite solution etc. led to β-4-methoxy-2 : 5-dimethylphenylethylamine, b. p. 120—122°/0·25 mm. [*hydrochloride*, m. p. 212—215° (decomp.); *acetyl* derivative, m. p. 147—148°], accompanied by a little *methyl* β-4-*methoxy*-2 : 5-*dimethylphenylethylcarbamate*, b. p. 175—185°/12 mm., m. p. 57·5°. β-4-*Methoxy*-2 : 5-*dimethylphenylethyl alcohol*, b. p. 125—126°/0·25 mm. (corresponding *phenylcarbamate*, m. p. 110°), isolated from the foregoing ethylamine by interaction with sodium nitrite in dilute acetic acid solution, gave with 45% aqueous hydrobromic acid β-4-*methoxy*-2 : 5-*dimethylphenylethyl bromide*, b. p. 128—130°/1 mm., which with ethyl sodiomalonate formed *ethyl* β-4-*methoxy*-2 : 5-*dimethylphenylethylmalonate*, b. p. 185°/0·25 mm., whence by hydrolysis with methyl-alcoholic potassium hydroxide the corresponding *ethylmalonic acid*, m. p. 145° (decomp.), and γ-4-*methoxy*-2 : 5-*dimethylphenylbutyric acid*, m. p. 101—102° (also formed by Clemmensen reduction of β-4-*methoxy*-2 : 5-*dimethylbenzoylpropionic acid*, m. p. 131°, obtained by the interaction of *p*-xylyl methyl ether, aluminium chloride, succinic anhydride, and benzene), were prepared successively. Brief heating of the foregoing butyric acid with concentrated sulphuric acid afforded 1-*keto*-7-*methoxy*-5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 63—64° (*dibromo*-derivative, by bromination in chloroform, m. p. 93°), which condensed with amyl nitrite in ether containing potassium ethoxide to give 2-iso*nitroso*-1-*keto*-7-*methoxy*-5 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 170—180° (decomp.).

β-4-*Methoxy*-2 : 5-*dimethylbenzoylacrylic acid*, m. p. 156—157°, from aluminium chloride, *p*-xylyl methyl ether, maleic anhydride, and light petroleum, at 70°, gave with hydrogen bromide in acetic acid α-*bromo*-β-4-*methoxy*-2 : 5-*dimethylbenzoylpropionic acid*, m. p. 144—147° (*ethyl* ester, m. p. 90—91°). The corresponding *ethyl* α-*chloro*-ester, m. p. 89—90°, was prepared analogously; amalgamated zinc and hydrochloric acid converted it into γ-4-methoxy-2 : 5-dimethylphenylbutyric acid, whilst condensation with ethyl sodiomalonate led to *ethyl* γ-4-*methoxy*-2 : 5-*dimethylbenzoylpropane*-αα*β*-*tricarboxylate*, an oil, hydro-

lysed by methyl-alcoholic potassium hydroxide to the related *acid*. The last compound, when (*a*) heated at 160°, gave *γ-4-methoxy-2 : 5-dimethylbenzoylpropane-αβ-dicarboxylic anhydride*, m. p. 152—153°, by elimination of carbon dioxide (corresponding *acid*, m. p. 148—150°), (*b*) reduced by amalgamated zinc and hydrochloric acid, formed *β-4-methoxy-2 : 5-dimethylphenylethylsuccinic acid*, m. p. 140—142°, which with sulphuric acid gave *7-methoxy-1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-acetic acid*, m. p. 143—145°, from which, by Clemmensen reduction, *7-methoxy-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-acetic acid*, m. p. 130—131°, was obtained. Brief heating of this methoxy-acid with hydriodic acid gave the related *7-hydroxy-acid* (*norsantonous acid*), m. p. 163—164°.

Ethyl α-chloro-β-4-methoxy-2 : 5-dimethylbenzoylpropionate and ethyl sodiomethylmalonate interacted to give *ethyl δ-4-methoxy-2 : 5-dimethylbenzoylbutane-ββγ-tricarboxylate*, m. p. 99°, b. p. (with slight decomp.) 220°/0·1 mm., hydrolysis of which with methyl-alcoholic potassium hydroxide gave 4-methoxy-2 : 5-dimethylacetophenone and the two racemic forms of *δ-4-methoxy-2 : 5-dimethylbenzoylbutane-βγ-dicarboxylic acid*, m. p. 155—162°, resolved by crystallisation from alcohol into mainly one form of the *acid*, m. p. 163—168°. Clemmensen reduction of the acid mixture of m. p. 155—162° gave small yields of an unknown *acid*, m. p. 181—182°, along with *α(β-4-methoxy-2 : 5-dimethylphenylethyl)-α′-methylsuccinic acid* (two forms : m. p. 169—171° and 130—132°, respectively). Either of the two preceding acids when warmed with sulphuric acid gave a *lactone*, m. p. 160—162°, alkaline hydrolysis of which produced a mixture of the two racemic forms of *α-7-methoxy-1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-propionic acid*, m. p. 105—115°. Clemmensen reductions of this mixture afforded the two possible racemic forms of *dl*-santonous acid methyl ether, m. p. 97—110°; these by boiling with hydriodic acid gave *dl*-santonous acid, m. p. 150—152° (ethyl ester, m. p. 125°), identical with santonous acid and its ester from santonin.

Attempts to condense β-methoxy-2 : 5-dimethylphenylethyl bromide with ethyl sodiopropane-ααβ-tricarboxylate yielded two *products*, b. p. 135—150°/12 mm. and b. p. 235—250°/12 mm. Treatment of the former with methyl-alcoholic potassium hydroxide gave 4-methoxy-2 : 5-dimethylstyrene(?), b. p. 120°/12 mm.

An improved preparation of *p*-xylene and *p*-xylenol from *p*-xylidine is described incidentally.

R. J. W. Le Fèvre.

Cryoscopic measurements with caoutchouc solutions and the separation of mixed phases from solutions of caoutchouc in benzene. IX. R. Pummerer, A. Andriessen, and W. Gündel (Ber., 1929, **62**, [*B*], 2628—2636; cf. A., 1928, 793).—Re-examination of the mol. wt. of caoutchouc in camphor shows that the hydrocarbon is not cracked at the high temperature (or cracking is complete within 5 min.), that melting camphor is not "catalytically" decomposed by caoutchouc and guttapercha, and that the depressions of the f. p. cannot be attributed to products of decomposition of oxygenated impurities in the caoutchouc, since camphor can be almost quantitatively sublimed from the mixture and is found practically unchanged in m. p. Re-determination of the mol. wt. of caoutchouc in menthol in an apparatus designed to examine the effect of delay in crystallisation gives values higher than those observed previously, which indicate the presence of 16—24 isoprene residues. Examination of sol caoutchouc in freezing benzene gives very varying results (mol. wt. 1500—8000) due to the separation of caoutchouc with the solid phase. No value can therefore be placed on determinations in benzene. In menthol, the variations are less marked, but more considerable than is usual, whereas in camphor the depressions proceed strictly stoicheiometrically and give almost the same values (about 1200) as the experiments in menthol.

H. Wren.

Iodine and oxygen values of sol and gel caoutchouc. X. R. Pummerer and F. J. Mann (Ber., 1929, **62**, [*B*], 2636—2647).—The iodine value is determined by means of iodine chloride in anhydrous chloroform, excess of the reagent being converted into iodine by addition of finely-divided potassium iodide. The acid liberated during the Wijs reaction is determined by a "dry" method, which consists in removing excess of iodine chloride in a parallel experiment by silver powder, distilling about half of the chloroform at about 20°/70 mm. into an excess of 0·1*N*-sodium hydroxide, and titrating the excess of the latter, and by a "wet" method in which the mixture remaining after use of thiosulphate is titrated directly with 0·1*N*-sodium hydroxide in presence of phenolphthalein. It is immaterial whether the experiment be performed at 0° or the ordinary temperature; the mixture is preserved for 6 or 72 hrs., and the solution contains 0·7 or 0·2% of caoutchouc. Addition of pyridine to sol caoutchouc (as offset against the nitrogenous impurities of gel caoutchouc) is without influence. The oxygen value is determined by means of perbenzoic acid in chloroform, the operation being complete within 48 hrs. Sol and gel caoutchoucs from latex, "revertex," crêpe, and smoked sheet are employed (cf. A., 1927, 1193; B., 1928, 793). Sol caoutchouc from latex and revertex gives almost the theoretical iodine values calculated for the absorption of 1 mol. of iodine per C_5H_8 group (denominated 100%). For sol caoutchouc from crêpe or smoked sheet the values 97·6% and 98·3% are observed. Halogen acid is not found in the chloroform. The oxygen values are 5—6% below the iodine values. For gel caoutchouc from latex, revertex, and crêpe the iodine values 108·6—110·3% and oxygen values 98·25—100·5% are observed. Gel caoutchoucs differ fundamentally from the sol products in that they evolve halogen acid in indifferent media. If it is assumed that the acid is formed by substitution, and 1 mol. of iodine is deducted for each mol. of hydrogen halide, the iodine value is almost exactly 100%, and the actual number of double linkings is identical in sol and gel caoutchouc. The "dry acid value" of gel caoutchouc is about 5% of the added halogen. If a correction based on the "wet acid value" (deduction of 1 mol. of iodine for 2 mols. of hydrogen halide) is applied to the iodine values, the corrected figure for all four pairs

of sol and gel caoutchouc is almost identical with the oxygen value.

If the sol caoutchouc–iodine solution is treated with water, 6—7% of the added halogen is eliminated as hydrogen halide which must be due to hydrolysis or ring formation [cf. the behaviour of hentriacontene dibromide towards alcohol (this vol., 1420)].

The original communication should be consulted for the detailed consideration of the theoretical aspects of the experiments. H. WREN.

Modified Curtius reaction. IV. Degradation of perhydronorbixin. C. NAEGELI and P. LENDORFF (Helv. Chim. Acta, 1929, **12**, 894—899).—Perhydronorbixin is converted by thionyl chloride into the acid chloride; this is treated with sodium azide, and the product is decomposed with hydrochloric acid (cf. this vol., 540). The main product is *bixamine hydrochloride*, an amorphous powder, sintering at 147° (*chloroplatinate*, sintering at 208°; *chloroaurate*, decomp. 65—70°; *dicarbamido*-derivative, pasty), accompanied by a mixture of ω-aminocarboxylic acids, from which a chloroplatinate is obtainable. R. K. CALLOW.

Conjugated unsaturated compounds. X. The ethylene group as chromophore. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1929, **12**, 899—903).—A reply to Faltis and Vieböck (this vol., 575). The intense colour of bixin is sufficiently accounted for by the cumulative effect of the nine conjugated unsaturated linkings and the two carboxyl groups in the formula proposed (A., 1928, 869). The colours of α-crocetin, norbixin, and bixin are comparable, respectively, with those of αo-diphenyltetradecaheptaene, αρ-diphenylhexadecaoctaene (A., 1928, 281), and with that to be expected in the next member of the series. Evidence is brought forward in support of the chromophoric equivalence of the phenyl and carboxyl groups. The formula of Faltis and Vieböck would correspond with a blue-black substance. R. K. CALLOW.

Conjugated unsaturated compounds. XI. Bixin and its degradation to bixane. R. KUHN and L. EHMANN (Helv. Chim. Acta, 1929, **12**, 904—915).—A further reply to Faltis and Vieböck (this vol., 575). In support of the formula $C_{25}H_{30}O_4$ for bixin new analytical data and molecular refractivities are given. The formula is also supported by the number of methyl groups determined (this vol., 425), and by the isomerisation phenomena (Karrer and others, this vol., 1075).

Details are given of an improved method of extraction of bixin from the seeds of *Bixa Orellana*. Perhydrobixin, b. p. 224°/0·30 mm., d_4^{20} 0·9368, n_D^{20} 1·4615, is obtained by hydrogenation of bixin in presence of platinum oxide–platinum-black, and is hydrolysed to perhydronorbixin, b. p. 227°/0·03 mm., 245·5°/0·24 mm., d_4^{20} 0·9528—0·9561, n_D^{20} 1·4685—1·4678, which is esterified to perhydromethylbixin, b. p. 219°/0·55 mm., d_4^{20} 0·9234, n_D^{20} 1·4658. Reduction of perhydromethylbixin with sodium in amyl alcohol yields the glycol, *αν-dihydroxybixane*, b. p. 198°/0·12 mm., and an acid *substance*, b. p. 281—285°/0·32 mm., n_D^{20} 1·4675. The glycol is converted by heating in a sealed tube with hydrobromic acid into the oily *dibromo*-compound, which is reduced by a zinc–copper couple in 60% acetic acid to the hydrocarbon *bixane* (*tetramethyleicosane*), b. p. 162°/0·52 mm., d_4^{20} 0·8054, n_D^{20} 1·4502. The b. p. of this hydrocarbon is concordant with its formulation as a homologue of farnesane and phytane. Reduction of perhydrobixin yields an *oil*, b. p. 254°/0·53 mm., from which a cyclic *hydrocarbon*, C_nH_{2n}, m. p. 66°, is obtained in 1% yield by boiling with acetic anhydride. R. K. CALLOW.

Strophanthin. XVII. Dehydration and lactone cleavage in *iso*strophanthic acid derivatives. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1929, **84**, 183—190).—β-*iso*Strophanthic lactone acid (A., 1927, 1194) when heated with acetic anhydride and acetyl chloride, gave an *anhydroanhydride acetate*, $C_{25}H_{30}O_7$, m. p. 280—281°, which, when hydrolysed with sodium hydroxide, neutralised 3 equivalents of alkali and yielded an *acid*, $C_{23}H_{30}O_7$, m. p. 230—232° (*dimethyl* ester, m. p. 199—200°, $[\alpha]_D^{20}$ −28·0° in methyl alcohol); treatment of the anhydride with methyl-alcoholic hydrogen chloride gave the *acetate* of the above ester, m. p. 170—171°. The ester was hydrogenated to give a saturated *ester*, $C_{25}H_{36}O_7$, m. p. 229—231°. The reaction is explained by cleavage of the unstable lactone ring, the liberated carboxyl forming a succinic anhydride with the carboxyl already free; the liberated hydroxyl is removed with introduction of a double linking and the second hydroxyl is acetylated (compare formulæ, A., 1928, 1376). The explanation is confirmed by the fact that the action of acetic anhydride and acetyl chloride on the methyl ester of β-*iso*strophanthic lactone acid leads only to the *acetate*, $C_{26}H_{34}O_8$, m. p. 235—237°. Also the prolonged action of methyl-alcoholic hydrogen chloride on β-*iso*strophanthic lactone acid leads to an unsaturated *dimethyl* ester, $C_{25}H_{34}O_7$, m. p. 154—155°, $[\alpha]_D^{20}$ +90° in methyl alcohol, the isomerism of which with the ester described above is explained by the fact that it belongs to the δ-*iso*strophanthic acid series (A., 1927, 1194). The *l*-ester was unchanged by heating with methyl-alcoholic hydrogen chloride, as was the *d*-ester after alkaline hydrolysis and re-esterification; the isomerisation must therefore involve carbon atom 6 (formulæ, *loc. cit.*) and have occurred prior to the opening of the lactone ring. C. R. HARINGTON.

Fungi resins. N. FRÖSCHL and J. ZELLNER (Monatsh., 1929, **53** and **54**, 146—152).—Hydrolysis of *Lentinus squamosus*, Schroet., with alcoholic potassium hydroxide and separation of the reaction mixture into (*a*) ether-soluble, (*b*) water-soluble, and (*c*) ether- and water-insoluble gelatinous products gives (*a*) a sterol-like substance, m. p. 152—154°, (*b*) amorphous acidic substances, and (*c*) resin acids and a neutral *substance* (termed *lentinol*), $C_{27}H_{41}O_3$, m. p. 265° after darkening at 250° (*triacetyl* derivative, m. p. 227—228°). This gives an olive-brown coloration with Liebermann's reagent and belongs to the resinol group. The alcoholic extract of the fungus contains the major part of the resin; this is separated into lentinol and resin acids. The resin from *Hypholoma fasciculare*, Huds., is separated as above into (*a*) a small amount of a substance, m. p. 173°, (*b*) acid products, and (*c*) a substance, m. p. 148—150° (cf.

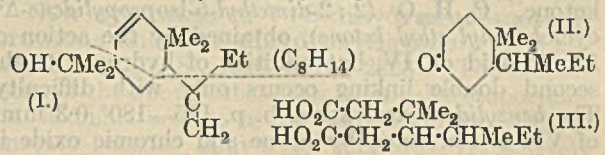
A., 1912, ii, 195). The resin acid fraction from *Polyporus pinicola*, Fr. (Hartmann and Zellner, this vol., 108), contains two isomeric *acids*, m. p. 208·5° after slight coloration at 198°, $[\alpha]_D^{20}$ +35·7° in alcohol, and m. p. 271° after darkening at 265°, $[\alpha]_D^{20}$ +23·4° in alcohol, termed α- and β-*pinicolic acids*, respectively. H. BURTON.

Breins from Manila elemi resin. A. ROLLETT (Monatsh., 1929, **53** and **54**, 231—236).—The commercial resin is freed from essential oil by steam-distillation and then extracted with alcohol. The residue from this extract deposits the brein *B*, m. p. 180—190°, of Vesterberg (A., 1906, i, 686). The residue from this contains brein (I), $C_{30}H_{50}O_2$(+EtOH), m. p. 218—219° [cf. *loc. cit.*; *dibenzoyl* derivative (+EtOH), m. p. (alcohol-free) 209—210°], obtained crystalline from an acetic acid solution, or as the acetyl derivative, m. p. 195°, by acetylation with acetic anhydride. Oxidation of I with chromic and acetic acids gives a small amount of a *substance*, $C_{30}H_{48}O_2$, m. p. 161—163° [*oxime*, m. p. 246—248° (decomp.)], probably a keto-alcohol. H. BURTON.

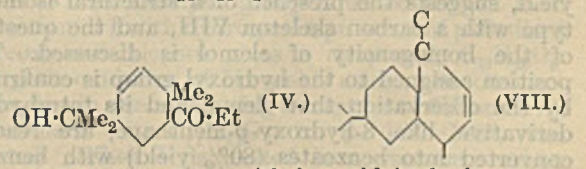
Constitution of resins. I. Boswellic acid from olibanum (frankincense). K. BEAUCOURT (Monatsh., 1929, **53** and **54**, 897—913).—Boswellic acid (I), $C_{32}H_{52}O_4$, m. p. 150—151° after sintering at 142° (Tschirch and Halbey, A., 1899, i, 69), on distillation at 245—260° (bath)/0·2 mm. gives acetic acid, an *acid*, m. p. 95—98° after sintering at 80°, isomeric with I, and a *hydrocarbon* (II), $C_{30}H_{48}$, m. p. 126—127°, $[\alpha]_D^{18\cdot5}$ +183° in benzene (crystallographic data given). The presence of one double linking in II is shown by bromine and perbenzoic acid titrations, and by catalytic reduction in presence of platinum-black or platinum oxide and amyl ether. The reduction product has m. p. 112—120°, and is probably a mixture. H. BURTON.

Behaviour of saturated di- and tri-cyclic terpene hydrocarbons towards catalytic reduction and dehydrogenation. N. D. ZELINSKI and R. J. LEVINA (Annalen, 1929, **476**, 60—70).—Reduction of di- and tri-cyclic terpenes containing a trimethylene ring with hydrogen and platinised charcoal at 160° readily causes fission of this ring (cf. Zelinski, A., 1913, i, 254). Thus carane gives *p*-menthane, *cyclo*fenchene gives *iso*bornylane identical with the product obtained by reduction of α-fenchene, whilst tricyclene yields camphane. Catalytic dehydrogenation with platinised charcoal at 300° in a current of carbon dioxide causes similar ring fission with the formation of an unsaturated hydrocarbon which, if hydroaromatic, is further dehydrogenated to the corresponding benzene derivative. Thus carane yields *p*-cymene, but thujane gives only a *hydrocarbon*, $C_{10}H_{18}$, b. p. 163·5—164·5°, n^{21} 1·4452, which may be 1 : 2-dimethyl-3-*iso*propylidene*cyclo*pentane, 1 : 2-dimethyl-3-*iso*propyl-Δ^2- or 1 : 3-dimethyl-3-*iso*propyl-Δ^1-*cyclo*pentene. Similar fission of a tetramethylene ring occurs, but less readily, pinane giving mainly *p*-cymene (oxidised to terephthalic acid), but the pentamethylene ring in fenchane or *iso*bornylane is unattacked. Similar dehydrogenation of *cyclo*fenchene causes partial fission of the trimethylene ring, giving a mixture of α- and β-fenchenes. J. W. BAKER.

Higher terpene compounds. XL. Constitution of elemol. L. RUZICKA, A. G. VAN VEEN [and, in part, D. KORVER, J. VAN DER KAMP, and H. J. WIGMAN] (Annalen, 1929, **476**, 70—112).—Further details concerning the structure of elemol and its degradation products (cf. A., 1926, 1148) have been elucidated, and on the basis of the results, which are briefly summarised below, the structure I is suggested for elemol. Catalytic dehydrogenation of elemene



with sulphur at 140—160° and removal of the thionaphthen derivative obtained by fractionation of the picrates and treatment with mercuric acetate in alcohol yields eudalene, which, together with an azulene, is obtained in 25% yield by two successive dehydrogenations with selenium at 280°, cyclisation of the side-chains occurring to form a second ring. Attempts to effect dehydrogenation of tetrahydroelemene to the corresponding benzene hydrocarbon were unsuccessful with a palladised-charcoal catalyst which was effective with hexahydrozingiberene. The formation of two isomeric tetrahydroelemenes (*loc. cit.*) by elimination of water (or hydrogen chloride) from tetrahydroelemol (or its chloride) receives support from the observation that elimination of hydrogen chloride from 8-chloro-*p*-menthane occurs in both possible directions, ozonolysis of the product giving formaldehyde, acetone, and ketones which are further oxidised by hypobromite to hexahydro-*p*-toluic and β-methyladipic acids. The mixed tetrahydroelemenes obtained either by the action of (1) 95% formic acid or magnesium phenyl bromide on tetrahydroelemol or (2) methyl-alcoholic potassium hydroxide or aniline on the corresponding chloride, give the same products on ozonolysis at 0° (cf. *loc. cit.*). Of these the ketone $C_{12}H_{22}O$, now identified as 4 : 4-*dimethyl*-3-sec.-*butyl*-cyclo*hexanone* (II) (*picrate* of *aminoguanidine* compound, m. p. 210°), forms a *benzylidene* derivative, b. p. 175—180°/0·5 mm., which ozonisation converts into the same dibasic acid, $C_{12}H_{22}O_4$ (III), as is obtained by hypobromite oxidation of the keto-acid, $[C_{10}H_{15}](CO_2H)(COPr^{\beta})$ (*loc. cit.*), obtained from the keto-aldehyde also formed in the original ozonolysis of tetrahydroelemene. The dimethyl ester of III is converted by cyclisation with sodium in boiling benzene and hydrolysis of the resulting keto-ester into 4 : 4-*dimethyl*-3-sec.-*butyl*cyclo*pentanone*, b. p. 90—95°/0·5 mm. (*semicarbazone*, m. p. 208°). The ketonic alcohol, $C_{14}H_{24}O_2$ (IV), b. p. 125—135°/0·3



mm., obtained together with formaldehyde, by ozonolysis of elemol, is reduced by hydrogen and platinum-

black in ethyl acetate to 2 : 2-*dimethyl*-5-(α-*hydroxy*-iso*propyl*)cyclo*hexyl ethyl ketone* (V), b. p. 132°/0·3 mm. (amorphous *semicarbazone*), which is converted by formic acid into 2 : 2-*dimethyl*-5-iso*propylidene*-cyclo*hexyl ethyl ketone* (VI), b. p. 125—135°/12 mm. (*semicarbazone*, m. p. 172°). This is reduced catalytically to 2 : 2-*dimethyl*-5-iso*propyl*cyclo*hexyl ethyl ketone* (VII), b. p. 131—133°/18 mm., d_4^{15} 0·9120, n_D^{15} 1·4702 (*semicarbazone*, m. p. 172°; *picrate* of *aminoguanidine* compound, m. p. 145°). The latter is also obtained by catalytic reduction of the doubly unsaturated ketone, $C_{14}H_{22}O$ (2 : 2-*dimethyl*-5-iso*propylidene*-Δ^3-cyclo*hexenyl ethyl ketone*), obtained by the action of formic acid on IV, but addition of hydrogen to the second double linking occurs only with difficulty. The *benzylidene* derivative, b. p. 175—180°/0·3 mm., of VII is converted by ozone and chromic oxide in acetic acid into 2 : 2-*dimethyl*-5-iso*propyl*cyclo*hexane*-1-*carboxylic acid* (*chloride*, b. p. 135°/12 mm.; amorphous *amide*), isolated as its *methyl* ester, b. p. 128—135°/12 mm. Catalytic reduction of elemol to its tetrahydro-derivative proceeds smoothly only with specimens purified through the benzoate or phenylurethane, specimens obtained merely by fractionation yielding *dihydroelemol*, b. p. 138°/12 mm., m. p. 47°, d_4^{15} 0·934, n_D^{15} 1·4925 (erroneously described by Jansch and Fantl, A., 1923, i, 814, as a dicyclic alcohol), which is actually a mixture of isomerides, an exocyclic double linking still being present. Thus ozonolysis of dihydroelemol gives acetaldehyde and formaldehyde, whilst by treatment of the main fraction of the neutral product in various ways the same (impure) semicarbazone, m. p. 171°, of V is obtained, although the pure ketone did not form a crystalline semicarbazone. This is converted by successive treatment with oxalic and 95% formic acids into VI, which is also obtained from the neutral fraction, b. p. 125—150°/3 mm., of the ozonolysis after oxidation with permanganate and successive treatment with alkali and 95% formic acid. The acid fraction of the products of ozonolysis of dihydroelemol is an *acid*, $C_{13}H_{24}O_3$, m. p. 145°, which is probably a γ- or δ-hydroxy-acid, since it lactonises by distillation in a high vacuum, and is converted by heating with either 85% formic acid or methyl-alcoholic potassium hydroxide into a *lactone*, $C_{13}H_{22}O_2$, m. p. 37°, b. p. 109—111°/high vacuum. When the ethereal extract of the acidified solution of this lactone in dilute alkali is evaporated on a water-bath, the original lactone is regenerated, but evaporation at the ordinary temperature in a vacuum yields a *substance*, m. p. 118°, which, however, is still contaminated with the lactone. The formation of the acid $C_{13}H_{24}O_3$ and acetaldehyde, together with the fact that from the products of oxidation of elemol with manganese dioxide and sulphuric acid trimellitic acid is isolated in small yield, suggests the presence of a structural isomeric type with a carbon skeleton VIII, and the question of the homogeneity of elemol is discussed. The position assigned to the hydroxyl group is confirmed by the observation that elemol and its tetrahydro-derivative, like 8-hydroxy-*p*-menthane, are readily converted into benzoates (80% yield) with benzoyl chloride and pyridine, whilst with 4-hydroxy-*p*-menthane only a 10% yield of the ester is obtained. No dimethylmalonic acid could be isolated by the successive action of formic acid and potassium permanganate on elemene, oxalic acid being the only product. Elemene is not reduced by sodium and amyl alcohol at 120—200°, and gives only a trace of condensation product with ethyl diazoacetate.

J. W. Baker.

Constitution of ψ-baptisin. E. Späth and O. Schmidt (Monatsh., 1929, **53** and **54**, 454—470).—When anhydrous ψ-baptisin (I), $C_{28}H_{30}O_{14}$, $[\alpha]_D^{14}$ −98·1° in methyl alcohol (crystallises also $+3H_2O$, which are lost at 120°) (cf. Gorter, A., 1897, i, 627; 1898, i, 39; 1906, i, 973; 1908, i, 97), is heated in a vacuum it sinters at 140°, melts at 140—150°, resolidifies at 180—210°, and re-melts at 249—251° with partial decomp. Hydrolysis of I with 10% sulphuric acid gives dextrose, rhamnose, and ψ-baptigenin (II), $C_{16}H_{10}O_5$ (cf. *loc. cit.*), m. p. 296—298° [acetyl derivative, m. p. 173°; the *ethyl ether* (III), m. p. 172°, and not ψ-baptigin (Gorter, *loc. cit.*), is obtained by the action of ethyl iodide on the sodium derivative of II]. Boiling 5% potassium hydroxide decomposes II, forming formic acid and ψ-baptigenetin (IV), $C_{15}H_{12}O_5$, m. p. 151° [*methyl ether*, m. p. 145°; *dimethyl ether*; *ethyl ether*, m. p. 129°, obtained also by decomposition of III with potassium hydroxide solution; *oxime*, m. p. 206° (slight decomp.)]. Treatment of IV with nitric acid (*d* 1·5) gives styphnic acid, whilst oxidation with 1% potassium permanganate at the ordinary temperature affords piperonylic acid. It is shown that IV is 2 : 4-*dihydroxyphenyl* 3 : 4-*methylenedioxybenzyl ketone* by the Hoesch condensation of resorcinol and 3 : 4-methylenedioxyphenylacetonitrile. Resorcinol and β-3 : 4-methylenedioxyphenylpropionitrile afford similarly 2 : 4-*dihydroxyphenyl* β-3 : 4-*methylenedioxyphenylethyl ketone*, m. p. 130° (*oxime*, m. p. 192—194°, not sharp). ψ-Baptigenin is, therefore, 7-*hydroxy*-3′ : 4′-*methylenedioxy*-iso*flavone*, and ψ-baptisin is the corresponding sugar derivative.

H. Burton.

α-Furfuryl chloride and derivatives. II. W. R. Kirner and G. H. Richter (J. Amer. Chem. Soc., 1929, **51**, 3131—3135).—The following compounds are prepared from α-furfuryl chloride (2-chloromethylfuran) (A., 1928, 1019) by the usual methods: ethyl α-furfurylmalonate, b. p. 125·5—127°/4 mm., d_4^{20} 1·10999, n_D^{20} 1·4591, ethylated to *ethyl α-furfurylethylmalonate*, b. p. 135·5—136·5°/5 mm.; 5-α-furfuryl-, m. p. 186—187·5° (lit. 193°), and 5-α-*furfuryl*-5-*ethyl-barbituric acids*, m. p. 144·5—145° [prepared from the above esters by the method of Dox and Yoder (A., 1922, i, 681)]; *ethyl α-furfurylacetoacetate*, b. p. 111—111·5°/4 mm., d_4^{20} 1·10366, n_D^{20} 1·4718 (hydrolysed to β-2-furylpropionic acid and α-furfurylacetone); *α-furylacetonitrile*, b. p. 74—75°/27 mm., d_4^{20} 1·04627, n_D^{20} 1·4833 (hydrolysed to 2-*furylacetic acid*, m. p. 108·5—109·5°), and *α-furfuryl thiocyanate*, b. p. 111·5—112·5°/27 mm., d_4^{20} 1·18709, n_D^{20} 1·5614. Condensation of α-furfuryl chloride with thiocarbamide and hydrolysis of the resulting product gives *α-furfuryl mercaptan*, b. p. 84°/65 mm., d_4^{20} 1·13186, n_D^{20} 1·5329, ethylated to *α-furfuryl ethyl sulphide*, b. p. 90·5—91°, d_4^{20} 1·04958, n_D^{20} 1·5140.

H. Burton.

1 : 6-Addition of hydrogen to unsaturated 1 : 4-diketones. R. E. LUTZ (J. Amer. Chem. Soc., 1929, **51**, 3008—3023).—Reduction of a series of unsaturated 1 : 4-diketones under various conditions gives chiefly the corresponding furan (in some cases exclusively). The corresponding saturated diketones afford little or no furan under the same conditions, indicating that 1 : 6-addition of hydrogen occurs thus: O:C·C:C·C:O + H_2 ⟶ HO·C:C·C:C·OH $\xrightarrow{-H_2O}$ ·C:C·C:C·. When a mixture of saturated ketone and furan is obtained, these compounds are, presumably, independent end-products of the reaction.

Bromine and *trans*-αβ-di-*p*-chlorobenzoylethylene in chloroform solution at 60° yield approximately equal amounts of *meso*- (Conant and Lutz, A., 1925, i, 681) and dl-αβ-*dibromo*-αβ-*di*-p-*chlorobenzoylethane*, m. p. 124·5°; in acetic acid solution the main product is the *meso*-derivative (cf. Lutz, A., 1927, 59). Treatment of the dibromoethane with sodium methoxide affords α-*methoxy*-αβ-*di*-p-*chlorobenzoylethylene* (I), m. p. 130°. When an alcoholic suspension of dibromodibenzoylethane is treated with an excess of phenol dissolved in 2·5% alcoholic sodium ethoxide a 63% yield of α-phenoxy-αβ-dibenzoylethylene (II) is obtained. Similarly, α-*p*-tolyloxy- (III) and α-m-*methoxyphenoxy*-αβ-*dibenzoylethylene*, m. p. 110° (10% yield), are prepared, using *p*-cresol and resorcinol monomethyl ether, respectively. A new α-m-*tolyloxy*-αβ-*dibenzoylethylene*, m. p. 95°, is obtained in addition to the form of m. p. 103° (Conant and Lutz, *loc. cit.*), when *m*-cresol is used in the above reaction; reduction of both forms by various reagents gives the same α-*m*-tolyloxy-αβ-dibenzoylethane (*loc. cit.*).

Reduction of α-methoxy-αβ-dibenzoylethylene with aqueous-alcoholic sodium hyposulphite (method *a*) gives mainly α-methoxy-αβ-dibenzoylethane (IV), which when heated at 210—215° decomposes into methyl alcohol and αβ-dibenzoylethylene. Reduction with zinc dust and acetic acid (sometimes with added acetic anhydride) (method *b*) affords 3-methoxy-2 : 5-diphenylfuran (V), whilst with alcoholic chromous chloride (method *c*) IV and V are obtained in varying amounts, depending on the conditions. αβ-Dibenzoyl-α-phenylethylene gives (*a*) mainly αβ-dibenzoyl-α-phenylethane, (*b*) a mixture of the ethane and 2 : 3 : 5-triphenylfuran. α-Methoxy-αβ-di-*p*-bromobenzoylethylene furnishes (*b*) mainly 3-*methoxy*-2 : 5-*di*-p-*bromophenylfuran*, m. p. 113°, (*a*) and (*c*) mixtures of the furan and α-*methoxy*-αβ-*di*-p-*bromobenzoylethane*, m. p. 72° (decomposes at 210—220° into methyl alcohol and αβ-di-*p*-bromobenzoylethylene). Reduction of I yields (*a*) α-*methoxy*-αβ-*di*-p-*chlorobenzoylethane* (VI), m. p. 58—59° (decomposes at 200°, forming methyl alcohol and αβ-di-*p*-chlorobenzoylethylene), or 3-*methoxy*-2 : 5-*di*-p-*chlorophenylfuran* (VII), m. p. 113°, according to the conditions, (*b*) a mixture of VI and VII. Reduction of II by method *b* gives a mixture of α-*phenoxy*-αβ-*dibenzoylethylene*, m. p. 120° (decomposes at 270° yielding phenol and dibenzoylethylene), and 3-*phenoxy*-2 : 5-*diphenylfuran*, m. p. 91°; similarly III furnishes a mixture of α-p-*tolyloxy*-αβ-*dibenzoylethane*, m. p. 108·5°, and 3-p-*tolyloxy*-2 : 5-*diphenylfuran*, m. p. 113°. In the above reductions variations in the conditions cause variations in the products formed. Treatment of the substituted ethanes under identical conditions gives either unchanged material or small amounts of furan; with the α-methoxy- and α-aryloxy-αβ-diaroylethanes elimination of the methoxy- or aryloxy-group occurs to varying extents.

α-Benzoyl-β-trimethylacetylstyrene is reduced by zinc dust and acetic acid and anhydride to desylpinacolin (Boon, J.C.S., 1910, **97**, 1258) which is unstable towards hot hydriodic acid. H. BURTON.

Synthetical experiments in chromone group. I. New syntheses of 7 : 8-dihydroxy-2-methylchromone and 7 : 8-dihydroxyflavone. K. VENKATARAMAN (J.C.S., 1929, 2219—2223).—The preparations of the above substances from gallacetophenone and sodium acetate–acetic anhydride or sodium benzoate–benzoic anhydride mixtures respectively are described. The m. p. of the two hydroxyl compounds are given as 241—242°, 246°, and of their corresponding diacetyl derivatives as 189° (after shrinking at 110° and losing water of crystallisation) and 194° (lit. 243°, 239°, 120°, 193°, respectively). The reactions and tinctorial properties of these substances are described in detail. R. J. W. LE FÈVRE.

Grape pigments. VI. Anthocyans in Ives grapes. R. L. SHRINER and R. J. ANDERSON (N.Y. Agric. Exp. Sta. Tech. Bull., 1929, No. 152, 11 pp.).—See this vol., 192.

