BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1930.

General, Physical, and Inorganic Chemistry.

New bands in the secondary spectrum of hydrogen. II. D. B. DEODHAR (Phil. Mag., 1930, [vii], **9**, 37—49).—A detailed examination of seven new band systems in the blue region of the secondary hydrogen spectrum is described. The frequencies of the null lines in each system have been determined from the $Q(1)$, $P(2)$, and $R(1)$ members and the values are in good agreement, those corresponding with the $Q(1)$ members being 21323·17, 21444·45, 21580·70, 21716·22, 21885·13, 22063·62, and 22261·70. In each band the initial moment of inertia is greater than the final one and the moment of inertia decreases gradually with the increasing frequency. The bands are attributed to excited hydrogen molecules and it is suggested that they are related to band systems in the yellow region of the spectrum previously described (A., 1928, 1067).   A. E. MITCHELL.

Theory of relativity and the spectral lines of hydrogen. T. RAMOS (Ann. Acad. Brasil. Sci., 1929, **1**, 20—27).—Mathematical. The Balmer series of the hydrogen spectra is discussed from the point of view of the general theory of relativity.
H. F. GILLBE.

Dissymmetry of emission of series lines. J. STARK (Naturwiss., 1929, **17**, 983).—Experiments on the line series of hydrogen and helium have shown in both cases that those lines which are shifted to the red by the electric field are emitted, along the axis of the field, with greater intensity against the field than in the direction of the field. The effect is reversed in the case of those lines which are shifted towards the violet.   G. E. WENTWORTH.

Radiation from the hydrogen–oxygen flame. W. E. GARNER and K. TAWADA (Trans. Faraday Soc., 1930, **26**, 36—45).—Measurements of the infra-red radiation from " wet " and " dry " hydrogen–oxygen explosions do not confirm the conclusions reached indirectly by Wohl and Elbe (A., 1929, 1394) that the " dry " flame exhibits chemiluminescence which is suppressed on saturation with water. The radiation–composition curve for mixtures of dry hydrogen and oxygen shows a maximum at 55% H and a subsidiary peak at 20%. The radiation decreases with the pressure more rapidly than the pressure itself. The density of an inert gas determines its effect on the amount of radiation emitted; thus argon, oxygen, and nitrogen increase it, whilst it is diminished by hydrogen or helium. When 2 volumes of argon are added to 3 volumes of the stoicheiometrical hydrogen–oxygen mixture, there is a threefold increase in the radiation

emitted. These effects are attributed to changes in the duration of the high temperature of the flame, and it is concluded that the phenomena are best explained by assuming that the radiation from this flame is thermal in character.   J. W. SMITH.

Lyman helium lines. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 662—666).—The calculation of the wave-lengths of spectral lines is now based on certain spectral laws. Many spectra are sufficiently accurately analysed to permit the calculation of short wave-lengths on the basis of their term systems, e.g., Al II and Hg II. The wave-lengths of the intensity maxima of the hydrogen and He II spectra are calculated with reference to the relativistic fine structure and intensity of the components. Using these as standards, the lines of the He I series discovered by Lyman are fixed. A spectrogram by Kruger on which the hydrogen series and both the helium spectra He I and He II were present with great sharpness was used.   A. J. MEE.

Fine structure and Zeeman effects in helium band lines. R. S. MULLIKEN and G. S. MONK (Physical Rev., 1929, [ii], **34**, 1530—1540).—Second and third order grating photographs of helium band lines λ 6400, 5733, 4546, and others, having the $2^3\Pi$ state as their final electron level show fine structure. The $3^3\Pi \longrightarrow 2^3\Sigma$ bands (λλ 4650, 4670) show no evidence of fine structure. The $2^3\Pi$ levels show types of fine structure for the odd and even K values. Theoretical interpretation of observed fine structures is discussed. The Zeeman effect of the λ 6400 band ($3^3\Sigma \longrightarrow 2^3\Pi$) was investigated at three field strengths. The Zeeman patterns replacing the original fine structures are in good agreement with predictions for a $^1\Sigma \longrightarrow {}^1\Pi$ transition, indicating that the spin effect giving rise to the original fine structure is overpowered by the external field.   N. M. BLIGH.

Spectrum of helium. D. BURGER (Arch. Néerland., 1929, [iii A], **12**, 147—163; cf. A., 1926, 985; 1929, 732).—A repetition of work already published.
C. A. SILBERRAD.

Hydrogen-like spectra of lithium and beryllium in the extreme ultra-violet. B. EDLÉN and A. ERICSON (Nature, 1930, **125**, 233—234).—The strongest lines 135·02 and 113·93 Å. in the hydrogen-like spectra of Li III and 75·94 Å. of Be IV have been observed.   L. S. THEOBALD.

Condensed spark spectra in the extreme ultra-violet to 88 Å. B. EDLÉN and A. ERICSON (Compt. rend., 1930, **190**, 116—118; cf. A., 1929,

1350).—By a further improvement of the apparatus previously used, lines down to $1'S_0 - 3'P_1$ of beryllium, 88·36 Å., have been measured, as also many additional lines in the spectra of O III, O IV, O V, and O VI, and lines belonging to Mg III, Al IV, and Si V. The ionisation potentials of O III, O IV, O V, and O VI are respectively 54·87, 76·99, 110·5 (uncertain), and 137·49 volts. C. A. SILBERRAD.

Perturbations in band spectra. II. J. E. ROSENTHAL and F. A. JENKINS (Proc. Nat. Acad. Sci., 1929, **15**, 896—902; cf. A., 1929, 866).—Perturbations in the carbon monoxide $^1S \longrightarrow {}^1P$ bands were investigated by measuring the band lines from a set of grating plates and plotting curves for deviations from the formulæ for regular lines of the band. An analysis of the rotation structure of the system had indicated abnormalities in the (0,0) and (1,0) bands, and some other anomalies. These irregularities are shown to be due probably to perturbations of the rotation terms of the ^1P state. Results indicate that the rotation terms of the ^1P state are crossed by terms of another electronic state in such a way that terms of equal j come into close coincidence. N. M. BLIGH.

Zeeman effect in the MgH bands. G. M. ALMY and F. H. CRAWFORD (Physical Rev., 1929, [ii], **34**, 1517—1529; cf. Watson and Perkins, A., 1928, 2).—The Zeeman effect in the MgH $^2\Pi \longrightarrow {}^2\Sigma$ bands at fields between 5000 and 28,000 gauss produced by a magnesium arc in hydrogen were investigated. Using Hill's results (cf. this vol., 265) the magnetic energy pattern is calculated and the line patterns in the λ 5211 band are plotted. A description of the observable patterns in this band and a quantitative comparison with theory are tabulated, and show good agreement. Qualitative intensities are discussed. N. M. BLIGH.

Emission spectrum of magnesium. D. VITALE (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], **35**, 155—157).—The spectrum of magnesium obtained by exploding a thin wire by the passage of an electric current has been mapped in the region 2733—2711 Å. Lines of both the arc and spark spectra are observed. The line at 4481 is obtained, but not the related line at 3104 Å. Reversal is shown in all cases where a tendency to this exists, with the exception of the triplet 5183, 5172, 5167 Å. R. K. CALLOW.

Spectrum of aluminium [and of other elements] in the extreme ultra-violet. B. EDLÉN and A. ERICSON (Compt. rend., 1930, **190**, 173—174; cf. this vol., 263).—The wave-lengths and intensities of lines of the spectra of Na III, Mg IV, Al V (group, $2s^2p^3 \, {}^2P - 2sp^6 \, {}^2S$) and F II, Ne III, Na IV, Al VI (pp' groups, $2s^2p^4 \, {}^3P - 2sp^5 \, {}^3P$) are tabulated. The strongest line obtained in the aluminium (Al V) spark spectrum is due to the hitherto unknown doublet of the lines 278·720 and 281·402 Å. (cf. Millikan and Bowen, A., 1924, ii, 214). J. GRANT.

Band spectra of aluminium hydride. E. BENGTSSON and R. RYDBERG (Z. Physik, 1930, **59**, 540—557).—The band spectra of aluminium hydride are investigated more completely. A new band system was found in the further ultra-violet at a wave-length of 2033 Å., which fits in very well with the scheme of electron levels in the molecule. It corresponds with the switch $^1\Sigma'' \longrightarrow {}^1\Sigma$. A further investigation of the effect of hydrogen pressure on the intensity of the bands was carried out. As the pressure is increased the series gradually lengthens, and the final lines become diffuse. The dissociation values for the different states can be derived on the basis of the relationship between the terms of AlH on the one hand, and those of the aluminium atom on the other. From the rotation terms some conclusions can be reached relative to the decomposition of the molecule. The intensity distribution inside a band is obtained from the relationship $I = i \cdot e^{E_0/RT}$. It is probable that the intensity effect is due to a labile change of the molecule into the $^1\Pi$ state. A. J. MEE.

Continuous spectra of flames containing the halogens. H. C. UREY and J. R. BATES (Physical Rev., 1929, [ii], **34**, 1541—1548; cf. Kondratéev, A., 1928, 1075).—The Franck–Condon theory for the dissociation of molecules by light (cf. A., 1929, 235) indicates that two colliding atoms may recombine with emission of light if appreciable quantities of the free atoms are present. Spectrograms were taken in the visible and ultra-violet of flames of chlorine and hydrogen, and hydrogen–oxygen flames containing the halogens, and the short wave-length limit of the spectra was determined and found to be in agreement with the hypothesis that they are due to the recombination of the normal and excited halogen atoms. Calculations show that there are enough collisions of this type in the flames to account for the intensity of the light emitted. N. M. BLIGH.