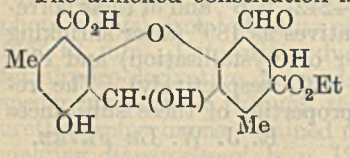
Constitution of cetraric acid. G. KOLLER and E. KRAKAUER (Monatsh., 1929, **53** and **54**, 931—951).—When cetraric acid (I), $C_{20}H_{18}O_9$ (Zopf, A., 1898, i, 489; Hesse, A., 1898, i, 531; 1901, i, 85; 1905, i, 138; Simon, A., 1903, i, 98; 1906, i, 961), is heated with hydriodic acid and phenol at 140—150°, ethyl iodide is formed and 2 mols. of carbon dioxide are eliminated. The ethoxyl group is present in the ester form, since I is hydrolysed by 10% sodium carbonate solution (in a current of hydrogen) at 50°. Acetylation of I with acetic anhydride and pyridine gives a *diacetate*. Methylation of I with methyl sulphate at 65—70° affords *methyl monomethylcetrarate* (II), $C_{22}H_{22}O_9$, m. p. 191—192° after sintering at 189° (contains a phenolic hydroxyl), and *methyl dimethylcetrarate* (III), $C_{23}H_{24}O_9$, m. p. 151—152°; a *compound* (IV), $C_{25}H_{30}O_{10}$, m. p. 99° (*ferrichloride*), is formed as a by-product. Further methylation of II gives a mixture of III and IV; similarly, III yields IV. The production of IV from III indicates the presence of an oxide ring in III; this undergoes fission. A free hydroxyl group is shown to be present in III (Zerevitinov), but phenolic groups are absent. The *oximes* of III and IV have m. p. 189—190° (decomp.) and 174—175°, respectively, and since oxidation of III with potassium permanganate in acetone solution affords an *acid*, $C_{23}H_{24}O_{10}$, m. p. 212—213°, an aldehyde group must be present in I. Reduction of I with hydrogen in presence of palladised charcoal and alcohol gives a *compound*, $C_{20}H_{20}O_9$. Energetic oxidation of III yields acidic, resinous products, but in one case (using a mixture of III and IV), a *substance* (V), $C_{11}H_{12}O_6$, m. p. 167—168°, was isolated. When V is heated in a vacuum, carbon dioxide is eliminated and sparassol (methyl 6-hydroxy-4-methoxy-*o*-toluate) (Späth and Jeschki, A., 1924, i,

513) is formed. Methylation of V affords *methyl* 3 : 5-*dimethoxytoluene*-1 : 4-*dicarboxylate* (VI), m. p. 56—57°; V is probably *methyl* (2) *hydrogen* 3-*hydroxy*-5-*methoxytoluene*-2 : 4-*dicarboxylate*.

Ethyl acetonedicarboxylate condenses with ethyl acetoacetate in presence of sodium, affording *ethyl orcinol*-2 : 4-*dicarboxylate*, m. p. 52—53°. Similar condensation of the methyl esters yields a mixture of methyl 2 : 4-dihydroxy-5-carbomethoxymethylbenzene-1 : 3-dicarboxylate (Dootson, J.C.S., 1900, 77, 1196) and *methyl orcinol*-2 : 4-*dicarboxylate*, m. p. 107—108°. Methylation of the last-named compound with diazomethane in ethereal methyl-alcoholic solution affords a mixture of *methyl* 3-*hydroxy*-5-*methoxytoluene*-2 : 4-*dicarboxylate*, m. p. 124—125°, and VI.

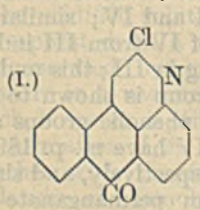
Zinc dust distillation of I in a current of hydrogen gives unidentified hydrocarbons similar to those obtained similarly from resacetophenone.

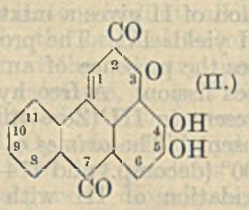
The annexed constitution is assigned provisionally to I. Methylation of the xanthhydrol hydroxyl group does not occur during the formation of II and III.



H. Burton.

Pyridanthrone and anthracoumarin syntheses. II. R. Seka, G. Schreckental, and P. S. Heilperin (Monatsh., 1929, 53 and 54, 471—484).—Treatment of 3-*phenylpropiolamido*-p-*toluic acid*, m. p. 260—261°, with sulphuric acid, first at the ordinary temperature and then at 60°, gives 13% of 4-*methylpyridanthrone*, decomp. 354—358° (for nomenclature see A., 1925, i, 1316), and a *substance*, $C_{17}H_{15}O_4N$, m. p. 215—216°, probably formed by addition of water to the triple linking of the original acid. Similarly, m-*phenylpropiolamidobenzoic acid*, m. p. 253—254°, affords pyridanthrone and the *substance*, $C_{16}H_{13}O_4N$, m. p. 207—208°. m-4′-*Methylcinnamoylamidobenzoic acid*, m. p. 264°, is converted by sulphuric acid at 90° into 9-*methylpyridanthrone*, m. p. 395—398°. Similarly, 3-4′-*methyl*- and 3-4′-*methoxycinnamoylamido*-p-*toluic acids*, m. p. 269° and 279° (decomp.), respectively, give 4 : 9-*dimethyl*-, m. p. 340° (decomp.), and 9-*methoxy*-4-*methyl-pyridanthrones*, m. p. (vac.) 312°, respectively. Treatment of pyridanthrone with phosphorus pentachloride in dichlorobenzene yields the *compound* (I), m. p. (vac.)



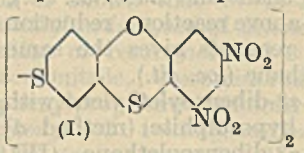


255°; methylation (methyl iodide) gives 3-*methylpyridanthrone*, m. p. 267—268°. Nitration of pyridanthrone with nitric acid (*d* 1·52) affords a *nitropyridanthrone*, m. p. 354—356°, which on boiling with aniline or *p*-toluidine furnishes *anilino*-, m. p. 385—390°, or p-*toluidino-pyridanthrone*, m. p. 388—392°, respectively. Reduction of the nitro-compound with alkaline sodium hyposulphite gives the unstable *aminopyridanthrone*, m. p. 364—368° (*benzylidene* derivative, decomp. 232—237°); attempted reduction with sodium stannite causes a considerable loss of nitrogen from the compound.

Treatment of a mixture of cinnamic and gallic acids with sulphuric acid at 90° gives 4 : 5-*dihydroxyanthracoumarin* (II), m. p. 392—394° (*diacetate*, m. p. 263—265°), described previously by Jacobsen and Julius (A., 1888, 56) as styrogallol, $C_{16}H_{10}O_5$. Cinnamic and 3 : 5-dihydroxybenzoic acids yield similarly 5-*hydroxyanthracoumarin*, m. p. 332—334° (cf. Kostanecki, A., 1888, 292) (*acetate*, m. p. 248—250°); 2 : 5-dihydroxybenzoic acid gives 6-*hydroxyanthracoumarin*, m. p. 282—285° (*acetate*, m. p. 237—239°). *m*-Hydroxycinnamic and gallic acids afford 4 : 5 : 10(or 8)-*trihydroxyanthracoumarin*, m. p. 388° (*triacetate*, m. p. 280—282°). H. Burton.

Sulphur dyes. III. Hydroxythiophenols. II. J. Pollak and E. Riesz (Monatsh., 1929, 53 and 54, 90—99).—Di- and tri-thiol derivatives of phenol are prepared by reduction of the corresponding phenolsulphonyl chlorides (cf. A., 1926, 514, 832; this vol., 60).

[With A. Nadel and (in part) R. Braun and P. Pollak.]—Phenol-2 : 4-disulphonyl chloride is reduced by zinc and hydrochloric acid in ethereal solution yielding impure 2 : 4-*dithiolphenol* (*tribenzoyl* derivative, m. p. 96°). Treatment of the *dipicryl* derivative, m. p. 155°, with alcoholic potassium hydroxide gives 2 : 4 : 2′ : 4′-*tetranitrodibenzophenoxthene* 6 : 6′-*disulphide* (I), decomp. when heated, which is reduced by sodium sulphide to a dye (light reddish-brown on cotton). Methylation of 2 : 4-dithiolphenol with methyl sulphate gives a *dimethoxydimethyldithioldiphenyl disulphide*, m. p. about 200° after some change at 77—90°. 2 : 4-*Dimethyldithiolanisole*, m. p. 38—39°, is obtained by methylation of 2 : 4-dithiolanisole (Gebauer-Fülnegg and von Meissner, A., 1928, 997) [*diacetyl*, m. p. 62°, *dicarbethoxy*-, m. p. 30—32°, *di*(*carboxymethyl*), m. p. 142—144°, and *dipicryl*, m. p. 190—194°, derivatives]. Phenol-2 : 4 : 6-trisulphonyl chloride is reduced to impure 2 : 4 : 6-*trithiolphenol* (*tetrabenzoyl* derivative, m. p. 132°; *tripicryl* derivative, decomp. 150—160° without melting). When cotton is treated with an alkaline solution of 2 : 4-dithiolphenol, dithiol-*o*-cresol, or 2 : 4 : 6-trithiolphenol, and then dyed with a concentrated solution of brilliant-green, the dyed fibre is stable towards short heating with potash soap.



[With A. Nadel.]—Chlorination of *p*-thioltoluene in hydrochloric acid suspension gives *p*-toluenesulphonyl chloride. Similarly, dithiol-*o*- and -*m*-cresols afford the corresponding cresoldisulphonyl chlorides, whilst I and its 7 : 7′-dimethyl derivative (this vol., 60) undergo fission and oxidation to phenol- and *m*-cresol-disulphonyl chlorides. The sulphur dyes from *o*- or *m*-cresol, sulphur, and sodium sulphide (G.P. 102,897) are chlorinated to *o*- or *m*-cresoldisulphonyl chlorides, but the corresponding dye from phenol gives *diphenyl*-4 : 4′-*disulphonyl chloride*, m. p. 203°. The diphenyl structure is presumably formed by the action of the intermediate sodium oxide on the

intermediate diphenylsulphone 4 : 4′-disulphide derivative (cf. Otto, 1886, 1031). H. BURTON.

Synthesis of 2-ethylpyrrolidine. A. MÜLLER and H. WACHS (Monatsh., 1929, **53** and **54**, 420—426).—Reduction of ethyl γ-keto-*n*-hexoate with sodium and alcohol gives *n*-hexane-αδ-diol (27% of theory) converted into *αδ-dibromo-n-hexane*, b. p. 94—97°/10 mm. Treatment of a mixture of this dibromide and *p*-toluenesulphonamide in boiling alcohol with alcoholic potassium hydroxide affords a 36% yield of the 1-p-*toluenesulphonyl* derivative, m. p. 76·9° (corr.), of *2-ethylpyrrolidine* (I), b. p. 122·4° (corr.)/744 mm., d_4^{15} 0·844, n_D^{15} 1·4442 [*hydrochloride*, m. p. below 100° (is very hygroscopic); *chloroplatinate*, decomp. 190—191°; *chloroaurate*, m. p. 96·2° (corr.); *picrate*, m. p. 85° (corr.); *phenylthiocarbimide* derivative, m. p. 89° (corr.)]. 1 : 1-*Dimethyl-2-ethylpyrrolidinium iodide*, m. p. about 220° (not sharp), is prepared from I and an excess of methyl iodide and methyl-alcoholic potassium hydroxide. The hexamethyleneimine described by Schmidt (A., 1922, i, 761) is probably I. H. BURTON.

Action of diazomethane on aromatic ketones. E. MOSETTIG and L. JOVANOVIĆ (Monatsh., 1929, **53** and **54**, 427—437; cf. this vol., 814).—Treatment of acetophenone with ethereal methyl-alcoholic diazomethane at about 20° gives phenylacetone and an oxide (probably α-phenyl-α-methylethylene oxide); the oxide is separated from unchanged acetophenone by conversion into the corresponding piperidino-alcohol (cf. *loc. cit.*) (*picrate*, m. p. 138—140°). Similarly, acetoveratrone affords small amounts of veratrylacetone [semicarbazone, m. p. 178—181° (lit. 175—176°)] and an oxide [the *picrate* (I) of the corresponding piperidino-alcohol has m. p. 150—152°]. Acetopiperone [obtained by the Friedel–Crafts reaction from methylenedioxybenzene, b. p. 55—56°/9 mm., n_D^{15} 1·5423 (*picrate*, m. p. 94—96°)], does not react with diazomethane. Piperonylacetone, b. p. 150—152°/11 mm. (*picrate*, m. p. 71—73°), yields with diazomethane about 60% of an *oxide* (probably α-3 : 4-methylenedioxybenzyl-α-methylethylene oxide), b. p. 152—156°/10 mm., converted by aqueous piperidine into *α-piperidino-β-3 : 4-methylenedioxybenzylpropan-β-ol* [*hydrochloride*, m. p. 162—163°; *picrate*, m. p. 152—154°; *chloroplatinate*, m. p. 172—175° (decomp.)], and by aqueous dimethylamine into *α-dimethylamino-β-3 : 4-methylenedioxybenzylpropan-β-ol* [*picrate*, m. p. 86—88°; *chloroplatinate*, m. p. 169—171° (decomp.)]. Veratrylacetone and diazomethane yield an *oxide* (probably α-3 : 4-dimethoxybenzyl-α-methylethylene oxide), b. p. 161—162°/10 mm., converted into *α-piperidino-β-3 : 4-dimethoxybenzylpropan-β-ol* (*picrate*, m. p. 152—153°, identical with I). H. BURTON.

Natural rotation of polarised light by optically active bases. IV. Rotation of synthetic *iso*quinoline derivatives. W. LEITHE (Monatsh., 1929, **53** and **54**, 956—962).—Reduction of 1-methyl-3 : 4-dihydro*iso*quinoline with sodium and alcohol gives dl-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, b. p. 233°/745 mm., resolved by *d*-tartaric acid into the l-*base* (I), d^{20} 1·024, $[\alpha]_D^{20}$ −79·5° (*hydrochloride*, m. p. 213°; d-*hydrogen tartrate*, m. p. 92°). dl-1-*Phenyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline*, m. p. 97°, furnishes similarly the corresponding l-*base* (II), m. p. 84°, $[\alpha]_D^{20}$ −43·4° in ether, +6·2° in alcohol (*hydrochloride*, m. p. 204°), and ethylation of *l*-α-phenylethylamine yields l-N-*ethyl-α-phenylethylamine* (III), b. p. 100° (bath)/16 mm., d^{20} 0·913, $[\alpha]_D^{20}$ −60·0°.

The effect of ring closure (comparison of III and I) is to cause an increase in the molecular rotatory power. Introduction of a second phenyl group into the ring system (as in II) lowers the rotatory power, probably because the molecule thereby acquires an increased symmetry. The rotatory powers of I in various solvents are analogous to those of phenylethylamine, whilst those of II are similar to pipecoline (cf. A., 1928, 1022; this vol., 647). The specific solution volume of II is highest in *cyclo*hexane; the orders of the values in various solvents agree with the rotatory powers in the same solvents (cf. this vol., 1079). H. BURTON.

Catalytic hydrogenation of 1-methylpyrrole and dehydrogenation of 1-methylpyrrolidine. N. D. ZELINSKI and J. K. JURJEV (Ber., 1929, **62**, [*B*], 2589—2590).—If pyrrole mixed with hydrogen is passed over palladised asbestos at 160°, smooth hydrogenation to pyrrolidine does not occur; the last-named compound is mainly decomposed with evolution of ammonia. Under these conditions, 1-methylpyrrole affords 1-methylpyrrolidine, b. p. 80°, d_4^{20} 0·8399, n^{20} 1·4480, in very good yield. Repeated passage of 1-methylpyrrolidine over palladised asbestos at 160° causes production of a certain amount of 1-methylpyrrole; the process becomes quantitative at 250°. H. WREN.

Additive compounds of organic bases with salts of heavy metals. J. V. DUBSKY and A. RABAS (Coll. Czech. Chem. Comm., 1929, **1**, 528—537).—Zinc chloride, either anhydrous or in aqueous solution, combines with pyridine to give the *compound* $ZnCl_2,2C_5H_5N$, m. p. 210—213°. Aniline and aqueous zinc chloride yield $ZnCl_2,2PhNH_2$, m. p. 266° (decomp.). *o*- and *p*-Toluidines in alcoholic solution combine similarly with (aqueous) zinc chloride to form the *compounds* $ZnCl_2,2(o\text{-}Me\cdot C_6H_4\cdot NH_2)$, m. p. 234°, and $ZnCl_2,2(p\text{-}Me\cdot C_6H_4\cdot NH_2)$, m. p. 267°, respectively. The corresponding hydrated compounds described by Lachowicz and Bandrowski (A., 1888, 1281) are non-existent. Zinc chloride (1 mol.) in aqueous solution and quinoline (2 mols.) in alcohol give the *compound* $ZnCl_2,2C_9H_7N$, m. p. 210°. Aqueous cupric sulphate and β-naphthylamine in benzene give the substance $CuSO_4,2(\beta\text{-}NH_2\cdot C_{10}H_7)$, m. p. 260° (decomp.), whilst with aniline the compound $CuSO_4,2PhNH_2$, m. p. 260° (decomp.), is produced. Dimethylaniline (2 mols.) with aqueous zinc chloride or cupric sulphate (1 mol.) yielded basic salts. An attempt to prepare $ZnCl_2,2C_5H_5N,2AcOH$ from zinc chloride in dilute acetic acid solution and pyridine afforded the compound $ZnCl_2,2C_5H_5N$, m. p. 196°. Contrary to the statement of Lachowicz and Bandrowski (*loc cit.*), zinc chloride (1 mol.) combines with glycine (0·75 mol.) to give the substance $ZnCl_2,3(NH_2\cdot CH_2\cdot CO_2H)$, m. p. 235° (decomp.). A. I. VOGEL.

4-Piperonyl-2 : 6-dimethylpyridine. A. STEIN and F. ULZER (Wiss. Mitt. Oesterr. Heilsmittelstelle,

1928, 15—16, 1929, 1—5; Chem. Zentr., 1929, i, 2778—2779).—Interaction of ethyl acetoacetate (2 mols.), piperonal (1 mol.), and alcoholic ammonia (1 mol.) affords ethyl 4-piperonyl-2 : 6-dimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate, which, by treatment in alcoholic suspension with nitrous acid affords ethyl 4-piperonyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate. Hydrolysis with alcoholic potassium hydroxide affords the acid ester (hydrochloride), which may be esterified with diazomethane. If the hydrolysis with alcoholic alkali is followed by long-continued hydrolysis with aqueous potassium hydroxide the dicarboxylic acid is produced. Distillation of the dicarboxylic acid with soda-lime affords the piperonyl-lutidine, which is formulated as 4-3′ : 4′-methylenedioxyphenyl-2 : 6-dimethylpyridine.

A. A. ELDRIDGE.

Manufacture of pyridines. I. OSTROMISSLENSKY etc.—See B., 1929, 958.

1 : 3-Dicarbonyl compounds. I. Mechanism of cyanoacetamide and cyanoacetic ester condensations. J. C. BARDHAN (J.C.S., 1929, 2223—2232).—Condensation of ethyl acetylpyruvate with cyanoacetamide in alcoholic solution containing diethylamine gave *ethyl 3-cyano-6-methyl-2-pyridone-4-carboxylate*, m. p. 219° (5-*bromo*-derivative, decomp. 232—233°), which by the action of methyl iodide, sodium methoxide, and methyl alcohol gave *ethyl 3-cyano-1 : 6-dimethyl-2-pyridone-4-carboxylate*, m. p. 177—179°. The last-named compound was converted by hydrochloric acid at 150—160° into *6-methyl-2-pyridone-4-carboxylic acid*, m. p. 314° (*methyl* ester, m. p. 228°), from which 2-chloro-6-methylpyridine-4-carboxylic acid (identical with the product of oxidation of 2-chloro-4 : 6-dimethylpyridine) was obtained by treatment with phosphoryl chloride and phosphorus pentachloride, followed by digestion with water.

Benzoylacetone and cyanoacetamide gave a mixed condensation product, m. p. 270—286°, resolved by fractional crystallisation into 3-cyano-6-phenyl-4-methyl-2-pyridone, m. p. 310° (decomp.) (*methyl* derivative, m. p. 267°), which when boiled with 80% sulphuric acid gave *6-phenyl-4-methyl-2-pyridone*, m. p. 182—183°, and 3-cyano-4-phenyl-6-methyl-2-pyridone, m. p. 249° (lit. 266—267°), identified by heating with hydrochloric acid, when 4-phenyl-6-methyl-2-pyridone was obtained.

Propionylacetophenone and cyanoacetamide yielded chiefly *3-cyano-6-phenyl-4-ethyl-2-pyridone*, m. p. 240° (decomp.).

Propionylacetone and cyanoacetamide condensed spontaneously, giving *3-cyano-4-methyl-6-ethyl-2-pyridone*, m. p. 240—241°, which when heated with concentrated hydrochloric acid passed into *4-methyl-6-ethyl-2-pyridone*, m. p. 144°; this in turn yielded *2-chloro-4-methyl-6-ethylpyridine*, b. p. 224°/765 mm., 124°/35 mm., by treatment with phosphorus pentachloride and water etc. The last-named compound, when heated with hydriodic acid (*d* 1·94) and red phosphorus or when its vapours were passed in a current of hydrogen over zinc dust heated to redness, was transformed into 4-methyl-6-ethylpyridine (picrate, m. p. 122—123°; lit. 115—116°, 120—121°).

C-Ethylacetylacetone and cyanoacetamide condensed readily, giving *3-cyano-4 : 6-dimethyl-5-ethyl-2-pyridone*, m. p. 272° (decomp. after previous darkening), and, by hydrolysis of this with hydrochloric acid, *4 : 6-dimethyl-5-ethyl-2-pyridone*, m. p. 150°.

Condensation of acetylacetone and cyanoacetamide produced successively 3-cyano-ψ-lutidocarbostyril, m. p. 289°, and ψ-lutidocarbostyril, m. p. 180—181°.

α-Cyanopropionamide (from ethyl α-cyanopropionate by the action of concentrated aqueous ammonia), m. p. 100—101° (lit. 81°, 105°), would not react with acetylacetone.

Propionylphenylacetylene condensed with ethyl malonate in ethyl-alcoholic sodium ethoxide solution, giving *ethyl 4-phenyl-6-ethyl-α-pyrone-3-carboxylate*, m. p. 72—73°, and with the sodium derivative prepared by addition of sodium ethoxide in absolute-alcoholic solution to cyanoacetamide in boiling alcohol, to form *3-cyano-4-phenyl-6-ethyl-2-pyridone*, m. p. 260°.

The results show that the β-diketones react with cyanoacetamide mainly in the keto-phase, producing in each case only one pyridine derivative, and also that the condensation is effected by the carbonyl group adjacent to the positive alkyl group in the diketone.

R. J. W. LE FÈVRE.

Manufacture of 6-ethoxy-2 : 4-dimethylquinoline. H. T. CLARKE and others.—See B., 1929, 935.

Unilaterally acylated diamines of therapeutic activity [quinoline derivatives]. I. G. FARBENIND. A.-G.—See B., 1929, 958.

Pharmaceutical products [quinolines and piperidines]. I. G. FARBENIND. A.-G.—See B., 1929, 958.

Vat dyes of the α-naphthaquinone [carbazole] series. I. G. FARBENIND. A.-G.—See B., 1929, 890.

Formation of 1-phenyl-5-methyl-3-pyrazolone. K. BRUNNER and H. MOSER (Monatsh., 1929, **53** and **54**, 682—686).—When a mixture of acetylphenylhydrazine, magnesium oxide, and fused potassium acetate is heated at 300—320° in a current of hydrogen, about 7·5% of 1-phenyl-5-methyl-3-pyrazolone (I), m. p. 166—167°, is obtained. The probable reaction is: $2NHPh{\cdot}NHAc \rightarrow NHPh{\cdot}NH_2 + H_2O + (I)$.

H. BURTON.

Derivatives of creatinine and diketopiperazine. L. R. RICHARDSON and C. E. WELCH [with S. CALVERT] (J. Amer. Chem. Soc., 1929, **51**, 3074—3079).—When creatinine is heated with aromatic aldehydes at 150° the corresponding 5-arylidene derivatives are formed. The benzylidene, m. p. 244° (formed similarly from creatinine and benzylideneaniline), m-*nitrobenzylidene*, decomp. 288°, and *4-hydroxy-3-methoxybenzylidene*, m. p. 267° (decomp.), derivatives are described. Diketopiperazine condenses with aromatic aldehydes only in presence of acetic anhydride and sodium acetate. The following are described: 2 : 5-*diketo-3 : 6-di-4′-acetoxy-3′-methoxybenzylidene-*, decomp. 310° after darkening at 290°; *-dicinnamylidene-*, decomp. 350° after darkening at 335°; *-dipiperonylidene-*, decomp. 320° after darkening at 290°; *-di-m-acetoxybenzylidene-*, m. p. 255°; *-di-m-toluylidene-*, decomp. 320° after darkening at 305°, and *-di-o-chlorobenzylidene-piperazine*, decomp. 340° after darkening at 330°. Aliphatic aldehydes do not give simple

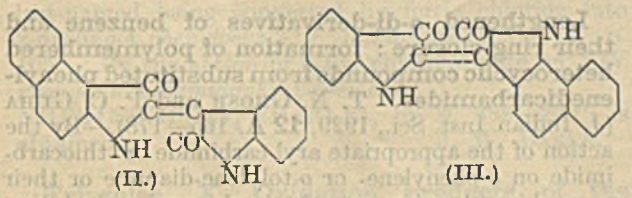
3 : 6-dialkylidene derivatives, poor yields of condensation products are obtained with *o*-hydroxybenzaldehydes, and condensation does not occur with amidines. Diketopiperazine furnishes a *bis-α-naphthylcarbimide* derivative, m. p. 232° (decomp.), which with *m*-nitrobenzaldehyde and *m*-tolualdehyde (as above) undergoes hydrolysis and subsequent condensation to the 3 : 6-diarylidene derivatives. The dienol form of diketopiperazine is therefore the 2 : 5-dihydroxy-compound. H. BURTON.

Naphtho*iso*indigotins. A. WAHL and J. LOBECK (Ann. Chim., 1929, [x], 12, 156—202).—In part, a more detailed account of work already described (this vol., 938). The following facts appear to be new: α-benzisatan (α-naphthisatan) has m. p. above 200° with blackening, whilst β-benzisatan, m. p. 199°, may be obtained by condensation of α-benzisatin and oxindole with hydrochloric acid or potassium hydroxide. Whilst α-benzisatin by treatment with hydrogen sulphide yields αα′-dibenzdisulphisatide, convertible into αα′-dibenz*iso*indigotin (I) (*loc. cit.*), β-benzisatin by similar treatment yields a sulphur compound, probably *ββ′-dibenzdisulphisatide*, which could not be converted into the corresponding ββ′-dibenz*iso*indigotin. Sulphuric acid converts I into *αα′-dibenziso*indigotindisulphonic acid (*sodium, potassium, barium*, and *silver* salts).

β-Naphthylamine and ethyl mesoxalate condense in 50% acetic acid to give *ethyl di-β-naphthylaminomalonate*, m. p. 150—152°, converted by hot glacial acetic acid into ethyl β-benzoxindole-3-carboxylate (ethyl β-naphthoxindole-3-carboxylate, cf. A., 1919, i, 457), also obtained directly from the reactants in glacial acetic acid. In the presence of dilute hydrochloric acid β-naphthylamine (1 mol.) and ethyl mesoxalate (2 mols.) undergo an oxidative reaction leading to β-benzisatin.

The action of cuprous chloride in acetic acid appears to be a general method for the conversion of disulphisatides into *iso*indigotins; in this way *pp′*-dimethyl-, *oo′*-dimethyl-, and *oo′*-dichloro-disulphisatide yield, respectively, pp′-*dimethyl*iso*indigotin* (55%), oo′-*dimethyl*iso*indigotin* (43%), and oo′-*dichloro*iso*indigotin* (55%), whilst disulphisatide (A., 1924, i, 322) affords *iso*indigotin (50%); ββ′-dibenzdisulphisatide furnishes an unstable, bluish-black, amorphous *substance*.

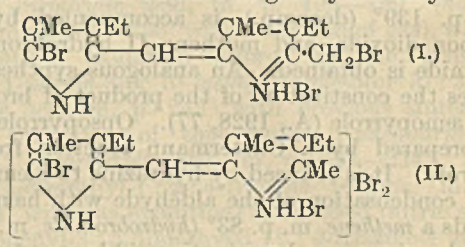
The method of Wahl and Bagard (Bull. Soc. chim., 1909, [iv], 5, 1039) has been applied to the synthesis of β-benzindirubin. β-Benzisatin and phosphorus pentachloride in chlorobenzene give *β-benzisatin chloride*, which reacts with oxindole in the same medium at 100—132° to furnish *β-benzindirubin* (II). α-Benzisatin by similar treatment gives an amorphous product. Condensation of α-benzisatin with



(II.) (III.)

indoxylic acid in the presence of hydrochloric acid in 50% alcohol gives *α-benzindirubin* (III). The corresponding β-benzindirubin could not be obtained, condensation of β-benzisatin and indoxylic acid under various conditions yielding only normal indirubin. C. W. SHOPPEE.

Halogenated pyrroles. VII. Halogenated methenes of cryptopyrrole and their constitution. H. FISCHER, E. BAUMANN, and H. J. RIEDL (Annalen, 1929, 475, 205—241).—The two brominated methene hydrobromides obtained by bromination of cryptopyrrole (A., 1926, 1261) have been further investigated and their constitution has been elucidated. Methene I hydrobromide, m. p. above 350°, is assigned the constitution I. It is formed in good yield only when



the bromination takes place at higher temperatures, and it yields more ætioporphyrin than methene II hydrobromide. Both facts support the assumption of bromination in the side-chain. When the preparation of the free base is attempted by treatment of the hydrobromide with alcohol and then with chloroform and sodium hydroxide, the product is a *base*, m. p. 73° [*picrate*, m. p. 145° (decomp.)], which is probably the compound containing an ethoxyl group in the side-chain mixed with a small amount of the hydroxy-compound. The analogous, partly methoxylated *base*, m. p. 84°, is obtained similarly. Treatment of the base, m. p. 73°, with bromine (1 mol.) in acetic acid yields methene I hydrobromide. Treatment with zinc dust in alcohol gives a *zinc* compound, $(C_{18}H_{24}ON_2Br)_2Zn$, m. p. 140°. Bromination of methene I hydrobromide yields a *perbromide*, $C_{16}H_{20}N_2Br_4$, m. p. 98°.

The second methene hydrobromide, m. p. 149°, is a perbromide, since it brominates acetone in the cold. It is assigned the constitution II. If this perbromide is warmed with alcohol containing a little sodium hydroxide it yields *methene II hydrobromide*, m. p. 215° (decomp.), which can be brominated in acetic acid at 50° to give the perbromide, or in boiling solution to give methene I hydrobromide, whilst treatment with sodium hydroxide solution and chloroform yields *methene II base*, m. p. 103° [*hydrochloride*, m. p. 212°; *hydriodide*, m. p. 213°; *picrate*, m. p. 188° (decomp.)]. Attempted debromination of this base by heating with aniline in toluene yields the *anilino*-derivative, m. p. 116° [*hydrochloride*, m. p. 234°; *hydrobromide*, m. p. 240°; *picrate*, m. p. 209°; complex salts with *copper*, $(C_{22}H_{26}N_3)_2Cu$, and with *iron*, *cobalt*, and *nickel*], from which the anilino-group cannot be eliminated. With zinc in alcohol the base yields a *zinc* compound, $(C_{16}H_{20}N_2Br)_2Zn$, m. p. 180°. The relationship of the two products of bromination of cryptopyrrole is shown by the fact that each yields the methene II hydriodide when heated with hydriodic acid in acetic acid. Again, the methene II base, by bromination in the cold with 1 or 2 mols. of bromine,

yields the hydrobromide or the perbromide, but in boiling acetic acid the methene I hydrobromide is formed, whilst the methene II hydrobromide perbromide, when boiled in acetic acid, yields, by migration of a bromine atom, methene I hydrobromide. Consistently poor yields of ætioporphyrin are given by methene II derivatives with the usual reagents, and from methene II hydrobromide perbromide and sulphuric acid the methene II base is produced.

The synthesis of methene II hydrobromide has been carried out by condensing cryptopyrrole with 4-methyl-3-ethylpyrrole-2-aldehyde-5-carboxylic acid. Bromination of the resulting *methenecarboxylic acid*, m. p. 139° (decomp.), is accompanied by loss of carbon dioxide, and methene II hydrobromide perbromide is obtained. An analogous synthesis establishes the constitution of the product of bromination of hæmopyrrole (A., 1928, 77). Opsopyrrolealdehyde is prepared by a Gattermann reaction from opsopyrrole. It is reduced by hydrazine to hæmopyrrole, and condensation of the aldehyde with hæmopyrrole yields a *methene*, m. p. 83° (*hydrobromide*, m. p. 188°), which gives on bromination (2-bromo-4-methyl-3-ethylpyrryl)-(2:3-dimethyl-4-ethylpyrrolenyl)methene hydrobromide perbromide, identical with the product from hæmopyrrole.

A method of synthesis of the corresponding methanes is described. The interaction of cryptopyrrole and magnesium ethyl bromide yields magnesium 5-cryptopyrryl bromide, which reacts with ethyl 4-methyl-2-bromomethyl-3-ethylpyrrole-5-carboxylate to yield (5-*carbethoxy*-4-*methyl*-3-*ethyl*)-(3′ : 5′-*dimethyl*-4′-*ethyl*)-2 : 2′-*dipyrrylmethane*, m. p. 142°, which gives phyllopyrrole when heated with hydriodic acid and phosphonium iodide. The *methanecarboxylic acid*, m. p. 145° (decomp.), obtained by hydrolysis of the ester, yields on bromination, with simultaneous loss of carbon dioxide, the above methene II hydrobromide perbromide. Interaction of the same Grignard compound with ethyl 4-methyl-3-ββ-dicarbethoxyethyl-2-bromomethylpyrrole-5-carboxylate (A., 1927, 1088) yields (5-*carbethoxy*-4-*methyl*-3-ββ-*dicarbethoxyethyl*)-(3′ : 5′-*dimethyl*-4′-*ethyl*)-2 : 2′-*dipyrrylmethane*, m. p. 139°. (5-*Carbethoxy*-4-*methyl*-3-ββ-*dicarbethoxyethyl*)-(3′ : 5′-*dimethyl*)-2 : 2′-*dipyrrylmethane*, m. p. 105°, and (5-*carbethoxy*-4-*methyl*-3-*ethyl*)-(3′ : 5′-*dimethyl*)-2 : 2′-*dipyrrylmethane*, m. p. 129°, are obtained similarly.

Chlorinated methenes have not been isolated from the reaction between chlorine and cryptopyrrole, but the action of sulphuryl chloride on the cooled ethereal solution yields a *chlorinated methene hydrochloride*, m. p. 203° (decomp. from 170°), the constitution of which is analogous to that of the brominated methene II hydrobromide. Only traces of ætioporphyrin are formed with the usual reagents. The hydrochloride is converted into the *hydriodide*, m. p. 179° (decomp.), by the action of potassium iodide in acetic acid. Bromination yields in the cold a *perbromide*, m. p. 156°, and in hot solution a *product*, m. p. above 350°, is obtained which probably contains a 2-bromomethyl group, since it readily yields ætioporphyrin. The action of pyridine or of sodium hydroxide and chloroform on the chlorinated methene hydrochloride yields the *base*, m. p. 106° [*picrate*, m. p. 183° (decomp.)], which is converted into the same anilino-derivative as that obtained from the brominated methene II base.

4-*Methyl*-3-*ethylpyrrole*-2 : 5-*dialdehyde*, m. p. 84°, is obtained in 1% yield by the interaction of sulphuryl chloride and cryptopyrrolealdehyde in ether.

R. K. Callow.

[Isomerism of diphenylmethylpyrazoles.] E. Ott (Ber., 1929, **62**, [*B*], 2685; cf. von Auwers and Schaum, this vol., 1082).—The occurrence of isomerism which cannot be satisfactorily explained in certain classes of compounds has been noted previously by the author (A., 1912, i, 828).

H. Wren.

Synthesis of pyrimidine-nucleosides. T. B. Johnson and G. E. Hilbert (Science, 1929, **69**, 579—580).—By heating the lactim ether, 2 : 4-dimethoxypyrimidine, slightly above the b. p., it is transformed into the lactam ether, whilst treatment with methyl iodide at the ordinary temperature converts it into the lactim lactam ether, 2-keto-6-methoxy-3-methyl-2 : 3-dihydropyrimidine. The corresponding ethoxy-compound can be formed in a similar manner. Hydrolysis of these two last-named compounds with acid yields 3-methyluracil. Bromotetra-acetylglucose gives with the 2 : 4-dimethoxypyrimidine at 50° a good yield of colourless needles of the pyrimidine-nucleoside, $C_{19}H_{24}O_{11}N_2$, m. p. 221°, having the formula $CH_2(OAc)\cdot CH(OAc)\cdot CH\cdot[CH(OAc)]_2\cdot CH\cdot N\cdot CH{:}CH\cdot C(OMe){:}N\cdot CO$ (O). Intense, but not mild, hydrolysis with hydrochloric acid gives rise to reducing substances.

L. S. Theobald.

Condensation products of the benzodiazine [quinazoline] series. I. G. Farbenind. A.-G.—See B., 1929, 935.

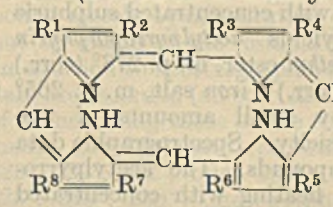
Derivatives of 6 : 7-benzo-1 : 8-naphthyridine. G. Koller and E. Strang (Monatsh., 1929, **53** and **54**, 952—955).—The condensation product, $C_{14}H_{10}O_4N_2$, from methyl 2-aminoquinoline-3-carboxylate and ethyl sodiomalonate (this vol., 76), is *methyl* 2 : 4-*dihydroxy*-6 : 7-*benzo*-1 : 8-*naphthyridine*-3-*carboxylate*. This is hydrolysed by potassium hydroxide solution to 2 : 4-*dihydroxy*-6 : 7-*benzo*-1 : 8-*naphthyridine*, m. p. 343° (elimination of carbon dioxide occurs during hydrolysis), converted by phosphoryl chloride at 100° into the 2 : 4-*dichloro*-derivative (I), m. p. 195·5—196·5°. Reduction of I with sodium and alcohol gives *octahydro*-6 : 7-*benzo*-1 : 8-*naphthyridine*, m. p. 158—159°, whilst treatment with methyl-alcoholic sodium methoxide affords 2 : 4-*dimethoxy*-6 : 7-*benzo*-1 : 8-*naphthyridine*, m. p. 152—153° [*methiodide*, m. p. 158° (decomp.)]. H. Burton.