Classification of the spectral lines of chlorine, bromine, and iodine. K. ASAGOE (Mem. Coll. Sci. Kyoto, 1929, **12**, 275—326).—The spectral lines of these three halogens were classified into arc and spark types by observing (1) the effect of constriction of a part of a Geissler tube on the intensities of the lines, (2) the change of relative intensities resulting from introduction of a capacity in the circuit, and (3) the effect of insertion of self-inductance in the condensed heavy discharge circuit. The spark lines were sorted out into spark and super-spark by varying the intensity of a magnetic field applied to a Geissler tube and by (2) and (3) above. Arc lines were found only in the visible region, whereas spark lines were distributed all over the region investigated. W. E. DOWNEY.

Wave-lengths of the blue argon spectrum with contributions to the term analysis. A. H. ROSENTHAL (Ann. Physik, 1930, [v], **4**, 49—81).—The intense blue glow excited in carefully purified argon using discharge tubes of various types has been studied in the region 2100—9000 Å., by means of a Rowland grating and prism spectrographs. The spectrum discloses a very large number of lines, many being recorded for the first time. Part of the spectrum can be classified in the doublet–quadruplet–multiplet system of A II with the limit ^3P, and 14 new terms of this system have been calculated. R. A. MORTON.

Atomic resonance radiation in potassium vapour. J. R. NIELSEN and N. WRIGHT (J. Opt. Soc. Amer., 1930, **20**, 27—30).—Resonance radiation was excited in a tube illuminated by a specially constructed argon-filled arc lamp containing potassium

vapour, and was observed first at 170°, increasing in intensity to 215°, at which temperature the red potassium doublet was observed spectroscopically. A line in the violet was faintly indicated.

N. M. BLIGH.

New band system of titanium oxide. A. CHRISTY (Astrophys. J., 1929, 70, 1—10).—Twenty-two bands between 5737 and 7988 Å. are now arranged in a new system, the lower level of which is the same as that of the blue-green system. Evidence has been obtained of the presence of Q-branches in these bands, indicating that the transition is a ^3P–^3S. The moment of inertia of the molecule in the ^3S-state is estimated to be 54.8×10^{-40} g.-cm.^{2}, and the corresponding nuclear separation is 1.66×10^{-8} cm. The heat of dissociation for the lowest level, with linear extrapolation, is 6.74 volts. The two systems are resonance systems of the TiO molecule. At 3300° Abs., the temperature at which the titanium bands persist in stellar spectra, $p_{\mathrm{Ti}} \cdot p_{\mathrm{O}}/p_{\mathrm{TiO}} = 10^{-3}$ atm., where p is the partial pressure. The partial pressure of oxygen in stellar reversing layers is estimated to be about 10^{-6} atm.

L. S. THEOBALD.

Structure of the cobalt spectrum. III. M. A. CATALÁN (Anal. Fís. Quím., 1929, 27, 832—845; cf. A., 1928, 338).—The previous work has been extended, and 70 new lines are recorded. The calculated minimum ionisation potential, i.e., the potential necessary for the separation of an electron of the $3d^7 4s^2$ configuration when the other $4s$ electron of the atomic residue occupies the $3d$ position, is 7.8 volts.

H. F. GILLBE.

Spectrum of trebly-ionised krypton. D. P. ACHARYA (Nature, 1930, 125, 204).—Strong lines having ν 42,475.1 (10) and 40,560.3 (9) have now been observed in the spectrum of krypton; they are the $^4P_3$–$^4D_4$ and $^4P_2$–$^4D_3$ lines. L. S. THEOBALD.

Separations in hyperfine structure. S. GOUD-SMIT and R. F. BACHER (Physical Rev., 1929, [ii], 34, 1501—1506).—Theoretical. The separations in hyperfine structure are due to the interaction energy between the nuclear moment and the total extranuclear moment. The quantum mechanics of the spinning electron in an s state is applied to a consideration of the hyperfine structure separations of those configurations which involve a deeply penetrating s electron. Results are applied to these configurations of Cd I, Tl I, Tl II, La I, and La II. N. M. BLIGH.

Spectrum of ionised xenon (Xe II). C. J. HUMPHREYS and T. L. DE BRUIN (Science, 1928, 68, 573).—The probable classification of combinations of the xenon spectrum from the data of Abbink and Dorgelo (A., 1928, 338) is given. The doublet separation is 9621 cm.$^{-1}$. L. S. THEOBALD.

Interpretation of hyperfine structure in spectral terms. H. E. WHITE (Physical Rev., 1929, [ii], 34, 1404—1410; cf. following abstract).—The hyperfine structures in cadmium, bismuth, and lanthanum are interpreted; term analysis indicates that for cadmium, the fine structures of $\lambda\lambda$ 5086, 4800, and 4678 are due to isotopes. Some of the fine structure terms in bismuth and lanthanum are inverted, and an explanation of term inversion, based on the penetration of an s valency electron, is advanced. N. M. BLIGH.

Hyperfine structure in singly-ionised praseodymium. H. E. WHITE (Physical Rev., 1929, [ii], 34, 1397—1403; cf. A., 1929, 1207).—Wave-lengths and frequency separations of the fine structure of 173 spectral lines of Pr II are given; about 100 have been resolved into six components, and each group reveals a decrease in intensity and interval towards either longer or shorter wave-lengths, and follows closely the Landé interval rule. The quantum theoretical interpretation of the fine structure is deduced from the assignment of angular momentum $5/2(h/2\pi)$ to the atomic nucleus. N. M. BLIGH.

Electric furnace spectrum of hafnium. A. S. KING (Astrophys. J., 1929, 70, 105—113).—The furnace, arc, and spark spectra of hafnium between 2640 and 6500 Å. have been photographed. In the carbon-tube furnace a temperature of 2600° is required to show any effective number of lines, whilst 2900—3000° is required for the neutral spectrum. 338 Lines are classified and compared with Meggers' data (A., 1929, 112). Lines belonging to the ionised atom are apparently absent from the furnace spectrum. Two new bands with heads at 3236 and 4101 Å. are added to those given by Meggers (loc. cit.) for the arc spectrum. The whole band system is attributed to the oxide since it is shown only in the arc in air and not by the vacuum-furnace spectrum.

L. S. THEOBALD.

Spectrum of ionised mercury hydride. T. HORI (Nature, 1930, 125, 131).—The system of mercury hydride bands appears when an arc discharge between mercury and tungsten electrodes takes place at a low voltage (60—70 volts) in an atmosphere of 2 mm. of hydrogen. The bands in the extreme ultraviolet recorded by Jezevski (A., 1929, 8) are to be associated with ionised mercury hydride; they belong to a $^1\Sigma \longrightarrow {}^1\Sigma$ system. The molecular constants are recorded. L. S. THEOBALD.

Series in the spectrum of radium emanation. E. RASMUSSEN (Naturwiss., 1930, 18, 84—85).—The arc spectrum of radium emanation has been investigated in the presence of argon and helium. Two strong lines, presumably the resonance lines, were observed in the Schumann region, at frequencies 55,997 and 68,889 ($\Delta\nu = 12,892$), corresponding with 6.905 and 8.494 volts, respectively. The infra-red, visible, and ultraviolet spectra were also photographed and many new lines observed. All the strongest terms are arranged in series which approach the same limits.

J. W. SMITH.

Zeeman effect in doublet band spectra. E. L. HILL (Physical Rev., 1929, [ii], 34, 1507—1516; cf. A., 1929, 1076).—Theoretical. The Zeeman effect in doublet bands is investigated by the application of perturbation quantum mechanics to Hund's case (b) for diatomic molecules. The magnetic terms are treated as a small correction to the coupling energy between the electron spin and orbital magnetic moments; the terms leading to a Paschen–Back effect are then included. A physical interpretation is discussed in relation to experiment. N. M. BLIGH.

Employment for spectrography of the extreme ultra-violet of gratings at grazing incidence. M. DE BROGLIE (Compt. rend., 1930, 190, 93—95;

cf. Thibaud, A., 1929, 225).—It is suggested that a crystal surface might serve as a (molecular) diffraction grating at grazing incidence for rays of very short wave-lengths. Dempster has apparently effected the diffraction of protons by this means.
C. A. SILBERRAD.

Spectral phenomena in spark discharges. J. W. BEAMS (Physical Rev., 1930, [ii], **35**, 24—33; cf. A., 1926, 1069).—The differences in the time of appearance of the spectrum lines in sparks was measured by two methods : (1) the Kerr cell method dependent on the rapid disappearance of the Kerr effect in some liquids after the electric field producing it is relaxed; (2) Henriot's method (cf. J. Phys. Radium, 1927, [vi], **8**, 443) for the rapid rotation of a mirror which either reflects the dispersed light of the spark to a photographic plate or the undispersed light to the slit of a spectrograph, the position of the beginning of a line on the plate giving its time of appearance. The second method was most suitable for studying the appearance and duration of the metallic lines not present in the earliest stages of the spark discharge, and the Kerr method for the air lines in the initial stages of the spark.
N. M. BLIGH.

Stark effect and polarisation. R. WIERL (Naturwiss., 1930, **18**, 86).—The recent observations of Stark (this vol., 263) are discussed in connexion with the views of the author (cf. A., 1929, 367, 963, 1354).
J. W. SMITH.

Spectrum of the solar corona. R. MECKE and R. WILDT (Z. Physik, 1930, **59**, 501—507).—The origin of the corona spectrum may possibly be explained on the basis of the Raman effect. This point of view is here considered, but no positive answer is reached. It seems possible, however, to explain the absorption-less continuum of the inner corona on the basis of the Raman effect.
A. J. MEE.

Thermal excitation of atoms in the reversing layer of the sun. A. UNSÖLD (Astrophys. J., 1929, **69**, 322—329).—By means of photometric measurements of the contours of a Fraunhofer line, the number of atoms in a particular state of excitation lying above 1 cm.^{2} of the photosphere, multiplied by the oscillatory power of the line, has been determined. The data thus obtained from Ca$^+$ and Ba$^+$ show that for excitation potentials below 1·7 volts Boltzmann's relation holds. An upper limit for the transition probability of the forbidden Ca$^+$ lines 4^2S-3^2D is derived, and the lifetime of the metastable 3^2D state must be greater than 10^{-2} sec. L. S. THEOBALD.

Stellar calcium lines in spectral types A and B. O. STRUVE and C. D. HIGGS (Astrophys. J., 1929, **70**, 131—134).—The contour of the K line of Ca^{++} has been determined in four class A stars; in only one case does the contour agree with the requirements of Unsöld's formula. The total numbers of atoms in the reversing layer have also been determined for many stars; the values range from 4×10^{16} for type $A2$ to 3×10^{15} for type $B5$. L. S. THEOBALD.

Composition of the sun's atmosphere. H. N. RUSSELL (Astrophys. J., 1929, **70**, 11—82).—A survey, and a discussion of existing evidence concerning the relative abundance of elements showing lines in the solar spectrum. The energy of binding of an electron in different quantum states is discussed for neutral atoms of atomic numbers 1—39 and for singly-ionised atoms of atomic numbers 2—32. The energy of binding for an electron in a given state increases with the atomic number and the increase of energy is most rapid when electrons are being added to complete a shell and when s electrons are being added. The characteristics of the spectra of the elements present are discussed and the ionisation potentials and most persistent lines are tabulated. The excitation potential, E, for the strongest lines in the observable part of the spectrum is the main factor; almost all the elements for which this is small appear in the sun and there are few solar lines for which $E > 5$ volts, the only strong ones being those of hydrogen. Using the calibration of Rowland's scale previously developed (ibid., 1928, **68**, 1) and Unsöld's investigations (A., 1928, 456) the abundance of various elements in the sun's atmosphere is calculated. The numbers of atoms in the more important energy states for each element are determined and are found to decrease with increased excitation, but somewhat more slowly than is demanded by thermodynamical considerations. The level of ionisation in the solar atmosphere is such that atoms of 8·3 volts ionisation potential are 50% ionised.

Tables of the relative abundance of 56 elements and 6 compounds show that sodium, magnesium, silicon, potassium, calcium, and iron form 95% of the whole mass. The number of metallic atoms above 1 cm.^{2} of the surface is 8×10^{20}, and 80% of these are ionised. The mean at. wt. is 32 and their total mass 42 mg./cm.^{2} The elements of even atomic number are ten times as abundant as those of odd atomic number. The hypothesis that the heaviest atoms sink below the photosphere is not confirmed. The metals from sodium to zinc, inclusive, are far more common than any others. Compounds are present only in small amounts, cyanogen being rarer than scandium, and the presence of band lines due to C_2, CH, CN, NH, and BO constitutes the chief evidence for the existence of carbon, nitrogen, and boron in the sun. Most of the elements which are absent should not show observable lines unless their abundance is much greater than is probable. The possibility of discovering faint lines of some additional rare earths and heavy metals, as well as of boron and phosphorus, still exists. The abundance of the non-metals, especially of hydrogen, is difficult to estimate from the scanty data available, but the solar atmosphere appears to contain 60 parts of hydrogen (by volume), 2 of helium, 2 of oxygen, 1 part of metallic vapour, and 0·8 of free electrons. The estimated temperature of the reversing layer is 5600° and the pressure at its base is 0·005 atm.
L. S. THEOBALD.

Spectrum of $B. D + 11°$ 4673. P. W. MERRILL (Astrophys. J., 1929, **69**, 330—378).—The spectrum of this star exhibits bright lines of H, He, Fe II, Al II, Al III, N II including two forbidden lines, Si I (?), Si II, Si III, Ti II, Cr II, Mg II, C II (?), and Sc II (?). The iron spectrum includes some forbidden lines. The lines of this star vary both in position and intensity.
L. S. THEOBALD.

New types of emission spectra. L. VEGARD (Naturwiss., 1930, **18**, 67—68).—Study of the luminescence of solidified gases has shown the existence of a new type of spectrum due to the combination of electron switches and atomic oscillations. It is a type of vibrational band spectrum uninfluenced by rotation. A number of spectra of this type have been investigated. The majority of series are not made up of single lines, but of two or more components, the splitting being more noticeable at the temperature of liquid helium than at that of liquid hydrogen. This multiplicity of lines does not depend on rotation energy, and the first explanation was based on a decomposition of the electron terms. Series with quite different electron terms and different principal vibration series show the same frequency difference between successive components. The separation is in some cases ten to fifteen times as large as that corresponding with the fundamental frequency of molecular rotation. It is shown that probably the force which binds the molecules in the crystal lattice and is closely bound up with the elastic forces of the crystal makes a molecule with oscillating atoms vibrate itself. As the distance between the molecules in the lattice is much greater than that between the atoms in a molecular element, the inner condition of the molecule will exert little effect on the molecular vibration. Hence the separation of lines in series derived from molecular oscillations will be nearly the same irrespective of the inner condition of the molecular elements.
A. J. MEE.

Indefinite characteristic spectra. E. SCHRÖDINGER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 668—682).—Theoretical. The treatment of wave mechanics is applied to unidimensional point motion, and in particular an extended spectrum is investigated. All so-called discrete characteristic spectra are really " almost " discrete, the former being an ideal case. A. J. MEE.

K-Absorption edges in X-ray spectrum. H. T. MEYER (Naturwiss., 1930, **18**, 34).—With bromates, structure lines which are absent in bromides are shown at the bromine absorption edge. The energy difference between the principal absorption edge and the shortest wave-length structure line reaches the high value of 240 volts. Very similar results are obtained with arsenates and selenates. Zinc sulphide gave no structure of the K-absorption edge, nor did rubidium carbonate and strontium nitrate. Yttria showed a bright absorption line on the short-wave side of the K-absorption edge, but no dark line, as in the bromates, selenates, and arsenates. Zirconium nitrate and oxychloride both exhibited a bright and a dark line, the difference in wave-length between the principal edge and the dark line being the same for both compounds. Niobium compounds indicated a very weak dark line. Molybdenum trioxide gave no certain evidence of structure. R. A. MORTON.

Form of the X-ray diffraction bands for regular crystals of colloidal size. C. C. MURDOCK (Physical Rev., 1930, [ii], **35**, 8—23).—Theoretical. The form of the diffraction bands of a fine uniform crystalline powder was computed for the (1,0,0), (1,1,0), and (1,1,1) planes for regular cubical and octahedral crystals and found to be approximately that of the Gauss error curve, the shape and half-intensity breadth varying from band to band characteristically with the shape of the crystals. There is a correlation between the form of the band and the direction of the corresponding Bragg planes with respect to the external features of the crystal.
N. M. BLIGH.

Scattering of X-rays by gases. G. HERZOG (Helv. phys. Acta, 1929, **2**, 169—216; Chem. Zentr., 1929, ii, 1379).—A new method for measuring the distribution of intensity is described, and the results of experiments with argon are recorded.
A. A. ELDRIDGE.

Raman effect in the X-ray region. A. CARRELLI (Nature, 1930, **125**, 201—202).—Theoretical. In order to observe this effect it is necessary to use substances presenting semi-optical lines, and of low atomic number, and to use wave-lengths, directions of observations, and substances for which the ratio $E_e/|E_\mu|$ is very high, where E_e is the kinetic energy of the electron emitted for the Compton effect in a particular direction of observation and for a given exciting frequency, and E_μ is the energy of the K level if the jump is $K \longrightarrow 1s$. L. S. THEOBALD.

Photometric determination of relative intensities in the β group in the L-spectrum of tungsten. W. H. LOVE (Med. J. Austral., 1929, **2**, 246).—For homogeneous radiations of wave-lengths corresponding with those in the $L\beta$ group of tungsten the relation between the photographic density of the line and the intensity of the radiation is linear when the time of exposure is constant and the density small. The relative intensities of the strongest four lines were evaluated. CHEMICAL ABSTRACTS.

Ionisation and dissociation processes in gases. H. KALLMANN and B. ROSEN (Physikal. Z., 1929, **30**, 772—773).—See this vol., 16.

Ionisation potential of atomic configurations with two electrons. E. A. HYLLERAAS (Naturwiss., 1929, **17**, 982).—The earlier calculation of the ionisation potential of helium (cf. A., 1928, 698; 1929, 616) has been applied to the results recently obtained by Edlén for the ionisation potential of Li+ and Be++ (A., 1929, 1350). The theoretical values are compared with Edlén's experimental values.
G. E. WENTWORTH.

Ionisation potential of atomic configurations with two electrons. G. W. KELLNER (Naturwiss., 1930, **18**, 86).—A claim for priority over Hylleraas (preceding abstract). The ionisation potentials of the configurations He, Li+, Be++, B+++, and C++++ had previously been calculated by Kellner using a similar method (cf. A., 1927, 912). J. W. SMITH.

Detection of excitation potentials of various spectra in gaseous discharge. E. LAU and O. REICHENHEIM (Naturwiss., 1930, **18**, 86—87).—A method is described whereby the excitation potentials of different spectral lines can be determined by observation of the spectra in various regions of the positive column and the Faraday dark space of a gaseous discharge tube, with and without the addition of a gas of lower ionisation potential than the gas

under investigation. Illustrations of the application of this method are given. J. W. SMITH.