Lengthened *o*-di-derivatives of benzene and their ring closure : formation of polymembered heterocyclic compounds from substituted phenylenedicarbamides. T. N. Ghosh and P. C. Guha (J. Indian Inst. Sci., 1929, **12 A**, 165—178).—By the action of the appropriate aryl-carbimide or -thiocarbimide on *o*-phenylene- or *o*-tolylene-diamine or their monothiocarbamides are obtained : o-*phenylene*-*di*-o- (I), m. p. 161°, and -*di*-p- (II), m. p. 178°, -*tolyl*-, *di*-

m-*xylyl-* (III), m. p. 145°, *-dimethyl-* (IV), m. p. 175°, -s-*phenylallyl-* (V), m. p. 245°, -s-*phenyl*-o-*tolyl-* (VI), m. p. 136°, -s-*phenyl*-p-*tolyl-* (VII), m. p. 165°, *-dithiocarbamides*, -s-*diphenyldicarbamide* (VIII), m. p. 220°; o-*tolylenediphenyldithiocarbamide* (IX), m. p. 142°; 1-*phenylcarbamido*-2-*phenyl-* (X), m. p. 220°, -2-p-*tolyl-* (XI), m. p. 165°, -2-*methyl-* (XII), m. p. 98°, and -2-*allyl-* (XIII), m. p. 160°, *-thiocarbamidobenzene*. By the action of boiling hydrochloric acid (*d* 1·19), I—VII and IX and similar known derivatives are converted into substituted aminoheptathiodiazines of the type $C_6H_4<^{NH\cdot CS>S}_{N=\!=C\cdot NHR'}$ aniline being eliminated in each case, and thus are obtained 4-*anilino-*, m. p. 290—291° (*acetyl* derivative, m. p. 160°, converted by the action of iodine into the *disulphide*, m. p. 210°), 4-o-*toluidino-*, m. p. 300° (*acetyl* derivative, m. p. 200°), 4-p-*toluidino-*, m. p. 300° (*acetyl* derivative, m. p. 200°; *disulphide*, m. p. 190°), 4-m-*xylidino-*, m. p. 295° (*acetyl* derivative, m. p. 296°; amorphous *disulphide*, m. p. 172°), 4-*methylamino-*, m. p. 168° (*disulphide*, m. p. 194°), 4-*allylamino-*, m. p. 293° (*disulphide*, m. p. above 300°), -2-*thioketo*-1 : 2-*dihydrobenz*-3 : 1 : 5-*thioheptadiazine*, and 4-*anilino*-2-*thioketo*-1 : 2-*dihydrotolu*-3 : 1 : 5-*heptatriazine*, but with *o*-phenylenediallyldithiocarbamide, hydrogen sulphide is eliminated with the formation of 2 : 4-*di*(*allylamino*)*benz*-3 : 1 : 5-*thioheptadiazine*, m. p. above 300° (*diacetyl* derivative, m. p. 185°). Boiling hydrochloric acid converts X, XI, XII, and XIII into, respectively, 3-*phenyl-*, m. p. 185° (*disulphide*, m. p. 128—130°), and 3-p-*tolyl-*, m. p. 175—176° (*disulphide*, m. p. 164°), -2-*keto*-4-*thioketobenz*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 5-*heptatriazine*, 2-*anilino*-4-*methylaminobenz*-3 : 1 : 5-*thioheptadiazine*, m. p. 195°, and 4-*anilino*-2-*keto*-1 : 2-*dihydrobenz*-3 : 1 : 5-*thioheptadiazine*, whilst *o*-phenylenedicarbamide gives 2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydrobenz*-1 : 3 : 5-*heptatriazine* $+2H_2O$, sublimes above 300° (*acetyl* derivative, m. p. 190°), and VIII is unattacked. *s-o*-Aminophenylphenyl- (XIV) (*disulphide*, m. p. 230°; *acetyl* derivative, m. p. 200°), o-*aminophenyl*-o-*tolyl-*, m. p. 160°, and -p-*tolyl-* (XV), m. p. 146—147°, and o-*aminophenylmethyl-*, m. p. 117°, *-thiocarbamides* all give *o*-phenylenethiocarbamide, m. p. 301—302° (lit. 290°), by boiling with hydrochloric acid, but s-o-*aminophenylallylthiocarbamide*, m. p. 115°, is converted into 1-*allylaminobenzthiazole*, m. p. 180° (*acetyl* derivative, m. p. 198°). By the action of ferric chloride XIV and XV are converted into 3-*anilino-*, m. p. 155—156°, and 3-p-*toluidino-*, m. p. 93°, *-benz*-2 : 1 : 4-*thiodiazine*, respectively, whilst by condensation of XIV with the appropriate aldehyde are obtained the o-*nitrobenzylidene*, m. p. 215°; m-*nitrobenzylidene*, m. p. 153—154°; o-*hydroxybenzylidene*, m. p. 180°; and *benzylidene*, m. p. 265—267°, derivatives, the last-named being converted by ferric chloride into 2-*anilino*-4-*phenylbenz*-3 : 1 : 5-*thioheptadiazine*, m. p. 105°. By the action of ethyl chloroformate on XIV *phenylthiocarbamidophenylurethane*, $NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot NH\cdot CO_2Et$, m. p. 288—290°, is obtained. J. W. BAKER.

Triazoles. X. Oxidation products of the three 1-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazoles. F. HERNLER (Monatsh., 1929, **53** and **54**, 668—681).—Oxidation of 1-*o*-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (I) with 25% nitric acid at 200° gives 1-*phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*-2′-*carboxylic acid* (II), m. p. 238—240° (*hydrochloride*, m. p. 243—245°); with 15% nitric acid at 150° or boiling 25% acid, the *nitrate*, m. p. 146—147° with previous sintering, of I is formed. Oxidation of I with alkaline potassium permanganate at 100° also gives II. Further oxidation of II with an excess of permanganate affords 1-*phenyl*-1 : 2 : 4-*triazole*-3(or 5) : 2′-*dicarboxylic acid* (anhydrous and $+H_2O$), m. p. 235—240°. Nitric acid oxidation of 1-*m*-tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (*nitrate*, m. p. 139—140°) furnishes 1-*phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*-3′-*carboxylic acid*, m. p. 198—199° (*hydrochloride*, m. p. 253—256° with evolution of gas), whilst permanganate oxidation affords as the primary product 1-*phenyl*-3(or 5)-*methyltriazole*-5(or 3) : 3′-*dicarboxylic acid*, m. p. 242° with previous sintering. Further oxidation of this yields 1-*phenyltriazole*-3(or 5) : 3′-*dicarboxylic acid*, m. p. 233—234°. 1-*p*-Tolyl-3 : 5-dimethyl-1 : 2 : 4-triazole (*nitrate*, m. p. 173—174° with gas evolution) is oxidised (nitric acid) to 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole-4′-carboxylic acid (III) (A., 1927, 1090) (*hydrochloride* $+H_2O$, m. p. 296—296·5° after sintering at 295°), whilst initial permanganate oxidation affords 1-*phenyl*-3(or 5)-*methyltriazole*-4′-*carboxylic acid* $+H_2O$ (IV). Further oxidation (permanganate) of III or IV gives 1-*phenyltriazole*-3(or 5) : 4′-*dicarboxylic acid* (anhydrous and $+H_2O$, m. p. 302—303°). H. BURTON.

Porphyrin syntheses. XXV. Chlorophyll. VIII. Syntheses of porphinmonopropionic acids VI, III, and I; conversion of pyrroporphyrin into porphinmonopropionic acid III. H. FISCHER, H. K. WEICHMANN, and K. ZEILE (Annalen, 1929, **475**, 241—266).—The remaining three of the eight isomeric porphinmonopropionic acids (cf. A., 1928, 651) have now been synthesised. "*Porphinmonopropionic acid VI*" (1 : 3 : 5 : 8-*tetramethyl*-4 : 6 : 7-*triethylporphin*-2-*propionic acid*; cf. annexed formula) [*methyl* ester, m. p. 246° (corr.); *copper* salt, $C_{33}H_{36}O_2N_4Cu$, and *iron* salt (*hæmin*), $C_{33}H_{38}O_2N_4ClFe$] is obtained by the usual method by condensation of (2-bromo-3-methyl-4-ethylpyrryl)-(2′-bromo-3′-methyl-4′-ethylpyrrolenyl)methene hydrobromide with (3-methyl-2-bromomethyl-4-ethylpyrryl)-(4′-methyl-5′-bromomethyl-3′-β-carboxyethylpyrrolenyl)methene hydrobromide by heating with hydrobromic acid. Modified methods are used for the synthesis of the other two acids on account of their unsymmetrical structure. (2 : 5-Dimethyl-4-ethylpyrryl)-(3′-methyl-4′-β-carboxyethylpyrrolenyl)methene hydrobromide and (2-bromo-3-methyl-4-ethylpyrryl)-(3′-methyl-5′-bromomethyl-4′-ethylpyrrolenyl)methene hydrobromide are condensed by fusion with succinic acid, and the porphinmonopropionic acid is separated by means of its insoluble sodium salt from the ætioporphyrin derived from the second reactant. The "*porphinmonopropionic acid*



III" (1 : 3 : 5 : 8-*tetramethyl*-2 : 4 : 6-*triethylporphin*-7-*propionic acid*) thus obtained yields a *methyl* ester, m. p. 271° (corr.) [*copper* salt, m. p. 223°; *iron* salt (*hæmin*), m. p. 265°; *phyllin*]. A better yield is obtained by another synthesis. (3 : 5-*Dimethyl*-4-β-*carboxyethylpyrryl*)-(3′-*methyl*-4′-*ethylpyrrolenyl*)-*methene hydrobromide*, decomp. slowly at 235—240°, is obtained by condensing opsopyrrole with 3 : 5-dimethyl-4-β-carboxyethylpyrrole-2-aldehyde, and condenses in turn with (3-methyl-2-bromomethyl-4-ethylpyrryl)-(2′-bromo-4′-methyl-3′-ethylpyrrolenyl)-methene hydrobromide (obtained by bromination of hæmopyrrole, cf. this vol., 1463), when fused with succinic acid to give the same "porphinmonopropionic acid III." (3-Methyl-4-ethyl-2-carboxypyrryl)-(3′ : 5′-dimethyl-4′-β-carboxyethylpyrrolenyl)methene hydrobromide (unpublished work with H. Berg) condenses with (2-bromo-3-methyl-4-ethylpyrryl)-(4′-methyl-2′-bromomethyl-3′-ethylpyrrolenyl)methene hydrobromide (obtained by bromination of cryptopyrrole, cf. this vol., 1463) when fused with succinic acid to yield "*porphinmonopropionic acid I*" (1 : 3 : 5 : 7-*tetramethyl*-4 : 6 : 8-*triethylporphin*-2-*propionic acid*), which yields the *methyl* ester, m. p. 237° (corr.) [*copper* salt, m. p. 226°; *iron* salt (hæmin), m. p. above 270°].

A further step in the orientation of the substituents in the chlorophyll porphyrins has been made by converting chlorophyll pyrroporphyrin, already known to be a tetramethyldiethylporphinmonopropionic acid, into the above porphinmonopropionic acid III by the introduction of an ethyl group, and the possible structures for pyrroporphyrin are reduced to three, of which XV (Annalen, 1929, **473**, 213) is most probable. The derivation of chlorophyll porphyrins from ætioporphyrin III is thus established, and hæmin and chlorophyll therefore have a similar arrangement of side-chains. The constitution of chlorophyll is discussed.

Pyrrohæmin in acetic anhydride is treated with stannic chloride; the reaction is not allowed to go to completion in order to avoid excessive decomposition. Treatment of the product with concentrated sulphuric acid to remove iron yields *acetylpyrroporphyrin* [*copper* and *iron* salts; *methyl* ester, m. p. 278° (corr.) (*copper* salt, m. p. 245° (corr.); *iron* salt, m. p. 265° (corr.))], accompanied by small amounts of two porphyrins of different basicity. Spectrographic data are given for these compounds. The acetylpyrroporphyrin is reduced by heating with concentrated alcoholic potassium hydroxide to the *carbinol*, which is accompanied by a spectroscopically similar porphyrin which is stable to concentrated sulphuric acid or heating in a vacuum. Reduction of the impure carbinol with hydriodic acid and phosphonium iodide yields porphinmonopropionic acid III, identical with the synthetic product and yielding the same derivatives. R. K. Callow.

Porphyrin syntheses. XXVI. Syntheses of mesoporphyrins I, IV, XIII, and XIV. H. Fischer and A. Kirrmann (Annalen, 1929, **475**, 266—287).—A detailed account is given of work already briefly summarised (this vol., 1316). An alternative synthesis of mesoporphyrin I (*copper* salt) is carried out by condensation of (4 : 5-dimethyl-3-β-carboxyethylpyrryl)-(3′-methyl-4′-β-carboxyethylpyrrolenyl)methene and (4 : 5-dimethyl-3-ethylpyrryl)-(2′-bromo-5′-methyl-4′-ethylpyrrolenyl)-methene by fusion with succinic acid. The coproporphyrin, m. p. 244° (corr.), obtained as a by-product in the first synthesis has been identified as coproporphyrin I. *Mesoporphyrin XIII*, m. p. above 280° (*copper* and *iron* salts, both m. p. above 280°), is obtained by condensation of (2-bromo-3-methyl-4-β-carboxyethylpyrryl)-(2′-bromo-3′-methyl-4′-β-carboxyethylpyrrolenyl)methene hydrobromide and (4-methyl-2-bromomethyl-3-ethylpyrryl)-(4′-methyl-2′-bromomethyl-3′-ethylpyrrolenyl)methene hydrobromide by fusion with succinic acid and converted into the *methyl* ester, m. p. 217° [*copper* salt, m. p. 238°; *iron* salt (*hæmin*), m. p. 257°]. The absorption spectra of the mesoporphyrins are indistinguishable, as are those of their corresponding derivatives.

Since it has been found that mesoporphyrins I and IX are readily separable, the identification of isomeric hæmins, if they occur, should be possible by conversion into the mesoporphyrins. However, fractionation of mesoporphyrin from ox blood yields only mesoporphyrin IX, identified as the methyl ester, and dog-fish blood and blood from a case of porphyrinuria yield the same mesoporphyrin. R. K. Callow.

Natural porphyrins. XXIV. Hæmatoporphyrin. H. Fischer, A. Treibs, and G. Hummel (Z. physiol. Chem., 1929, **185**, 33—73).—An attempt to reduce hæmatoporphyrin hydrochloride with boiling alcoholic potassium hydroxide was unsuccessful. The product was converted into the hydrochloride and then represented the dihydrochloride of hæmatoporphyrin with 1 mol. of water, although the carbon percentage was low. It was shown spectroscopically to contain 10% of protoporphyrin. The potassium salt with methyl-alcoholic hydrogen chloride gave the crystalline *dimethyl* ester, m. p. 212°, chief absorption bands, 624·8, 575·6, 569·5, 529·3, 495·7. This was converted into *tetramethylhæmatoporphyrin*, m. p. 120°. The dimethyl ester at 185—195° gave protoporphyrin ester. *Tetramethylhæmatoporphyrin* ester *C*, m. p. 145°, which lost methyl alcohol only at 185°, showed a higher m. p. after rubbing (185°). *Tetraethylhæmatoporphyrin*, m. p. 149°, was prepared by esterification of the potassium salt with alcoholic hydrogen chloride (chief absorption bands 495·9, 530·1, 569·5, 576·2, 624·7). When the temperature of the hæmatoporphyrin-alcoholate mixture rose to 180°, reduction occurred, giving the meso-ester, m. p. 194°. The Busch reduction to indicate the hydroxyvinyl radical met with no success. With hydrogen iodide and acetic acid, reduction to mesoporphyrin was effected. Bromination of the hæmatoporphyrin dimethyl ester yielded dibromodeuteroporphyrin. Acetic acid and hydrobromic acid gave hæmatoporphyrin. Hæmatoporphyrin is easily converted into mesoporphyrin by way of a hydrobromic acid additive product, which also points to the equivalence of the side-chains. The oxidation of tetramethylhæmatoporphyrin decided this point. Methoxymethylmaleimide, m. p. 59°, was obtained and hæmatinic acid in yield corresponding with two pyrrole nuclei. Oxidation of meso-

porphyrin likewise gave a yield of more than 1 mol. of methylethylmaleimide. Bromoporphyrin I gave more than 1 mol. of bromocitraconimide. The action of bromine on tetramethylhæmatoporphyrin in chloroform gave dibromodeuteroporphyrin ester. The brominated imide, m. p. 76°, of Küster and Grosse could not be obtained. In place of the dichlorodimethylhæmin of Küster and Schlayer a crystalline chlorohæmin of a *monochlorotetramethylhæmatoporphyrin* was obtained. Oxidation gave a small amount of chlorocitraconimide. It is doubtful if the imide, m. p. 76°, has the constitution assigned to it. Bromination of mesoporphyrin ester, its copper salt, and of ætiohæmin gave well-crystallised perbromides which were debrominated by acetone.

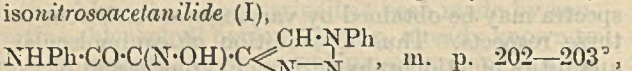
Oxidation of 2-methyl-4-ethylpyrrole gave ethylmaleimide, m. p. 80°, bromination gave the crystalline (3 : 5-*dibromo*-4-*ethylpyrryl*)-(5′-*methyl*-3′-*ethyl*-4′-*bromopyrrolenyl*)*methene hydrobromide*. By the action of sodium hydroxide, the free *methene*, m. p. 133°, was obtained; this on fusion with succinic acid gave *tetrabromotetraethylporphin* (?). Oxidation of the iron salt of tetramethylhæmatoporphyrin gave the *methoxylated imide*, m. p. 58°. J. H. Birkinshaw.

Molecular compounds of porphyrins. A. Treibs (Annalen, 1929, 476, 1—60).—A comprehensive investigation of the salts and molecular additive compounds formed by a large number of porphyrins and their esters with styphnic, picric, picrolonic, and flavianic acids, and of their spectra both in powder form and in solution, is described. For details in individual cases the original must be consulted, the main general conclusions being briefly summarised below. Coloured compounds of 1 mol. of the porphyrin with 1—5 mols. of the acid are formed, exhibiting all variations of solubility, the m. p. of which are reproducible only with very rapid heating and are of no value for mixed m.-p. determinations. Like the spectra of the porphyrins themselves, the spectra of these compounds are not trustworthy as a guide to constitution, since they fall into three definite types, individual compounds within each type having closely similar spectra. Thus in ethereal solution the spectra of ætio-, meso-, deutero-, copro-, and pyrroporphyrins exhibit four chief bands of approximately equal intensity (neutral type). In hydrochloric acid an entirely different type of spectrum (type II) is obtained consisting of three bands of very unequal intensity in the green, two additional weak bands appearing with increasing concentration of hydrochloric acid, which also causes a general shift towards the red. With the molecular compounds, however, increase in the concentration of the acid component causes a shift towards the violet, and in these compounds an intermediate spectrum type (type I) due to the presence of mono-acid salts is obtained. A corresponding type [type (I)] is obtained with powder spectra (such spectra being indicated by the bracketed type number), these showing a shift of 6—10 μμ towards the red compared with the corresponding solution spectra. Each spectrum type corresponds with a definite type of compound. Thus most compounds in which the ratio porphyrin : nitrophenolic acid is 1 : 1 give spectra of type (I) and are true mono-acid salts. In this group, however, dibromodeuteroporphyrin picrate and ætioporphyrin 2 : 6-dinitrobenzoate give the neutral type spectra and are therefore true molecular additive compounds, similar results being obtained with the picryl chloride additive *compounds* of ætioporphyrin-I, m. p. 251°, and mesoporphyrin ester, m. p. 158°, and with the bromo-2 : 4-dinitrobenzene additive *compound* (1 : 2), m. p. 188°, of ætioporphyrin-I. Most compounds with the porphyrin : acid ratio 1 : 2 give spectra of type (II) and are true di-acid salts, but the picrolonates give type (I) spectra and are, therefore, additive compounds of the mono-acid salts. The spectra of these change to type II, however, in the presence of a large excess of picrolonic acid. Compounds with the ratio 1 : 3 give type II spectra and are additive compounds of the di-acid salts. Such compounds, with the exception of the styphnate of ætioporphyrin-II, are found only in the flavianic acid series. The 2 : 6-*dinitrobenzoates* of ætioporphyrin-I, m. p. 203°, and mesoporphyrin ester, m. p. 153°, are the only examples, respectively, of compounds with the ratio 1 : 4 and 1 : 5, and are additive compounds of the di-acid salts. Dissociation of these molecular compounds occurs in solution, its extent depending on the solvent and increasing with rise of temperature, so that different types of spectra may be obtained by varying the conditions in these respects. Thus by addition of equimolecular quantities of ætioporphyrin-I in chloroform and picric acid in methyl alcohol, the solution, after concentration, exhibits a type I spectrum in which the neutral type can still be observed. The latter disappears on addition of 10—15% excess of picric acid, but for this solution of homogeneous spectrum type the 1 : 2 picrate showing spectrum type (II) is obtained, whilst the mother-liquor still has the type I spectrum, proving the existence of an equilibrium in solution. Explanations of the detailed results are discussed, and it is concluded that the porphyrin molecule exhibits residual affinity and hence that the iron in hæmin and the magnesium in chlorophyll are not bound merely by substitution of 2 atoms of hydrogen, but by means of the residual affinity of the complex. In addition to spectrographic data the following m. p. data are recorded (all corr. and with decomp.), each set of values being those of the styphnate, picrate, picrolonate, and flavianate, respectively: ætioporphyrin-I, 223°, 232°, 262°, indef. 230°; ætioporphyrin-II, 217°, 223°, 228°, 250°; mesoporphyrin, 232°, 178°, 204°, indef. 215°; mesoporphyrin ester, 185°, 145°, 195°, 235°; protoporphyrin, 234°, indef. 180° (1 : 1) and 157° (1 : 2), indef. 160°, 211° (1 : 2) and 215° (1 : 3); protoporphyrin ester, 135°, 150°, 143° (1 : 1) and 115° (1 : 2), decomp. 260° (1 : 2) and decomp. 230° (1 : 3); deuteroporphyrin, 183°, indef. 240°, 118°, 275°; deuteroporphyrin ester, 127° (1 : 1) and 188° (1 : 2), 148°, 212° (1 : 1) and 141° (1 : 2), 204°; hæmatoporphyrin, —, —, decomp. 180°, decomp. 200°; tetramethylhæmatoporphyrin, 171°, 155°, 132° and 110° (two forms both 1 : 1), 183°; coproporphyrin-I, 295, 251°, 256°, indef. 310°; coproporphyrin-I ester, 143° and 154° (both 1 : 2), 146°, 245°, 225°; uroporphyrin ester, —, —, —, 176°; *iso*uroporphyrin ester, 232°, 240°, —, 215°; dibromodeuteroporphyrin ester, —, 177°, —, indef. 165°; phylloporphyrin, 163°, 156°,

212°, 235°; phylloporphyrin ester, 210°, indef. 135°, —, indef. 230°; pyrroporphyrin, 206°, 152°, 154°, indef. 220°; pyrroporphyrin ester, 177°, 169°, 175°, indef. 262°; rhodoporphyrin, 257°, —, —, —, mesorhodin ester, 169°, 211°, 135°, decomp. 300°. Ætioporphyrin-I forms additive *compounds* with chloranilic acid, m. p. 251°, 2 : 4 : 6-trinitro-, m. p. 304°, and 2 : 6-dinitro-, m. p. indef. 175° (1 : 1) and 203° (1 : 4), -benzoic acids, and bromo-2 : 4-dinitrobenzene, m. p. 188°. J. W. BAKER.

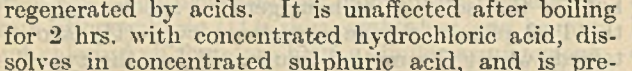
Phylloerythrin. L. MARCHLEWSKI (Z. physiol. Chem., 1929, **185**, 8).—Phylloerythrin forms a stable additive product with chloroform, but the latter can be eliminated by dissolving the complex in warm pyridine and pouring into a large volume of alcohol or acetic acid. J. H. BIRKINSHAW.

Fulminic acids. VIII. Constitution of polymerised fulminic acids. Erythrocyanilic acid and β-*iso*cyanilic acid. H. WIELAND, W. FRANK, and Z. KITASATO (Annalen, 1929, **475**, 42—54).—The reaction between erythrocyanilic acid and aniline incompletely studied by Will (Diss., München, 1923) has been fully investigated. Erythrocyanilic acid and aniline (2 mols.) react in warm ethyl acetate solution with the formation of 1-*phenyl*-4-*triazolyl*-iso*nitrosoacetanilide* (I),



NHPh·CO·C(N·OH)·C<CH·NPh / N=N>, m. p. 202—203°, and hydroxylamine. The former slowly dissolves in boiling methyl-alcoholic potassium hydroxide and the solution on dilution yields the *potassium* salt, m. p. 212—213° (decomp.), from which the anilide is regenerated by acids. It is unaffected after boiling for 2 hrs. with concentrated hydrochloric acid, dissolves in concentrated sulphuric acid, and is precipitated unchanged on the addition of water, is unaffected by bromine or by chromic acid in acetic acid and also by nitrous acid. The *acetyl* derivative of I has m. p. 171—172°, and is converted into I by boiling with dilute alkali. Thionyl chloride and I give 4-*cyano*-1-*phenyl*-1 : 2 : 3-*triazole*, m. p. 121—122°, converted by prolonged hydrolysis with *N*-alcoholic potassium hydroxide into an insoluble *compound*, m. p. 232°, and 1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid, m. p. 150°. The last-named affords 1-phenyltriazole, m. p. 55—56°, when heated above the m. p. for several minutes. The mechanism of the reaction between erythrocyanilic acid and aniline and the subsequent transformations is given (cf. A., 1925, i, 1048). Erythrocyanilic acid and phenylhydrazine react in alcohol to give a *compound*, $C_{22}H_{25}O_4N_9$ (1 mol. acid, 3 mols. phenylhydrazine, loss of 1 mol. NH_3), m. p. 217—218° (decomp.), which reduces ammoniacal silver nitrate containing a little sodium hydroxide, is dehydrated by bromine in glacial acetic acid to an azo-compound, and gradually dissolves in boiling concentrated hydrochloric acid to a solution from which a *compound*, m. p. 261—262°, is precipitated by water.

*iso*Cyanilic acid (Steinkopf, A., 1910, i, 305) and benzoyl chloride (3 mols.) in pyridine yield a *dibenzoyl* derivative, m. p. 155°, whilst boiling with aniline hydrochloride in aqueous solution affords an anil-oxime, m. p. 121—122°, identical with the compound obtained from the α-acid (cf. A., 1925, i, 1049). The open-chain structure originally assigned to this anil-oxime is withdrawn and the cyclic structure



NPh:CH·C(:NO)<OH·N:CH·C=N>O substituted. When β-*iso*cyanilic acid is warmed with thionyl chloride for a short time, *cyanofuroxanaldoxime*, m. p. 90—91°, is formed (also obtained by boiling the acid with water), which when treated with 1 equivalent of 0·1*N*-sodium hydroxide, followed by acidification, is converted into anhydro-*iso*cyanilic acid, m. p. 185—186° (lit. 180°), identical with the substance obtained from *iso*cyanilic acid and phosphorus pentachloride. With dilute hydrochloric acid alone no change takes place, thus indicating that the original oxime undergoes a preliminary Beckmann transformation in presence of alkali. β-*iso*-Cyanilic acid reacts slowly with ammonia to give peri*cyanilic acid*, m. p. 187°, and meta*cyanilic acid*, m. p. 70°. Dicyanofuroxan, m. p. 40—41°, is produced when β-*iso*cyanilic acid is vigorously boiled with thionyl chloride. A. I. VOGEL.

Fulminic acids. IX. Constitution of polymerised fulminic acids. peri*Cyanilic*, epi*cyanilic*, and meta*cyanilic acids*. H. WIELAND and Z. KITASATO [with F. FROMM] (Annalen, 1929, **475**, 54—78).—*peri*Cyanilic acid, m. p. 187° (decomp.) (previously called hydrato*iso*cyanilic acid), prepared by the action of mild alkalis, *e.g.*, ammonia, on *iso*cyanilic acid, is best purified by decomposing the characteristic sparingly soluble *ammonium* salt with dilute hydrochloric acid. It forms a sparingly soluble *pyridine* salt, m. p. 179° (decomp.), a *trimethyl* ester, m. p. 128°, when treated in methyl-alcoholic solution with diazomethane in ether at 0°, a *tribenzoyl* derivative, m. p. 189° (decomp.) (4 mols. of benzoyl chloride in pyridine solution), and a *triacetyl* derivative, m. p. 162° (decomp.), when boiled for a short time with acetic anhydride. When *peri*cyanilic acid in chloroform solution is warmed with thionyl chloride at 70° for 3 hrs., *anhydro*epi*cyanilic acid*, m. p. 102°, is formed. This acid is unaffected by cold concentrated sulphuric acid or by hot concentrated hydrochloric acid at 100°, is decomposed by alkali giving ammonia and carbon dioxide, yields a *dibenzoyl* derivative, m. p. 158° (benzoyl chloride in pyridine), and is decomposed by boiling *N*-baryta solution into ammonia and 3-hydroxyfurazan-4-carboxylamide, m. p. 202—204°, identical with the previously known *iso*fulminuric acid (*benzoyl* derivative, m. p. 212°), and separated by means of the sparingly soluble barium salt; prolonged boiling with baryta yields hydroxyfurazancarboxylic acid, m. p. 175°. 3-*Hydroxy*-4-*furazan*iso*nitrosoacetic acid*, m. p. 165° (decomp.), was isolated from the filtrate of the barium salt separation.

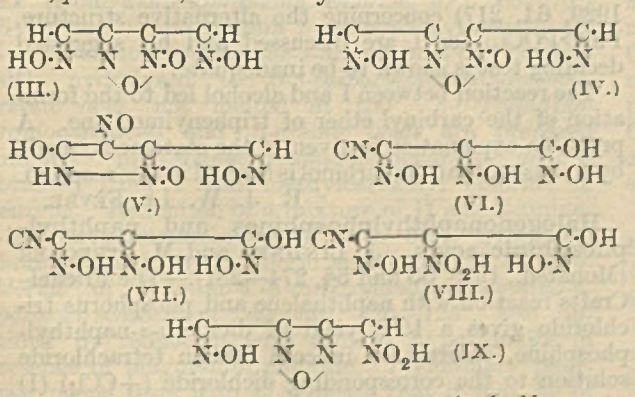
α-epi*Cyanilic acid*, m. p. 170° (decomp.), is formed by heating *peri*cyanilic acid with aqueous aniline hydrochloride at 100° or by dissolving *peri*cyanilic acid in concentrated sulphuric acid at 10° and later pouring the solution on to ice. The acid yields a *tetrabenzoyl* derivative, m. p. 179° (decomp.), which gives no coloration with ferric chloride; when boiled with thionyl chloride *anhydro*epi*cyanilic acid*, m. p. 102°, is produced. Cyanoglyoximecarboxylic acid

(I), m. p. 162° (decomp.), is obtained from the α-acid by heating with concentrated hydrochloric acid; it gives a brownish-red colour with ferric chloride, whilst the α-acid gives a carmine-red colour. I is also produced from the β-acid (Thiele, Diss., München, 1921) and undergoes decarboxylation when heated with 2*N*-methyl-alcoholic potassium hydroxide, giving cyanoglyoxime, m. p. 175° (also produced directly from the β-acid by boiling with 2*N*-methyl-alcoholic potassium hydroxide), identical with the compound obtained from *amphi*chloroglyoxime and sodium cyanide in alcohol.

*meta*Cyanilic acid, m. p. 70°, is best prepared by the addition of excess of concentrated aqueous ammonia to a solution of *peri*cyanilic acid in pyridine, keeping, removing the precipitated ammonium *peri*cyanilate, acidifying with hydrochloric acid, and extracting with ether; yield, 50%. This acid is characterised by its great stability to alkalis. With benzoyl chloride and pyridine at 0°, *meta*cyanilic acid yields *dibenzoylhydroxamyl chloride*, m. p. 168°. Gentle warming with thionyl chloride in ether gives a 50% yield of aci-*nitromethylfurazancarboxylamide*, m. p. 105°, whilst vigorous boiling with thionyl chloride furnishes aci-*nitromethylcyanfurazan* (or *anhydro*meta*cyanilic acid*) (II), b. p. 98°/2 mm. (*benzoyl* derivative, m. p. 157°). When II is boiled with 2 mols. of *N*-baryta, 4-aci-*nitromethylfurazan-3-carboxylic acid*, m. p. 100° (decomp.), is formed (this compound decomposes on keeping); benzoylation at 0° affords *benzoylfurazanhydroxamyl chloride*, m. p. 211—212°, whilst benzoylation at 20° gives a *compound*, $C_{17}H_{10}O_4N_3Cl$, m. p. 221°, identical with the substance obtained by benzoylation of cyanometazonic acid. *meta*Cyanilic acid and bromine water give *tribromo*meta*cyanilic acid*, m. p. 122°; the bromine is immediately eliminated by alcoholic potassium hydroxide at 0°.

The various reactions described in this and the previous paper are interpreted by the following formulæ for the acids:

β-*iso*- III, α-*iso*- IV, erythro- V, α-*epi*- VI, β-*epi*- VII, *peri*- VIII, and *meta*-cyanilic acid IX.



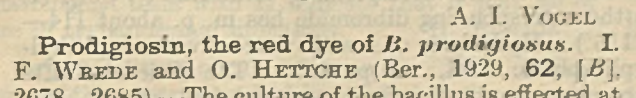
A. I. Vogel

Prodigiosin, the red dye of *B. prodigiosus*. I. F. Wrede and O. Hettche (Ber., 1929, 62, [*B*], 2678—2685).—The culture of the bacillus is effected at about 25° on agar in presence of peptone, Maggi meat extract, dextrose, and magnesium sulphate. The red mass is treated with sodium hydroxide and extracted with light petroleum. The dye is precipitated from the extract as the *hydrochloride*. *Prodigiosin* is an amorphous compound which softens at 70—80°. It appears to have the composition $C_{20}H_{25}ON_3$. The mol. wt. in freezing acetic acid or of the salicylate in bromoform corresponds with the simple formula, whereas double this value is observed in freezing benzene. In boiling alcohol it gives colloidal solutions. Its spectroscopic behaviour shows that it does not belong to the rosaniline group. It is not readily reduced. It absorbs about 13 atoms of oxygen per mol. from permanganate in acetone solution, whereby oxalic acid is formed. It is readily oxidised by chromic acid or hydrogen peroxide. An acyl derivative could not be prepared. It appears to contain one methoxyl or ethoxyl group, but not a methylimino-radical. A primary amino-group is not present. The following salts are described: *perchlorate*, m. p. 228° after softening at 226°; *picrate*, m. p. 176° after softening at 173°; *salicylate*, m. p. 178° after softening at 176°; *benzoate*, m. p. 170° after softening at 168°.

H. Wren.

Thiazole derivatives. E. Riesz and R. Hübsch (Monatsh., 1929, **53** and **54**, 111—118).—Treatment of diazotised dehydrothiotoluidine (1-*p*-aminophenyl-5-methylbenzthiazole) (I) with an alkaline xanthate solution and subsequent hydrolysis of the intermediate product with alcoholic potassium hydroxide affords 1-p-*thiolphenyl-5-methylbenzthiazole* (II) [*acetyl* derivative, m. p. 198°; *benzoyl* derivative, m. p. 253°; S-*methyl* derivative, m. p. 186°; corresponding *thioglycollic acid* (III), m. p. 233°]. Oxidation of II to the corresponding disulphide (IV) occurs readily in air. Chlorination of a chloroform suspension of II or IV gives 1-*phenyl-5-methylbenzthiazole-4′-sulphur chloride*, m. p. 162°, which with aniline yields the corresponding S-*anilino*-derivative, m. p. 278°. An alkaline solution of II and diazotised I afford the dye

(yellow on cotton). When III is treated with chlorosulphonic acid at −10° ring closure occurs and 3-*keto-5-(5′-methyl-1-benzthiazolyl)-2 : 3-dihydrothionaphthen* (V) is formed; at 90° ring closure and oxidation take place and the *thioindigotin* derivative is isolated (an alkaline vat dyes cotton reddish-violet). Treatment of an alkaline solution of V with alcoholic *p*-nitrosodimethylaniline gives the 2-p-*dimethylaminoanilo*-derivative, m. p. above 300°, of V. This dyes tannined cotton with a red shade. The *benzylidene* and p-*dimethylaminobenzylidene* (dyes tannined cotton orange) derivatives of I have m. p. 158° and 218°, respectively. 4-Chloro-2-nitrophenylsulphur chloride and I react in ethereal solution yielding the *compound*



m. p. about 300°.