Emission of electrons from conductors under intense fields. P. W. BRIDGMAN (Physical Rev., 1929, [ii], **34**, 1411—1417; cf. A., 1928, 213, 682).— Theoretical. The current drawn from metals by intense fields produced by the Volta *P.D.* between two metals is discussed thermodynamically, using the classical concept of the electron, and modifications required by the wave mechanical picture are examined. Expressions are given for the change in heat of evaporation of electrons and in the photo-electric threshold efficiency produced by intense fields in terms of a slight change of Volta difference.
N. M. BLIGH.

Effect of light on the electron emission from oxide-coated filaments. K. NEWBURY (Physical Rev., 1929, [ii], **34**, 1418—1425; cf. Crew, A., 1927, 85).—The increase in electron emission from oxide-coated platinum filaments when light is focussed on them was studied as a function of applied potential, filament temperature, and wave-length of the incident light. The effect was zero at zero applied field and reached a saturation value at from 2 to 10 volts, depending on the thickness of the oxide coating. At an applied potential giving saturation the effect reached a maximum at a filament temperature of about 1000° and then decreased. The long wave-length limit of the effect was about 4000 Å.; there is a sharp increase in sensitivity for wave-lengths less than about 2500 Å. Results can be explained on the assumption that the normal photo-electric emission so modifies the distribution of the intrinsic surface field as to alter the effect of the externally applied field on the work function of the surface.
N. M. BLIGH.

Investigations on secondary emission. K. SIXTUS (Ann. Physik, 1929, [v], **3**, 1017—1054).—The emission of secondary electrons at the anode of technical tubes with different cathode materials has been studied. The differences in secondary emission arise from changes in the condition of the anode following volatilisation of the cathode material. The geometrical arrangement of electrodes affects the results. Striking irregularities in the course of the anode characteristic between 0 and 10 volts in tubes with oxide-equipotential cathodes probably arise from selective absorption and reflexion in the electrode surface. The measured contact *P.D.* between tungsten and thoriated tungsten is about 10% smaller than the difference in the work of escape for the two materials. The magnitude of the secondary emission is independent of the temperature of the emitting substance over a wide range. Whilst the primary emission of a tungsten wire is increased 10^5 times when it is thoriated, the secondary emission or the secondary yield is increased by not more than 20%. The high characteristic velocity of the secondary electrons accounts for smallness of the increase, a small reduction in the work of escape making no important difference. By assuming Maxwellian velocity distribution of secondary electrons (the data show approximate agreement), the mean velocity of the secondary electrons of metals is calculated. The

measurements concerning electrodes carrying a layer of oxide disclose no clear relationship between work of escape and the strength of the secondary emission.
R. A. MORTON.

Electron velocities in a high-frequency discharge in hydrogen. C. J. BRASEFIELD (Physical Rev., 1930, [ii], **35**, 92—97; cf. A., 1929, 1115).— The mean velocity of the electrons in a high-frequency discharge in hydrogen, obtained by applying undamped high-frequency voltages to the movable electrodes of a cylindrical tube, was determined from the ratio of the densities of certain singlet and triplet lines of the molecular spectrum of hydrogen. It was found that the electron velocity increases with rise of voltage at constant gas pressure and oscillation frequency, is greater the longer is the wave-length of oscillation at given voltage, and decreases as the pressure is increased. The mechanism of the discharge is discussed and an explanation of its behaviour is proposed. N. M. BLIGH.

Ionisation of alkali atoms by slow electrons. H. FUNK (Ann. Physik, 1930, [v], **4**, 149—184).—The question of ionisation-sharing for ionisation brought about by collision of slow electrons is dealt with. An apparatus for the determination of the sharing is described. The substances investigated were sodium and potassium, which were obtained in the form of an atomic radiation. An electron beam of approximately uniform velocity was directed perpendicularly to the atomic radiation, and the primary electron current and the resulting ionic current were measured. From these quantities the sharing can be calculated. The sharing can be given on the one hand as a cross-section in $cm.^2/cm.^3$, by analogy with a Ramsauer cross-section, or as a percentage. The experiments show a maximum effect in the neighbourhood of twice the ionisation potential. The value obtained for sodium was 29 $cm.^2/cm.^3$, and for potassium 11 $cm.^2/cm.^3$ This is in agreement with the theory of Sir J. J. Thomson on ionisation by electron collision, and the theoretical values are 54% for sodium and 50% for potassium. There is thus also agreement as regards the relative size of the effect for the two metals, but the difference between the values is different.
A. J. MEE.

Effect of light on the electron emission from cerium dioxide. C. E. BERGER (Physical Rev., 1929, [ii], **34**, 1566—1574; cf. Crew, A., 1927, 85).— An increase in photo-emission with rise of temperature was found for calcium iodide, calcium oxide, thorium oxide, and cerium oxide on platinum, calcium oxide and cerium oxide on tungsten, and cerium oxide on nichrome. No effect was found for barium iodide on platinum and zirconium oxide on tungsten. For cerium dioxide on platinum at about 1000° the photo-emission varied linearly with the intensity of the ultra-violet light; wave-lengths above 3000 Å. were not effective. Air, hydrogen, or oxygen in small amounts caused a decrease in the photo-emission. The saturation photo-currents showed an increase with rise of temperature. The explanation of results as a variation of the true photo-electric effect or as due to some cause such as change of surface by bombardment is discussed. N. M. BLIGH.

Scattering of positive lithium ions in mercury vapour. I. W. Cox (Physical Rev., 1929, [ii], **34**, 1426—1437).—An apparatus giving a high-speed vacuum system constantly flushed with mercury vapour is described. The number of positive lithium ions passing through a fixed distance was observed with different mercury vapour pressures. Kennard's method (cf. A., 1928, 453) giving curves showing the variation of the electrometer current with magnetic field current for a particular pressure, and a second method using two coaxial Faraday cylinders and added collimating slits in front of the absorption chamber, were used. The rate of absorption depended on the aperture of the apparatus, indicating that the absorption is largely due to small angle scattering of the ion at a collision with a mercury atom, and incompatible with elastic collision scattering.
N. M. Bligh.

Secondary electrons of high velocity from metals bombarded with cathode rays. P. B. Wagner (Physical Rev., 1930, [ii], **35**, 98—106).—The work of Stehberger (A., 1928, 1069) and Lorenz (A., 1929, 14) is discussed critically, and to investigate further the secondary emission process, the magnetic spectra of high-speed secondary electrons emitted by gold, silver, and aluminium when bombarded by cathode rays of from 16 to 40 kilovolts were photographed and densitometer graphs obtained. From the high-velocity end the density is zero down to the energy eV_0, equal to that of a primary ray, then rises rapidly to a maximum at about $0.94eV_0$ for gold or silver and $0.85eV_0$ for aluminium, and then decreases. The density is continuous, but there is apparently a discontinuity in the first derivative in every spectrum at the high-velocity end, and occurring at a velocity equal to that of the primary cathode rays. The resemblance of spectra for thin and thick targets indicates that most of the secondary electrons come from very near the surface. N. M. Bligh.

Ions produced by discharges at liquid surfaces. J. J. Nolan and J. G. O'Keeffe (Proc. Roy. Irish Acad., 1929, **A**, **39**, 21—30).—Chattock's method (Phil. Mag., 1899, **48**, 401) can be applied to measure the mobilities of the ions concerned in the discharge from liquid surfaces. The mobilities observed show that these ions are of the same character as the ordinary small ions produced by discharge at a metal point or by the ionising radiations. The observation of Tyndall and Phillips (A., 1926, 877) that in air saturated with n-butyl or n-amyl alcohol at the ordinary temperature, the mobility of the positive ion is greater than that of the negative ion is confirmed.
R. A. Morton.

Crucial experiment on diffusion of electrons. F. Dacos (Bull. Acad. roy. Belg., 1929, [v], **15**, 452—460).—The calibration and arrangement of the apparatus are described. Electrons accelerated at 360 volts pass in a parallel pencil between two slits, then pass through a **V**-shaped slit and impinge on a photographic plate. The influence of a magnetic field on the results is discussed. W. R. Angus.

Radiation of free electrons in a Coulomb field. J. A. Gaunt (Z. Physik, 1930, **59**, 508—513).—Mathematical. An error in Oppenheimer's recent work on the subject is pointed out. When corrected this leads to a smaller deviation from Kramers' theory than was previously the case. A. J. Mee.

Intensity of electron interference. F. Kirchner (Naturwiss., 1930, **18**, 84).—The order of magnitude of the influence of the electron shell on the nuclear scattering by gold atoms can be estimated if the electron shell be assumed to be, as a whole, like that of hydrogen. On this basis wave-mechanical calculations lead to a value of the scattering intensity expressed approximately by the wave function $1/(\sin^2 \theta/2 + \alpha^2)^2$ instead of $1/\sin^4 \theta/2$ ($\alpha = \lambda/2\pi r$; $\lambda = h/mv$, the De Broglie electronic wave-length; $r =$ the "mean radius" of the electron shell). If $\alpha = 0.02$ and $\lambda = 7 \times 10^{-10}$ cm. this equation agrees well with the results of Thomson (A., 1929, 1209) and corresponds with a "mean radius" of the electron shell of about 0.5 Å. J. W. Smith.