H. Burton.

Sinomenine and disinomenine. XIII. Reduction of bromosinomenine. K. Goto and T. Nakamura (Bull. Chem. Soc. Japan, 1929, 4, 195—197).—Reduction of bromosinomenine with palladised charcoal and 1 mol. hydrogen yields *bromodihydrosinomenine*, m. p. 237° (decomp.), $[\alpha]_D^{20}$ in chloroform, +102·4° [*hydrobromide*, m. p. 229—232° (decomp.);

methiodide, m. p. 225° (decomp.); *semicarbazone*, m. p. 250°], identical with the compound obtained in 80% yield by the bromination of hydrosinomenine in glacial acetic acid solution. With 2 mols. of hydrogen a mixture of bromo- and hydro-sinomenine is formed.
A. I. VOGEL.

Strychnos alkaloids. LIII. Oxidation products of the reduced Hanssen acid. H. LEUCHS and F. KRÖHNKE (Ber., 1929, **62**, [*B*], 2598—2603; cf. this vol., 1320).—Oxidation of the reduced Hanssen acid with potassium permanganate at 0° leads to the consumption of about six equivalents of oxygen and production in 30% yield of an *acid*, $C_{19}H_{24}O_9N_2,H_2O$, which does not yield stable salts with mineral acids. The presence of a ketonic group is not established with certainty, although phenylhydrazine gives an amorphous *product*, $C_{19}H_{24}O_7N_2(:N\cdot NHPh)_2$.

The reduced Hanssen acid, $C_{19}H_{24}O_6N_2$, is converted by oxidation with bromine into a compound, $C_{19}H_{26}O_9N_2$, which gives a *semicarbazone hydrobromide*, $C_{20}H_{27}O_8N_5,HBr$, a *phenylhydrazone*, $C_{25}H_{30}O_7N_4$, and *oxime hydrochloride*, $C_{19}H_{25}O_8N_3,HCl$, decomp. 240° without melting below 300°, derived from the anhydride, $C_{19}H_{24}O_8N_2$. The *dimethyl* ester, $C_{21}H_{28}O_8N_2$, m. p. 147—148° [*hydrochloride*, m. p. about 265° (decomp.)], of the anhydride is described. Reduction of the acid, $C_{19}H_{26}O_9N_2$, with water and sodium amalgam affords the *compound* $C_{19}H_{26}O_8N_2$, isolated as the *hydrobromide*. Oxidation of the acid, $C_{19}H_{26}O_9N_2$, by permanganate yields an *acid*, $C_{19}H_{24}O_9N_2$ [*dimethyl* ester *hydrochloride*, m. p. 255° (decomp.) after softening].
H. WREN.

Halogenotolylphosphines. J. LINDNER [with O. BRUGGER, A. JENKNER, and L. TSCHEMERNIGG] (Monatsh., 1929, **53** and **54**, 263—273).—Halogenophosphines have been prepared for possible use in the author's method of volumetric determination of carbon and hydrogen (A., 1922, ii, 657; 1925, ii, 901). A large proportion of the paper is a repetition of Michaelis and Paneck's work (A., 1882, 958). Dichloro-*p*-tolylphosphine dichloride, m. p. 69—91° (cf. Michaelis and Paneck, *loc. cit.*), when heated at 98° in a current of dry air evolves hydrogen chloride; chlorination of the methyl group occurs. Dichloro-*p*-tolylphosphine dibromide has m. p. 128—130° (sealed tube) with elimination of bromine. Reduction of this dibromide with sulphur dioxide gives the substance $Me\cdot C_6H_4\cdot POClBr(?)$, m. p. 5—8°. Dibromotolylphosphine dibromide, m. p. 160—161° with elimination of bromine, also eliminates hydrogen bromide when kept at 160°. During the Friedel–Crafts preparation of dibromotolylphosphine a small amount of the *o*-derivative is probably formed in addition to the *p*-isomeride.
H. BURTON.

Formation of triphenylmethylphosphinic acid from triphenylmethoxyphosphorus dichloride. II. Mechanism of the reaction. H. H. HATT (J.C.S., 1929, 2412—2422).—The alcoholysis of triphenylmethoxyphosphorus dichloride (I) by alcoholic sodium ethoxide solution led to the formation of triphenylmethylphosphinic acid, rearrangement taking place. This reaction has been studied in detail by observing the rate of formation of sodium chloride and also by examination of the phosphorus-containing products. With 2·5*N*-alcoholic sodium ethoxide removal of chlorine atoms proceeded in definite stages, thus leading to the isolation of intermediates. The first halogen was removed rapidly, the velocity being governed chiefly by the rate of dissolution of the phosphorus dichloride in the alcohol; the second halogen was removed more slowly. The final product was *ethyl hydrogen triphenylmethylphosphinate*, m. p. 259° (*silver* salt).

The course of the reaction is considered to be $Ph_3C\cdot O\cdot PCl_2$ (I) $\longrightarrow$ $Ph_3C\cdot O\cdot PCl(OEt)$ (II) $\longrightarrow$ $Ph_3C\cdot POCl(ONa)$ (III) $\longrightarrow$ $Ph_3C\cdot PO(OEt)\cdot ONa$, and is supported by the isolation by acidification with alcoholic hydrogen chloride at the appropriate stage of *triphenylmethylchlorophosphinic acid* (III), m. p. 233—234° (*aniline* salt +EtOH, m. p. 182—182·5° or 151—156° on rapid heating; *quinoline* salt, m. p. 181—182·5°), and, when 0·2—0·5*N*-sodium ethoxide was employed, the *chloro-ester*, II, m. p. 135—137°, in 85% yield. Heating with 2*N*-sodium ethoxide solution or hydriodic–acetic acid mixture transformed II into III.

In concentrated solutions an alternative course existed: (I) $\longrightarrow$ $Ph_3C\cdot O\cdot PCl(OEt)$ $\longrightarrow$ $Ph_3C\cdot PO(OEt)_2$ $\longrightarrow$ $Ph_3C\cdot PO(OEt)\cdot ONa$, indicated by the isolation of diethyl triphenylmethylphosphinate, m. p. 120—121° (also obtained by shaking together silver monoethyl triphenylmethylphosphinate, ethyl iodide, and dry benzene), in 20% yield when 4*N*-solutions of sodium ethoxide were used. This ester underwent sulphonation with concentrated sulphuric acid, but hot aqueous sulphuric acid effected hydrolysis first into the monoethyl ester, then into the phosphinic acid itself. Triphenylmethylphosphinic acid and phosphorus pentachloride at 70° gave triphenylchloromethane, m. p. 106—109°.

The varying stabilities towards hydrolysing agents of the compounds isolated are noted and tentative explanations given. No decision is reached regarding the stage at which during alcoholysis migration of triphenylmethyl from oxygen to phosphorus occurs; the structure of II is therefore left open. The indefinite conclusions of Arbusov (J. Russ Phys. Chem. Soc., 1929, **61**, 217) concerning the alternative structure, $Ph_3C\cdot POCl_2$, for I are discussed and his suggested deciding test is shown to be inadequate.

The reaction between I and alcohol led to the formation of the carbinyl ether of triphenylmethane. A probable explanation is given of the statement, made by Arbusov, that the carbinol is formed in this reaction.
R. J. W. LE FÈVRE.

Halogenonaphthylphosphines and naphthylphosphinic acids. J. LINDNER and M. STRECKER (Monatsh., 1929, **53** and **54**, 274—281).—The Friedel–Crafts reaction with naphthalene and phosphorus trichloride gives a 15% yield of dichloro-α-naphthylphosphine, chlorinated in cold carbon tetrachloride solution to the corresponding dichloride (+CCl_4) (I) (the corresponding dibromide has m. p. about 114—116°). Hydrolysis of I with water gives α-naphthylphosphinic acid, m. p. 189°. The Friedel–Crafts reaction is not a suitable method for preparing dibromonaphthylphosphine. Parts of the paper have been reviewed previously (A., 1922, ii, 657; 1925, ii, 901).
H. BURTON.

Nitration of halogenophenylarsinic acids. H. J. BARBER (J.C.S., 1929, 2333—2337).—2-Bromophenylarsinic acid [the corresponding *di(carbamylmethyl) o-bromophenylthioarsinite* has m. p. 137—138°], prepared from *o*-bromoaniline by Bart's reaction, gave on nitration 2-*bromo*-5-*nitrophenylarsinic acid* (anhydrous and monohydrated) (corresponding *thiolacetamide*, m. p. 171—172°) (also obtained from 2-bromo-5-nitroaniline by diazotisation), alkaline hydrolysis of which gave 5-nitro-2-hydroxyphenylarsinic acid (*thiolacetamide* derivative, m. p. 194—195°). Only small yields of 2-*iodophenylarsinic acid monohydrate* were obtained from *o*-iodoaniline owing to interaction between the arsinic acid and excess of sodium arsenite in the presence of copper arsenite with production of *o*-phenylenediarsinic acid (also obtained by boiling 2-iodophenylarsinic acid with aqueous sodium arsenite and copper arsenite). With copper powder, sodium 2-iodophenylphenylarsinate in boiling aqueous solution gave a mixture of phenylarsinic acid, 2-hydroxyphenylarsinic acid, and diphenyl-2 : 2′-diarsinic acid (?).

2-Iodophenylarsinic acid on nitration as for the bromo-acid above produced 2-*iodo*-5-*nitrophenylarsinic acid* (*thiolacetamide*, m. p. 158—160°), hydrolysis of which afforded 5-nitro-2-hydroxyphenylarsinic acid.

Application of Bart's reaction to 3-chloro-, 3-bromo-, and 3-iodo-anilines led solely to 3-chloro-, 3-*bromo*- (*thiolacetamide*, m. p. 131—132°), and 3-*iodo-phenylarsinic acids*, respectively. These on nitration gave 3-chloro- (*thiolacetamide*, m. p. 172—173°), 3-*bromo*-, and 3-*iodo*-6-*nitrophenylarsinic acids*, identified by a new method of dearsinification by boiling with aqueous alkali (an arsinic acid grouping in the *o*-position to a nitro-group being labile).

4-*Bromo*- and 4-*iodo*-3-*nitrophenylarsinic acids* are also described. R. J. W. LE FÈVRE.

β-Anilinopropionamide-4-arsinic acid and related compounds. C. S. HAMILTON and C. L. SIMPSON (J. Amer. Chem. Soc., 1929, **51**, 3158—3161).—β-Iodo- or β-*bromo-propionamide*, m. p. 110—111° (from β-*bromopropionyl chloride*, b. p. 65—70°/25—30 mm.), and sodium *p*-aminophenylarsinate (I) give β-*anilinopropionamide*-4-*arsinic acid* (II) (*sodium* salt), hydrolysed to p-β-*carboxyethylaminophenylarsinic acid*, not melted at 250°. β-o-*Toluidinopropionamide*-4- and -5-*arsinic acids* are prepared similarly. p-N-*Methylcarbamidophenylarsinic acid* is obtained from I and methylcarbamyl chloride in benzene. Reduction of a mixture of II and 3-amino-4-hydroxyphenylarsinic acid with 50% hypophosphorous acid in hydrochloric acid gives the *dihydrochloride* of 3-*amino*-4′-β-*carboxylamidoethylamino*-4-*hydroxyarsenobenzene*, decomp. 120—125°, also obtained by reduction with sodium hyposulphite in presence of magnesium chloride. Preliminary pharmacological tests with II indicate that it may be of use in trypanosomal infections. H. BURTON.

Organic compounds of arsenic. XV. Existence of the arsenoazo-linking and phosphoarsenobenzene. W. STEINKOPF and H. DUDEK (Ber., 1929, **62**, [*B*], 2494—2497; cf. A., 1928, 1230).—If nitrosobenzene and phenylarsine are mixed in alcohol and ether in an atmosphere of carbon dioxide, the green solution immediately becomes pure yellow and, after some time, arsenobenzene is deposited; the filtrate yields phenylarsine oxide and the residual oil yields aniline and azobenzene when treated with steam. Reaction is presumed to occur as follows: $2PhAsH_2 + 2Ph{\cdot}NO = 2AsPh{:}NPh + H_2O$; $2AsPh{:}NPh = AsPh{:}AsPh + NPh{:}NPh$ and $AsPh{:}NPh + H_2O = PhAsO + PhNH_2$ or $PhAsH_2 + Ph{\cdot}NO = PhAsO + PhNH_2$.

Phenylarsine and phosphorus phenyl chloride afford *phosphoarsenobenzene*, PPh:AsPh, m. p. 181°, which is disproportioned when crystallised from xylene into arsenobenzene and phosphobenzene.

Contrary to previous observations, diphenylarsine and arsenic phenyl dichloride in ether afford a mixture of phenylcacodyl and arsenic diphenyl chloride. In light petroleum only traces of phenylcacodyl are observed, the main products being arsenobenzene and arsenic diphenyl chloride, presumably arising by decomposition of primarily formed chlorotriphenyldiarsine. H. WREN.

Arsenical azo-derivatives. S. BERLINGOZZI (Annali Chim. Appl., 1929, **19**, 397—406).—By coupling with diazophenylarsinic acid (cf. A., 1928, 1146), the following compounds are obtained: from *o*-hydroxybenzyl alcohol 1-*hydroxy*-2-*hydroxymethylbenzene*-4-*azo*-p-*phenylarsinic acid*, $O{:}As(OH)_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH$, not melting below 250°; with salicylaldehyde, 1-*hydroxy*-2-*aldehydobenzene*-4-*azo*-p-*phenylarsinic acid*; with salicylic acid, 1-*hydroxy*-2-*carboxybenzene*-4-*azo*-p-*phenylarsinic acid*; with guaiacol, 1-*hydroxy*-2-*methoxybenzene*-4-*azo*-p-*phenylarsinic acid*, m. p. 215° (decomp.); with 1-phenyl-3-methyl-5-pyrazolone, 1-*phenyl*-3-*methyl*-5-*hydroxypyrazolebenzene*-4-*azo*-p-*phenylarsinic acid*, not melted at 250°; with benzidine, the *hydrochloride* of the *compound* $O{:}As(OH)_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(NH_2){\cdot}C_6H_4{\cdot}NH_2$, not melting at 250°, which, on diazotisation and coupling with phenol, gives the *compound* $C_{24}H_{20}O_4N_5As$, not melted at 250°; with *m*-aminophenol, 1-*amino*-3-*hydroxybenzene*-4-*azo*-p-*phenylarsinic acid*. The last-named gives the *compound* $O{:}As(OH)_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(OH)(NH_2){\cdot}N_2{\cdot}C_6H_4{\cdot}AsO(OH)_2$, unchanged below 250°, when coupled with diazophenylarsinic acid and the *compound* $O{:}As(OH)_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(OH)(NH_2){\cdot}N_2{\cdot}C_{10}H_7$, unchanged at 250°, when coupled with α-diazonaphthalene. T. H. POPE.

Pyridine and quinoline derivatives. V. Derivatives of 2-hydroxypyridine-5-arsinic acid. A. BINZ, C. RÄTH, and E. URBSCHAT (Annalen, 1929, **475**, 136—147).—Nitration of 2-hydroxypyridine-5-arsinic acid (Binz and Räth, A., 1927, 890) with mixed acids at water-bath temperature gives 3-*nitro*-2-*hydroxypyridine*-5-*arsinic acid* (I), decomp. 250°, converted by alkaline hypoiodite into 5-*iodo*-3-*nitro*-2-*hydroxypyridine*, m. p. 246° (decomp.), which is reduced by stannous chloride and hydrochloric acid to the *hydrochloride*, m. p. 218° (darkens at 196°), of 5-iodo-3-amino-2-hydroxypyridine. This is converted by the diazo-reaction into 5-iodo-2-hydroxypyridine-3-arsinic acid, m. p. 270—272° (Scheller, B., 1928,

140). Reduction of I with hyposulphite converts it into 3-*amino*-2-*hydroxypyridine*-5-*arsinic acid*, m. p. 228—229° (decomp.) (N-*acetyl* and N-*acetamido*-derivatives), isolated as its *hydrochloride* and converted by carbonyl chloride in toluene solution into amorphous *pyridine*-2 : 3-*oxazolone*-5-*arsinic acid*, and reduced by sulphur dioxide and potassium iodide to 3-*amino*-2-*hydroxy*-5-*pyridylarsinoxide*. Reduction of I with concentrated hydrochloric acid and 50% hypophosphorous acid gives 5 : 5′-*diamino*-6 : 6′-*diketo*-1 : 6 : 1′ : 6′-*tetrahydro*-3 : 3′-*arsenopyridine*, which exhibits no basic character, but is soluble in sodium hydroxide solution, the amphoteric character of its benzene analogue salvarsan being absent in the pyridine series. It does, however, form a red condensation product with dimethylaminobenzaldehyde. It is oxidised by iodine in sodium hydrogen carbonate solution to the arsinic acid : $(C_5H_5ON_2As)_2+8I+6H_2O=2C_5H_5ON_2\cdot AsO_3H_2+8HI$. J. W. BAKER.

Meriquinonoid derivatives of the phenarsazine series. III. Reduction of derivatives of 5 : 10-dihydrophenarsazine with formic acid. G. RAZUBAIEV [with W. MALINOVSKI] (Ber., 1929, **62**, [*B*], 2675—2677; cf. this vol., 585, 834).—If 5 : 10-dihydrophenarsazine oxide is warmed with formic acid and the coloured solution so produced is decolorised with oxygen, and the sequence is repeated until further development of colour does not occur, two reactions take place resulting (1) in the formation of phenarsazinic acid and (2) in that of arsenic and *N*-formyldiphenylamine. If dihydrophenarsazine derivatives are warmed for a protracted period with formic acid, quantitative precipitation of arsenic and evolution of carbon dioxide occur. 3 : 7-Dimethyl-5 : 10-dihydrophenarsazine oxide is similarly reduced to arsenic, carbon dioxide, and *N*-formyldi-*m*-tolylamine. H. WREN.

Mercurated nitrobenzenes. G. SACHS and K. FÜRST (Monatsh., 1929, **53** and **54**, 550—553).—Reduction of mercury *o*-nitrophenyl chloride with sodium hyposulphite in aqueous-alcoholic solution gives a *mercury di*-o-*nitrophenyl* (I), m. p. 220—230° after sintering at 170°, differing from the form of m. p. 206—207° (II) described by Hein and Wagler (A., 1925, i, 1341). Decomposition of I with 66% hydrobromic acid in alcohol gives nitrobenzene, and treatment with sodium methoxide affords II. Reduction of I with 1% sodium amalgam and alcohol furnishes azobenzene. H. BURTON.

Position occupied by acetatomercuri- (Hg·OAc′) groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. V. L. VECCHIOTTI and S. COPERTINI (Gazzetta, 1929, **59**, 525—543).—As a result of the completion of previous work on the action of mercuric acetate on *o*-substituted anilines the following rules are stated. A single acetatomercuri-group enters position 4 only, except in *o*-chloroaniline (A., 1925, i, 1058). Disubstitution takes place in positions 4 and 6, except with *o*-chloroaniline (*loc. cit.*) and *o*-toluidine, which form in addition 4 : 5- and 3 : 4-derivatives, respectively, and *o*-iodoaniline (A., 1926, 1163), which forms no stable disubstituted derivative. No more than two acetatomercuri-groups can be introduced.

As a by-product in the preparation of 2-bromo-4-acetatomercurianiline (A., 1928, 783), 2-*bromo*-4 : 6-*diacetatomercurianiline*, m. p. 183—184°, separates very slowly from the mother-liquors. The *acetyl* derivative, m. p. 204—205°, yields 2 : 4 : 6-tribromoacetanilide with bromine and potassium bromide.

The action of mercuric acetate on *o*-toluidine has been reinvestigated. Addition of *o*-toluidine to aqueous mercuric acetate (2 mols.) yields 4 : 6-diacetatomercuri-*o*-toluidine, m. p. 223° (Schrauth and Schoeller, A., 1912, i, 930), from which the corresponding 4 : 6-dihydroxy-, 4 : 6-*dichlorido*-, m. p. 170° (decomp.), and 4 : 6-*dibromido*- (decomp. below m. p.) -*mercuri*-derivatives are prepared. The *acetyl* derivative, m. p. 231°, yields 4 : 6-dibromoacet-*o*-toluidide with bromine and potassium bromide, and 4 : 6-dichloroacet-*o*-toluidide with chlorine and sodium chloride. Vecchiotti's compound (A., 1926, 747), 3 : 4-diacetatomercuri-*o*-toluidine, m. p. 208°, is obtained when the reaction with mercuric acetate is carried out in aqueous-alcoholic solution at 55°. The acetyl derivative yields 3 : 4-dibromoacet-*o*-toluidide, m. p. 199° (Verda, A., 1903, i, 21), which is hydrolysed to 3 : 4-*dibromo*-o-*toluidine*, m. p. 44—45° (*hydrochloride*, m. p. 170—171°); this, when diazotised, reduced with sodium stannite, and decomposed, yields the known 2 : 3-dibromotoluene, thus proving the constitution of the preceding compounds and that of the 3 : 4-dichloro-*o*-toluidine, m. p. 41—42° (previously given, in error, as 161—162°), already prepared (Vecchiotti, *loc. cit.*). 4-*Acetatomercuri*-o-*toluidine*, m. p. 129—130° (accompanied by the 3 : 4-derivative), is obtained by interaction of *o*-toluidine (2 mols.) with mercuric acetate (1 mol.) in aqueous alcohol at 55° (10 min.) followed by keeping at 25° for 24 hrs. The *acetyl* derivative, m. p. 212—213°, yields 4-bromoacet-*o*-toluidide (hydrolysed to 4-bromo-*o*-toluidine) or 4-chloroacet-*o*-toluidide by the usual methods. R. K. CALLOW.

Lead diaryldialkyl compounds. H. GILMAN and L. BALASSA (Iowa State Coll. J. Sci., 1929, **3**, 105—107).—Lead diphenyl-dibutyl, -di*iso*butyl-, -di-*sec*.-butyl, and -di-*tert*.-butyl (m. p. 177°) were prepared by treating lead diphenyl dibromide with the appropriate magnesium butyl bromide. The anti-knock properties of the substances were examined. CHEMICAL ABSTRACTS.

Preparation of lead triphenyl chloride and lead diphenyl dichloride. H. GILMAN and J. D. ROBINSON (J. Amer. Chem. Soc., 1929, **51**, 3112—3114).—Lead triphenyl chloride is obtained in 75% yield by passing hydrogen chloride into a warm solution of lead tetraphenyl in chloroform until lead diphenyl dichloride begins to separate. The residue from the filtered solution is extracted with alcohol, which separates the chloride from the unchanged material (20%). The dichloride is obtained in 98·5% yield when hydrogen chloride is passed into a benzene solution of lead tetraphenyl at 50°. H. BURTON.

Heterocyclic systems containing selenium. II. *cyclo*Selenopentane. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1929, 2197—2202).—The action of

αε-pentamethylene dibromide at 80° in an atmosphere of hydrogen on aqueous sodium selenide (prepared *in situ* from hydrogen selenide and alcoholic alkali) gave cyclo*selenopentane*, b. p. 158°/759 mm., n_D^{18} 1·5475, d_4^t 1·424—0·001236*t* (*mercurichloride*, m. p. 175—176°; *methiodide*, sublimes in open tube at 160°, m. p. in closed tube 165—166°). Carbon tetrachloride solutions of the last compound gave with solutions of the appropriate halogen: cyclo*selenipentane* 1 : 1-*dichloride*, m. p. 103° [dilute aqueous solutions of which gave with chloroplatinic acid cyclo*selenipentane* 1-*chloroplatinate*, m. p. 216° (decomp.) after shrinking at 190°, whilst hot concentrated solutions formed *bis*-1-*chloro*cyclo*selenipentane* 1-*chloroplatinate*, decomp. 160°]; cyclo*selenipentane* 1 : 1-*dibromide*, m. p. 117—118° (*perbromide*, $C_5H_{10}SeBr_2,Br_5$, decomp. in air, leaving dibromide); and the corresponding 1 : 1-*di-iodide*, m. p. 114°.

Treatment of the above dichloride or dibromide in aqueous solution with excess of fresh silver oxide gave cyclo*selenipentane* 1 : 1-*dihydroxide*; this by mixing with an equimolecular proportion of the 1 : 1-dichloride or by treating the 1 : 1-dichloride with sufficient silver oxide to remove only half its chlorine gave cyclo*selenipentane* 1-*hydroxy*-1-*chloride*, decomp. at 110—111°.

By heating *cyclo*selenopentane with ethylene dibromide and water for 1 week in a sealed tube at 100° 1-β-*bromoethyl*cyclo*selenipentane* 1-*bromide*, m. p. 88°, was formed. With moderately concentrated nitric acid *cyclo*selenopentane gave the 1 : 1-dinitrate; fuming nitric acid and aqueous potassium permanganate caused rupture of the ring. The derivatives described are less stable than the corresponding derivatives of *cyclo*selenobutane. The parachor, 264·2, is considered evidence that *cyclo*selenopentane is a normal liquid.

Potassium selenocyanate and pentamethylene dibromide, heated in acetone solution, gave αε-*pentamethylene diselenocyanate*, a viscous oil, which, by treatment with alcoholic potassium hydroxide, formed cyclo*pentamethylene diselenide* (cyclo*diselenopentane*). This by heating strongly produced *cyclo*selenopentane or by the action of bromine in chloroform solution yielded *cyclo*selenipentane 1 : 1-dibromide or *cyclo*pentamethylene diselenide tetrabromide according to the amount of bromine used. The last substance decomposed with production of *cyclo*selenipentane 1 : 1-dibromide. R. J. W. LE FÈVRE.

Interactions of basic tellurium chloride and the cresols. G. T. MORGAN and H. BURGESS (J.C.S., 1929, 2214—2219).—Addition of the cresol to "basic tellurium chloride" (prepared by oxidising tellurium with nitric acid, removal of excess of nitric acid, and repeated evaporation with concentrated hydrochloric acid) suspended in dry ether, followed by distillation of the ether and maintenance at 120—130° for *o*- or *m*-cresol or 110—120° for *p*-cresol gave, respectively, 4-*hydroxy*-3-*methylphenyltellurium trichloride*, decomp. 208—209°, and two isomeric *di*-o-*hydroxyditolyl telluridichlorides*, A, decomp. 198—198°, B, decomp. 177—178°, one of which is probably $(OH{\cdot}C_6H_3Me)_2TeCl_2$ (Me : OH = 3 : 4); *di*-4-*hydroxydi*-2-*methyldiphenyl telluridichloride*, which by boiling with 95% alcohol or by dissolution in hot aqueous sodium carbonate followed by acidification passed by elimination of one third of the tellurium into *tri*-4-*hydroxytri*-2-*methyltriphenyltelluronium chloride dihydrate*, m. p. 184—185° (the corresponding *telluronium hydroxide* gave a *sodium* salt, m. p. 137—138° with subsequent resolidification); and *tri*-2-*hydroxytri*-5-*methyltriphenyltelluronium tellurium oxychloride*, $[(HO{\cdot}C_7H_6)_3Te]TeOCl_3$, decomp. 229—230°, *di*-2-*hydroxydi*-5-*methyldiphenyl telluridichloride*, decomp. 213—214°, and *tri*-2-*hydroxytri*-5-*methyltriphenyltelluronium chloride dihydrate*, m. p. 244—245° (decomp.). Interaction of *m*-cresol and tellurium tetrachloride, both in ethereal solution, gave an oil which was converted by ice-cold potassium metabisulphite solution into small yields of *di*-4-*hydroxydi*-2-*methyldiphenyl telluride*, m. p. 143—144°. The low yield is taken as indicating that the effective agent in this condensation is the small amount of basic tellurium chloride produced by the action of moisture on the tetrachloride. R. J. W. LE FÈVRE.

Constitution of triphenylsilicane and its reaction with sodium in liquid ammonia. H. H. REYNOLDS, L. A. BIGELOW, and C. A. KRAUS (J. Amer. Chem. Soc., 1929, **51**, 3067—3072).—Magnesium phenyl bromide (4·5 mols.) and trichlorosilicane afford 73% of triphenylsilicane (I), m. p. 36—37° (cf. Ladenburg, A., 1907, i, 668, who gives m. p. 200—203°). Kipping and Murray's triphenylsilicane (this vol., 586) is impure. Bromine in carbon tetrachloride converts I into triphenylsilicyl bromide, which is decomposed by boiling dilute sodium hydroxide to triphenylsilicol. When I is treated with sodium in liquid ammonia 0·66 g.-atom of sodium is used, but 1·9 atoms of hydrogen are evolved. Decomposition of the product formed with ammonium bromide affords a viscous oil and *bistriphenylsilicylamine* (II) $(SiPh_3)_2NH$, m. p. 175°; decomposition with ethyl bromide, bromobenzene, or oxygen also gives II. Hydrolysis of II with 6*N*-hydrochloric acid affords ammonium chloride and triphenylsilicol. II is stable towards dilute sodium hydroxide and air. H. BURTON.

Series arrangement of organic groups. I. As determined by halogenation of mixed stannanes. R. H. BULLARD (J. Amer. Chem. Soc., 1929, **51**, 3065—3067).—*Triphenylbenzylstannane*, m. p. 90—91°, prepared from sodium triphenylstannide and benzyl chloride in liquid ammonia, is converted by bromine (2 mols.) in benzene and carbon tetrachloride solution into *phenylbenzylstannic dibromide*, m. p. 74—75°. The series arrangement of groups based on the ease of their removal from stannanes by halogen is: Ph, $\cdot CH_2Ph$, Me, Et, Pr. H. BURTON.

Reaction between proteins and diazotised aromatic amines in neutral solution. M. HEIDELBERGER and F. E. KENDALL (Proc. Soc. Exp. Biol. Med., 1929, **26**, 482—484).—Chemical interaction, with formation of dyes, takes place in neutral mixtures of diazotised aromatic amines and proteins. CHEMICAL ABSTRACTS.

Structure of silk fibroin. E. ABDERHALDEN and H. BROCKMANN (Biochem. Z., 1929, **211**, 395—411).—Silk fibroin dispersed in concentrated lithium bromide solution could not be separated into different fractions by dialysis, precipitation with ammonium

sulphate solution, or fractionation of the benzoyl derivative. Silk fibroin was condensed with benzoyl chloride, also with *p*-chloro- and *p*-bromo-benzoyl chloride. The introduction of the simple or halogenated benzoyl radicals into the dispersed fibroin gave derivatives containing chiefly easily hydrolysable groups and a smaller amount hydrolysed only with difficulty. The ratio of these was approximately the same for all three benzoyl groups, indicating that silk fibroin is homogeneous. The easily hydrolysed groups are probably attached to hydroxyl and the others to amino-groups of tyrosine and serine; thus the hydroxyl groups are presumably not concerned in the linking up of the amino-acids. Silk fibroin and sericin can be separated by means of ammonium sulphate. J. H. BIRKINSHAW.

Electrolyte-free proteins. VIII. Free charge and neutral salt effects of pure proteins. T. ITO and W. PAULI (Biochem. Z., 1929, **213**, 95—108; cf. this vol., 394).—The conductivity of solutions of pure egg-albumin, serum-albumin, glutin, and pseudoglobulin was determined. Chlorides of the alkali metals up to concentrations of 0·2*M* were unable to change the anodic migration of egg- and serum-albumin. The alkaline-earth chlorides at 0·05*M* produced migration in both directions. Glutin was more susceptible to the action of salts, the migration being actually reversed by 0·004*M*-barium chloride. Potassium salts change the cathodic migration of pseudoglobulin in concentrations varying from 0·05*M* for the chloride to $2·5 \times 10^{-5}$ for the ferrocyanide. The direction of migration cannot be inferred from the position of the isoelectric point.

J. H. BIRKINSHAW.

Analytical reactions of lead tetraethyl. G. EDGAR and G. CALINGAERT (Ind. Eng. Chem. [Anal.], 1929, **1**, 221—222).—The lead in the organic compound is converted into bromide by treatment with a 30% solution of bromine in carbon tetrachloride, and the lead bromide either converted into chromate and weighed, or dissolved in ammonium acetate and titrated with standard molybdate solution. The method is available both for a concentrated preparation of lead tetraethyl and for its dilute solution in petrol. An alternative method in the former case is to decompose the material in benzene solution with 0·1*N*-iodine and titrate the excess of iodine with thiosulphate. If a mixture of lead triethyl and tetraethyl salts is present, the former may be removed by extracting the solution in light petroleum twice with concentrated aqueous ammonia; the lead in the extract and residual solution is then determined as above. H. F. HARWOOD.

Determination of quinol and pyrocatechol in presence of resorcinol and other phenols. I. F. BÖCK and G. LOCK (Monatsh., 1929, **53** and **54**, 888—896).—The determination of *p*-benzoquinone may be effected by shaking a chloroform solution with 10% potassium iodide and 10% sulphuric acid for a short time, and then titrating the liberated iodine with thiosulphate (cf. Willstätter and others, A., 1909, i, 535; 1910, ii, 553; Wieland, A., 1910, i, 243). Oxidation of a 0·2% aqueous solution of quinol with 10% ferric chloride solution, and determination of the *p*-benzoquinone formed (extracted by chloroform), gives practically quantitative results; 0·01 g. can be determined. The method gives values of 98·3—99·5% in presence of phenol, resorcinol, orcinol, phloroglucinol, pyrogallol, or hydroxyquinol. Pyrocatechol is determined similarly, using 0·05% aqueous solutions.

A preliminary account of the separation of quinol and resorcinol by initial oxidation with ferric chloride, extraction of the quinone with chloroform, and subsequent reduction of this with sodium hyposulphite is given. H. BURTON.

Application of semicarbazones to the determination of ketones. S. VEIBEL (J.C.S., 1929, 2423—2424).—A claim to priority (A., 1927, 1172) against Hobson (this vol., 949) and a comparison of the details of the two methods. J. W. BAKER.

Determination of small amounts of carotinoids. H. VON EULER, H. HELLSTRÖM, and M. RYDBOM (Mikrochem., 1929, Pregl Fest., 69—76).—Carotin and allied compounds such as dihydro-α-crocetin methyl ester can be determined colorimetrically when dissolved in dry chloroform with addition of antimony trichloride, a Lovibond tintometer being employed.

H. F. HARWOOD.

Microchemical method for determination of cerebrosides. P. KIMMELSTIEL (Mikrochem., 1929, Pregl Fest., 165—177).—The material (0·25 g.) is cooled in liquid air, powdered, and extracted with hot alcohol. A portion of the extract is hydrolysed by heating with 11% hydrochloric acid, the solution neutralised with sodium hydroxide, and the reducing substances present determined by Hagedorn and Jensen's method with potassium ferricyanide. The reducing substances present in the original alcoholic extract are determined similarly after removal of alcohol by evaporation, and the figure deducted from that previously obtained. The resultant value which represents the galactose formed by hydrolysis of the cerebrosides is multiplied by 4·6 to obtain the amount of cerebrosides present in the original material.

H. F. HARWOOD.

Biochemistry.

The respiratory enzyme and oxidases. O. WARBURG (Biochem. Z., 1929, **214**, 1—3).—When an extract of cells contains several oxidases, these do not represent enzymes present in the living cell, but are different breakdown products of a single substance therein. From the author's previous work it is likely that all the iron atoms in a cell which act as oxygen carriers in respiration are bound identically and that the respiratory enzyme is the same for different cells (cf. A., 1928, 537, 549, 795). P. W. CLUTTERBUCK.

The respiratory enzyme and oxygen storage. O. WARBURG (Biochem. Z., 1929, **214**, 4).—The red blood-corpuscle of a bird contains, besides the iron of

the respiratory enzyme, an iron compound—hæmoglobin—which stores oxygen. Displacement of oxygen from this store by carbon monoxide has no influence either at constant or decreasing oxygen tension on the respiration and can bring about with decreasing oxygen tension only an acceleration and never an inhibition of respiration. P. W. CLUTTERBUCK.

Respiration at low oxygen tensions. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, **214**, 5—18).—The respiration of cell suspensions (of *Micrococcus candicans*) measured by differential manometer at oxygen tensions as low as 10^{-5} atm. (0·008 mm.) is at 1° the same as, at 5° only a little greater, and at 10° slightly greater than the respiration in air. The importance of these results for the mathematical theory of respiration is indicated.

P. W. CLUTTERBUCK.

Is the inhibition of respiration by carbon monoxide complete? O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, **214**, 19—23).—The inhibition of respiration of cell suspensions (of *Torula utilis*) by carbon monoxide is the greater the greater is the carbon monoxide tension and the less is the oxygen tension and is as complete as the law of distribution will permit. Under the conditions used, 99% inhibition of respiration was readily obtained.

P. W. CLUTTERBUCK.

Action of carbon monoxide on the respiration of *Aspergillus oryzæ*. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, **214**, 24—25).—If 15-hr. agar cultures of *Aspergillus oryzæ* are placed in a mixture of 5% of oxygen and 95% of carbon monoxide, a smaller respiration is obtained than in oxygen of the same partial pressure diluted with argon. The respiration of these, as with most other cells, is reversibly inhibited by carbon monoxide.