Collision between two electrons. N. F. Mott (Proc. Roy. Soc., 1930, **A**, **126**, 259—267).—Mathematical. The exclusion principle is applied to the problem of the collision between two particles possessing spin (e.g., electrons), and also between two particles without spin (e.g., α-particles). Assuming an inverse square law between the particles and neglecting the actual spin forces, a scattering law, differing considerably from that of the classical theory, is deduced from the symmetry properties of the wave functions. Some experimental evidence in favour of the theory is advanced.
L. L. Bircumshaw.

Effective cross-section of non-inert-gas molecules with respect to electrons below 1 volt. C. Ramsauer and R. Kollath (Ann. Physik, 1930, [v], **4**, 91—108).—Methods already applied to the inert gases have been extended to hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and methane. Cross-section/volt¹ curves for velocities down to 0.16 volt have been obtained. The curves for nitrogen and carbon monoxide are similar, whilst the methane curve resembles that of argon and of krypton, the resemblances extending over the range 0.16—36 volts. The similarity between hydrogen and helium does not extend into the region below 1 volt. Some of the curves indicate increasing cross-section as the electron velocity decreases from 1 to 0.16 volt; in others the reverse is the case, but the existence of a very sharp minimum in oxygen at 0.24 volt demonstrates the risk involved in extrapolation towards zero velocity. The influence of the gas on photo-electric emission is vanishingly small for nitrogen, hydrogen, carbon monoxide, and carbon dioxide, considerable for methane, and very strong for oxygen. R. A. Morton.

Report of the German Commission on atomic weights. X. M. Bodenstein, O. Hahn, O. Hönigschmid, and R. J. Meyer (Ber., 1930, **63**, [B], 1—24).—The report is drawn up on the same lines as its predecessors (cf. A., 1929, 232). No change is made in the table of practical atomic weights except that Re=188.7 is introduced. H. Wren.

Arithmetical relation between at. wt. and atomic number. G. Fournier (Compt. rend.,

1930, **190**, 118—119; cf. A., 1929, 863).—p_n is plotted against p_n+i_n as abscissa, where p_1, p_2, . . . are the odd prime numbers 1—59, and i_1, i_2, . . . the odd numbers 1—33; $p_{17}+i_{17}$ thus=92, the atomic number of uranium. On the same scale $A/4$, where A is the number of protons in successive elements, is plotted against N, the corresponding atomic number, each isotope being separately indicated. The two curves are nearly coincident.
C. A. SILBERRAD.

Vibrational quantum analysis and isotope effect for the lead oxide band spectra. S. BLOOMENTHAL (Physical Rev., 1930, [ii], **35**, 34—45). —Measurements were made of the wave-lengths of the band heads from moderate-dispersion spectrograms of the lead arc in air, and from high-dispersion spectrograms taken with a lead arc and with a uranium-lead arc. Each strong line ($Pb^{206}O$) in the band spectrum from the uranium-lead arc is represented by three lines ($Pb^{208, 207, 206}O$) in the band spectrum from the lead arc with relative intensities in agreement with Aston. Corresponding band line separations of isotopic molecules are in good agreement with the isotope effect theory with PbO as the emitter. Vibrational quantum analysis gives an expression for a new band system D in the region 3209—3594 Å. The systems A, B, and C (very weak), all having a common lower state, are discussed. N. M. BLIGH.

Fine structure analysis of the bands in the A and D systems of lead oxide. A. CHRISTY and S. BLOOMENTHAL (Physical Rev., 1930, [ii], **35**, 46—50; cf. preceding abstract).—Theoretical. The bands of the A and D systems are composed of single R and P branches only; the rotational constants of the molecule are determined by application of the combination principle. The nuclear separation of the common final state is found to be 1.9207×10^{-8}, that of the upper state of A, 2.0927×10^{-8}, and of D, 2.0424×10^{-8} cm. No Q branches have been found for the two systems, the electronic levels of which are singlets. The electron states involved are probably all $^1\Sigma$ states. N. M. BLIGH.

Isotopy. A. VAN DEN BROEK (Arch. Néerland., 1929, [iii A], **12**, 143—146; cf. A., 1920, ii, 540; 1921, ii, 295).—An elaboration of the author's views on isotopy. Atoms with even atomic number and mass number divisible by 4 are regarded as normal, intermediate members of the series are abnormal (" polytopes ") and interabnormal (" interpolytopes ").
C. A. SILBERRAD.

Application of adiabatic microcalorimeter to measurements of the heats of radiation of uranium, thorium, and radioactive minerals. A. DORABIALSKA (Bull. Acad. Polonaise, 1929, **A**, 487—496).—See A., 1929, 1358.

Status of the γ-ray change. N. FEATHER (Physical Rev., 1929, [ii], **34**, 1558—1565).— Theoretical. The work of Jacobsen (cf. A., 1928, 104) is considered in connexion with the view that the emission of γ-rays in radioactive disintegration is subsidiary to the ejection of the α- or β-particle from the nucleus, and is shown to imply that the emission of a quantum of γ-radiation between the β-particle disintegration of radium-C and the α-par-

ticle disintegration of radium-C' is essential. The difficulties attending this condition are discussed. An attempt is made to connect the complexity of the " normal " α-radiation of thorium-C and the emission of long-range α-particles from radium-C and thorium-C with the occurrence of certain lines in the γ-ray spectra of these elements. N. M. BLIGH.

Passage of " fast " β-particles through gases. E. J. WILLIAMS and F. R. TERROUX (Proc. Roy. Soc., 1930, **A**, **126**, 289—309).—The Wilson cloud method is applied to an investigation of phenomena representing loss of energy by fast β-particles in oxygen and in hydrogen. A radioactive source of high-speed β-particles, with energy varying from about 100 to 1500 kilovolts, is used, and the phenomena investigated include the primary ionisation, the frequency of production of branches, and the momentum relations in branch collisions. The results indicate that the classical theory gives only the order of magnitude of the observed effects. For both the primary ionisation and the frequency of branch production the observed values are much greater than the classical theoretical values, and vary with the velocity according to a different law. In both cases the ratio of the observed to the theoretical value decreases with decreasing velocity, and for " slow " β-particles the number of branches may be equal to or less than the classical number. If it is assumed that an electron has a magnetic moment equal to one Bohr magneton, then the classical calculations for the theoretical number of branches gives values of a different order of magnitude from those observed, and from the actual ratios of the observed and calculated numbers it is inferred that the maximum magnetic moment is considerably less than a Bohr magneton. Observations are described which show that the deflexion of fast β-particles due to the production of branches corresponds approximately with the ratio of the momentum of the branch to that of the β-particle. L. L. BIRCUMSHAW.

Radioactive disintegration of potassium. O. HÖNIGSCHMID (Nature, 1930, **125**, 91).—The methods and data of Frost and Frost (this vol., 130) are considered to be insufficiently trustworthy to permit conclusions concerning the formation of calcium isotopes from potassium to be reached.
L. S. THEOBALD.

Scattering of α-particles by light atoms. A. C. BANERJI (Nature, 1930, **125**, 167—168).—An expression for scattering of α-particles giving good agreement with the results obtained by Rutherford and co-workers has been obtained by using the law $F=Ze^2/r^2-\mu/r^n$ when $n=3$. The assumption of the same law in Schrödinger's equation permits the calculation of the " Eigenwerte " of α-particles in the nucleus; positive and negative values result and the former explain the γ-radiations of the six radioactive elements which so far have been accurately measured.
L. S. THEOBALD.

Effect of solar radiation on radioactive phenomena and transmutation. (MLLE.) S. MARACINEANU (Bull. Acad. Sci. Roumaine, 1929, **12**, 5—9).— Lines characteristic of mercury have been found in the spectrum of lead which has been exposed to sun-

light. Solar radiation can cause the transmutation of 0·001% of lead into gold. C. W. GIBBY.

Supposed transmutation of lead by sunlight. C. FABRY and E. DUBREUIL (Compt. rend., 1930, **190**, 91).—The experiments described by Maracineanu (cf. preceding abstract) as resulting in the formation of gold, mercury, and helium from lead by prolonged exposure to sunlight have been repeated with old roof lead. No trace of any such transmutation was found. C. A. SILBERRAD.

Quantum mechanics of α-radiation. T. SEXL (Z. Physik, 1930, **59**, 579—582).—Mathematical.

Anode spots and their relations to the absorption and emission of gases by the electrodes of a Geissler discharge. C. H. THOMAS and O. S. DUFFENDACK (Physical Rev., 1930, [ii], **35**, 72—91).— An investigation was made of the anode spots into which the anode glow breaks up in a Geissler discharge containing hydrogen, nitrogen, carbon monoxide, and mixtures of hydrogen or mercury vapour with the rare gases, but not oxygen, argon, or neon. One electrode was allowed to serve as a cathode for a given time, during which it absorbed gas through positive ion bombardment; the polarity of the electrodes was then reversed. Spots formed on iron, nickel, aluminium, copper, brass, and mercury; a necessary condition for their formation was found to be the emission of gas from the anode surface. Conditions governing the size, number, and duration of the spots were determined. It is concluded that their formation and existence depend on the joint action between the gases released from, and the electron stream to, the anode, and that they are manifestations of a splitting up of the electronic current into discrete " rays " or current-beams. An explanation of their formation is advanced. It is shown that in a Geissler discharge between cold electrodes, the cathode absorbs and the anode emits gas at rates which are functions of the current density, gas pressure, kind of gas, and electrode temperature.
N. M. BLIGH.