P. W. CLUTTERBUCK.

Carbylamine-hæmoglobin and the photochemical dissociation of its carbon monoxide compound. O. WARBURG, E. NEGELEIN, and W. CHRISTIAN (Biochem. Z., 1929, **214**, 26—63).—The displacement of carbon monoxide and oxygen from iron–porphyrin compounds by the N:C grouping on addition of methylcarbylamine is investigated quantitatively. If a suitable amount of methylcarbylamine is added to a solution of oxyhæmoglobin through which oxygen at atmospheric pressure is passing, the red colour changes to violet and oxygen escapes. Bivalent iron is then present in solution and when carbon monoxide is passed, 1 mol. is absorbed per atom of iron. Manometric determination of the displacement of oxygen and carbon monoxide by methylcarbylamine shows that 1 mol. of carbylamine is absorbed for the displacement of 1 mol. of oxygen or carbon monoxide. In order to convert an appreciable fraction of hæmoglobin into its carbylamine compound, a carbylamine concentration of 0·001*M* is required. In presence of oxygen or carbon monoxide this concentration must be greater and then depends on the pressure of oxygen or carbon monoxide. Carbon monoxide-hæmoglobin in carbylamine solutions is the most highly light-sensitive carbon monoxide–iron–porphyrin compound as yet described. The distribution constant $K = C_{FeMeNC} \times C_{CO} / C_{FeCO} \times C_{MeNC}$ in yellow light of intensity 1 g.-cal./sq. cm. per min. at 10° increases to 3600 times its value in the dark, whereas for carbon monoxide-hæmoglobin in water under the same conditions no displacement of the dark equilibrium is obtained. The dark dissociation constant of the carbon monoxide compound in presence of methylcarbylamine is very much less than in its absence, thus falling into line with the requirements of the mathematical theory of photochemical dissociation. P. W. CLUTTERBUCK.

Absorption spectrum of the respiratory enzyme. O. WARBURG and E. NEGELEIN (Biochem. Z., 1929, **214**, 64—100).—To the six wave-lengths for which the absorption coefficients of the respiratory enzyme have been determined (A., 1928, 549; this vol., 216, 470) nine further wave-lengths are added, the spectral range now being from 254 to 603 μμ. The absolute absorption spectrum of the carbon monoxide compound of the enzyme is portrayed graphically. The methods are described whereby the fifteen wave-lengths are isolated, and the mathematical theory is given whereby the relative and absolute absorption coefficients of the enzyme are calculated. A photoelectric method is described for the determination of the absolute absorption spectrum of iron–porphyrin compounds over a spectral range of 250—600 μμ, thus avoiding the tedious photographic method.

P. W. CLUTTERBUCK.

Absorption spectrum of the respiratory enzyme of the retina. O. WARBURG and E. NEGELEIN (Biochem. Z., 1929, **214**, 101—106).—Using the wave-length 436 μμ, that intensity which appreciably dissociates the carbonyl compound of the respiratory enzyme of yeast (10^{-4} g.-cal./sq. cm./min.) also dissociates the carbonyl compound of the respiratory enzyme of retinal cells. In order to find the region of maximal absorption, the ratio of the light absorption coefficients for the wave-lengths 436 and 405 μμ was obtained; this was almost identical for the retinal and yeast respiratory enzymes.

P. W. CLUTTERBUCK.

Respiratory enzyme in the serum of suffocated animals. O. WARBURG and F. KUBOWITZ (Biochem. Z., 1929, **214**, 107—109).—Kempner's result (Klin. Woch., 1927, **6**, 2386) that the plasma of normal hens showed no respiration, whereas that of pest-infected hens used 5 c.mm. per c.c. per hr., is due, not to the infection, but to the suffocation causing death. Thus the plasma of normal hens suffocated by placing in an atmosphere of nitrogen shows quantitatively the same respiration, and it must be assumed that during suffocation the respiratory enzyme passes from the body-cells into the blood. P. W. CLUTTERBUCK.

Gasometric control of standard solutions for the Palmer hæmoglobin method. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1929, **84**, 211—216).—If the standard hæmoglobin solutions employed by Palmer (A., 1918, ii, 88) be saturated with pure carbon monoxide, and be kept in the dark at 7°, they remain unchanged for 32 weeks. The condition of the standard solutions can readily be controlled by determination of the carbon monoxide-combining capacity (A., 1928, 1149). C. R. HARINGTON.

Hæmoglobin maintenance on synthetic diets. D. L. DRABKIN and C. S. WAGGONER (Science, 1929, **69**, 480).—Dogs fed on the Karr–Cowgill diet maintained a normal hæmoglobin level and addition of copper sulphate was without effect on this and on recovery after bleeding. Growth, appearance, and hæmoglobin maintenance were normal in rats fed on both a copper-free diet and on a diet to which copper salts were added, and rats rendered anæmic by a milk diet were cured by the copper-free diet.
L. S. THEOBALD.

Relation of iron and copper to hæmoglobin synthesis in the chick. C. A. ELVEHJEM and E. B. HART (with A. R. KEMMERER) (J. Biol. Chem., 1929, **84**, 131—141).—In the chick as in rats (A., 1928, 790) both iron and copper are necessary for the normal synthesis of hæmoglobin. C. R. HARINGTON.

New amino-acid from hæmoglobin. S. FRÄNKEL and G. MONASTERIO (Biochem. Z., 1929, **213**, 65—71).—After digestion of oxyhæmoglobin with trypsin for 2 years a crystalline *amino-acid*, $C_{22}H_{46}O_7N_4$, m. p. 270° (decomp.), α_D^8 $-11{\cdot}76°$, was isolated from the methyl-alcoholic portion of the non-crystallisable dialysable syrup obtained. It has three carboxyl and four amino-groups.
J. H. BIRKINSHAW.

Absorption of ultra-violet light by oxyhæmoglobin and by some of its derivatives. C. S. HICKS and H. F. HOLDEN (Austral. J. Exp. Biol., 1929, **6**, 175—186).—Observations have been made of the absorption bands in the ultra-violet region of hæmoglobin (ox) and of certain related compounds. The following are the wave-lengths (in $\mu\mu$) at which maximum absorption takes place: oxyhæmoglobin, 411·5; hæmoglobin, 429·5; carbon monoxide-hæmoglobin, 417·9; methæmoglobin, 404·5; alkaline methæmoglobin, 410·6; alkaline hæmatin (in water) 384·7; alkaline hæmatin (in alcohol), 402·5; acid hæmatin (in water), 379·3; acid hæmatin (in alcohol), 398·7; globin, 279·0; denatured globin, 274·0.
W. O. KERMACK.

Gasometric determination of methæmoglobin. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1929, **84**, 205—210).—The method of Van Slyke for the determination of methæmoglobin (A., 1926, 443) has been combined with the technique employed for determining the carbon monoxide-combining capacity of blood (A., 1928, 1149), so that the whole operation can be carried out in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to 0·1—2 c.c. of blood. C. R. HARINGTON.

Gasometric determination of oxalic acid and calcium; application to serum analysis. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1929, **84**, 217—232).—Blood-serum or -plasma is freed from protein with trichloroacetic acid; an aliquot portion of the filtrate is treated with sodium acetate, ammonium oxalate, and ammonia to p_H 5·0 and kept over-night. The calcium oxalate is separated and washed with dilute ammonia at the centrifuge, and dissolved in *N*-sulphuric acid; the solution is transferred to the apparatus of Van Slyke and Neill (A., 1924, ii, 872), and, after extraction and rejection of dissolved gases, is treated with acid permanganate solution and shaken under diminished pressure, and the carbon dioxide evolved is determined in the usual manner. With samples of 1—2 c.c. of serum the results agree with those obtained by the titrimetric method to within $\pm 5\%$. With solutions of pure oxalic acid or calcium salts agreement to within $\pm 1\%$ can be obtained. C. R. HARINGTON.

Possibility of individual chemical synthesis of blood-proteins. I. Tryptophan content of human serum-proteins. K. LANG (Arch. exp. Path. Pharm., 1929, **145**, 88—99).—The tryptophan contents of 60 pathological sera were determined by the method of Fürth (A., 1924, ii, 576) or calculated from the albumin–globulin ratio. No correlation between tryptophan content and rate of sedimentation of erythrocytes was found (cf. Fischer and Weiss, Z. ges. exp. Med., 1925, **48**, 111—118). The results showed no agreement in 50% of the sera examined. These results are said to afford further experimental support for the views of Herzfeld and Klinger (A., 1918, i, 87). C. C. N. VASS.

Blood-tryptases and a micro-method for their determination. O. SOKOLNIKOV (Biochem. Z., 1929, **213**, 414—418).—The amount of protease in human blood is altered by the application of very slight physiological stimuli. By means of a modification of the method of Utkin-Ljubovzov (A., 1926, 648) the tryptase content of 0·1 c.c. of blood is deduced from determinations of total and residual nitrogen in the caseinogen precipitate.
W. MCCARTNEY.

Antitryptic activity of sera. G. YAMANAKA (Sei-i-kwai Med. J., 1929, **48**, No. 3, 62—78).—The antitryptic activity of serum is increased during menstruation, is greater in acute than in chronic diseases, is increased after ultra-violet irradiation, treatment with the vaccine of *B. coli communis* or egg-albumin, or injection of adrenaline, but is decreased during fasting. CHEMICAL ABSTRACTS.

Influence of hydrogen-ion concentration of the medium on the amylase activity of horse serum. B. ROUSSEU, Z. GRUZEWSKA, and G. ROUSSEL (Compt. rend., 1929, **189**, 589—590).—The amylase activities of blood obtained at successive bleedings of a horse show marked fluctuations. These fluctuations are similar in the same series of samples whatever be the p_H at which the activity is measured, but their amplitudes are most marked at p_H 6·4, the reaction at which the activity of amylase is maximum.
W. O. KERMACK.

Uric acid of the blood. D. LIOTTA (Arch. Farm. sperim., 1929, **46**, 241—258).—Experiments on dogs show that injection of lutein has no appreciable influence on the level of the uric acid of the blood, whereas suprarenal and pituitary extracts cause a lowering. Insulin and iodothyrin produce increases in the total and plasma-uric acid, in relation to that of the corpuscles; "caseum" behaves similarly, but the total uric acid of the blood varies markedly, whereas the increase in the plasma is more constant. In human beings, suprarenal extract especially causes a distinct diminution of the uricæmia and constant variations in the ratio between the plasmatic and corpuscular uric acid. With pituitrin and

"caseum" only very slight effects are observed. The influence of insulin is similar to that noticed with dogs. T. H. POPE.

Bang's method for the determination of fatty substances in blood. W. RADSMA and PIRNGADI (Arch. Néerland. Physiol., 1929, **14**, 345—358).—The times allowed for extraction and for oxidation of the fats in the method of Bang ("Mikromethoden zur Blutuntersuchung," 1922) have little effect on the values obtained, but the vessel must be open to the air during oxidation. In the precipitation of cholesterol by digitonin better results are obtained if the light petroleum is first entirely removed. K. V. THIMANN.

Fatty substances in the blood of Indonesians and Europeans in the tropics. PIRNGADI (Arch. Néerland. Physiol., 1929, **14**, 359—370).—A series of determinations has been made by Bang's method (cf. *supra*) on whole blood and on serum. Native employees exhibited a slightly lower content of cholesteryl esters and fatty acids than native students or Europeans. K. V. THIMANN.

Cholesterol content of blood of tropical inhabitants. W. RADSMA (Arch. Néerland. Physiol., 1929, **14**, 371—385).—The colorimetric method of Bloor for determination of cholesterol gives results about 40% higher than those obtained by precipitation with digitonin. This is ascribed, not to the presence of other colour-producing substances in blood, but to a difference between the cholesterol of blood and the pure commercial product. The cholesterol content of the blood of native employees is lower than that of students or of Europeans. One cause of this is ankylostomiasis. K. V. THIMANN.

Micro-determination of free cholesterol in blood. L. TUTKEVITSCH (Biochem. Z., 1929, **213**, 439—442).—Blood (100—120 mg.) is weighed on filter-paper, which is then extracted for some hours with light petroleum. The extract is concentrated to 1·0 c.c., transferred to a centrifuge tube, 0·1 c.c. of 0·5% digitonin solution is added, and the mixture, after being warmed, is kept over-night. The digitonin compound is then decomposed by the addition of 0·3 c.c. of 25% sodium hydroxide solution. After the mixture has been heated and cooled, 1·5 c.c. of chloroform are added and then anhydrous sodium dihydrogen phosphate is stirred in until the precipitate formed begins to settle. The colour of the liquid is compared with that of a standard. The error of the method amounts to ±2—3 mg. per 100 c.c. W. MCCARTNEY.

Cholesterol in the blood of the fresh-water mussel *Anodonta cygnæa*. A. DE WAELE (Natuurwetensch. Tijds., 1929, **11**, 154—157).—Cholesterol was identified after separation from the ether extract of the whole organism. Determinations of cholesterol on 100 c.c. of the blood showed the presence of 0·36 mg. in the plasma and 0·9 mg. in the corpuscles. S. I. LEVY.

Lipoid layer of sheep's chromocytes. F. GRENDEL (Biochem. Z., 1929, **214**, 231—241).—The lipins of sheep's erythrocytes when extracted and spread in a unimolecular layer occupy a surface which amounts to double the total surface of the chromocytes and since lipin does not exist within the cells it must be assumed that they are surrounded by a bimolecular layer of lipins, the thickness of which is shown to be 31 Å. The lipins after extraction are shown to contain 36% of cholesterol, 50% of kephalin, and 13% of sphingomyelin. The area occupied by the lipins is 10% greater on buffered solutions not containing calcium than on distilled water. It is also a little greater on addition of 3·75—5 mg. of calcium per 100 c.c., but is 12% smaller with 11 mg. of calcium (an amount corresponding with the calcium content of blood). Decrease of plasma-calcium, therefore, is accompanied by decrease of the lipoid layer of the corpuscles. P. W. CLUTTERBUCK.

Fixation of dextrose by blood-corpuscles. H. HÄUSLER and O. LOEWI (Biochem. Z., 1929, **214**, 229—230).—A reply to Högler, Thomann, and Überrack (this vol., 1096). P. W. CLUTTERBUCK.

Reducing power of blood after acid hydrolysis. F. SILBERSTEIN, F. RAPPAPORT, and M. WACHSTEIN (Biochem. Z., 1929, **213**, 355—374).—The methods so far used for the determination of the total carbohydrate content of blood have been examined and the following procedure is now recommended: 0·1 c.c. of blood is heated for 4 hrs. at 100° with 1·0 c.c. of 0·67*N*-sulphuric acid. To the cooled solution 5 c.c. of water and 1 c.c. of 10% sodium tungstate solution are added and the mixture is heated for 3 min. at 45°, cooled, diluted with water to 15 c.c., and filtered. To 5 c.c. of the filtrate, 2 c.c. of 8·2% potassium carbonate solution are added and the original procedure of Hagedorn and Jensen is then followed. This method is shown to determine accurately the chief carbohydrates which occur in blood in pathological conditions. It gives results higher than those found with other methods, partly because it determines glucosamine. It has been found that blood contains substances which reduce potassium ferricyanide in the cold, but the amount of these does not vary much in the same animal. The blood of normal and of diabetic dogs to which peptone or dextrose was administered and of normal and diabetic dogs to which insulin was subcutaneously administered with and without simultaneous administration of sugar has been examined by determining both the direct reducing power and the reducing power after hydrolysis. These reducing powers varied and the results are discussed. W. MCCARTNEY.

Rôle of reducing colloids in blood-sugar determination. S. DONHOFFER and M. MITTAG-DONHOFFER (Biochem. Z., 1929, **213**, 195—201).—The method of Bang gives higher results than that of Hagedorn and Jensen for sugar in plasma, serum, and egg-albumin. This is due to a reducing, non-fermentable substance of colloid nature precipitated by zinc hydroxide, but not completely by uranyl acetate. It is present as both a coarse and a fine dispersion. The method of Hagedorn and Jensen gives results corresponding closely with fermentable sugar. J. H. BIRKINSHAW.

Reducing powers of different sugars for ferricyanide. J. A. HAWKINS (J. Biol. Chem., 1929, **84**, 79—82).—Figures are given for the relative reducing

powers of different sugars for the alkaline ferricyanide reagent employed in the gasometric method of Van Slyke and Hawkins (A., 1928, 1358).

C. R. HARINGTON.

Micro-determination of reducing sugars in blood and urine. J. A. HAWKINS (J. Biol. Chem., 1929, **84**, 69—77).—The method of Hawkins and Van Slyke (this vol., 462) has been modified so as to be applicable to 0·2 c.c. of blood, the error of the determination remaining ±5%. C. R. HARINGTON.

Micro-determination of chlorides in blood. W. B. ROSE and C. J. STUCKY (Mikrochem., 1929, Pregl Fest., 300—301).—The method of Van Slyke has been modified to permit the determination in 0·1 c.c. of blood. The blood is measured out by a micro-pipette, added to distilled water, and 1 c.c. of a standardised solution of silver nitrate added. The whole is heated until the supernatant liquid is clear and the silver chloride coagulated, and the excess of silver is then titrated with a solution of potassium thiocyanate containing 0·554 g. per litre.

H. F. HARWOOD.

Influence of protein and inorganic phosphorus on serum-calcium. J. P. PETERS and L. EISERSON (J. Biol. Chem., 1929, **84**, 155—166).—The indications of previous work (cf. Binger, A., 1917, i, 677; Salvesen and Linder, A., 1924, i, 442), that the concentration of calcium in the blood-serum falls with increase in the inorganic phosphate and with decrease in the protein, are confirmed. The relationship $Ca = -0{\cdot}255P + 0{\cdot}566 \times \text{protein} + 7$, where Ca and P represent the calcium and inorganic phosphorus in mg. per 100 c.c., and the protein is expressed in g.-%, was found to hold good in a large series of pathological cases. C. R. HARINGTON.

Condition of calcium in body fluids. K. KLINKE (Biochem. Z., 1929, **213**, 177—189).—The calcium of serum ultrafiltrate is not precipitated by freezing. It is precipitated as carbonate by shaking with calcium phosphate (avoiding loss of carbon dioxide). More carbon is precipitated than stoicheiometric theory expects. The calcium of serum ultrafiltrate, contrary to that in supersaturated Ringer's solution, wanders in the electric field to both cathode and anode; there is present in serum a negatively-charged calcium compound. By addition of caffeine the ultrafiltrability of serum-calcium is increased by 40%. Only about 2 mg. per 100 c.c. of the calcium of serum is ionised. J. H. BIRKINSHAW.

Blood coagulation. XXII. Significance for blood coagulation of nitrogenous substances. B. STUBER and K. LANG (Biochem. Z., 1929, **213**, 460—468).—When blood coagulates there is no measurable change in its residual nitrogen content. No relation can be found between the formation of ammonia in blood and its coagulation. The preparation "18 Promonta," which is hydrolysed by trypsin-kinase, inhibits glycolysis of blood *in vitro* and *in vivo*, the extent of the inhibition being parallel to the retardation of coagulation. Proteolysis is not a cause of blood coagulation. W. MCCARTNEY.

Immunisation and the nitrogenous constituents of the blood. M. F. GUYER and S. LEPKOVSKY (J. Immunol., 1929, **16**, 175—207).—When a foreign protein is injected into the blood-stream of rabbits the blood-amino-nitrogen (except in moribund animals) tends to diminish, the non-protein-nitrogen increases, the p_H and alkaline reserve are lowered, and the body tissues exhibit acidosis.

CHEMICAL ABSTRACTS.

Chemical nature of the constituent of fowl serum responsible for non-specific precipitations. G. S. SCHILLING (J. Immunol., 1929, **16**, 439—449).—The constituents of fowl sera responsible for non-specific precipitations appear to be lipoproteins and neutral fats. CHEMICAL ABSTRACTS.

Mode of action of formaldehyde on complement-fixation systems. C. E. REYNER (J. Immunol., 1929, **16**, 1—16).

CHEMICAL ABSTRACTS.

Carbohydrate group of ovomucoid. P. A. LEVENE and T. MORI (J. Biol. Chem., 1929, **84**, 49—61).—Coagulated egg-white was hydrolysed for 7 hrs. with 10% barium hydroxide. After removal of barium the solution was cleared with basic lead acetate and concentrated; the carbohydrate in the residue was precipitated with basic lead acetate and barium hydroxide. The solution obtained after decomposition of the lead precipitate with carbon dioxide was treated with mercuric sulphate to remove traces of peptide; mercury and sulphuric acid having been removed, the solution was concentrated and poured into excess of methyl alcohol, yielding 1·9% of polysaccharide. The same material was obtained in yields of 0·26% and 5·1% by similar treatment of crystalline egg-albumin and of ovomucoid, respectively. In agreement with Fränkel and Jellinek (A., 1927, 862) the material was found to yield, on complete hydrolysis, exclusively glucosamine and mannose; it had $[\alpha]_D^{20}$ about +30° in water, and, contrary to Fränkel and Jellinek (*loc. cit.*), analysed as a trisaccharide. Dialysis failed to separate it into different constituents. On partial hydrolysis, it gave a reducing trisaccharide.

C. R. HARINGTON.

Molecular size of carbohydrates from egg-proteins. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1929, **84**, 63—68).—Determinations by the diffusion method indicate for the polysaccharide obtained from egg-proteins (cf. preceding abstract) a mol. wt. of 2000 and, for its partial hydrolysis product, one of 500. The polysaccharide therefore consists of four trisaccharide units, each containing 1 mol. of glucosamine and 2 mols. of mannose.

C. R. HARINGTON.

Distribution and variation of glycogen in the intestinal mucous membrane of the mammalian embryo. I. MARUYAMA (Okayama J. Med., 1928, **40**, 1296—1333).—Results for rabbit's, marmot's, and dog's intestinal mucous membrane are recorded. Changes in the quantity of free and lactacidogen phosphoric acid with lapse of time after conception are recorded. The intestinal mucous membrane of marmots contains much, and that of dogs little, insulin-like substance. CHEMICAL ABSTRACTS.

Glycogen in the central nervous system of some mammals. III. Effects of inanition. H. TANAKA (Sei-i-kwai Med. J., 1929, **48**, No. 2, 51—81).

—Experiments with rabbits and guinea-pigs are described. CHEMICAL ABSTRACTS.

Glycogen. I. S. HARADA (Sei-i-kwai Med. J., 1929, **48**, No. 1, 46—83).—The glycogen in the kidney, pelvis of the kidney, ureter, and bladder epithelium is formed locally from blood- and urine-sugar. CHEMICAL ABSTRACTS.

Glycogen content of the liver of cadavers. H. POPPER and O. WOZASEK (Wien. med. Woch., 1929, **79**, 456—458; Chem. Zentr., 1929, i, 2788).

Mineral content of the skin. I. Micro-determination of potassium and calcium. E. NATHAN and F. STERN (Dermat. Z., 1928, **53**, 451—456; Chem. Zentr., 1929, i, 2800).—The skin (0·5 g.) is incinerated with nitric acid and hydrogen peroxide and the determination then made in the usual way. Variable results (potassium, 53—145 mg.-%; calcium 5·96—17·81 mg.-%) were obtained for the skin of cadavers. A. A. ELDRIDGE.

Inorganic constituents of the musculature of the Fallopian tubes (of the sow) and their physiological variations. F. KOK and W. BERGMANN (Biochem. Z., 1929, **213**, 424—438).—The water, ash, potassium, sodium, calcium, magnesium, phosphorus, sulphur, chlorine, and nitrogen contents of the musculature of the Fallopian tubes of sows have been determined at different stages during the œstral period. Important differences have been found between the contents of inorganic constituents of smooth muscle and of transversely striated muscle and great differences in this content are also found between the musculature of the Fallopian tubes and that of other smooth muscle organs of the same animal. During œstrus, also, both the total ash content and the relative proportions of the various inorganic constituents of the musculature of the tubes vary considerably. W. MCCARTNEY.

Cerebronic acid. F. A. TAYLOR and P. A. LEVENE (J. Biol. Chem., 1929, **84**, 23—37).—A large amount of cerebronic acid was oxidised by the method of Levene and Taylor (A., 1922, i, 714) and the oxidation product was esterified; the esters were submitted to repeated fractional distillation at 0·1 mm. The distillation residues, when hydrolysed, yielded acids with mol. wt. 367—374; on reoxidation, followed by esterification and fractionation, this part of the material yielded a *tetracosoic acid*, m. p. 78·5—79·5°. The distillates gave acids of mol. wt. 351—356, and from this portion, by fractional crystallisation, was obtained an apparently pure tricosoic acid which is probably that described by Klenk (A., 1928, 868). This material was, however, not in reality homogeneous, since more exhaustive fractionation of the esters from which it was derived yielded, together with acids of higher mol. wt., a fraction which gave the analytical figure for docosoic acid, although this fraction contained material of still lower mol. wt. The results indicate that cerebronic acid contains, in addition to α-hydroxypentacosoic acid, lower hydroxy-acids or hydroxypentacosoic acids with the hydroxyl group in different positions; the m. p. of the impure acids obtained in the above experiments render it doubtful whether they belong to the lignoceric acid series. C. R. HARINGTON.

Conditions for the combination of the grey matter of the brain with quinine. P. I. BORISSOV, A. PETRUNKINA, and M. PETRUNKIN (Biochem. Z., 1929, **213**, 419—423).—At low hydrogen-ion concentrations the grey matter of the human brain combines not at all or only very slightly with quinine. At p_H 3—4 the extent of combination begins to increase and reaches considerable magnitude at p_H 6—7. The amount of quinine which enters into combination increases with increase of the protein content of the grey matter, but this may also contain substances, other than proteins, which combine with quinine. W. MCCARTNEY.

Extractive substances of muscle. XXVIII. Extractive substances of hen's flesh. N. TOLKATSHEVSKAYA (Z. physiol. Chem., 1929, **185**, 28—32).—From hen's flesh a base, $C_{10}H_{16}O_3N_4$, was isolated, agreeing closely in properties with anserine. J. H. BIRKINSHAW.

Lower enzymic fission products of muscle-adenylic acid. K. POHLE (Z. physiol. Chem., 1929, **185**, 9—27).—Although purine bases and nucleosides could not be obtained from fresh rabbit's muscle this was easily effected after exposure of the muscle at 40° to sodium hydrogen carbonate for a few hours. Addition of adenylic acid increases the amount of these substances—an indication of their origin. There were isolated carnine, m. p. 235—245°, hypoxanthine, and xanthine, and small amounts of a substance probably identical with thymine. The presence of pentosephosphoric acid was probable. Muscle-adenosinephosphoric acid is suggested as the precursor of endogenous uric acid. J. H. BIRKINSHAW.

Determination of carbon dioxide content of muscle. J. K. W. FERGUSON and L. IRVING (J. Biol. Chem., 1929, **84**, 143—153).—Muscle is fixed by freezing in liquid air, and a sample of about 1·5 g. is introduced into the extraction chamber (made for this purpose in two sections connected by a ground joint) of the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The carbon dioxide is extracted by shaking for 45 min. with excess of dilute hydrochloric acid, and is then determined in the usual manner. The error is within 2%. C. R. HARINGTON.

Acetylcholine. H. W. DUDLEY (Biochem. J., 1929, **23**, 1064—1074).—Acetylcholine chloroplatinate, which crystallises in anisotropic needles, forms with choline chloroplatinate an equimolecular co-ordination compound, m. p. 260—261°, which is less soluble than either of its components and crystallises in isotropic octahedra. Its significance in connexion with the isolation of acetylcholine from natural sources is discussed. A further identification of acetylcholine isolated from horse's spleen as *choline–acetylcholine dichloroplatinate* is provided by the preparation of acetylcholine chloroaurate from the double chloroplatinate. Acetylcholine chloride is liberated quantitatively from acetylcholine chloroaurate by shaking an aqueous solution of the latter with metallic silver. This method can be applied generally to the preparation of chlorides or hydrochlorides of bases from their

chloroplatinates and chloroaurates, and is particularly useful with salts of relatively unstable bases. A structural basis for the well-known dimorphism exhibited by choline chloroplatinate is suggested.
S. S. ZILVA.

Condition of creatine in amphibian voluntary muscle. W. DULIÈRE (Biochem. J., 1929, **23**, 921—925).—In many cases of resting muscles the ratio of free creatine to free orthophosphate is practically unity, but exceptions to this rule are not infrequent, the ratio reaching sometimes a value of two. The combined creatine and the labile phosphate occur in the ratio of unity. The total creatine and the total "directly determinable phosphate" (orthophosphate and labile phosphate) are present consequently in many cases in approximately equimolecular amounts. In resting, well-oxygenated muscles the free creatine may be no more than 50 mg. per 100 g. of fresh muscle.
S. S. ZILVA.

Change in the condition of equilibrium of cell components. III—IV. Proteins. T. CAHN and A. BONOT (Ann. Physiol. Physicochim. Biol., 1928, **4**, 781—845; Chem. Zentr., 1929, i, 2890).—The structure of protein molecules is discussed. The arginine content of the protein of various organs is constant. The arginine : cystine ratio for the kidney, muscle, or brain protein is 8 : 3; for that of the lungs, intestinal mucous membrane, or intestinal muscle other values are obtained. A. A. ELDRIDGE.

Determination of the density of small fragments of [human] organs. M. DE CRINIS (Mikrochem., 1929, Pregl Fest., 25—26).—An account of a method for determining the density of small fragments of brain material, using a torsion balance.
H. F. HARWOOD.

Existence of the hæmolytic complement in human cerebrospinal fluid. I. T. OKADA (Sei-i-kwai Med. J., 1929, **48**, No. 3, 41—61).
CHEMICAL ABSTRACTS.

Amphibian poisons. O. GESSNER (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1927, **61**, 138—250; Chem. Zentr., 1929, i, 2788—2789).—A discussion of toad, frog, and salamander toxins.
A. A. ELDRIDGE.

Effect of various substances of the quinine group on the enzymic functions of the organism. XII. Effect of quinine on the secretion of the gastric juice in man. I. A. SMORODINCEV, A. N. ADOVA, and I. N. PIKOUL (Biochem. Z., 1929, **213**, 380—390).—Quinine when orally administered reduces the hydrogen-ion concentration of the gastric juice, stimulates the secretory activity of the stomach, and inhibits the digestion of protein. It is retained in the stomach somewhat longer than is methylene-blue.
W. MCCARTNEY.

Excretory function of the stomach. II. Excretion of hexamethylenetetramine by the stomach wall. G. DE TONI (Biochim. Terap. sperim., 1928, **15**, 7 pp.; Chem. Zentr., 1929, i, 3002).—When the amount of hexamethylenetetramine injected into rabbits exceeded 0·002 mol. per kg., the substance could be detected in the gastric juice. With children, the limits were 0·0005 mol. (intramuscular) and 0·001—0·0015 (rectal). The gastric juice liberates formaldehyde from hexamethylenetetramine. A. A. ELDRIDGE.

Heller's test for blood in urine. BECKER (Med. Welt, 1929, **3**, 134—135; Chem. Zentr., 1929, i, 2675).—The test is not specific. A. A. ELDRIDGE.

Detection of minute amounts of bismuth in urine. H. K. BARRENSCHEEN and M. FREY (Mikrochem., 1929, Pregl Fest., 1—5).—Feigl's reaction has been applied to the detection of bismuth in urine. To 100 c.c. of the urine three drops of 3% lead acetate solution are added, followed by ammonia to strongly alkaline reaction. The precipitate is centrifuged, dissolved in concentrated nitric acid, and the solution evaporated and ignited. The residue is dissolved in hydrochloric acid, and the diluted solution tested with an alkaline solution of sodium stannite. In the presence of bismuth the resulting precipitate rapidly turns black, or in the presence of very small amounts, brownish. The reaction will detect 0·00005 mg. of bismuth in 5 c.c. of solution; small amounts of iron and copper do not interfere. H. F. HARWOOD.

Determination of the oxidation quotient of urine. H. MÜLLER (Biochem. Z., 1929, **213**, 116—122).—The method previously described (A., 1927, 996) for determination of the oxidation quotient of urine gives low values. An improved method consists in boiling 5 c.c. of urine with the requisite amount of potassium iodate and 20 c.c. of sulphuric acid for 3 hrs. under reflux. The mixture is then diluted, the free iodine boiled out, and the excess of iodate titrated. For chloride determinations the method of Votocek is recommended.
J. H. BIRKINSHAW.

Reduction of mercury salts by normal urine. H. PÉNAU and G. TANRET (Compt. rend., 1929, **189**, 713—715).—The method of Baudouin and Lewin gives the total reducing power of the urine. From determinations performed after previous treatment with basic lead acetate and acid mercuric nitrate respectively, conclusions are reached concerning the amounts of substances of the uric acid, creatinine, and carbohydrate groups present. A. A. GOLDBERG.

Change of hydrogen-ion concentration in the urine at low atmospheric pressure. S. MATSUKA (Naval J. Med., 1928, **17**, 261—263).—Excretion of alkali is increased. CHEMICAL ABSTRACTS.

Reaction of urine. G. KAYE (Austral. J. Exp. Biol., 1929, **6**, 187—214).—An alkaline tide in the urine is usually but not constantly observed 3—4 hrs. after the taking of a meal, being less marked in the case of a carbohydrate meal than in the cases of a mixed meal or of a meat meal. It is concluded that the alkaline tide is dependent on the gastric secretion of acid and not on increased respiration with subsequent loss of carbon dioxide. The clinical bearings of the observations are discussed. W. O. KERMACK.

Reaction of the morning urine. R. S. HUBBARD (J. Biol. Chem., 1929, **84**, 191—197).—In individuals with normal gastric function there is usually an increase in the alkalinity of the urine after breakfast. In cases of achlorhydria there may be no change in reaction, or there may be a progressive increase in acidity from the time of waking. Finally some cases

with normal gastric function secrete an alkaline urine throughout the morning. The results are explained by the combined effect of two "alkaline tides," one due to secretion of hydrochloric acid in the stomach, and the other to respiratory elimination of carbon dioxide which has accumulated over-night.

C. R. HARINGTON.

Variations in the morning alkaline tide of normal individuals. R. S. HUBBARD and T. M. STEELE (J. Biol. Chem., 1929, **84**, 199—204).—No consistent effects on the reaction of the morning urine in normal individuals were obtained by varying the food taken at breakfast (cf. preceding abstract).

C. R. HARINGTON.

Peptidase in diseases. R. KRAFT (Deut. Z. Chir., 1928, **208**, 126—151; Chem. Zentr., 1929, i, 2675).

Post-operative blood. K. REUTERSKIOLD and E. ANDREWS (Proc. Soc. Exp. Biol. Med., 1928, **26**, 17—18).—After surgical operations under ether anæsthesia the calcium : potassium ratio in dogs' blood was temporarily lowered.

CHEMICAL ABSTRACTS.

Iron in nutrition. X. Specificity of copper as a supplement to iron in the cure of nutritional anæmia. J. WADDELL, H. STEENBOCK, and E. B. HART (with E. VAN DONK) (J. Biol. Chem., 1929, **84**, 115—130).—Zinc, chromium, germanium, nickel, cobalt, lead, antimony, tin, cadmium, mercury, and manganese were unable to relieve the nutritional anæmia of rats on a diet of whole milk and iron salts. Arsenic had a slight temporary effect, which did not approach that of copper (A., 1928, 790); in this respect, therefore, copper is a unique and necessary element in nutrition.

C. R. HARINGTON.

Hæmoglobin percentage and the red blood-cell count in Bright's disease, myocardial insufficiency, and hypertension. B. ASHE (Arch. Int. Med., 1929, **44**, 506—530).—The theoretical and practical importance of the red blood-cell count and hæmoglobin index in cases of nephritis and allied conditions is emphasised.

W. O. KERMACK.

***d*-Lactic acid in gastric juice [in cancer].** T. KUBO (J. Kyoto Pref. Med. Coll., 1928, **2**, 261—292).—In the cancerous stomach one third of the lactic acid present is usually *d*-lactic acid; the presence of this acid, probably derived from the stomach wall involved, is believed to be peculiar to the disease.

CHEMICAL ABSTRACTS.

Arginine metabolism in tuberculosis and carcinoma. H. FUJIWARA (Z. physiol. Chem., 1929, **185**, 1—7).—The arginase values of tuberculous guinea-pigs and carcinomatous mice were recorded over long periods. Tuberculosis causes a steady decline in the value for liver, kidneys, and total arginase, but a definite increase for muscle and spleen. In carcinoma, the arginase value of the kidneys begins to fall a few days after inoculation and decreases with the development of the tumour. The difference in value between males and females is confirmed.

J. H. BIRKINSHAW.

Biometry of calcium, inorganic phosphorus, cholesterol, and lecithin in the blood of rabbits. IV. Effects of a malignant tumour. A. R. HARNES (J. Exp. Med., 1929, **50**, 109—120).—Blood-cholesterol and serum-inorganic phosphorus increased. The ratios cholesterol : calcium and lecithin : calcium tended to increase, whilst the ratios calcium : inorganic phosphorus, lecithin : cholesterol, and lecithin : inorganic phosphorus tended to decrease.

CHEMICAL ABSTRACTS.

Rôle of calcium in senile cataract. D. R. ADAMS (Biochem. J., 1928, **23**, 902—912).—In patients with senile cataract the serum-calcium is appreciably higher than normal. There is no age-variation in the serum-calcium either of normal subjects or of those with senile cataract. Calcium salts acting on fresh ox lenses do not cause opacity except in unphysiological concentrations, nor do they act as "sensitisers" in the production of opacity by ultra-violet radiation. Dialysed solutions of the lens proteins, α- and β-crystallin, exhibit a certain sensitivity to solutions of calcium salts. The experimental production of a persistently raised blood-calcium in rabbits does not cause cataract, nor accelerate the development of naphthalene cataract, although it causes a corresponding rise of calcium in the aqueous humour. There is no age-variation in the calcium content of normal or of cataractous human lenses. The calcium content of cataractous lenses is much greater than that of normal lenses, whilst the potassium content is considerably less. Individual cataract lenses show a wide variation in calcium content which may be attributed to an erratic local deposition of calcium in the lens. There is an increase of calcium in the blood of patients with senile cataract and an abnormal deposition of calcium in the lens.

S. S. ZILVA.

[Non-]occurrence of cystine in sweat in cystinuria. H. B. LEWIS (Proc. Soc. Exp. Biol. Med., 1928, **26**, 69—70).