Charging of small suspended particles in the corona discharge. H. SCHWEITZER (Ann. Physik, 1930, [v], **4**, 33—48).—The number of elementary charges carried by droplets of paraffin oil of radius $2—5 \times 10^{-5}$ cm. in a corona discharge of $1—2 \times 10^{-6}$ A. varies between 20 and 100 for the large majority of the particles. A small percentage of highly charged particles is observed, the number of elementary charges being 42 for droplets of radius $2·44 \times 10^{-5}$ cm. and 694 when the radius is $6·3 \times 10^{-5}$ cm. The normal values are in good agreement with the calculations of Arendt and Kallmann (Z. Physik, 1926, **35**, 421), whilst the small proportion of highly charged particles possess values approaching the extrapolated maximum values arrived at by Deutsch (Z. tech. Physik, 1926, **17**, 628) for cigarette smoke.
R. A. MORTON.

Stern–Gerlach experiment with active nitrogen. L. C. JACKSON (Nature, 1930, **125**, 131).— The presence of the $^2P_{\frac{1}{2}}$ state in active nitrogen is considered to be established by an analysis by the Stern–Gerlach method of a stream of nitrogen,

activated by means of a condensed electrical discharge. L. S. THEOBALD.

Peculiar behaviour of nitrogen on ionisation by X-rays. K. BRUMMER (Strahlenther., 1929, **32**, 759—760; Chem. Zentr., 1929, ii, 1628).—Of the gases examined, only with nitrogen was the ionisation affected by the velocity of passage of the gas. With increasing velocity the ionisation rose to a maximum value, then diminished somewhat to constant value.
A. A. ELDRIDGE.

Quantum mechanics of chemical reactions : predissociation and unimolecular decompositions. O. K. RICE (Physical Rev., 1929, [ii], **34**, 1451—1462; cf. A., 1929, 734, 1016).—Theoretical. The processes of activation, reaction of the activated products, and deactivation in a chemical change can be described quantum mechanically, and are illustrated by consideration of the predissociation of diatomic molecules activated by light. The wave function immediately after the excitation can be described as the wave function of a discrete state which interacts with a continuum. Wentzel's calculation of the rate of dissociation can be applied with some limitations which are discussed. Predissociation and unimolecular decompositions of complex molecules are compared, and the difficulties of theoretical treatment in the latter case are considered; although the perturbations giving rise to the decompositions are of the same nature, there will be many intermediate states before the final state of the molecule is reached, and the perturbations cannot be put into the same equation to give the rate of reaction. The decomposition of azomethane is considered.
N. M. BLIGH.

Theory of electrons and protons. P. A. M. DIRAC (Proc. Roy. Soc., 1930, **A**, **126**, 360—365).— The relativity quantum theory of an electron moving in a given electromagnetic field involves the difficulty that the wave equation has, besides the wanted solutions referring to positive kinetic energy, an equal number of solutions for negative kinetic energy of the electron, which appear to have no physical meaning. The fact that an electron with negative energy can be shown to move in an external field as though it carried a positive change has led to the suggestion that a close connexion exists between the negative-energy electron and the proton. The view, however, that a negative-energy electron is a proton would lead to a number of paradoxes. Accordingly, a new theory is now advanced which postulates only one fundamental kind of particle instead of electron and proton. It is assumed that protons are simply holes in the distribution of negative-energy electrons, and that when an electron of positive energy drops into a hole and fills it up, an electron and a proton disappear together with emission of radiation. The problem of the scattering of radiation by an electron, free or bound, is considered in the light of the above ideas.
L. L. BIRCUMSHAW.

Test of quantum mechanics of hydrogen by measurements of absorption in the Balmer series. J. L. SNOEK, jun. (Arch. Néerland., 1929, [iii A], **12**, 164—204).—A more detailed account of work previously published (cf. A., 1928, 1293).

Measurements of the absorption of H_a, H_β, and H_γ are recorded. The results obtained are in satisfactory agreement with the theoretical considerations advanced. C. A. SILBERRAD.

Probability of the simultaneous action of two light quanta in one elementary process. (FRL.) M. GÖPPERT (Naturwiss., 1929, **17**, 932).—A probability calculation. H. F. GILLBE.

Theory of intermittent action and infra-red band spectrum. K. C. KAR and B. BISWAS (Z. Physik, 1930, **59**, 570—572).—Mathematical. The theory of intermittent action previously put forward is here applied to the problem of the anharmonic oscillator and leads to the well-known formula for the infra-red band spectrum. A. J. MEE.

X-Ray search for the origin of ferromagnetism. J. C. STEARNS (Physical Rev., 1930, [ii], **35**, 1—7).— With the object of ascertaining whether inner-orbit electrons are responsible for ferromagnetism, a sensitive null method employing two crystals and two ionisation chambers was used to detect any change in intensity of an X-ray beam reflected from a crystal of magnetite or silicon steel when magnetised. Although the sensitivity was several times that theoretically necessary, no change was observed. Results indicate that the spinning electron and not an orbital electron should be identified with the ultimate magnet. N. M. BLIGH.

Gibbs–Ewald reciprocal lattice. A. L. PATTERSON (Nature, 1930, **125**, 238).—A simple analytical expression for defining this lattice is developed. L. S. THEOBALD.

Correct formulation of Pauli's exclusion principle. J. FRENKEL (Nature, 1930, **125**, 235—236). —Theoretical. The usual statement of this principle as applied to the two-electron or two-proton system is incorrect. L. S. THEOBALD.

Influence of foreign gases on the absorption spectrum of nitric oxide. M. LAMBREY (Compt. rend., 1930, **190**, 261—263; cf. A., 1929, 1363).— The increase in absorption of nitric oxide due to the presence of non-absorbing foreign gases may be expressed by $f(\pi/p)=k'(\pi/p)^{0.90}$, where π and p are the respective pressures of the mixture and of the foreign gas, and k' has the values for hydrogen 0·69, nitrogen 0·87, argon 0·91, and carbon dioxide 0·87. This function was deduced for the (0,0) band of the γ-system from measurements of the pressure required to give the same optical density in pure nitric oxide under the same conditions as in the mixture. A similar study of the equilibrium $2NO_2 \rightleftharpoons 2NO + O_2$ showed that the presence of nitrogen dioxide, an absorbing gas, increases the optical density of nitric oxide. J. GRANT.

Existence of two limits of pre-dissociation in the nitrogen peroxide molecule and the heat of dissociation of oxygen. V. HENRI (Nature, 1930, **125**, 202).—In the absorption spectrum of nitrogen peroxide vapour the first limit of pre-dissociation occurs between 3800 and 3700 Å., whilst that of the second limit occurs between 2459 and 2200 Å. These limits correspond with the two limits of dissociation of the nitrogen peroxide molecule into nitric oxide

and a normal or an activated oxygen atom. The corresponding energies are $NO_2 \longrightarrow NO + O - 77,000$ g.-cal. (3700 Å.) and $NO_2 \longrightarrow NO + O^* - 116,000$ g.-cal. (2459 Å.), from which the calculated heat of dissociation of the oxygen molecule is $-128,000$ g.-cal. and the heat of activation of an oxygen atom is $-39,000$ g.-cal. L. S. THEOBALD.

Colours of inorganic salts. M. N. SAHA (Nature, 1930, **125**, 163—164).—An hypothesis to explain the colours of inorganic salts is advanced and is illustrated by a consideration of the case of chromium. The absorption of light in the visible region is due to a change from $\frac{1}{2}$ to $-\frac{1}{2}$ in the r-vector of some of the α-electrons. This type of transition is possible only in transitional groups, and although usually forbidden, becomes prominent in all molecular formations. L. S. THEOBALD.

Absorption by carboxyl groups in the short-wave ultra-violet. H. LEY and B. ARENDS (Z. physikal. Chem., 1929, **B, 4**, 234—238).—The absorption bands in the short-wave ultra-violet have been determined for pure acetic acid and ethyl acetate, for solutions of these two, and also for solutions of sodium acetate. Acetic acid, both homogeneous and in solution, has a marked absorption band at 2040 Å., although the maximum for the pure acid appears to be shifted slightly towards the long-wave region. There is probably a second, more intensive band at still shorter wave-lengths. Ethyl acetate behaves similarly, the maximum being at about 2090 Å. No such band is observed in the case of sodium acetate solutions. It is possible that this difference may be associated with some difference in the carbonyl chromophore group due to electrolytic dissociation. M. S. BURR.

Absorption spectrum of histidine and histamine in the ultra-violet. F. ELLINGER (Biochem. Z., 1929, **215**, 279—285).—The ultra-violet absorption spectra of a 1-cm. layer of 1% solutions of histidine and histamine hydrochloride were measured by photographic and photo-electric methods. Histidine showed a steep increase of absorption commencing at 313 $\mu\mu$ with a maximum at 275 $\mu\mu$ succeeded by a minimum at 254 $\mu\mu$ and then followed by a further steep increase. With histamine hydrochloride a linear increase of absorption was obtained starting at 366 $\mu\mu$ and increasing continuously toward the shorter wave-length region. P. W. CLUTTERBUCK.

Absorption of light by nitrophenols. I. Weakly alkaline aqueous solutions. J. EISENBRAND and H. VON HALBAN (Z. physikal. Chem., 1930, **146**, 30—40).—Absorption spectra of mono- and di-nitrophenoxide and picrate ions have been examined over the range 250—550 $\mu\mu$. Alteration of the position of a nitro-group in the nucleus exercises a powerful influence on the value of the extinction coefficient, which may be changed ten-fold. Introduction of a second or a third nitro-group produces a change in the extinction coefficient of the same order of magnitude as above if the group introduced occupies a new position relative to the hydroxyl group; otherwise the effect is of a lower order of magnitude. F. L. USHER.