Rôle of enzyme action in the formation of dental calculi. K. T. ADAMSON (Austral. J. Exp. Biol., 1929, **6**, 215—227).—Extracts of the fresh gum tissue of dog or man exhibit a definite phosphatase action, but no pyrophosphatase action. When an extract is incubated with normal human saliva or blood-serum an increase occurs in the inorganic phosphate, showing that these fluids contain a substrate, presumably a phosphoric ester, on which the enzyme acts. Normal saliva from which the protein had been removed yielded a solution free from inorganic phosphate from which inorganic phosphate was liberated by hydrolysis with acid. The reducing power of this solution was approximately doubled by treatment with dilute acid and the reducing power of normal human saliva was also approximately doubled when treated in the same way. The deposits of calcium phosphate which form the main portion of dental calculi are probably produced as the result of an increase of the phosphate ions in the saliva in the mouth produced by the action of the enzyme, liberated from the tissues of the gum, on the organic phosphate occurring in the saliva.

W. O. KERMACK.

Relation of calcium in the saliva to dental caries. K. HORTON, J. MARRACK, and I. PRICE (Biochem. J., 1929, **23**, 1075—1078).—Dental caries is associated with a reduction of the concentration of

calcium in saliva. This reduction appears to be secondary to the caries. S. S. ZILVA.

Metabolism in diabetics. H. GLATZEL (Arch. exp. Path. Pharm., 1929, **145**, 154—170).—20-Hr. respiratory experiments were conducted on diabetics of moderate severity on a constant and moderate carbohydrate and protein diet. Insulin causes an increased carbohydrate metabolism at the expense of the fat metabolism. The basal metabolism of diabetics of light or moderate severity on a carbohydrate and protein diet is comparable with that obtained for healthy subjects. C. C. N. VASS.

Day- and night-fluctuations of the blood-sugar in non-diabetics, diabetics, and hypertonics. J. JACOBI and F. BAUMANN (Arch. exp. Path. Pharm., 1929, **145**, 24—34).—The regular fluctuations of the blood-sugar curve occur throughout the night as well as during the day and observe a close correspondence in non-diabetics, diabetics with and without insulin treatment, and hypertonics. In general minimum values are shown in the early part of the evening and in the early hours of the morning, whilst maxima are recorded towards midnight and 8 a.m. In non-diabetics, administration of opium does not modify the general character of the blood-sugar curve. C. C. N. VASS.

Influence of insulin on diabetic lipæmia. I. DONOMAE (Folia endocrinol. japon., 1928, **4**, 54).—Treatment with insulin reduced the lipoid content of the serum; the effect was greatest in the fatty acids and slight in the lecithin. CHEMICAL ABSTRACTS.

Treatment of diabetes with vitamin-*B*. C. A. MILLS (Amer. J. Med. Sci., 1928, **175**, 376).—Cold aqueous ethyl-alcoholic hydrochloric acid extracts of various plants were neutralised and filtered from protein. The extracts depressed the excretion of sugar. CHEMICAL ABSTRACTS.

Carbohydrate metabolism in eclampsia. H. J. STANDER and E. P. HARRISON, jun. (Amer. J. Obstet. Gynæcol., 1929, **17**, 17—27).—Eclampsia is generally associated with a tendency towards hyperglycæmia. CHEMICAL ABSTRACTS.

Fluctuations in blood-sugar during eclampsia. III. Relationship between plasma-sugar and corpuscular sugar variations. P. TITUS and E. W. WILLETTS (Amer. J. Obstet. Gynæcol., 1929, **17**, 27—35).—The plasma-sugar is the most mobile and readily available. Convulsions occur when the corpuscles are deprived of their sugar. CHEMICAL ABSTRACTS.

Intravenous injection of phosphates. A. BOLLIGER (Med. J. Austral., 1929, **1**, 650—655).—Injection of sodium phosphate solutions into fasting dogs caused a brief increase in plasma-phosphate. With long-continued injections the phosphorus elimination gradually decreased. The behaviour in nephritis was studied. CHEMICAL ABSTRACTS.

Renal insufficiency associated with Bence-Jones proteinuria. E. G. BANNICK and C. H. GREENE (Arch. Int. Med., 1929, **44**, 486—501).—Bence-Jones protein is frequently found in the urine of patients suffering from a type of nephritis characterised by marked proteinuria, secondary anæmia, nitrogen retention, and delayed excretion of phenolsulphonephthalein, little or no œdema and little or no hæmaturia, hypertension, or retinitis. W. O. KERMACK.

Bence-Jones proteins. L. F. HEWITT (Biochem. J., 1929, **23**, 1147—1152).—The examination of Bence-Jones proteins obtained from five cases of myelomatosis showed that the proteins from different patients differ in properties. Not all are redissolved in boiling salt solutions. In the presence of alcohol both Bence-Jones proteins and serum-proteins are dissolved when the coagulated suspensions are boiled. S. S. ZILVA.

Biochemistry of experimental rabies in rabbits. D. ZUVERKALOW, I. GOLDBERG, and A. SILBERSTEIN (Biochem. Z., 1929, **213**, 109—115).—Injection of rabbits with "virus fixe" (rabies) lowers the total nitrogen and phosphorus of the blood; calcium and potassium are also diminished, the residual nitrogen and inorganic phosphorus are almost unchanged, and hyperglycæmia is often observed. J. H. BIRKINSHAW.

Rickets. E. FREUDENBERG (Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg, 1927, **61**, 83—96; Chem. Zentr., 1929, i, 2791).—Rickets is usually accompanied by hypophosphatæmia. In normal infants and in rickets glycolysis to the extent of 17—48% and 0—21%, respectively, of the sugar administered was observed. A similar inhibition of glycolysis was observed with rachitic rats. Hexosephosphate is readily glycolysed by rachitic blood. Glycolysis in the tissue of rachitic animals is also observed. A. A. ELDRIDGE.

Blood-sugar regulation in idiopathic steatorrhœa. II. Origin of the low blood-sugar curve. T. E. H. THAYSEN (Arch. Int. Med., 1929, **44**, 477—485).—The low blood-sugar curve in idiopathic steatorrhœa (fatty diarrhœa) is not due to defective absorption or to destruction of dextrose in the intestine. W. O. KERMACK.

Isoelectric point in the blood. P. H. ROSSIER (Ann. Méd., 1928, **23**, 248—380; Chem. Zentr., 1929, i, 2656).—A discussion. A. A. ELDRIDGE.

Changes in the isoelectric point of the serum in syphilis. P. H. ROSSIER and R. LUCHSINGER (Arch. Phys. biol., 1928, **6**, 310—315; Chem. Zentr., 1929, i, 2656).—In recent, but not in long-established, syphilis the isoelectric point of the serum is raised. A. A. ELDRIDGE.

Colloidal properties of Wassermann antigens. II. W. O. KERMACK and W. T. SPRAGG (Biochem. J., 1929, **23**, 959—974; cf. Kermack and MacCollum, A., 1925, i, 197).—The observations made on the effect of calcium chloride on a Wassermann antigen hold true for salts of other bivalent cations, whilst the salts of univalent cations with the exception of hydrogen ion, which acts like bivalent cations, do not cause complete precipitation at any concentration. Experiments on the action of mixtures of two of the four salts, lithium chloride, sodium chloride, magnesium chloride, and calcium chloride, on the precipitation of the turbid antigen showed that the addition of a sufficient quantity of another salt, whether of a univalent or bivalent cation, to a salt (with a bivalent cation) present in concentration sufficient to cause precipit-

ation if it were alone, tends to prevent precipitation. Hydrogen chloride behaves in this respect like a salt with a bivalent cation. The protective effect of the antigen on gold sol is excited by the presence of salts, but especially by salts with bivalent cations or hydrogen ions much more than with salts of the other univalent cations. The clear antigen exhibits rather greater protective power than the turbid antigen. The protective power of the antigen has also been determined, using cholesterol, gum mastic, or gum benzoin sol; it is most marked in the first and least in the last. Sols of commercial lecithin possess only in small degree the peculiar properties of the Wassermann antigens. Standard methods of preparation of turbid and clear antigens are described.

S. S. ZILVA.

Colloidal properties of serum. C. I. B. VOGE (Biochem. J., 1929, **23**, 1137—1146).—In syphilitic serum a zone of precipitation exists which is not present in normal serum. An abnormal substance is present in syphilitic serum which possesses the power of conferring a positive charge on the serum-proteins and so rendering them unstable in the presence of a negatively-charged sol such as gum benzoin. Syphilitic serum loses this property after being heated at 55° for 90, but not for 30 min., whilst normal serum undergoes little change after this treatment. The abnormal substance is present in the serum-euglobulin fraction of syphilitic serum when separated from the other serum fractions. The addition of small quantities of a protamine to normal serum causes the latter to simulate syphilitic serum in its precipitating and complement-fixing powers. The conferred changes disappear on heating. Normal serum and antiserum possess a similar precipitating power on gum benzoin sol. An almost similar degree of agglutinating power is shown by normal serum on an antigen of *B. abortus*. The marked agglutinating power of antiserum on a suspension of *B. abortus* is greatly diminished by subjecting the antiserum to preliminary heating. The substance responsible for the agglutinating power is associated with the serum-euglobulin fraction.

S. S. ZILVA.

Distribution of gold in the organs of healthy and tuberculous rabbits following administration of gold preparations. II. Tuberculous rabbits. K. HENIUS and G. WEILER (Biochem. Z., 1929, **214**, 204—215).—The distribution is indicated in a series of tables. The preparation "lopion" is stored chiefly in the liver, whereas "solganol" and "sanocrysin" are found chiefly in the kidney. The total storage is greatest with "lopion" (67% of the amount injected) and least with "solganol" (15%). With "lopion" the storage is the same for healthy and tuberculous animals. With "solganol," 13 mg. of gold per 100 g. of tissue are recovered in the lungs of tuberculous and only 2·5 mg. per 100 g. in the lungs of healthy animals (cf. A., 1928, 1156).

P. W. CLUTTERBUCK.

Blood-sugar and amino-acid-nitrogen in lactation in women; lipoid and inorganic phosphorus. V. J. HARDING and C. E. DOWNS (J. Biol. Chem., 1929, **84**, 335—344).—Normal values were found for the total sugar, non-fermentable sugar, and amino-acid-nitrogen in the blood of lactating women. The inorganic phosphorus of the blood averaged 3·9 mg. per 100 c.c. and the lipoid phosphorus 10·8 mg. per 100 c.c. during lactation.

C. R. HARINGTON.

Carbohydrate metabolism of muscular tissue. I. F. USUELLI (Arch. Fisiol., 1928, **26**, 14 pp.; Chem. Zentr., 1929, i, 3004).—During pregnancy the lactacidogen content of the uterine musculature (of rabbits) increases; the total carbohydrate and sometimes also the glycogen are increased during pregnancy.

A. A. ELDRIDGE.

Carbohydrate exchange and degradation of the dextrose molecule. II. Lactic acid. E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1929, **8**, 466—648; Chem. Zentr., 1929, i, 2792).—A dihydroxyacetone–lactic acid interconversion was not detected. In resting tissue the venous lactic acid is higher than the arterial. Methylglyoxal may suffer conversion into dihydroxyacetone.

A. A. ELDRIDGE.

Appearance of glycogen in the mucous membrane of the alimentary canal. XVI, XVII. K. YOSHIDA (J. Study Micro-organisms, 1928, **22**, 2385—2402, 2403—2424).—Injection of starch, insulin [inulin?], or glycogen into a rabbit seldom causes formation of glycogen in the alimentary mucous membrane. The liver-glycogen was only slightly increased by the injection of glycogen. The appearance of glycogen is attributed to a polymerising action of the superficial intestinal cells on the excessive accumulation of blood-sugar.

CHEMICAL ABSTRACTS.

Influence of unphysiological nutrition on the composition of the organs and on metabolism. II. Glycogen-forming diet. P. JUNKERSDORF and K. WITSCH (Arch. exp. Path. Pharm., 1929, **145**, 171—187).—Fasting dogs were fed on a diet of flesh, potato, rice, and raw sugar for periods up to 30 days. The increase in weight of the dogs, and the weights of the liver and heart as percentages of the total weight were recorded. The water, glycogen, and fat contents of the liver, muscle, and heart were determined. The liver increased to a maximum weight after 8 days' feeding and gradually returned to normal; its water content primarily increased and then decreased to a value below that normally observed. The glycogen content was always above normal, whereas with one exception the fat content varied only slightly from the normal. The water content of the muscle reached a minimum after 20 days' feeding, whilst its glycogen content was always above normal. In the heart, the weight and the water and glycogen contents fell below normal and the fat content increased. Blood-sugar determinations were made every fifth day. Up to the tenth day a fall in the blood-sugar was observed; thereafter a gradual rise was recorded, in good agreement with the deviation of the liver during the experiment.

C. C. N. VASS.

Glycogen metabolism of the snail. M. OKADA (Okayama J. Med., 1928, **40**, 1402—1407).—On resumption of activity after hibernation the glycogen content was 0·82—2·39 (average 1·63), at maximum activity 0·35—0·81 (0·61), and on hibernation 3·52—7·61 (4·63) per 100 g.

CHEMICAL ABSTRACTS.

Possible significance of *d*-xyloketose (urinary pentose) in normal metabolism. I. GREENWALD (Proc. Soc. Exp. Biol. Med., 1929, **26**, 321—322).—*d*-Xyloketose *p*-bromophenylhydrazone has m. p. 127—128°, [α] (1% in alcohol) 1·87°→2·43°; the free ketose has $[\alpha]_D^{22}$ 34·8°. Injection of the pentose (3·05 g. during 2 hrs.) into a dog increased the urinary sugar by 6% of the quantity injected; on further injection, 60% appeared in the urine.

CHEMICAL ABSTRACTS.

Increase in blood-sugar following ingestion of glycerol. J. FERBER and S. RABINOWITSCH (Amer. J. Med. Sci., 1929, **177**, 827—832).—Glycerol ingested in hunger causes hyperglycæmia in man. In diabetes glycerol may produce glycosuria.

CHEMICAL ABSTRACTS.

Lactic acid content of the brain under differing conditions of respiratory want. R. COBET (Arch. exp. Path. Pharm., 1929, **145**, 140—145).—The cerebrum of living rabbits contains less than 10 mg. of lactic acid per 100 g., but on extirpation the amount increases rapidly and reaches a maximum value of 120 mg. per 100 g. The amount of lactic acid in the cerebrum remains uninfluenced in a pure carbon dioxide hyperpnœa. In anoxæmia, oxygen deficit causes a rapid increase of lactic acid in the living brain which acts on the respiratory centre and is reduced to its normal value as soon as normal respiration is established. C. C. N. VASS.

Gas exchanges of nerves during and after anaërobiosis. F. O. SCHMITT (Biochem. Z., 1929, **213**, 443—445; cf. Gerard, A., 1928, 910).—The oxygen deficit in frog's nerves kept in nitrogen increases with the time of asphyxiation up to 15 hrs. and the deficit produced by stimulation is greater than that in resting nerves. Paralysis of the conducting mechanism of the nerves with potassium chloride has no effect on the oxygen deficit. The respiratory quotient of the nerves in the hour following re-admission of oxygen, calculated for the extra oxygen consumed, is not much above zero. The rate of production of carbon dioxide by nerves in nitrogen falls rapidly during the first 6 hrs., but remains at about 1·5 c.c. per g. after 15 hrs. Anaërobic stimulation does not cause production of extra carbon dioxide.

W. MCCARTNEY.

Metabolism in muscular work on a pure fat diet. V. HATTINGBERG (Arch. exp. Path. Pharm., 1929, **145**, 72—87).—The energy balance sheet on a pure fat diet has been computed wherein almost one half of the energy consumed is derived from the fatty acids. The various mechanisms by which this might be accomplished are discussed, preference being given to the view that the fatty acids are first converted into sugar-like substances. C. C. N. VASS.

Influence of ingestion of trihexoin on body-fat of the white rat. H. C. ECKSTEIN (J. Biol. Chem., 1929, **84**, 353—357).—Feeding with trihexoin as the sole fat of the diet caused the deposition, in white rats, of body-fat of a more saturated character than that found in the same animal on a fat-free diet. On the other hand, an increase in the proportion of fatty acids of low mol. wt. could not be detected in the newly-deposited fat. C. R. HARINGTON.

Serum-cholesterol, lecithin-phosphorus, and fatty acids of pigeons after feeding with ox tissues. G. L. MULLER (J. Biol. Chem., 1929, **84**, 345—352).—Exclusive feeding with various ox tissues following a fasting period caused an increase in the cholesterol of the blood-serum of pigeons, the lecithin-phosphorus and fatty acids not being affected. The greatest effect was obtained with liver and kidney and little with spleen; brain did not constitute a complete food and in this case the cholesterol of the blood was diminished. The stimulating effect of the various tissues on formation of red blood-corpuscles and hæmoglobin was in inverse proportion to the effect in increasing the blood-cholesterol.

C. R. HARINGTON.

Connexion between oxidative and anoxidative deamination and the rôle of aminopurines in intermediate tissue metabolism. J. K. PARNAS (Klin. Woch., 1929, **8**, 506—507; Chem. Zentr., 1929, i, 2662).—Under physiological conditions the ammonia irreversibly produced in frog's muscle arises finally from oxidative deamination, the intermediately deaminated adenine nucleotide being continually reaminated. A. A. ELDRIDGE.

Origin of creatine or creatinine in the animal organism. Purine metabolism. E. ABDERHALDEN and S. BUADZE (Med. Klinik, 1929, **25**, 11—12; Chem. Zentr., 1929, i, 2897).—In presence of arginine, choline, and arginase, formation of creatine or creatinine results. After addition of adenine, guanine, and nucleic acid muscular tissue contains an increased amount of creatine or creatinine. Histidine, hydantoin, and *N*-methylhydantoin, but not uric acid or uracil, increase the amount of creatine in minced muscle. A. A. ELDRIDGE.

Diffusion experiments with the phosphorus-containing compounds of muscle. P. ROTHSCHILD (Biochem. Z., 1929, **213**, 251—261).—The velocities of dialysis of inorganic phosphate and of various phosphorus compounds of muscle extracts have been measured. Isolated compounds as well as natural and artificial mixtures were used. From the results obtained and from determinations of diffusion coefficients it is concluded that the preformed inorganic phosphate, the creatine-phosphoric acid, and the adenylpyrophosphoric acid of the extracts do not form parts of protein-like complexes. W. MCCARTNEY.

Decomposition of creatine-phosphoric acid in relation to the activity of muscle. III. Extent of decomposition and rate of stimulation. D. NACHMANSOHN (Biochem. Z., 1929, **213**, 262—300).—The influence of temperature, fatigue, nerve degeneration, and of curarisation on the decomposition of creatine-phosphoric acid has been studied and it has been shown that the extent of the decomposition runs parallel with the rate of excitation. The increase in the extent of decomposition caused by veratrine was exactly proportional to that rate; strychnine did not affect the extent of decomposition; curare, sparteine, and the ammonium bases greatly reduced it. Of the substances which caused reduction the most powerful was trimethyloctylammonium iodide. Long times of action and large doses greatly reduced the extent of the decomposition. W. MCCARTNEY.

Intermediate protein metabolism. I, II. F. SILBERSTEIN, F. RAPPAPORT, and M. WACHSTEIN (Biochem. Z., 1929, **213**, 312—339, 340—354).—I. Analyses have been made of samples of blood taken at intervals during 24 hrs. from dogs to which meat or peptone was orally administered after a long preliminary period of feeding with food either rich or poor in protein, the total non-protein-, urea-, amino-acid-, and polypeptide-nitrogen, and the uric acid and total creatine-nitrogen being determined. The influence of the food consumed during the preliminary period and of the meat or peptone administered on the changes which take place in the amounts of these forms of nitrogen has been followed. The blood contained nitrogenous substances ("undetermined nitrogen") of unknown nature.

II. The pancreas was removed from dogs used in the first series of experiments and these were then continued as before with necessary changes.

W. McCARTNEY.

Influence of carbohydrate consumption on the protein metabolism at a high-temperature environment. S. HAMADA and M. EMA (Nat. Hyg., 1928, **5**, 718—743).—Experiments on a dog showed that feeding with carbohydrate inhibits the decomposition of protein at ordinary temperatures and may at high temperatures tend to reduce the increase of protein decomposition. CHEMICAL ABSTRACTS.

Effect of an exclusive meat diet on chemical constituents of the blood. C. W. LIEB and E. TOLSTOI (Proc. Soc. Exp. Biol. Med., 1929, **26**, 324—325).—A slight increase in blood-uric acid and temporary lipæmia were observed in man.

CHEMICAL ABSTRACTS.

Production of œdema and serum-protein deficiency in white rats by low-protein diets. R. A. FRISCH, L. B. MENDEL, and J. P. PETERS (J. Biol. Chem., 1928, **84**, 167—177).—Young white rats were kept on diets deficient in protein. The serum-proteins were reduced in all cases, and in a large proportion of the animals œdema developed.

C. R. HARINGTON.

Effect of indole derivatives in a diet deficient in tryptophan. R. W. JACKSON (J. Biol. Chem., 1929, **84**, 1—21).—The effect was investigated of adding to the tryptophan-deficient diet of rats the following substances: hypaphorine, β-indolyl-α-benzamido-acrylic acid, *γ-indolylbutyric acid* (by the Fischer synthesis from ethyl hydrogen α-ketopimelate phenylhydrazone), m. p. 123—124° (corr.), β-indolylpropionic acid, indolylethylamine, indolylethyl alcohol, *β-indolyl-α-carbamidopropionic acid*, m. p. 200° (corr.), indolylpyruvic acid, and the condensation product of formaldehyde and tryptophan described by Homer (A., 1913, ii, 451). The only one of these compounds which was able to replace tryptophan was indolylpyruvic acid. After a period of stunting extending over 232 days as the result of deficiency of tryptophan, a rat resumed normal growth when tryptophan was restored to the diet. C. R. HARINGTON.

Calcium and phosphorus metabolism in dairy cows. III. Adequate ration for high-producing cows and the effect of exercise on calcium, phosphorus, and nitrogen balances. W. A. TURNER and A. M. HARTMAN (J. Nutrition, 1929, **1**, 445—454).—Exercise affected the nitrogen metabolism, but that of calcium and phosphorus only slightly. CHEMICAL ABSTRACTS.

Magnesium sulphate as a factor in retention of calcium and phosphorus in cattle. L. S. PALMER C. H. ECKLES, and D. J. SCHUTTL (Proc. Soc. Exp. Biol. Med., 1928, **26**, 58—62).—Water containing magnesium sulphate, when consumed by cattle, may cause important losses of calcium when the phosphorus content of the ration is low. CHEMICAL ABSTRACTS.

Results of ingestion of certain calcium salts and of lactose. C. S. ROBINSON, C. F. HUFFMAN, and M. F. MASON (J. Biol. Chem., 1929, **84**, 257—267).—In feeding experiments with normal calves, ingestion of calcium chloride raised the blood-calcium, but caused a large loss of phosphorus from the body; about 10% of the calcium administered was retained. Administration of calcium lactate with lactose raised the calcium and reduced the inorganic phosphorus of the blood-serum; 50% of the calcium was retained, and there was also improved retention of food-phosphorus. Ingestion of bone meal resulted in increase in the inorganic phosphorus of the blood and in retention of 20% of the calcium and phosphorus, these amounts being doubled by simultaneous administration of lactose. Lactose alone reduced the calcium and increased the inorganic phosphorus of the blood. C. R. HARINGTON.

Iodine as biogenic element. XXI. Feeding experiment with iodine on milch-cows. W. SCHROPP. **XXII. Feeding experiment with increasing doses of iodine on milch-cows.** K. SCHARRER and W. SCHROPP. **XXIII. Chemistry of animal iodine metabolism.** K. SCHARRER and J. SCHWAIBOLD (Biochem. Z., 1929, **213**, 1—17, 18—31, 32—39; cf. this vol., 715).—XXI. The addition of 100 mg. of iodine as potassium iodide to the daily ration of milch-cows increased the milk yield by 4·53% over a period of 99 days and was in no way detrimental to the health of the animals.

XXII. Higher doses of iodine, 200, 400, and 600 mg. of iodine *per diem*, did not further increase the milk yield, but had a definite effect in prolonging the lactation period. The absolute amount of milk-fat was increased by iodine; the percentage was unchanged except with the highest dose, when there was a small diminution. The body temperature and general health were unaffected.

XXIII. A daily dose of 100 mg. of iodine increased the iodine content of the milk about five times, and higher doses in proportion. The amount excreted in the urine was also proportional to the dose. The iodine content of various milk products was examined; the greater part of the iodine was found in the skim-milk, buttermilk, and whey, but little in the butter. Iodine feeding had no effect on the p_H of milk.

J. H. BIRKINSHAW.

Significance of the "internal cycle" for crystalloids, especially the iodine ion. W. LIPSCHITZ (Klin. Woch., 1929, **8**, 116—117; Chem. Zentr., 1929, i, 2075).—Iodide injected into dogs remains ionised for a considerable time and forms a

"mobile deposit." Buchholz' method is suitable for the determination of small quantities of iodide in gastric juice. Experiments with salicylate, hydroferrocyanic acid, lactic acid, and dextrose are described. The method of excretion of iodine is examined.

A. A. ELDRIDGE.

Transport and transformation of organically bound plant-iodine in the animal body. G. PFEIFFER and H. COURTH (Biochem. Z., 1929, **213**, 74—85).—Yellow carrots and radishes are able to store up large amounts of iodine (500—700 times normal), of which a large proportion is organically bound. The normal iodine content of the thyroid gland of dogs is very low, but it can be greatly increased by feeding plant-iodine. The assimilation and deposition of organic plant-iodine by dogs is very great.

J. H. BIRKINSHAW.

Iodine content of the thyroid and ovary of the fowl during the growth, laying, and moulting periods. E. M. CRUICKSHANK (Biochem. J., 1929, **23**, 1044—1049).—The thyroid weight and total thyroid iodine increase in proportion to increase in body-weight in the growing birds. The average thyroid weight from mid-March to mid-July is about 35% less than from January to March. The seasonal variation in both percentage and total iodine tends to follow the seasonal variation in thyroid weight. The average weight of fresh gland and the thyroid weight per kg. body-weight is low compared with the values obtained for the same breed in the goitre belt of the United States of America. The weight of thyroid per kg. body-weight, the percentage of iodine, and the total thyroid iodine per kg. body-weight are higher than in mammals. The ovary contains only a trace of iodine, yolk of egg contains an appreciable amount. The histological appearance of the thyroid suggests a state of relatively great activity in the immature bird and of relative inactivity in the laying and moulting birds.

S. S. ZILVA.

Metabolism of iron. IV. (Supplement; see A., 1928, 542.) Iron in urine. V. Iron requirement of man. W. LINTZEL (Z. Biol., 1929, **89**, 342—349, 350—352).—IV. Under normal conditions the kidneys do not excrete iron, as no trace of that metal could be found in the urine of three normal men by the method of Henriques and Roland (this vol., 93). The sensitiveness of the method is such that 0·02 mg. of iron per litre gives a positive result.

V. In normal adult men the daily iron requirement is less than 0·9 mg. per day, any excess being excreted.

W. O. KERMACK.

"Active" iron. H. PETOW and H. KOSTERLITZ [in part with PROBST] (Klin. Woch., 1929, **8**, 600—601; Chem. Zentr., 1929, i, 2793).—An examination of the benzidine activity as differentiating "active" iron compounds. All the iron compounds examined, except ferric ions, form under favourable conditions a larger amount of benzidine-blue than corresponds with their molecular concentration; the amount depends on the p_H, of which the optimal value is 5·0. The reaction with complex salts and with hæmoglobin, but not with ferrous salts, is dependent on the hydrogen peroxide concentration. Mineral waters containing iron behave like ionised ferrous salts. Complex salts behave qualitatively like hæmoglobin. Experiments on therapeutic activity were performed.

A. A. ELDRIDGE.

Micro-determination of arsenic in cadavers. P. SZENDRŐ and G. FLEISCHER (Mikrochem., 1929, Pregl Fest., 323—328).—The usual methods for determining arsenic in human organs are tedious and lengthy. Wintersteiner's method permits a satisfactory determination in 1½ hrs. of amounts of arsenic down to 0·1 mg., employing only 2 g. of material. The organic matter is destroyed with sulphuric and nitric acids, and the iron invariably present is determined colorimetrically in a portion of the solution. The remainder is treated with hydrochloric acid and potassium iodide, and after 10 min. the liberated iodine is titrated with 0·01*N*-thiosulphate. A correction for the amount of iron found is subtracted from the titration value. Copper if present must be removed by Pregl's micro-method before determining the arsenic.

H. F. HARWOOD.

Metabolic activity of arsenic. A. BICKEL (Med. Welt, 1929, **3**, 5—6; Chem. Zentr., 1929, i, 2661).—A discussion.

A. A. ELDRIDGE.

Passage of arsenic through the placenta. E. ZIEMKE (Deut. Z. ges. gerichtl. Med., 1929, **13**, 217—225; Chem. Zentr., 1929, i, 2794).—Arsenic administered to the mother is largely withheld from the fœtus by the placenta.

A. A. ELDRIDGE.

Effect of phosphorus on nitrogenous substances in the bile. Effect on amino-acids. K. SUGIU (Okayama J. Med., 1928, **40**, 1481—1506, 2202—2213).—When yellow phosphorus is administered to a dog with gall-bladder fistula the coagulable protein of the bile begins to increase in 4 days and becomes normal in 3—4 weeks. Urea begins to increase in 4 days and is normal after 30 days. The increase in urea, ammonia, and coagulable protein following administration of phosphorus diminishes on administration of dextrose. The increase when adrenaline is first given is marked; when insulin is first injected there is a decrease. Phosphorus increases the amino-acid-nitrogen of the bile unless dextrose, insulin, or adrenaline is first administered.

CHEMICAL ABSTRACTS.

Distribution of lead in the body after absorption. R. W. TANNAHILL (Med. J. Austral., 1929, I, 216—217).—The lead is chiefly stored in the bones; some is excreted in the urine and fæces.

CHEMICAL ABSTRACTS.

Copper in the organism. F. B. FLINN and J. M. INOUYE (J. Biol. Chem., 1929, **84**, 101—114).—Administration of small amounts of copper over long periods to rats leads to deposition of the metal for the most part in the liver, this being the organ which, in normal animals of other species, shows the highest copper content. Neither copper nor lead salts give insoluble phosphates when their solutions are brought into contact with calcined bones. One hr. after injection of copper salts into the intestine the copper content of the blood-plasma is about twice that of the corpuscles. No hæmolysis or formation of methæmoglobin was observed as the result of an increased copper concentration in the blood; on the

contrary, the oxygen-carrying capacity of the blood was increased. A definite improvement in growth was observed in guinea-pigs which received small amounts of copper in the food.

C. R. HARINGTON.

Chronic mercury poisoning. A. HERTZ (Klin. Woch., 1929, 8, 541—544; Chem. Zentr., 1929, i, 2667).—Mercury ingested orally appears to be excreted chiefly in the fæces, whilst that inhaled is chiefly excreted in the urine. Traces of mercury were commonly detected in the fæces of persons not exposed to mercury. The danger of poisoning by dental amalgams etc. is not as great as Stock supposes.

A. A. ELDRIDGE.

Distribution of mercury in the various organs in cases of mercurial poisoning. J. BUCHTALA (Mikrochem., 1929, Pregl Fest., 20—24).—An examination of the various organs in a case of poisoning by mercuric chloride showed the largest amount (0·1616 g.) in the stomach, and the least (0·00039 g.) in the brain. The mercury is best determined electrolytically, using a carbon anode and gold or platinum cathode, the deposit being subsequently identified by conversion into red mercuric iodide.

H. F. HARWOOD.

Pharmacology of rare-earth metals. III. Samarium. H. STEIDLE and H. DÜRR (Arch. exp. Path. Pharm., 1929, 145, 19—23).—The action of solutions of samarium nitrate on proteins, yeast fermentation, isolated frog's heart and preparations, ox-blood, muscle, and mucous membrane, and their toxicity towards certain animal species are recorded.

C. C. N. VASS.

Reactivity and physiological action. K. KINDLER (Arch. Pharm., 1929, 267, 541—555).—A lecture.

H. BURTON.

Factors influencing bone formation in the albino rat. I. Effect of guanidine intoxication produced by the successive injection of sub-lethal doses of guanidine salts. II. Effect of injection of parathyroid extract. C. M. BURNS (Biochem. J., 1927, 23, 840—852, 853—859).—I. Injections of guanidine cause no deposition of calcium in faultily-calcified bones nor decalcification of formed bone. They may retard ossification very slightly in growing animals by limiting the amount of available calcium, but this influence is not detected where the growth of the injected animals is markedly retarded. No important interrelation between mild guanidine poisoning and bone-formation was detected.

II. The injection of the extract did not produce any retardation either in body or in bone growth, nor was the deposition of calcium in the bones influenced by it. Unlike the females, the male animals which received the parathyroid extract showed unusually large deposits of fat.

S. S. ZILVA.

Effect of continued ingestion of mineral acid on growth of body and bone and on the composition of bone and soft tissues. C. M. BURNS (Biochem. J., 1929, 23, 860—867).—In rabbits receiving acid daily for periods varying from 17 to 35 days there was a reduction in the base content of the muscles, but not of the viscera. There was also a marked reduction in the percentage of ash of the bones, but not in the fat content. Growth was retarded. In rats receiving daily doses of acid for a period of more than 9 weeks there was no appreciable reduction in the fat content of the bones nor was the ash content changed. Growth was retarded and considerable loss of weight occurred when the dose was increased. The base content of the soft tissues was increased slightly where death was preceded by marked loss in weight.

S. S. ZILVA.

Ethyl alcohol in fowls after exposure to alcohol vapour. T. M. CARPENTER (J. Pharm. Exp. Ther., 1929, 37, 217—259).—The concentration of alcohol has been determined in the blood and various organs of hens exposed for 2—29 hrs. to an atmosphere containing ethyl alcohol vapour. The concentration of alcohol in the blood is usually higher than in any of the organs and is exceeded only occasionally by that in brain and the immature eggs. With low concentrations in the blood very little is found in the liver, but with higher concentrations in the blood the concentration in the liver approximates to that in heart, lungs, kidney, and spleen. The lowest concentration of alcohol was found in the fat.

W. O. KERMACK.

Absorption, distribution, and excretion of carbon tetrachloride in dogs under various conditions. B. H. ROBBINS (J. Pharm. Exp. Ther., 1929, 37, 203—216).—Carbon tetrachloride is absorbed from the intestine of the dog, less rapidly from the colon, and not from the stomach, the absorbed compound being almost quantitatively excreted through the lungs. The rate of absorption is increased when fat or alcohol is simultaneously administered. After absorption of carbon tetrachloride from the intestinal tract it is found in comparatively high concentrations in the bone marrow, the organs next richest in the compound being the liver, pancreas, and brain.

W. O. KERMACK.

Blood changes caused by histamine. G. DE TONI (Boll. Soc. Ital. Biol. sper., 1928, 3, 87—92; Chem. Zentr., 1929, i, 3002).—Injection of histamine usually increases the blood-sugar; in young children the water is increased, but in older children diminished.

A. A. ELDRIDGE.

Relationship of heterocyclic compounds to the autonomic nervous system. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1929, 37, 177—191).—A large number of heterocyclic compounds, including derivatives of quinoline, pyridine, piperidine, and pyrrolidine, have been investigated in respect of their pharmacological actions on the autonomic nervous system of the cat. In general, most of the compounds investigated were not highly active, but β-phenoxyethyl-*N*-methylpyrrolidinium iodide had a marked nicotine-like action.

W. O. KERMACK.

[Pharmacological action of] ethers of formocholine and choline. R. HUNT and R. R. RENSHAW (J. Pharm. Exp. Ther., 1929, 37, 193—202).—The pharmacological action of formocholine chloride (hydroxymethyltrimethylammonium chloride) and of various ethers and closely related compounds derived therefrom has been investigated on the autonomic nervous system of the cat. The *n*- and *iso*-butyl ethers as well as the allyl ether have a marked muscar-

inc and also a marked nicotine action. The introduction into the benzene ring of the phenyl ether of choline of a hydroxy-, methoxy-, or benzoyloxy-group diminished the nicotine-like action of the compound, whilst an acetamido-group completely abolished it. Compounds of this type possess no muscarine-like action. W. O. KERMACK.

Carbamide synthesis in fatty livers. K. IMHÄUSER (Arch. exp. Path. Pharm., 1929, **145**, 120—130).—Fasting dogs treated *per os* with infusions of *Amanita phalloides* (*i.e.*, poisoning with amanitatoxin; cf. Abel and Ford, Heffter's "Handb. exp. Pharmakol.," 1924, **2**, 1712) show the typical poisoning symptoms. A steep fall in the blood-sugar occurs, followed by convulsions which can be temporarily relieved by injection of dextrose. Artificially perfused livers extirpated from these animals show no variation from normal livers in carbamide synthesis. C. C. N. VASS.

Extraction of strychnine in forensic investigations. A. I. PORTNOW (Pharm. Zentr., 1929, **70**, 661—663).—To prevent strychnine from being extracted by acid ether or chloroform extraction, addition to the material of not less than 2·5% of tartaric acid is necessary. Extraction of strychnine by chloroform containing 10% of alcohol is inadmissible. T. H. POPE.

Effect of *Vinca rosea* [leaves] on the blood-sugar of rabbits. D. H. K. LEE and W. R. M. DREW (Med. J. Austral., 1929, I, 699—701).—No change in blood-sugar could be ascribed to feeding an infusion or extract of the leaves.
CHEMICAL ABSTRACTS.

Diuretin hyperglycæmia. N. SUGIMOTO (Okayama Ig. Zasshi, 1927, **39**, 719—742).—Insulin or atropine inhibits diuretin hyperglycæmia, and diuretin inhibits insulin hypoglycæmia.
CHEMICAL ABSTRACTS.

Seventh report of the Committee on Contact Catalysis. Enzyme catalysts. E. F. ARMSTRONG and T. P. HILDITCH (J. Physical Chem., 1929, **33**, 1441—1455).—A summary. After a discussion of the factors controlling the rate of enzyme action, the analogy between inorganic catalysts and enzymes, and the nature of enzymes, the following conclusions are reached. The physical form of the enzyme is that of a dispersed colloidal sol in which the molecule is of considerable complexity and protein, carbohydrate, phosphorus, and iron compounds are not necessarily integral components. Further, it is unlikely that the whole of the molecular complex is involved in enzymic changes and only certain groupings of highly specific character and configuration are able to enter into combination with specific substrates. The whole molecule, however, is liable to form associated complexes with other large molecular species, and the presumed groupings, the rate of action, and the optimum character of the reaction medium must be considerably affected by this feature. Only the specific nature of the change effected by the enzyme itself persists unaltered. Hydrolytic action is exerted by enzymes through the presence of definite groupings adapted to form intermediate complexes with the substrate and water, and specificity is due, in all probability, to their asymmetric configuration. Co-enzymic activity appears to be closely connected with the combinations which occur with other colloidal molecules. Finally, the catalytic properties of an enzyme are at present best ascribed to a catalyst which by reason of this capacity for interaction is in a labile or dynamic condition and the activity of which is very sensitive to a variety of conditions and is controlled by its environment at a given time. L. S. THEOBALD.

Kinetics of cell fermentation from the point of view of a reaction in a closed space. V. Mechanism of enzyme action. F. F. NORD and J. WEICHHERZ.—See this vol., 1397.

Enzymes and bacteria in the honey bee. F. M. BROWN (Amer. Mus. Nov., 1928, No. 304, 5).—The enzymes normally native to the digestive system of the honey bee are: invertase, both peptic and tryptic proteolytic enzymes, and a lipase.
CHEMICAL ABSTRACTS.

Dilatometric studies in enzyme action. M. SREENIVASAYA and B. N. SASTRI (Biochem. J., 1929, **23**, 975—981).—In the cases of the hydrolytic action of diastase, invertase, emulsin, amidase, and tannase, there was a good agreement between the results obtained by the dilatometer and by the usual methods. The dilatometer is described. S. S. ZILVA.

Enzyme action. III. Amylase from Cumbu (*Pennisetum typhoideum*). D. NARAYANAMURTI, C. V. R. AYYAR, and R. V. NORRIS (J. Indian Inst. Sci., 1929, **12 A**, 105—108).—The hydrolytic action on starch of filtered and dialysed extracts of malted Cumbu seeds has been determined at various hydrogen-ion concentrations. When the period of action is 15 min. and the temperature 37°, the maximum hydrolysis occurs at p_H 5·1 and with longer periods the optimum is at a more acid reaction, whilst with rise in temperature the optimum occurs at a less acid reaction. The malt extract also contains maltase and for this enzyme two optima exist when the period of reaction is more than 30 min., namely, at p_H 4·8 and 6·2. W. O. KERMACK.

Chemistry of starch. F. POLAK and A. TYCHOWSKI (Biochem. Z., 1929, **214**, 216—228).—Starch consists of amylopectin which is converted by the action of β-diastase into a reducing dextrin and further hydrolysed only with great difficulty, and amylose which is converted into maltose by α-diastase and into a dextrin by β-diastase, the dextrin being hydrolysed to maltose only by α-diastase. The preparation of amylose, the behaviour of its solutions to α- and β-diastase, and attempts at fractionation of starch are described. P. W. CLUTTERBUCK.

Malt catalase. M. MATSUYAMA (Biochem. Z., 1929, **213**, 123—137).—The optimum p_H for malt catalase action is 7·4—7·5 in 0·05*M*-hydrogen peroxide. The unimolecular reaction constant for malt catalase action in 0·0125*M*-hydrogen peroxide falls, but the C_1-value of Maximovitsch and Avtonomova is constant; the *D*-value, however, does not agree with the results for blood catalase. The optimum temperature in 0·025*M*-hydrogen peroxide buffered to p_H 7·4 is 30°; at 40° the enzyme is destroyed. The

inactivation of malt catalase is not a unimolecular reaction. The temperature sensitivity is dependent on the acidity and enzyme concentration; the stability is highest at p_H 7·2. J. H. BIRKINSHAW.

Indophenol reaction in biological oxidations. D. C. HARRISON (Biochem. J., 1929, **23**, 982—999).—The secondary oxidation of dimethyl-*p*-phenylenediamine leading to a positive indophenol reaction can be brought about during the oxidation of hypoxanthine by xanthine-oxidase from milk or liver in presence of peroxidase. *p*-Phenylenediamine increases the oxygen uptake of yeast, which does not give an indophenol reaction unless it is previously heated at 52° for 1·5 hrs. (cf. Keilin, this vol., 470). The destruction of the reducing power of yeast when heated at 52° is not due to any appreciable exhaustion of oxidisable substances, but probably to the destruction of the enzyme, involved in reducing systems. The initial rate of reduction of methylene-blue by warmed yeast is much more rapid than that shown by unwarmed yeast, but in the final stages the reduction is relatively very slow in the warmed yeast. The rate of reduction of methylene-blue by yeast treated with toluene is doubled by plasmolysis by increasing the accessibility of the dye to the reducing systems, but there is a lowered oxygen uptake owing to the partial destruction of the oxidising systems by this treatment. Also although warmed and unwarmed yeasts do not reduce indigo-carmine, yeast after treatment with toluene does so. Although the indophenol reaction becomes positive in yeast either after warming or after treatment with toluene, it is destroyed by the double effect of warming and toluene treatment. Unwarmed yeast reduces indophenol-blue more rapidly than warmed yeast. A scheme of reactions is described to explain the significance of the indophenol reaction in cell oxidations; cytochrome may be involved in a similar series of reactions. The indophenol reaction is no criterion for the presence of an activator of oxygen. A method for the preparation of an active solution of xanthine-oxidase of the liver is based on precipitating an aqueous extract of the liver by acidification to p_H 5 with acetic acid and treating the neutralised protein layer obtained after centrifying with ammonium sulphate. S. S. ZILVA.

Behaviour of dextrose-oxidase towards dialysis, hydrocyanic acid, carbon monoxide, and methylene-blue. D. MÜLLER (Biochem. Z., 1929, **213**, 211—219; cf. A., 1928, 1291).—Dextrose-oxidase is stable and non-hydrolysable and is not affected by a co-enzyme from boiled juice of *A. niger*. After 24 hrs.' dialysis the oxygen uptake in absence of sugar is nil. The action of dextrose-oxidase in presence of dextrose decreases rapidly, due to inhibition chiefly by hydrogen ions but partly by gluconate ions. It is inhibited by hydrocyanic acid at concentrations above 0·01*N*, but not by carbon monoxide. In presence of dextrose and absence of oxygen methylene-blue is not reduced more quickly than in dextrose-free solution.

J. H. BIRKINSHAW.

Dehydrogenation of citric acid. A. HAHN and W. HAARMANN (Z. Biol., 1929, **89**, 332—334).—In presence of fresh muscle pulp with or without the addition of methylene-blue citric acid is oxidised with loss of carbon dioxide and formation of pyruvic acid. W. O. KERMACK.

Enzyme action. IV. Tyrosinase. I. D. NARAYANAMURTI and C. V. R. AYYAR (J. Indian Inst. Sci., 1929, **12 A**, 109—129).—The tyrosinase activity of extracts of ungerminated *Dolichos lablab* is at a maximum at p_H 6·5. The isoelectric point of the tyrosinase as determined by migration experiments is also in the neighbourhood of this p_H. The kinetics of tyrosinase action have been investigated and the effects of concentrations of enzyme and of substrate, temperature, and reaction have been determined. The reaction appears to be essentially unimolecular. Irradiation of the enzyme solution with ultra-violet light increases its activity. The enzyme may be separated from inorganic electrolytes by electrodialysis or by ultra-filtration. As neither of the processes brings about a decrease in activity, it is concluded that the enzyme action does not depend on the presence of small quantities of iron or manganese salts. W. O. KERMACK.

Influence of temperature on acetaldehyde production [in blood or organs]. C. KAWAMURA (J. Kyoto Prefect. Med. Coll., 1928, **2**, 211—222).—Calcium sulphite and a phosphate buffer (p_H 6·5) were added to rabbit's blood or pulped organs and the acetaldehyde produced at 30°, 34°, and 38° was determined. In 5 hrs. the amounts produced (max., 38°) were: liver 2·4 mg., muscle 1·13 mg. per 100 g., blood 1·08 mg. per 100 c.c. CHEMICAL ABSTRACTS.

Tissue glycolysis. Effect of fluoride and some other substances. F. DICKENS and F. ŠIMER (Biochem. J., 1929, **23**, 936—958).—Fluoride and oxalate inhibit anaërobic glycolysis very strongly in all the tissues examined. There is a simple relationship based on the law of mass action between the concentration of fluoride and the percentage inhibition of glycolysis in Jensen rat sarcoma, rat brain, and rat testes. This relationship, although of a similar type, is not identical in these tissues. There is a variation which is due to a difference in the order of the reaction and the affinity of fluoride for the glycolytic enzyme. The approximate values of the affinity constant of the fluoride–enzyme complex have been determined for these tissues. Fluoride most probably forms an active compound with some substance essential for glycolysis. This reaction follows the ordinary laws of chemical equilibria. The effect of temperature on this equilibrium is described; the enzyme–fluoride compound is exothermic. Fluoride also has a strongly inhibitory action on glycolysis in the case of rat retina, rat kidney, and two specimens of human carcinoma. The effect of oxalate is less than that of fluoride, whilst cyanide inhibits glycolysis only when present in very high concentration. Fluoride and oxalate do not appreciably influence tissue respiration in the concentrations used, and the former does not inhibit conversion by tissues of dihydroxyacetone into lactic acid. Aërobic glycolysis is inhibited by fluoride in the case of Jensen rat sarcoma, but not in that of rat testes. S. S. ZILVA.

Stability of luminous substances of luminous animals. E. N. HARVEY (Proc. Soc. Exp. Biol. Med., 1928, **26**, 133—134).—Dry *Cypridina* luciferin and luciferase can be kept unchanged for a long period. An aqueous solution of luciferin is stable in absence of oxygen, whilst luciferase is decomposed in aqueous solution. CHEMICAL ABSTRACTS.

Effect of electrolytes on glycerophosphatase. K. INOUYE (J. Biochem. Japan, 1929, **10**, 395—408).—The activity of pure glycerophosphatase is inhibited only by fluorine, oxalate, and sulphate ions which are also anticoagulants for fibrinogen. Unlike the latter, the former effect cannot be attributed to removal of calcium ions. CHEMICAL ABSTRACTS.

Fat-decomposing enzyme. XII. Activation of lipase by bile, and the relation between the stomach lipase and the activating action of bile. K. GYOTOKU and S. MATSUBARA (Tokyo J. Med., 1928, **42**, 2147—2161).—The splenic lipase of the dog is first activated and subsequently deactivated by the bile of man or of the dog. The activation is most marked at p_H 7·6. Purified stomach lipase is similarly activated. The activating agent is thermostable and non-dialysable, but dried bile dissolved in water has no effect. CHEMICAL ABSTRACTS.

Chemical equilibria in enzymic systems. E. SYM (Compt. rend. Soc. Biol., 1928, **99**, 1011—1013, 1013—1015; Chem. Zentr., 1929, i, 2997).—In the systems amyl butyrate, picric acid, lipase, and amyl alcohol, butyric acid, lipase the equilibrium depends on the difference in the activity of the catalyst and enzyme. A. A. ELDRIDGE.

Action of substances containing alcoholic hydroxyl groups on pancreatic lipase. A. DI FRISCO (Boll. Soc. Ital. Biol. sper., 1928, **3**, 299—303; Chem. Zentr., 1929, i, 2998).—The activity of stored pancreatic juice is increased by addition of sodium potassium tartrate, sodium citrate, or glycerol. A. A. ELDRIDGE.

Behaviour of aromatic esters towards extracts of organs. I—III. G. YOSHIMATSU (Acta Schol. Med. Univ. Imp. Kyoto, 1929, **11**, 599—615, 617—638, 639—648).—The comparative efficiencies of rabbit's liver, kidney, muscle, spleen, and pancreas, and of pig's organs, in hydrolysing ethyl, *iso*butyl, amyl, glyceryl, and phenyl benzoate, and ethyl, *iso*butyl, amyl, and phenyl salicylate, have been measured. CHEMICAL ABSTRACTS.

Behaviour of ethyl- and phenyl-sulphuric acids towards extracts or organs. G. YOSHIMATSU (Acta Schol. Med. Univ. Imp. Kyoto, 1929, **11**, 649—660).—Glycerol extracts of pig's liver, kidney, pancreas, and stomach and intestinal mucous membrane affected tributyrin, but not potassium ethyl or phenyl sulphate. CHEMICAL ABSTRACTS.

Nephelometric determination of pepsins. C. G. VAN ARKEL (Pharm. Weekblad, 1929, **66**, 857—864).—The intensity of the opalescence following addition of sulphosalicylic acid to diluted ox-serum which is undergoing hydrolysis by pepsin is used to determine the degree of hydrolysis for a given time and hydrogen-ion concentration. Curves are given showing the effect of time for a given p_H, and of p_H for a given time. S. I. LEVY.

Crystalline pepsin. J. H. NORTHROP (Science, 1929, **69**, 580).—Dialysis under pressure at p_H 3·0 and 5° of a concentrated solution of commercial pepsin gave 1—2% of crystalline material having the properties of pepsin with an activity slightly less than certain amorphous preparations. The small, hexagonal prisms containing 14·5% N can be recrystallised by dissolving in sodium hydrogen carbonate at 37° and precipitation with dilute sulphuric acid. More concentrated acids and alkali dissolve them, but the material is precipitated by half saturation with ammonium sulphate, copper salts, lead acetate, trichloroacetic acid, and safranine, and coagulates on boiling. The diffusion coefficient indicates a mol. wt. of 10,000. L. S. THEOBALD.

Action of papain on polarisation of gelatin. H. C. GORE (Ind. Eng. Chem. [Anal.], 1929, **1**, 203—205).—The mutarotation of gelatin solution is lessened by digestion with proteolytic enzymes, such as papain, and the relationship between the decline in mutarotation at 20° and the quantity of enzyme present is linear up to the point when 40% of the former has been destroyed. It is proposed to utilise this as a means of determining the proteolytic activity of papain. 50 C.c. of 2% gelatin solution of p_H 4·8 and 10 c.c. of Walpole's acetate buffer of p_H 4·8 are mixed at 45° with 40 c.c. of papain solution and digested at this temperature for 1 hr. The mixture is cooled in ice water, kept for 16 hrs. at 5°, warmed to 20°, and the mutarotation determined after maintenance for 1 hr. at this temperature. In order to calculate the percentage of gelatin digested, determinations under similar conditions must be made of the polarisation values of the original gelatin and of completely digested gelatin, when the proteolytic power of the papain can be calculated from the formula $P=W/wt$, where W=weight of gelatin digested, w=weight of papain used, and t=time in hours. H. F. HARWOOD.

Proteolytic enzymes of green malt. I. Adsorption and elution. R. H. HOPKINS (Biochem. J., 1929, **23**, 1022—1029).—A cold aqueous extract of green malt appears to contain at least two proteolytic enzymes, a protease which renders egg-albumin non-coagulable at p_H 4·6 and 100° and attacks Witte's peptone, and a peptidase which attacks Witte's peptone and Roche peptone. The enzymes are maximally adsorbed at about p_H 4·7. They may be separated by elution by 0·1*M* phosphate. By adsorption and elution twice at p_H 4·5 a preparation of the protease almost free from peptidase is obtained and by adsorption at p_H 7·0 and elution at p_H 9·2 and a repetition of both processes a preparation of peptidase almost free from protease is obtained. S. S. ZILVA.

Structure and enzymic degradation of the acetylated polypeptide associates obtained from gelatin by degradation with acetic anhydride. V. A. FODOR and C. EPSTEIN (Biochem. Z., 1929, **214**, 242—252).—*N*-Acetylated tripeptide complexes (associations of three tripeptides such as glycylprolylalanine, glycylhydroxyprolylalanine, etc.; cf.

this vol., 1188) are hydrolysed by trypsin but not by yeast maceration juice. Gelatin peptone which contains the same complexes in the non-acetylated condition is attacked fairly readily by yeast, and it must be assumed that *N*-acetylation inhibits the action of yeast. P. W. CLUTTERBUCK.

Physiology of digestion in infants. VI. Effect of *B. coli* fermentation on erepsin and trypsin. VII. Excretion of tryptase and peptidase in the fæces of infants. O. BUDDE (Z. Kinderheilk., 1928, **46**, 195—201, 202—209; Chem. Zentr., 1929, i, 2552).—The action of erepsin is inhibited by butyric, hexoic, acetic, or lactic acid, or peptone, whereas the amines, formic acid, and succinic acid produced do not affect it. *B. coli*, living or dead, usually inhibits the action of erepsin; trypsin is not affected by any of the substances.

The trypsin and peptidase content of the fæces of breast-fed infants was smaller than that for bottle-fed infants. The peptidase is apparently affected by fermentation acids. A. A. ELDRIDGE.

Dismutation of methylglyoxal and of phenylglyoxal by the enzyme from green leaves (of the lime tree). C. PI-SUÑER BAYO (Biochem. Z., 1929, **213**, 495—500).—The enzyme from green leaves of the lime tree (*Tilia grandifolia*) converts phenylglyoxal hydrate into mandelic acid. The yield of 83% consists almost entirely of the *l*-acid. Methylglyoxal is converted into *i*-lactic acid by the enzyme.

W. MCCARTNEY.

Production of methylglyoxal in the fermentation of sugar with extract of macerated yeast. C. PI-SUÑER BAYO (Biochem. Z., 1929, **213**, 489—494).—Methylglyoxal is easily obtained in yields of up to 100% from magnesium hexosediphosphate by the action of extracts of macerated yeast. It follows that living yeast cells or cells partly damaged act in the same way as do cell-free organisms.

W. MCCARTNEY.

Proteolytic action of yeasts. F. ZARIBNICKY (Mikrochem., 1929, Pregl Fest., 338—340).—A number of different kinds of yeast in sterile milk showed marked differences in proteolytic action after 14 days, and the differences were still more sharply defined after a period of 8 weeks. H. F. HARWOOD.

Effect of "bios" on the growth and metabolism of certain yeasts. A. M. COPPING (Biochem. J., 1929, **23**, 1050—1063).—The type of yeast and the composition of the medium influence the requirements for "bios." There is an increased oxygen uptake and carbon dioxide output in the presence of this factor, but whether this is due to the greater number of cells produced by the stimulating action of "bios" on growth or to a change in their metabolic processes has not been ascertained.

S. S. ZILVA.

Detection of pyruvic acid in yeast fermentation. G. KLEIN and W. FUCHS (Biochem. Z., 1929, **213**, 40—64).—Benzhydrazide and di(phenylacet)-hydrazide are well suited for the characterisation of pyruvic acid; the corresponding hydrazones have m. p. 92° and 170—172°, respectively. The two hydrazides were successfully used for the interception of acetaldehyde under various conditions, but in no case could methylglyoxal or pyruvic acid be detected.

J. H. BIRKINSHAW.

Rates of sugar disappearance and carbon dioxide formation during fermentation of dextrose. J. A. HAWKINS and D. D. VAN SLYKE (J. Biol. Chem., 1929, **84**, 243—247).—During the first few minutes of fermentation of dextrose by yeast the rate of disappearance of the sugar is twice as rapid as the production of carbon dioxide; the lag in carbon dioxide production persists after 1 hr.

C. R. HARINGTON.

Effect of hydrogen-ion concentration on the toxicity of sodium benzoate to micro-organisms. W. V. CRUESS and P. H. RICHERT (J. Bact., 1929, **17**, 363—371).—The retardation of the growth of, or of alcoholic fermentation by, *Saccharomyces ellipsoideus* by sodium benzoate is much more marked at p_H 2·5—4·5 than at p_H 5·0—9·0. Other food preservatives behave similarly. CHEMICAL ABSTRACTS.

Glutathione. (Sir) F. G. HOPKINS [with a Section by L. J. HARRIS] (J. Biol. Chem., 1929, **84**, 269—320).—The fact that prolonged boiling of aqueous solutions of the substance previously described (A., 1921, i, 635) as glutathione led to the separation of glycylcystine dianhydride indicated that the constitution assigned to the compound was erroneous (cf. Hunter and Eagles, A., 1927, 477, 478). Further investigation of means of purification led to the development of the following method. Pressed yeast was twice extracted with boiling 0·1% acetic acid, and the filtered extracts were treated with lead acetate and mercuric sulphate; the washed precipitate was decomposed with hydrogen sulphide, and, after removal of the latter, the solution was treated with sulphuric acid to 0·5*N* concentration; cuprous oxide was then added cautiously to the point of maximum precipitation, the temperature being maintained at 50°. The white, crystalline *precipitate*, $C_{10}H_{16}O_6N_3Cu$, was separated at the centrifuge, washed, and decomposed with hydrogen sulphide; the filtrate from the cupric sulphide was concentrated in a vacuum, treated with 0·5 vol. of alcohol, and allowed to crystallise in a desiccator; the yield was 1·25 g. per kg. of yeast. A similar preparation was made from red blood-corpuscles, the yield in this case being very much less. The *glutathione* then obtained had the formula $C_{10}H_{17}O_6N_3S$; when hydrolysed with 25% sulphuric acid it yielded cysteine (as cystine), glutamic acid, and glycine in amounts of 84·5—92% of those demanded by the theory that the compound is a tripeptide containing these three amino-acids. When the tripeptide was kept for 5 hrs. at 37° in 0·33*N*-barium hydroxide in presence of lead acetate, more than 50% of the sulphur was removed. Boiling (of the disulphide form) for 24 hrs. in 2% aqueous solution led to elimination of 27·9% of the sulphur as hydrogen sulphide and in the free state, a further 31% of the sulphur being isolated in the form of *glycylcystine dianhydride*, $C_{10}H_{14}O_4N_4S_2$, m. p. 262° (decomp.); (reduction of the above, or boiling of the aqueous solution of the reduced form of glutathione, led to the more soluble *glycylcysteine anhydride*, $C_5H_8O_2N_2S_2$, m. p. 203°); in addition to the above anhydride, the solution contained glutamic

acid and α-pyrrolidonecarboxylic acid, together with unidentified decomposition products. The fission by boiling with water was accompanied by elimination of a part of the carbon as carbon dioxide. Oxidation of the reduced form of the tripeptide by aëration of its solution at p_H 7·6 in presence of a trace of iron was accompanied by destruction of 20% of the material with loss of nitrogen and sulphur; this phenomenon is peculiar to the pure tripeptide as contrasted with the earlier (impure) preparations.

[By L. J. HARRIS.] Application of the author's titrimetric methods of determination of amino- and carboxyl groups (A., 1924, ii, 73, 355) to the reduced form of glutathione affords confirmatory evidence that the compound is a tripeptide with an equivalent weight of 307. C. R. HARINGTON.

Titration curve of glutathione. N. W. PIRIE and K. G. PINHEY (J. Biol. Chem., 1929, **84**, 321—333).—Titration curves have been determined for reduced and (impure) oxidised glutathione; the pK values found for the reduced compound were 2·12, 3·53, 8·66, and 9·62. Consideration of the magnitude of these constants leads to the conclusion that the compound is probably glutaminylglycylcysteine, the carboxyl group of glutamic acid which is adjacent to the amino-group being free. C. R. HARINGTON.

Exchange of ions between yeast cells and solutions of lead nitrate. P. GÉNAUD (Compt. rend., 1929, **189**, 591—592).—When yeast-cells are immersed in a solution of lead nitrate an exchange of cations takes place, the lead ions penetrating the yeast cells and an equivalent number of potassium and calcium ions being liberated. With fresh yeast there is a rapid uptake of lead during the first minute, after which time it is found in the cell capsule. This is followed by slow uptake and lead is then also found in the vacuoles. Complete saturation of living yeast with lead affects only the capsule and vacuoles, whereas in the case of dead cells the protoplasm also takes it up. W. O. KERMACK.

Proteins of egg-white. II. Transformation of crystallised ovalbumin into non-crystallisable conalbumin. L. HEKTOEN and A. G. COLE (J. Infect. Dis., 1929, **44**, 165—166).—Crystallised ovalbumin is not converted by putrefaction into conalbumin. CHEMICAL ABSTRACTS.

Irradiated proteins. VIII. Relation of the velocity of coagulation by light of protein solutions to their sterility. M. SPIEGEL-ADOLF and K. F. POLLACZEK (Biochem. Z., 1929, **214**, 175—186).—The velocity of coagulation by light of 14 protein solutions is investigated. Sterile solutions readily coagulated, but all spontaneously infected solutions (chiefly *B. subtilis*) showed considerable retardation of coagulation, which persisted after the infection had spontaneously died. With sterile solutions, retardation of coagulation was obtained 24 hrs. after sowing with bacteria. Electrodialysis of spontaneously or artificially infected solutions restores the velocity of coagulation to the original values for a short time. P. W. CLUTTERBUCK.

Growth of moulds. I. R. G. TOMKINS (Proc. Roy. Soc., 1929, **B**, **105**, 375—401).—The influence of the temperature, humidity, and the nutrients in the medium on the rate of germination of the spores of fungi and on the growth of colonies has been investigated. W. O. KERMACK.

Relation between the carbohydrates digested and secreted by *Aspergillus niger*. F. OBATON (Compt. rend., 1929, **189**, 711—713).—The amounts of trehalose and mannitol in the mycelium of *A. niger* at various stages in the growth of this organism on cultures containing dextrose and lævulose, respectively, have been determined. There is a marked relation between the nature of the sugar secreted by the organism and that from which it derives its nourishment. A. A. GOLDBERG.

Acetic fermentation. A. BERTHO (Annalen, 1929, **474**, 1—64).—An extension of the investigations of Wieland and Bertho (this vol., 219). In addition to *B. orleanense* and *B. Pasteurianum*, cultures of *B. ascendens* and *B. aceti* are employed. An apparatus for determining the rate of dehydrogenation by the decolorisation of methylene-blue, in which the air is displaced by nitrogen instead of being exhausted, and permits the addition of the reagents and continuous shaking, is described. The degree of adsorption of methylene-blue and Lauth's violet by the bacteria is very high and the values obtained approximate to Freundlich's adsorption isotherm. For this and other reasons these dyes are less suitable as hydrogen-acceptors than is quinone. Neither diethyl peroxide nor potassium persulphate can act as acceptor. Of the substances examined, methyl, ethyl, propyl, *iso*butyl, *iso*amyl alcohols, and their corresponding aldehydes, phenylethyl alcohol, *iso*propyl alcohol, and dextrose act as donators, but not benzyl alcohol, saligenin, salicylaldehyde, acetone, acetic acid, or succinic acid. No evidence could be found for the further oxidation or dehydrogenation of acetic acid. *iso*Propyl alcohol is dehydrogenated entirely to acetone. The relative rates of dehydrogenation by two acceptors vary with different donators. The velocity of the reaction is studied systematically, using varying concentrations of acceptor and donator with constant concentration of donator and acceptor, respectively, ethyl alcohol, aldehyde, and *iso*propyl alcohol being the donators, and quinone and (with *iso*propyl alcohol) oxygen the acceptors. Preparations of bacteria killed by acetone treatment contain too little dehydrogenase for such kinetic studies, but it is noted that owing to damage to the cell structure the rate of reduction of methylene-blue then approximated to that of oxygen. The fact that the dehydrogenation of alcohol proceeds in two stages prevents the working out of the p_s curves for that reaction, but curves are given for the dependence of the velocity of the reaction on the concentrations of aldehyde, *iso*propyl alcohol, and quinone. The dissociation constants are 0·001 for the system aldehyde $\rightleftharpoons$ dehydrogenase–quinone, 0·0025 for aldehyde–dehydrogenase $\rightleftharpoons$ quinone and *iso*propyl alcohol–dehydrogenase $\rightleftharpoons$ quinone, and 0·125 for *iso*propyl alcohol $\rightleftharpoons$ dehydrogenase–quinone. The complex aldehyde–dehydrogenase–quinone decomposes at about twice the rate of *iso*propyl alcohol–dehydrogenase–quinone. Using *iso*propyl alcohol as

donator, the velocity of the reaction is directly proportional to the concentration of oxygen when that acceptor is used, indicating the very high affinity of the natural acceptor for the enzyme. With quinone, the velocity is relatively slower at low concentration, an optimum being reached at about 0·016*N* in presence of aldehyde, 0·01*N* with *iso*propyl alcohol. Except in the case of fresh bacteria, which are apparently damaged by concentrations of *iso*propyl alcohol at concentrations below the optimum when oxygen is the acceptor, the optimum concentration of donator or quinone can be considerably exceeded without relative retardation of the reaction velocity. Thus neither donator nor acceptor excludes the other from the enzyme surface, although it has been shown (*loc. cit.*) that quinone appears to exclude oxygen, possibly on account of its relatively large molecules. Comparison of the activity of fresh with that of 5 weeks old cultures indicates a decrease to about 60% of the dehydrogenating power of the latter for both ethyl alcohol and aldehyde, to about 70—75% for *iso*propyl alcohol with both oxygen and quinone, supporting the idea of the identity of the enzyme. Comparison of the rate of aldehyde dismutation with that of dehydrogenation with various cultures of the four bacterial species gave ratios of 1 : 25 to 1 : 500. The temperature coefficient of both reactions is about 2. Bacterial cultures in wort showed acid production at a rate at least six times as great as the highest rate of dismutation observed under experimental conditions and there was no accumulation of aldehyde. No confirmation was found for the previous supposition that oxygen might possibly accelerate aldehyde dismutation, and the results indicate that mutase action plays only a minor part in the acetic fermentation. F. E. DAY.

Mechanism of the degradation of citric acid by *B. pyocyaneus*. I. J. BUTTERWORTH and T. K. WALKER (Biochem. J., 1929, **23**, 926—935).—*B. pyocyaneus*, when grown on ammonium citrate at 34°, produces acetonedicarboxylic acid. The acid has only a transitory existence. The total "acetone bodies" reached, under the experimental conditions, their highest value 56 hrs. after inoculation; thereafter they decreased rapidly in quantity and disappeared entirely after 80 hrs. The production of malonic acid reached a maximum 96 hrs. after inoculation, followed by entire disappearance after 133 hrs. Succinic acid too was present and reached its maximum at 167 hrs. Volatile acids, principally acetic acid, appeared in the early stages of fermentation and persisted during the experiment. An acidity curve correlating the formation of volatile acid and the appearance, accumulation, and disappearance of the other degradation products is given. Acetic acid was isolated in the fermentation of ammonium malonate. S. S. ZILVA.

Nitrogen circulation. I. Proteolytic power of microbes in general and of *B. coli* in particular. A. JANKE and H. HOLZER (Biochem. Z., 1929, **213**, 142—153).—The action of mass cultures of *B. coli*, *B. putidum*, and *B. fluorescens* on caseinogen was studied. The basic difference between non-liquefiers and liquefiers is that with the former only those cells rendered incapable of reproduction (by chloroform) show a proteolytic activity, whilst with the latter the active proliferating individuals bring about proteolysis. J. H. BIRKINSHAW.

Endocellular enzymes of *B. coli communis*. E. G. YOUNG (Biochem. J., 1929, **23**, 831—839).—The cells of the organism were destroyed by repeated freezings and thawings. The cellular extracts obtained after centrifuging and filtration through a Berkefeld candle, when tested anaërobically, hydrolysed peptone at p_H 7—8, but did not decompose dextrose in absence or presence of phosphate. No hexosephosphate was formed. The dehydrogenase activity on succinic and formic acids is independent of living cell concentration and is associated with cell stroma. In the case of acetic acid, lactic acid, alcohol, or dextrose the activity is temporarily independent of living cell concentration, but is rapidly destroyed by the freezing. The action of toluene towards dehydrogenase activity was similar to that of freezing. There is an increased enzymic (dehydrogenase) power after the early freezings and thawings. S. S. ZILVA.

Biologically active lipins of tubercle bacilli. R. J. ANDERSON (Proc. Nat. Acad. Sci., 1929, **15**, 628—633).—The lipoid fractions of tubercle bacilli were separated by extraction with alcohol, ether, and chloroform, and the fractions, consisting of acetone-soluble fat, a phosphatide, crude wax, and polysaccharide, were analysed. The crude liquid saturated fatty acids obtained after saponifying the acetone-soluble fat were converted into methyl esters, which on distillation gave two principal fractions, which were saponified and the free acids isolated. One of these, m. p. 14—15°, was isomeric with stearic acid; the name *tuberculostearic acid* is proposed. The other is phthioic acid (see this vol., 1108); the m. p. is now given as 28°, $[\alpha]_D^{20}$ +7·98°, mol. wt. 398, and it is stated to be isomeric with cerotic acid. The two acids appear to belong to a new series of fatty acids; a method of separation is outlined. N. M. BLIGH.

Chemotherapy of tuberculosis. E. CHERBULIEZ (Helv. Chim. Acta, 1929, **12**, 920—921).—The copper derivative of 3 : 5-di-iodosalicylaldehyde, $[C_6H_2I_2(CHO)\cdot O]_2Cu$, and the corresponding didymium compound, in oil solution have been used with favourable results in the treatment of tuberculosis in the guinea-pig and man (cf. Stephani, Rev. de la Tuberculose, 1928, **9**, 898). R. K. CALLOW.

Purification of anticarbuncle serum. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1929, **17**, 49—58).—Dilution of anticarbuncle serum with four volumes of distilled water, or, better, of distilled water saturated with carbon dioxide, precipitates the active part quantitatively, mixed with a minimum quantity of proteins (chiefly pseudoglobulins). Dialysis of the serum causes a less complete precipitation of a more concentrated material. Electrodialysis causes complete precipitation of the active material accompanied by pseudoglobulins, and the solution of the precipitate in physiological saline solution is stable when kept. R. K. CALLOW.

Proposed gold chloride titration for determining the toxicity of diphtheria toxin. E. SANDERSON and J. H. YOE (J. Immunol., 1929, **16**, 429—438).—The green colour zone produced in mixtures of gold chloride and toxic broths is not specific for toxin. CHEMICAL ABSTRACTS.

Sterilising action of silver and copper on bacteria. C. EGG and A. JUNG (Mikrochem., 1929, Pregl Fest., 46—60).—0·04 Mg. of silver per litre sufficed to sterilise cultures of *B. coli* within 24 hrs., and a marked effect was produced with concentrations as low as 0·001 mg. The active principle is the silver ion, slightly dissociated silver salts such as the sulphide having no sterilising action. Colloidal solutions of silver and solutions containing complex silver ions may also in certain cases act as sterilisers, but this action is due to the liberation of silver ions through secondary reactions. The sterilising effect of copper compounds is also due to copper ions, but in this case a minimum concentration of 0·6 mg. per litre is necessary for complete sterilisation. No other metals have been found with sterilising power equal to the above. H. F. HARWOOD.

Oligodynamic action of silver. R. WERNICKE and F. MODERN (Biochem. Z., 1929, **214**, 187—197).—Distilled water which has acquired an oligodynamic activity by contact with silver contains 0·00005 mg. per c.c. of this metal in the ionised condition. The activity is lost on electrolysis, the silver being precipitated at the cathode. The oligodynamic action of silver and copper solutions is also obtained in an atmosphere of hydrogen. P. W. CLUTTERBUCK.

Combined action of formaldehyde and salts of certain heavy metals (zinc, copper, cadmium) on proteins and micro-organisms. M. DEGANELLO (Arch. Farm. sperim., 1929, **47**, 177—212).—The character of the flocculent coagulum rapidly produced by the action of zinc, copper, or cadmium sulphate on protein solutions is altered in presence of formaldehyde, which renders it gelatinous. The antiseptic properties of the two components are also enhanced when mixed. Similar results were obtained by Simon (Pathologica, 1915). T. H. POPE.

Disinfecting properties of alkylphenols. II. *n*-Butylphenol. L. F. RETTGER, W. N. PLASTRIDGE, and G. VALLEY (Zentr. Bakt. Par., 1929, I, **111**, 287—296; Chem. Zentr., 1929, i, 2544).—The disinfecting action is enhanced by hydrogen ions (optimal p_H 5·0) and inhibited by hydroxyl ions or soaps. Experiments with *n*-butylphenol and *n*-butylresorcinol are described. A. A. ELDRIDGE.

Diminution of activity of pathogenic bacteria by potassium tellurite. R. GOSIO (Ann. Igiene, 1929, **39**, 112—120; Chem. Zentr., 1929, i, 3000).

Effect of certain factors on the growth of the pneumococcus. H. D. WRIGHT (J. Path. Bact., 1929, **32**, 203—227).—A small amount of fermentable carbohydrate is necessary; excess leads to high acidity. Thermolabile nitrogenous substances essential to growth are present in yeast extract and blood in large quantity, and in meat extract, serum, and peptone in small quantity. After being heated the organic materials inhibit growth, the effect being diminished by reducing conditions. In presence of yeast extract, but not of blood or serum, a small amount of calcium favours growth. CHEMICAL ABSTRACTS.

Use of bacteriostatic dyes in the isolation of *Rhizobium leguminosarum*, Frank. I. A. ANDERSON (Soil Sci., 1929, **28**, 305—313).—*R. leguminosarum* from nodules of lucerne and beans can be successfully isolated by treatment of cultural media with suitable dyes in such concentration as to inhibit the growth of other organisms. Best results were obtained by the use of Ashby's agar containing 1 : 10,000—15,000 parts of crystal-violet. Rosaniline hydrochloride and malachite-green also gave promising results. A. G. POLLARD.