Absorption spectra of the azobenzene crystal. J. W. OBREIMOW and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1324—1328).— The change of colour of crystals at low temperatures is a general phenomenon, probably due to the contraction of absorption bands. The spectrum of azobenzene at 20° Abs. is very regular. It has been measured by the use of a plane grating, and the lines are classified. At this temperature and below, azobenzene shows a line spectrum when the light vector is parallel with the b-axis of the crystal. Spectral photographs were taken at 14° and 4·22° Abs. It was not possible to measure all the lines with the apparatus used. There is a continuous background of diffuse bands as well as the lines; these diffuse bands become stronger towards the violet. At 4·22° Abs. the absorption lines are considerably sharper than at 14°, but the same lines appear at both temperatures, with nearly the same distribution of intensity. The absorption spectrum was also investigated for the component of the light perpendicular to the b-axis, but no structure could be found in this spectrum even at 4·22° Abs. There was a continuous absorption in the violet without discrete bands. In the spectrum of the vapour of azobenzene under atmospheric pressure, no lines or bands could be found.   A. J. MEE.

Relation between ultra-violet absorption spectra and heats of combustion. E. P. CARR (Nature, 1930, **125**, 237).—The heat of combustion of a hydrocarbon in the liquid state containing m double linkings can be represented by the equation $Q = (3n+1)52\cdot1 - m(Nh\nu_2 - Nh\nu_1)$, where ν_1 and ν_2 are the centres of the absorption bands. For acetylenic hydrocarbons $2m$ replaces m in the above formula where m now stands for the number of triple linkings present.   L. S. THEOBALD.

Infra-red absorption spectra of benzene and its halogen derivatives. J. F. DAUGHERTY (Physical Rev., 1929, [ii], **34**, 1549—1557; cf. Ellis, A., 1924, ii, 219; 1926, 454; Dreisch, A., 1925, ii, 627).— With the view of discovering series relations or any shifting of the maxima due to halogen substitution, the infra-red absorption spectra of benzene and its monohalogen derivatives were measured from 1 to 7·5 μ, and several previously unobserved weak bands were found. Good agreement with existing data was found for other bands. In the region 1—1·9 μ, a maximum at 1·12 is associated with a smaller maximum at 1·14 (cf. Barnes, A., 1928, 1306); an intense maximum at 1·66 and smaller maxima at 1·72, 1·78, and 1·88 μ were found. The region at 3·3 μ showed maxima at 3·29, 3·32, and 3·44 μ; the region 5—7·5 μ showed bands for benzene at 5·06, 5·56, 6·20, 6·74, and 7·16 μ. The spectra showed a general similarity, but no definite rule for shifting was found. Calculations of combination bands and harmonics are given.   N. M. BLIGH.

Infra-red investigations of molecular structure. IV. Overtone of nitric oxide. C. P. SNOW and E. K. RIDEAL (Proc. Roy. Soc., 1930, A, **126**, 355—359).—The NO overtone ($n'' = 1/2 \longrightarrow n' = 5/2$) has been detected with the gas at atmospheric pressure, and partly resolved at 0·5 atmosphere.

It consists, like the fundamental, of R, P, and Q branches, the existence of the Q branch (at 3744± 1·5 cm.$^{-1}$) being explained by the 2Π character of the molecule. The constants ω_0 and $\omega_0 x$ are evaluated as 1895·2 and 12·2, respectively, in fair agreement with the electronic band spectral values of 1892 and 13·7. From these, the constants of the Mecke value are obtained. The ratio of the intensities of the fundamental and overtone is compared with the theoretical value.   L. L. BIRCUMSHAW.

Infra-red spectra. XIV. Band attributed to amino-nitrogen. G. B. BONINO (Atti Soc. Ligustica Sci. Lett., 1926, **5**, 6 pp.; Chem. Zentr., 1929, ii, 1507).—All compounds with nitrogen directly united with hydrogen show a band at about 3 μ. With increasing mol. wt. the compounds in a particular series with the same number of amino-hydrogen atoms have almost equal maximal molecular absorption coefficients for 3 μ, whilst for the 3·4—3·5 μ bands the values may vary considerably.   A. A. ELDRIDGE.

Short-duration phosphorescence in fused quartz. H. W. WEBB and (MISS) H. A. MESSENGER (Physical Rev., 1929, [ii], **34**, 1463—1465; cf. Gillam and Morton, A., 1929, 240).—Radiation from a water-cooled quartz-mercury arc was passed through a narrow slit and fell on a sample of fused quartz. The phosphorescence, measured by Zemansky's rotating device (cf. A., 1927, 491), was found to have a decay constant of approximately 5×10^3 sec.$^{-1}$; the wave-length of the exciting radiation was less than 2270 Å. The phosphorescence radiation is a continuous band from 3700 to 4750 Å. with a maximum at 4000 Å., and is unaffected by temperature changes from 20° to 240°; it was not observed in crystalline quartz.   N. M. BLIGH.

Light absorption and dispersion in phosphorescent alkali halides containing a known number of heavy metal ions. W. KOCH (Z. Physik, 1930, **59**, 178—385).—The absorption and dispersion of phosphorescent potassium bromide containing lead and of potassium chloride containing thallium have been determined and the number of electrons causing dispersion calculated by means of the classical electron theory. The numbers calculated from the height and width of the absorption band are in good agreement with those calculated from the nature of the anomalous dispersion. Using potassium chloride crystals containing a varying and experimentally determined number of thallium ions (Koch, A., 1929, 1364), the short- and long-wave absorption bands were investigated and the number of dispersing electrons calculated. For the long waves about one electron was found for every 10 thallium ions present, and for the short waves about one for every 2 thallium ions, the relation being linear in each case. From this it is deduced that single thallium ions replace single potassium ions in the lattice, but that since doubling the ion content does not quite double the number of dispersing electrons, some of the thallium exists in colloidal form at the higher concentrations. Potassium chloride crystals containing lead were similarly investigated but no such definite relationship was found and it is inferred that the lead is mainly colloidal.   H. A. JAHN.

Phosphorescence. R. TOMASCHEK (Sitzungsber. Ges. Beförd. ges. Wiss., 1928, **63**, 119—136; Chem. Zentr., 1929, ii, 1382).—Spatial differentiation between the excitation and emission processes at a centre of phosphorescence is postulated and the appearance of the sodium D-lines in after-glow is interpreted. The phenomena of phosphorescence, photo-electric conductivity, solid catalysis, and chemiluminescence are correlated.   A. A. ELDRIDGE.

Photo-voltaic properties of phototropic mercury compounds. S. V. R. RAO (J. Indian Inst. Sci., 1929, **12A**, 225—232; cf. A., 1929, 627, 660).— Of eleven phototropic mercury compounds previously described, seven have been found to show a " dark potential " between the light- and dark-coloured modifications. In general the dark potential increases linearly with the duration of the time of previous exposure of the preparation to the light, this in turn being proportional to the quantity of the dark-coloured compound. The potential reaches a maximum value, at which it remains constant in less than an hour. The highest value recorded was about 140 millivolts for the compound IHg·CNS. Exposure to light causes a photo-potential which increases to a maximum, at which it remains constant without fatigue. The original condition is rapidly regained on cutting off the light, the fall in potential amounting to 50% in 30 sec.

In many cases the photo-potential is proportional to the light intensity up to a value at which a saturation potential occurs. The maximum potential measured was 170 millivolts for the compound HS·Hg·CNS. With visible light the shortest wave-lengths produce the highest potential, and dyeing the electrodes with erythrosin caused an increase in potential.

The dark potential of most of the compounds is almost independent of temperature in the range 30—50°, but in a few cases, notably that of the compound $HgBr_2,2HgS$, it has a negative temperature coefficient.   F. G. TRYHORN.

Raman effect. P. DAURE (Ann. Physique, 1929, [x], **12**, 375—441; cf. A., 1929, 11, 240, 865, 866).— The Raman effect was investigated for a number of pure substances, mixtures, and solutions, and liquefied gases. Results are given and discussed for liquefied hydrogen chloride, ammonia, and carbon tetrachloride, the chlorides of arsenic, phosphorus, carbon, antimony, bismuth, silicon, titanium, and tin, and for a number of organic series. A constant difference, the characteristic frequency, was found between the exciting frequency and that of the negative secondary radiation. A liquid mixture gave a superposition of the spectra of the constituents; dissociation was marked by a broadening of the lines, and the view of a molecular origin for the Raman lines was supported. The spectra of the inorganic chlorides and the organic series showed, respectively, marked analogies, indicating a connexion with molecular constitution. Spectro-photometric measurements verified the theoretical law for the decrease, with respect to the characteristic frequency, of the ratio of the intensities of the corresponding positive and negative lines; showed that the Raman intensities for a given charac-teristic frequency were proportional to the intensities of the diffuse lines of the same exciting frequency, and vary as the fourth power of the exciting frequency, and allowed a comparison of the intensities of some diffuse and Raman lines. A comparison of the positions and intensities of infra-red absorption bands and Raman lines showed a similarity and a greater intensity for high-frequency Raman lines of hydrogen compounds. No general results were obtained relating Raman spectra and molecular structure, but certain lines were found to be associated with certain molecular linkings for hydrogen, the carbon chain, and the CO group.   N. M. BLIGH.