Variation in staining character of bacteria as related to the reserve food material within the organism. E. W. STEARN and A. E. STEARN (Stain Tech., 1929, **4**, 105—109).—When *B. cereus* is starved at 37° it tends to lose its Gram-positivity. This is thought to be due to depletion of its reserve of acidic food material, *e.g.*, nucleoprotein. H. W. DUDLEY.

Chemical basis of staining. I. Reaction between dyes, proteins, and nucleic acid. A. E. STEARN and E. W. STEARN (Stain Tech., 1929, **4**, 111—119).—Basic dyes cause an increase in hydrogen-ion concentration when added to nucleic acid, although both solutions are originally at the same p_H. Acid dyes have no effect on nucleic acid solutions. Basic dyes exhibit the same behaviour when treated with solutions of proteins. Acid dyes when treated with protein solutions show an analogous, though opposite, effect. The bearing of these observations on the theory of staining is discussed. H. W. DUDLEY.

Influence of adrenaline on blood-sugar utilisation of functionally hepatectomised rats. C. F. CORI and G. T. CORI (Proc. Soc. Exp. Biol. Med., 1929, **26**, 345—347).—Rats which have fasted for 24 hrs. contain 5·8±1·4 mg. of liver-glycogen per 100-g. rat. When 0·03 mg. of adrenaline is injected subcutaneously and dextrose is supplied at the rate of 100 mg. per 100-g. rat per hr., 75% of the dextrose remains unutilised in the blood and body-fluids. In functionally hepatectomised rats the blood-sugar and lactic acid were higher after administration of dextrose and adrenaline than after that of dextrose alone. CHEMICAL ABSTRACTS.

Automatin. I. H. G. K. WESTENBRINK and P. ARONS (Arch. Néerland. physiol., 1929, **14**, 394—406).—When solutions of automatinogen are flocculated by irradiation automatin is set free. This substance re-establishes the beating of the heart of the eel, which has been arrested by rinsing with potassium-free Ringer's solution, even after a lapse of 30—40 min. Automatinogen probably consists of automatin adsorbed on phosphatides or other colloidal substances. The unit of automatin is defined as the smallest quantity which, when dissolved in potassium-free Ringer's solution, re-establishes a pulsation of 20 beats per min. in the heart of the eel. Automatin is not destroyed by nitrous acid nor precipitated by silver nitrate, and is therefore not identical with

vitamin-*B*, adrenaline, or histamine. It occurs mainly in the skeletal muscles and heart of the dog and ox.
K. V. THIMANN.

Heart hormone. G. ZUELZER (Med. Welt, 1929, **3**, 304—305; Chem. Zentr., 1929, i, 2547). L. HABERLANDT (Med. Welt, 1929, **3**, 307; Chem. Zentr., 1929, i, 2547).—A discussion. A. A. ELDRIDGE.

Influence of the pituitary on metabolism, growth, and sexual organs of male rats and rabbits. I. Influence of extracts of pituitary on nitrogen metabolism. V. KORENCHEVSKY and M. H. DENNISON (Biochem. J., 1929, **23**, 868—875).—Administration by mouth of anterior or posterior lobe of the pituitary gland dried at the ordinary temperature in a vacuum does not influence definitely the urinary flow or the nitrogen metabolism of rats and rabbits. Subcutaneous injections of glycerol-aqueous extracts of the anterior lobe of fresh pituitary produced on the day of injection a decreased urinary flow (to 35% below normal) and a decrease in the nitrogen metabolism (to 27% below normal). On the days following the injection the nitrogen excretion remained depressed in rabbits but increased to 28% above normal in rats; the volume of urine excreted was much above normal. No special difference was noticed in the response of cryptorchid animals as compared with that of normal animals, nor in the influence of the extracts prepared from bull's or bullock's pituitary. S. S. ZILVA.

Tethelin as a tissue-culture medium. K. C. RICHARDSON and E. S. HORNING (Austral. J. Exp. Biol., 1929, **6**, 137—141).—The growth of cultures of intestinal epithelium from a 7-day embryo chicken in a medium of plasma is markedly increased by the presence of tethelin from the anterior lobe of the pituitary. W. O. KERMACK.

Oestrin. I. Preparation from urine and separation from an unidentified solid alcohol. G. F. MARRIAN (Biochem. J., 1929, **23**, 1090—1098).—Methods of preparing active œstrus-producing concentrates from the unsaponifiable fraction obtained from the urine of pregnant women are described. There is present in the unsaponifiable fraction of the ether-soluble material from the urine of pregnancy varying amounts of a solid saturated *alcohol* $C_{19}H_{32}O_2$ or $C_{20}H_{34}O_2$, m. p. 232—234·5° (uncorr.) (*acetate*, m. p. 177·5—178·5°). This compound has not been detected in the urine of normal males and normal non-pregnant females. S. S. ZILVA.

Testicles and water metabolism. T. YAMAMOTO (Okayama J. Med., 1928, **40**, 1467—1480).—Castration causes a change in the water and sodium chloride metabolism; injection of spermatin slightly restores the metabolic function.
CHEMICAL ABSTRACTS.

Insulin. H. MATHIS (Biochem. Z., 1929, **213**, 72—73).—The non-cystine sulphur of insulin (3·72% as cystine) is not present as a sulphuric ester.
J. H. BIRKINSHAW.

Composition of insulin and its relation to enzymes and activators. E. GLASER and G. HALPERN (Wien. Med. Woch., 1929, **79**, 363—366; Chem. Zentr., 1929, i, 2656).—Insulin is regarded as a compound of guanidine with amino-acids. Similar substances are present in fungi and beet. Various enzymes exert a hypoglycæmic action. Peroxidases and aldehydases are found in insulin. The action of insulin is enhanced by certain enzymes.
A. A. ELDRIDGE.

Reversible inactivation of insulin. F. H. CARR, K. CULHANE, A. T. FULLER, and S. W. F. UNDERHILL (Biochem. J., 1929, **23**, 1010—1021).—Ethyl alcohol and hydrochloric acid inactivate insulin. The rate of inactivation is increased by raising the temperature or the concentration of either the acid or the alcohol. Coincident with the inactivation there is a gradual change in the final precipitation point towards the alkaline side. The activity can be completely recovered and the original final precipitation point obtained by treatment with dilute sodium hydroxide. The process may be repeated with a small amount of loss in activity. Other strong acids with primary or secondary alcohols have a similar action on insulin. Insulin most probably undergoes an esterification on inactivation. S. S. ZILVA.

Production of insulin after administration of lævulose. F. SILBERSTEIN and M. WACHSTEIN (Biochem. Z., 1929, **213**, 301—311).—Experiments on dogs and rabbits according to Pollak's modification (A., 1927, 1115) of Staub and Traugott's method show that after administration of dextrose there is always a positive insulin effect. Administration of lævulose produces typical insulin effect, sometimes in dogs, never in rabbits. The positive results found with some dogs are attributed to the fact that lævulose is not an adequate food for carnivorous animals.
W. MCCARTNEY.

Action of insulin, particularly on cell and tissue metabolism. H. J. ARNDT (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1927, **61**, 116—133; Chem. Zentr., 1929, i, 2789).—A discussion of morphological results. A. A. ELDRIDGE.

Influence of insulin on glycogen formation in macerated liver or muscle and in the liver during perfusion with sugar-saline solutions. K. OTANI (Okayama Ig. Zasshi, 1928, **40**, 727—745).—Macerated liver of *Bufo japonicus* can form glycogen from either dextrose or lævulose, whilst resected muscle can convert only dextrose. Addition of insulin reduces the glycogen content of both muscle and liver. When liver is perfused with a sugar-saline solution glycogen is formed from both dextrose and lævulose, insulin respectively retarding or accelerating the action. CHEMICAL ABSTRACTS.

Influence of insulin and synthalin on the gastric secretion. L. G. BUSTAMANTE (Arch. Endocrinol. Nutric., 1928, **6**, 295—333; Chem. Zentr., 1929, i, 3002).—Insulin increases the acidity of the gastric secretion; the effect of synthalin is indefinite. The action of insulin is suppressed by atropine.
A. A. ELDRIDGE.

[Physiological] action of pancreatic secretin. A. FIESCHI (Biochim. Terap. sper., 1927, **14**, 5 pp.; Chem. Zentr., 1929, i, 3001).—Intravenous injection of pancreatic secretin causes a fall in blood-sugar; long-continued injection does not influence the blood-sugar, but increases the carbohydrate tolerance.
A. A. ELDRIDGE.

Secretin in Japanese plants. T. OKANO (Japan. J. Int. Secr., 1928, **4**, 1350—1354).—Substances (soluble in water or ethyl alcohol, but not in ether) which excite or inhibit the motion of isolated rabbit's intestine were extracted from fresh plants with warm, dilute hydrochloric acid. CHEMICAL ABSTRACTS.

Vitamin-*A*, polyenes, and ergosteryl phosphate. H. VON EULER and M. RYDBOM (Svensk Kem. Tidskr., 1929, **41**, 223—227).—The effect of administration of carotinoids on the red blood-cell count of rats has been investigated. Experiments have also been carried out on the antimony trichloride tests as applied to the blood-serum and the extracts of the liver of rabbits. *Diergosteryl phosphate* has m. p. 180—182°, $[\alpha]_D^{20}$ −68·9° in chloroform; *ergosteryl phosphite* has m. p. 146°. W. O. KERMACK.

Relation of vitamin-*A* content to size of leaves. L. MCLAUGHLIN (with E. S. HABER) (J. Biol. Chem., 1929, **84**, 249—256).—Small spinach leaves contain relatively more vitamin-*A* than large ones, the determining factor being the surface area. C. R. HARINGTON.

Assimilation of vitamin-*A* when dissolved in liquid paraffin. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1929, **18**, 997—998).—No differences in vitamin-*A* activity were detected between solutions of cod-liver oil concentrate in olive oil and liquid paraffin. E. H. SHARPLES.

Biology of iodine compounds. I. Effect of cuprous iodide in avitaminosis-*A* and -*D*. G. VON WENDT (Med. Welt, 1928, **3**, 527—528; Chem. Zentr., 1929, i, 2896—2897).—With rats, doses of 0·15—0·25 mg. of cuprous iodide per 100 g. had an immediate effect on the assimilatory processes in avitaminosis-*A* or -*D*. A. A. ELDRIDGE.

Vitamin contents of grass seeds from treated plots. M. I. ROWLANDS (Nature, 1929, **124**, 760).—Grass seed from plots manured with dung, when fed to rats, gives a much steeper growth curve than does seed from plots treated with artificial manures. A. A. ELDRIDGE.

Nutritive value of the garbanza pea. H. S. MITCHELL (West. Hosp. Rev., 1928, **11**, No. 6, 26, 27, 52, 53).—The garbanza (Idaho) pea is approximately equivalent to caseinogen in the quantity of protein, is a rich source of vitamin-*B*, and has a slight potential alkalinity. CHEMICAL ABSTRACTS.

Comparison of the vitamin-*B* content of fresh yeast and of the dried yeast produced from it. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1929, **213**, 220—225).—The processes involved in the manufacture of dried yeast from fresh brewery yeast do not lessen its content of vitamin-*B*. J. H. BIRKINSHAW.

So-called refection. I. Vitamin-*B* testing. A. SCHEUNERT, M. SCHIEBLICH, and J. RODENKIRCHEN (Biochem. Z., 1929, **213**, 226—233).—The phenomenon of sudden increase of growth in rats fed on a diet deficient in vitamin-*B* ("refection") is not due to coprophagy alone, but chiefly to a special type of micro-organism capable of forming vitamin-*B* in the food or fæces. This anomalous effect is best avoided by keeping the animals on wire netting, by the use of carefully extracted starch, and by microscopical examination of the fæces in cases under suspicion. J. H. BIRKINSHAW.

Influence of different samples of "casein" on vitamin tests. K. H. COWARD, K. M. KEY, B. G. MORGAN, and M. CAMBDEN (Biochem. J., 1929, **23**, 913—920).—The growth response of rats given cod-liver oil after they have ceased to grow in a preparatory period may vary greatly according to the sample of casein used in the basal diet. "Light-white casein" even after extraction with alcohol and ether contains some growth-promoting factor which is not necessarily present in other samples of casein. For vitamin-*B* testing "light-white casein" (B.D.H.) as the source of protein gives more uniform results than "vitamin-free casein" (Glaxo). As it contains neither vitamin-B_1 nor -B_2 it does not need to be extracted before use in vitamin-*B* testing. S. S. ZILVA.

Concentration of vitamin-*B*. B. C. GUHA and J. C. DRUMMOND (Biochem. J., 1929, **23**, 880—897).—Two methods of preparation of vitamin-B_1 concentrates from wheat embryo are described. In one the procedure consisted of adsorbing the vitamin on norite after clearing the alcoholic extract of the embryo with lead acetate and further purification by precipitation with phosphotungstic acid, adsorption on silver oxide, and clearing with picrolonic acid. In the second method the vitamin was adsorbed on fuller's earth and fractionated with silver nitrate and baryta, phosphotungstic acid, platinic chloride, and gold chloride. In the last stage the precipitate was active only in large doses, whilst the filtrate was inactive; on combining the two, however, the activity was very much increased. Concentrates of which 0·005 mg. was active as pigeon-curative day-dose and which promoted good growth in rats in daily doses of 0·015 mg. when supplemented by vitamin-B_2 were obtained. Nucleic acid, nicotinic acid, betaine, and a substance, m. p. 234—235°, obtained by Drummond and Funk possess no vitamin-B_1 activity, nor does marmite liberate an active base on boiling with 20% sodium hydroxide solution. The "bios" activities of the concentrates are given. S. S. ZILVA.

Alleged antineuritic properties of certain quinoline and glyoxaline derivatives. J. M. GULLAND and R. A. PETERS (Biochem. J., 1929, **23**, 1122—1125).—Neither 4(5)-glyoxalinemethylethylcarbinol hydrochloride nor 2 : 6-dihydroxyquinoline has antineuritic vitamin properties similar to those of torulin. A number of compounds containing glyoxaline and pyrimidine rings have also given negative results. S. S. ZILVA.

Carbohydrate metabolism in birds. I. The relation between the lactic acid content of brain and the symptoms of opisthotonus in rice-fed pigeons. H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1929, **23**, 1126—1136).—Pigeons in the terminal stages of vitamin-B_1 deficiency showing symptoms of opisthotonus have an increased amount of lactic acid (95 mg. per 100 g. of tissue) in the brain as compared with the normal (55 mg. per 100 g. of tissue). This increase disappears within a short time

after dosing with torulin. It is not a consequence of the high blood-sugar and tends to follow the blood-lactic acid, which is raised. At the end of a period of 40 sec. after death about 70% of the lactic acid maximum is formed in the brain. Stunning produces lactic acid more rapidly than careful anæsthesia with ether. S. S. ZILVA.

Colour reaction for vitamin-*C*. I. Dispersion and behaviour of substances specific for Bezssonov's reagent towards various adsorbents. B. DOGADKIN and B. I. YANOVSKAYA (Biochem. Z., 1929, **213**, 86—94).—The substances in lemon and cabbage juice giving the Bezssonov reaction are in a state of molecular dispersion. Like quinol, they are adsorbed by animal and plant carbons. Unlike quinol, when adsorbed on charcoal they are not removed by capillary-active substances. The specific violet colour is probably due to the decomposition products of vitamin-*C*. J. H. BIRKINSHAW.

Production of avitaminosis: vitamin-*C*. L. RANDOIN and R. LECOQ (J. Pharm. Chim., 1929, [viii], **10**, 337—344).—A review of the previous methods of producing a diet deficient in vitamin-*C* is given, and the following is found to be an efficient modification which is rapidly prepared: peptone 17%, powdered brewer's yeast 3%, butter fat 5%, maize starch 64%, sodium chloride 1·5%, calcium lactate 5%, filter paper 2·5%, and Osborne and Mendel's salt mixture 2%. On this diet guinea-pigs show the first symptoms of scurvy from the 14th to the 18th day, and a few days later diarrhœa and gross digestive disorders set in, accompanied by a rapid loss of weight. Death occurs from the 25th to the 30th day. *Post-mortem* examination reveals the characteristic lesions of scurvy. The spleen alone of the body organs does not appear to be hypertrophied. The daily addition of 2—3 c.c. of lemon juice to the diet (according to the weight of the animal) ensures proper growth of the young and maintenance of adults, and will cure animals already showing the earlier symptoms of scurvy. P. G. MARSHALL.

Vitamin-*D* content of the fat of marine mammals. S. N. MATZKO (Biochem. Z., 1929, **213**, 391—398).—The subcutaneous fat of the seal (*Phoca capsica*, Nils) and of the dolphin (*Delphinus Delphis*, L.) contain considerable amounts of vitamin-*D*. W. MCCARTNEY.

Hypervitaminosis and vitamin balance. IV. An instance of vitamin balance. L. J. HARRIS and T. MOORE (Biochem. J., 1929, **23**, 1114—1121).—The need of the rat for marmite (vitamin-*B* complex) is increased as the vitamin-*A* and -*D* (cod-liver oil concentrate) content of the diet is increased. The extra amount of vitamin-*B* can also be supplied in the form of wheat germ extract. It is probable that the antagonistic effect is exerted between the vitamin-*B* complex and the vitamin-*A* of the concentrate or cod-liver oil. The possible action of other unidentified substances is not excluded. S. S. ZILVA.

Vitamin-*D*. I. Its influence on vitamin-*A*. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 795—800).—The growth-promoting activity of vitamin-*A* ("Riken-biosterin") is greater when vitamin-*D* (irradiated ergosterol) is also administered than in the absence of the latter vitamin. W. O. KERMACK.

Effect of cod-liver oil feeding on the calcium and phosphorus content of cows' milk. E. J. SHEEHY and B. J. SENIOR (Biochem. J., 1929, **23**, 898—901).—The addition of 6—8 oz. of cod-liver oil daily to the diet of milking cows which were fed on a winter ration including hay, roots, and meals and had reached the 14th, 11th, and 19th week, respectively, of the lactation period did not alter the calcium or phosphorus content of the milk produced. S. S. ZILVA.

Diet and calcium assimilation. XI. Influence of cod-liver oil on calcium metabolism of milking cows. XII. Influence of hays cured with varying exposure to sunlight on calcium metabolism of milking cows. E. B. HART, H. STEENBOCK, E. C. TEUT, and G. C. HUMPHREY (J. Biol. Chem., 1929, **84**, 359—365, 367—376).—XI. No effect on the calcium metabolism of milking cows was observed as the result of adding 0·5 lb. of cod-liver oil, rich in vitamin-*D*, to the daily diet.

XII. Although all hays tested possessed antirachitic properties, the relative activity was not proportional to the exposure of the material to sunlight, nor was 10 lb. of the best hay *per diem* sufficient to maintain calcium equilibrium in a milking cow. C. R. HARINGTON.

Decrease in bone-phosphatase in overfeeding with irradiated ergosterol. L. BAUMGARTNER, E. J. KING, and I. H. PAGE (Biochem. Z., 1929, **213**, 170—176).—The administration to rabbits of large doses of "vigantol" (irradiated ergosterol) produces, in addition to pathological phenomena, a considerable decrease in bone-phosphatase. J. H. BIRKINSHAW.

Acidity relations of the *Sarracenias*. E. T. WHERRY (J. Washington Acad. Sci., 1929, **19**, 379—390).—A detailed study of the p_H values etc. of soils in which 8 species and a number of hybrids of *Sarracenias* or pitcher plants grow, and of the liquids in the hollow leaves or "pitchers" of these plants. Some of these plants are able to obtain nitrogen, phosphorus, and other essential elements through digestion of insects which drown in the pitcher liquor, and can thus grow in soils lacking in available nutrients. E. HOLMES.

[Biochemical factors in] heredity. III. H. VON EULER and D. RUNEHJELM (Z. physiol. Chem., 1929, **185**, 74—80; cf. this vol., 1197).—Chlorophyll-normal and chlorophyll-defective mutants of barley were germinated in the dark. The catalase action of the yellow (normally green) plants was about double that of the white mutants. J. H. BIRKINSHAW.

Photosynthetic reaction [of sugar]. R. B. GORDON.—See this vol., 1405.

Determination of aluminium in plants. II. O. B. WINTER and O. D. BIRD (J. Amer. Chem. Soc., 1929, **51**, 2964—2968; cf. this vol., 1397).—The colorimetric method previously described is applied to the determination of aluminium in plants. The metal was found in all the substances investigated, particularly in lettuce. The method yields fairly accurate

results, and aluminium added to the plant material is accurately determined. S. K. TWEEDY.

Luxury consumption of potassium by plants. R. P. BARTHOLOMEW and G. JANSSEN (J. Amer. Soc. Agron., 1929, 21, 751—765).—Plants absorb more potassium during early periods of growth than is necessary for normal growth. Potassium can be translocated within and re-utilised by the plant.

CHEMICAL ABSTRACTS.

Iodine from Black Sea weeds. N. D. AVERKIEV (Farm. Zhur., 1928, 176—179).—The seaweed red *Phyllophora* is exceptionally rich in iodine; its technical extraction is described.

CHEMICAL ABSTRACTS.

Iodine content of the principal marine algæ of the coasts of Galicia. I. P. PONDAL (Datos Geoquím. Galicia, 1927, 1—30).—The percentage of iodine in a number of varieties of algæ from the Galician coasts has been determined by the incineration method, and varies from 0·001 to 0·55. The quantity of iodine present in a given species is the same as that present in the corresponding French and Scottish species. The economic aspect of iodine production is discussed. H. F. GILLBE.

Potato as an index of iodine distribution. R. E. REMINGTON, F. B. CULP, and H. VON KOLNITZ (J. Amer. Chem. Soc., 1929, 51, 2942—2947).—The average iodine content of Irish potatoes from several American localities was determined by the method previously described (this vol., 413). It increases progressively as the locality is removed from the sea coast and approaches the Appalachian Mountains; the relative amount of clay in the soil increases in the same manner. The iodine content also varies for different samples raised in the same area and identical soil type. Immediate influence of the sea is not apparent beyond a very narrow belt along the coast. It is suggested that the principal source of iodine is the disintegration of granite rocks supplemented by the use of commercial fertilisers.

S. K. TWEEDY.

Significance of methods of botanical microscopic work for botanical microchemistry and histochemistry. J. KISSER (Mikrochem., 1929, Pregl Fest., 178—191).—A definition of the field covered by botanical microchemistry is given, and the methods employed in botanical microscopy are discussed. H. F. HARWOOD.

Microchemical detection and localisation of glucosides. L. ROSENTHALER (Mikrochem., 1929, Pregl Fest., 302—307).—A discussion and criticism of the various microchemical methods available for the detection and localisation of glucosides in plant material. H. F. HARWOOD.

Determination of lignin by acid hydrolysis. L. PALOHEIMO (Biochem. Z., 1929, 214, 161—174).—Restricting the term "ortholignin" to that type of lignin which is resistant to the action of concentrated hydrochloric acid and 70% sulphuric acid for 24 hrs. and is scarcely attacked by boiling with dilute alkali, the author finds that pine wood contains 25%, aspen wood 6%, clover 5%, and various grasses 2—5% of ortholignin. Other kinds of lignin, readily hydrolysed by strong acids and dilute alkalis, are grouped as "hydrolysable lignin." Pine wood contains very little and hay and straw chiefly hydrolysable lignin. In strongly acid solutions, hydrolysable lignin readily forms secondary condensation products which coagulate on dilution and in undiluted solution are partly absorbed on undissolved constituents of the cell wall. Part of the protein is as resistant to strong acids as ortholignin. Pringsheim's lignin contains ortholignin, unhydrolysed protein, and coagulated and adsorbed condensation products of hydrolysed lignin.

P. W. CLUTTERBUCK.

Plant phosphatides. VII. Escape of proteins and tannins into the dialysate of barley. V. GRAFE and K. FREUND (Beitr. Biol. Pflanzen, 1928, 16, 140—156; Chem. Zentr., 1929, i, 2999).—Hordein is slightly soluble in water, and less soluble in barley dialysate, which always gives Millon's reaction. Tannin substances could not be detected, but a hydroxy-fatty acid was probably present.

A. A. ELDRIDGE.

Allantoinase and the origin of allantoic acid in vegetables. R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, 189, 716—717).—Fermentation of the juice expressed from the green haricot gave rise to allantoic acid, due to the action of allantoinase on allantoin contained in the sugar. The presence of ammonium carbonate augments the amount of allantoic acid formed.

A. A. GOLDBERG.

Metabolic products of certain fucoids. I. Sugar. II. Mannitol and mannitan. P. HAAS and T. G. HILL (Biochem. J., 1929, 23, 1000—1004, 1005—1009).—I. There is present in *Pelvetia canaliculata* and *P. canaliculata forma libera*, but not in *Ascophyllum nodosum* and *Fucus serratus*, plants of a lower level of the emerging zone, a small amount of free reducing sugar, probably a pentose. In *Pelvetia* there is also a dialysable pentose complex which reduces Fehling's solution only after hydrolysis. Plants air-dried for some time and extracted in the same way as the freshly-gathered material do not give any sugar reactions. This complex is probably a transient labile disaccharide.

II. *Pelvetia canaliculata* and *P. canaliculata f. libera* contain mannitol. Its presence has also been confirmed in *Ascophyllum nodosum*, *Fucus serratus*, and *Laminaria digitata*. A *dibenzylidene* derivative of mannitan, m. p. 165—166°, has been isolated from *P. canaliculata* and its form *libera* which occupy the highest position in the emerging zone. After heating mannitol for 1·5 hrs. at 300—308° an isomeric *dibenzylidenemannitan*, m. p. 113—115°, can be isolated.

S. S. ZILVA.

Decomposition of hexoses in plants. IV. Stimulating effect of atmospheric oxygen on the post-mortal alcoholic fermentation of peas. W. ZALESKI and L. NOTKINA (Biochem. Z., 1929, 213, 406—413).—Atmospheric oxygen stimulates the alcoholic fermentation of pea-meal. Acetaldehyde and methylene-blue also have this effect, although the influence of the latter is pronounced only when the fermentation is anaërobic. The fermentation of meal from peas which are incapable of germinating is not stimulated by either atmospheric oxygen or

methylene-blue. $10^{-3}M$-Potassium cyanide restricts both the aërobic and anaërobic fermentation of meal from peas capable of germination, but has no effect on meal from those incapable of so doing. The influence of methylene-blue is not affected by potassium cyanide. Sodium pyrophosphate does not interfere with the stimulating effect of atmospheric oxygen. Meal from peas capable of germination contains glutathione, which is present only in traces in those which are incapable of germination. The fact that meal from unground peas behaves quite differently shows that the changes which occur during grinding favour the fermentation process, which is also greatly promoted by preliminary germination.

W. McCartney.

Tobacco. II. Protein complexes in tobacco. N. Gavrilov and A. Koperina. **III. Determination of protein in tobacco.** N. Gavrilov and A. Taranova (Biochem. Z., 1929, **214**, 134—149, 150—157).—II. An aqueous or faintly alkaline extract of tobacco does not contain either protein, peptone, or polypeptide. The ammonia obtained on hydrolysis is largely obtained from purine substances. By autoclaving tobacco and water, condensation occurs with considerable decrease of amino-nitrogen and carbohydrate content.

III. Determination of the protein content of albumin solutions before and after partial hydrolysis and of tobacco extracts is carried out by a variety of methods, *e.g.*, by precipitation of the protein by tannin, lead acetate, phosphotungstic acid, 0·5% acetic acid (Mohr's method), with subsequent determination of the nitrogen by Kjeldahl's method. It is shown that although the methods give good results with pure protein solutions, they give widely varying results for both the tobacco extracts and the hydrolysates. Of the methods, Mohr's probably gives the most trustworthy results. P. W. Clutterbuck.

Glutathione in plants. W. H. Camp (Science, 1929, **69**, 458).—Fink's micro-method for glutathione (*ibid.*, 1927, **65**, 143) has been used to detect this substance in plants. The stem apex of *Helianthus annuus*, the staminate tissue of *Alocasia odora* (distinction from the carpellate tissue), and especially the normal, staminate tassels of *Zea mais* all showed the presence of this substance, and the nitroprusside reaction can thus be used to measure the metabolic level of various tissues. L. S. Theobald.

Constituents of *Matteucia orientalis*. S. Fujise (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 111—118).—A pure specimen was obtained and the constitution established of the matteucinol first isolated from this source by Munesada (J. Pharm. Soc. Japan, 1924, 185). The analytical data correspond with the formula $C_{18}H_{18}O_5$, and the methoxyl content corresponds with one methoxy-group in the molecule. From 570 g. of the stalk 11 g. of a solid are obtained by acetone extraction and, after five crystallisations from methyl alcohol, 0·5 g. of matteucinol is obtained. An acetone extract of the leaves gives a solid which is contaminated with chlorophyll; the products are purified as follows. Calcium hydroxide and water are added to the acetone extract to form a paste which is filtered; the precipitate formed on addition of hydrochloric acid to the filtrate is extracted with ether, and the residue obtained on evaporating the ethereal extract is repeatedly crystallised from methyl alcohol and finally from xylene, yielding *demethoxymatteucinol*, m. p. 200°. The early filtrates from crystallisations of demethoxymatteucinol are evaporated and the residue is dissolved in ethyl alcohol. Precipitation from this by addition of light petroleum gives a product which, after four crystallisations from dilute alcohol, is pure matteucinol, m. p. 174°. Its colour reactions and absorption spectrum agree with those of the flavanone group. Methylation with diazomethane in dry ether gives a *monomethyl ether*, $C_{19}H_{20}O_5$, m. p. 100°. *Demethoxymatteucinol monomethyl ether*, $C_{18}H_{18}O_4$, m. p. 109°, is prepared similarly. By a mild fusion with potassium hydroxide of impure matteucinol (containing demethoxymatteucinol, with which it forms mixed crystals, m. p. 165—168°), it is possible to isolate (1) a *substance* of empirical formula $C_{17}H_{16}O_4$ considered to be a cinnamoyldimethylphloroglucinol, derived from demethoxymatteucinol, (2) 2 : 4-dimethylphloroglucinol, and (3) *p*-methoxycinnamic acid; (2) and (3) are derived from matteucinol, the constitution of which is confirmed (by synthesis from 2 : 4-dimethylphloroglucinol and *p*-methoxycinnamic acid chloride) as 5 : 7-dihydroxy-4′-methoxy-6 : 8-dimethylflavanone. Demethoxymatteucinol is considered to be 5 : 7-dihydroxy-6 : 8-dimethylflavanone.

P. G. Marshall.

Natural resins and resin acids. F. Balás (Časopis Českoslov. Lék., 1927, **7**, 320—338; Chem. Zentr., 1929, i, 2530—2531).—The resin of (American) *Pinus palustris* afforded *n*-heptacosane, a diterpene, $C_{20}H_{32}$, b. p. 192—195°/12 mm., and the corresponding diterpene alcohol. The resin of (French) *Pinus maritima* afforded a sesquiterpene, $C_{15}H_{24}$, b. p. 120—123°/12 mm. (which on dehydrogenation with selenium gave cadalin), a diterpene, $C_{20}H_{32}$, b. p. 188—192°/12 mm., and *n*-hentriacontane, m. p. 68·5°. From the resin acids of *P. palustris* were isolated: *l*-pimaric and *d*-pimaric acids [nitrosite, m. p. 79—80° (decomp.)]. Reduction (platinum and hydrogen) of *d*-pimarol gave dihydro-*d*-pimarol. *d*-Pimaric acid forms three hydrochlorides, m. p. 232° (decomp.), 184° (decomp.), and 125° (decomp.), respectively. Oxidation with alkaline permanganate gave two isomeric dihydroxy-*d*-pimaric acids, m. p. 224° (diacetate, m. p. 235°) and 239°, respectively. The following *d*-pimarates are described: *propylamine*, m. p. 158°; *dipropylamine*, m. p. 112°; *diamylamine*, m. p. 113°; *piperidine*, m. p. 133°; *quinine*, m. p. 195°; *quinidine*, m. p. 90°; *cinchonidine*, m. p. 175°. The following abietates are described: *dipropylamine*, m. p. 160°; *diamylamine*, m. p. 133°.

A. A. Eldridge.

Origin of essential oils, balsams, and resins. A. Ossowski (Rocz. Farm., 1927, **5**, 1—65; Chem. Zentr., 1929, i, 2999—3000).—The influence of season and time of day on vegetable secretions was examined.

A. A. Eldridge.

Microdetermination of water in connective tissue. J. García-Blanco (Arq. Seminario Est. Galegos, 1929, **5**, 1—2).—The tissue (0·2—1·0 g.) is subjected to distillation with 15 c.c. of xylene and

the quantity of water evolved is measured directly by centrifuging the cold distillate in a graduated tube. The determination can be completed in about 10 min., and the results are concordant to within about 5%. H. F. GILLBE.

Colorimetric determination of arsenic. A. POLJAKOV and N. KOLOKOLOV (Biochem. Z., 1929, **213**, 375—379).—Organic matter in the material (biological fluid) is destroyed with aqua regia and the arsenic is then precipitated by sodium hypophosphite, collected, and dissolved in hydrogen peroxide. The solution is evaporated to dryness, the residue dissolved in water, and to the solution are added a saturated solution of ammonium molybdate and a solution of stannous chloride in hydrochloric acid. The blue colour which is produced is extracted with amyl alcohol and compared with a standard in a colorimeter. W. MCCARTNEY.

Electrolytic determination of small amounts of mercury in body fluids and tissues. A. G. YOUNG and F. H. L. TAYLOR (J. Biol. Chem., 1929, **84**, 377—391).—The reason for the loss of mercury which occurs in the wet incineration of biological material containing the metal with sulphuric acid is the reduction of the mercury salt by the organic matter to the metal, which is then volatilised. Mercury is not completely precipitated on copper from biological fluids even after oxidation of the organic matter. Diluted urine was treated with nitric and sulphuric acids and potassium permanganate until destruction of organic matter was complete; the mercury was then deposited electrolytically on a platinum electrode, from which it was subsequently dissolved with nitric acid, and titrated with thiocyanate. Mercury can be determined in cerebrospinal fluid without preliminary oxidation; muscle and fæces are first treated with concentrated sulphuric acid and the diluted fluid is analysed by the method described for urine. The method is accurate to within ±0·1 mg. of mercury. C. R. HARINGTON.

Micro-determination of silver in blood and physiological material. L. PINCUSSEN and W. ROMAN (Mikrochem., 1929, Pregl Fest., 296—299).—The blood or other material is treated with concentrated nitric acid, hydrogen peroxide, and a few drops of hydrochloric acid, and heated until organic matter is destroyed. The precipitate of silver chloride is repeatedly centrifuged with water until free from soluble chloride, and reduced by treatment with 1 c.c. of concentrated ammonia and a boiling 25% solution of dextrose. If any brown colloidal silver forms the solution must be centrifuged until clear after addition of solid magnesium sulphate. The metallic silver is dissolved in nitric acid and the solution titrated with 0·001*N*-ammonium thiocyanate. 0·01 Mg. of silver in blood can be determined by the above method with a maximum error of 2%. H. F. HARWOOD.

Colorimetric micro-determination of sulphur and of sulphates in biological fluids. K. LANG (Biochem. Z., 1929, **213**, 469—474).—Inorganic sulphate in 1·0 c.c. of urine is determined by adding 9·0 c.c. of 0·01*N*-barium chromate solution, allowing the barium sulphate formed to settle, precipitating the excess of barium chromate with solid calcium hydroxide, removing the precipitates by filtering or centrifuging, and adding 1·0 c.c. of a solution of 2·0 g. of diphenylcarbazide in 10 c.c. of acetic acid and 90 c.c. of 96% alcohol. The reddish-violet colour produced is compared after 20 min. with that of a standard. The total sulphate is determined in the same way after the organic sulphate has been decomposed with hydrochloric acid and the amount of organic sulphate is obtained by difference. The total sulphur in urine or serum is determined after organic matter has been destroyed with nitric acid and hydrogen peroxide. The average error is less than 2%. Salts of heavy metals, if present in large amount, interfere with the process. W. MCCARTNEY.

Micro-methods. C. HABLER and B. NOETZEL (Biochem. Z., 1929, **214**, 201—203).—A modification of Bang's micro-burette is described. By combining Volhard's macro-method and Claudius' micro-method (Arch. Med. Scand., 1924, **61**, 3) for the determination of chlorine, the chloride content of 0·5 c.c. of body-fluid can be obtained with an accuracy of 2 mg. per 100 c.c. P. W. CLUTTERBUCK.

Micro-determination of the residual nitrogen content of tissues. F. LEÖVEY (Biochem. Z., 1929, **214**, 198—200).—The tissue (0·3—0·4 g.) is ground with sand, the pulp washed into a measuring flask with phosphomolybdic acid and, after shaking and keeping for 24 hrs., is filtered. The nitrogen content of an aliquot of the filtrate is then determined by Kjeldahl's method. Parallel determinations differ by not more than 4—5%. The values for different samples show considerable variation, the most constant results being obtained for different samples of brain and muscle (especially heart-muscle). P. W. CLUTTERBUCK.

Solubility of uric acid in presence of proteic acids. K. YABANA (Biochem. Z., 1929, **213**, 456—459).—The amount of uric acid dissolved by 100 g. of pure water at 22° is 5·0 mg., but in the presence of proteic acids this quantity is increased by from 6% to 32%. In the determination of uric acid with permanganate 1·0 c.c. of 0·05*N*-solution is equivalent to 3·8 mg. of uric acid. W. MCCARTNEY.