Constitution of water and the Raman effect. W. GERLACH (Naturwiss., 1930, **18**, 68).—Experiments on the magnetic and optical properties of salt solutions led to the conclusion that in certain solutions a change in the constitution of the water may take place. The Raman photographs of pure water and of 60% solutions of lithium and calcium chlorides were taken. Distilled water showed only a trace of fluorescence. The Raman spectrum gave the double band in the blue and a very wide, sometimes unresolved band in the violet. The salt solutions, prepared from pure salts and the same water as used above, showed only the long-wave component of the blue band with any great intensity. The short-wave part was missing. With the lithium chloride solution the violet band was small and quite weak, whilst the blue band was fairly intense. For calcium chloride, the violet band has a very sharp maximum. The explanation is the depolymerisation of water. The present work leaves open the possibility of the existence of a new Raman band for lithium chloride at λ 4850 Å.   A. J. MEE.

Raman effect for some organic substances. J. SÖDERQVIST (Z. Physik, 1930, **59**, 446—465).— The Raman spectra for benzene, toluene, ethylbenzene, ethyl chloride, ethyl bromide, allyl chloride, n-propyl chloride, and n-propyl bromide were examined. It was found that substances frequently gave similar Raman frequencies, especially if their structures were similar. Pringsheim and Rosen (cf. A., 1928, 1307) have proved that a Raman frequency of 3050 cm.$^{-1}$, corresponding with a wave-length of 3·3 μ, is obtained with all organic substances containing the CH linking. This value is, however, a little different for aromatic and for aliphatic compounds, the former showing a value of 3·27 μ and the latter one of 3·37 μ. The aromatic substances investigated also showed a wave-length almost twice this, and this, as well as the 10 μ and 16 μ wave-lengths also investigated, were given by Kohlrausch and Dadieu as characteristic values for ring compounds (cf. A., 1929, 976). It was found that substances containing the methyl group gave a characteristic Raman frequency of wave-length 3·40 μ. In cases where the methyl occurs in an aromatic compound, this wave-length is found in addition to those mentioned above. With the aromatic substances investigated a line was found at approximately 8·5 μ. This may be characteristic of benzene and its derivatives. Aliphatic substances, especially the halides, often gave similar Raman lines. The two propyl halides gave values very

near each other, the greatest difference being $0.2\,\mu$. The wave-lengths of the bromide were always greater than those of the chloride, owing presumably to the greater mass of the bromine. A. J. MEE.

Raman effect in liquid pyridine. S. VEN-KATESWARAN (J. Physical Chem., 1930, **34**, 145—152).—The Raman effect in liquid pyridine has been investigated, using the light from a mercury arc as the incident source. The spectrum of the scattered light exhibits several modified lines, which have been measured, and a faint continuous spectrum. The corresponding infra-red wave-lengths for pyridine are 16.58, 15.36, 11.32, 10.12, 9.735, 8.214, 6.343, and $3.271\,\mu$. The modified lines are differently polarised and the two most prominent lines corresponding with $10.12\,\mu$ and $9.735\,\mu$ are the most strongly polarised. A comparison of the Raman effect in benzene and pyridine indicates that the two substances possess a similar structure. L. S. THEOBALD.

" Common third level " in the Raman effect. R. C. MAJUMDAR and D. S. KOTHARI (Nature, 1930, **125**, 165).—Theoretical. Combination scattering of light (Raman effect) is dependent on the existence of a third common level E_n whereby a molecule may pass from E_l to E_n and may return from E_n to E_l or E_n to E_k. L. S. THEOBALD.

Molecular scattering of light. J. R. NIELSEN (Science, 1929, **69**, 15).—The wave-length shift reported by Cabannes and Daure (A., 1928, 812) may be due to the Compton effect, but no unmodified line was reported. An interpretation in terms of the Raman effect is also out of the question. Further investigation is desirable. L. S. THEOBALD.

Raman effect with optically active substances. S. BHAGAVANTAM and S. VENKATESWARAN (Nature, 1930, **125**, 237—238).—Differences in the relative intensities of some of the lines of the spectra of d- and l-pinene especially in the Raman line about $74\,\mu$ have been observed. L. S. THEOBALD.

Ionisation produced in the oxidation of nitric oxide. L. A. M. HENRY (J. Physical Chem., 1929, **33**, 1941—1952).—In connexion with a study of the reaction $2NO + O_2 \rightleftharpoons 2NO_2$ an apparatus capable of measuring currents of 10^{-15} to 10^{-16} amp. is described. At temperatures up to $100°$ the introduction of the reacting mixture into the ionising chamber produced no permanent ionisation; only short-lived, temporary effects were observed when nitric oxide was introduced into and cut off from a stream of oxygen. At $300°$, a permanent ionisation, proportional to the $P.D.$ in the chamber and to the percentage of nitric oxide, was observed. Possible explanations are discussed, the most probable one being that ionisation results from the dissociation of nitrogen peroxide.
L. S. THEOBALD.

Molecular polarisation of symmetrical but non-rigid molecules. G. JUNG and A. SCHLEEDE (Z. physikal. Chem., 1929, **B**, **4**, 207—216).—Theoretical. The relationship between temperature and the molecular polarisation P which can be induced in a symmetrical but non-rigid molecule (i.e., one capable of rotation of one part with respect to another), is of the form $p_{(\text{non-rigid})} = \alpha' - b'T$, whilst Debye's

equation for the natural polarisation of an unsymmetrical molecule is $p_{(\text{rigid})} = \alpha + b/T$. Thus by determining the way in which P depends on T it is possible to distinguish between the two types of molecule. M. S. BURR.

Effect of temperature on the molecular polarisation of gases and vapours. R. SÄNGER and O. STEIGER (Helv. phys. Acta, 1929, **2**, 136—144; Chem. Zentr., 1929, ii, 1135).—The dielectric constants of methyl, ethyl, and propyl ether vapour between $300°$ and $400°$ Abs. at constant density have been measured. The relation between dielectric constant and density accords with Debye's theory. The electric moment diminishes with increasing mol. wt.
A. A. ELDRIDGE.

Variation of dielectric constant with frequency. J. H. L. JOHNSTONE and J. W. WILLIAMS (Physical Rev., 1929, [ii], **34**, 1483—1490).—The dielectric constants of solutions of nitrobenzene and p-dichlorobenzene in mineral oil of high viscosity were measured at three concentrations, and the critical frequency at infinite dilution was found by extrapolation. The dielectric constant of nitrobenzene decreased with increasing frequency, and was constant for the non-polar p-dichlorobenzene, which showed no dispersion effect, in accordance with Debye's dipole theory. The diameter of the nitrobenzene molecule is calculated to the correct order of magnitude.
N. M. BLIGH.

Dielectric constants of solutions of oximes and ketones in benzene. Dipole moment of benz-aldoxime O-methyl ether, acetophenone, and benzophenone. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1929, **B**, **4**, 217—222).—The method employed for the determination of dielectric constants is described. By the dissolution of oximes in benzene only a small increase in the dipole moment of benzene takes place, in spite of the large dipole moment of the simple oxime molecule. This behaviour is to be attributed to the association of the oxime molecules in solution. This association annuls the dipole moments. The dipole moment of the O-methyl ether of $anti$-benzaldoxime is 0.86×10^{-18} e.s.u. It is known that aliphatic ketones have practically the same dipole moment, but the results obtained show that the substitution of alkyl by phenyl groups leads to an increase in the dipole moment. The dipole moments of acetone, acetophenone, and benzophenone are 2.72×10^{-18}, 2.97×10^{-18}, and 3.13×10^{-18} e.s.u., respectively.
M. S. BURR.

Variation of the dielectric constants of some organic liquids with frequency in the range 1—10^3 kilocycles. R. W. LUNT and M. A. G. RAU (Proc. Roy. Soc., 1930, **A**, **126**, 213—230).—By measuring the capacities of condensers comprising two metal surfaces separated by air or by the liquid under examination, the dielectric constants of benzene, ethyl ether, methyl ether, chloroform, ethyl alcohol, acetone, aniline, and nitrobenzene, and the conductivities of the last four substances have been determined in the frequency range 1—10^3 kilocycles. The results show that within the limits of experimental error (0.5%) there is no change in the dielectric

constant of benzene, ethyl ether, methyl ether, or chloroform over the range studied, whilst for the remaining liquids a slight increase takes place at frequencies higher than 10^2 kilocycles. Bryan's work on nitrobenzene (Physical Rev., 1922, **22**, 391) is confirmed. The conductivity of aniline diminishes slowly up to 10^2 kilocycles and then more rapidly, so that at 10^3 kilocycles it cannot be measured on the bridge available. It is considered possible that the degree of dehydration of aniline determines the conductivity.   L. L. BIRCUMSHAW.

Dipole moment of s-trinitrobenzene. A. PARTS (Z. physikal. Chem., 1929, **B**, **4**, 227—233).—The dielectric constants of solutions of s-trinitrobenzene in benzene, between 10° and 50°, have been determined by a method which is described. The total polarisation appears to be independent of concentration, at least up to a mol. fraction of trinitrobenzene of 0·0389, and is approximately 54 at 25°. From optical data the electron polarisation is 40. Hence the combined atomic and dipole polarisation are 14, giving a dipole moment of $0·8 \times 10^{-18}$ e.s.u. on the assumption that the atomic polarisation is zero (cf. Williams, A., 1928, 1180).   M. S. BURR.

Refraction of light by alkali hydrides. H. BODE (Z. physikal. Chem., 1930, **B**, **6**, 251—255).—The molecular refractions of sodium and potassium hydrides have been determined and those of lithium, rubidium, and cæsium calculated from them. The hydrogen anion itself has a high refraction. In the alkali hydrides hydrogen is analogous to the halogens. Both the mol. vols. and refractions of hydrogen and the halogens increase in the order F', H', Cl'.
                                              F. L. USHER.

Optical properties of mixed crystals. T. F. W. BARTH (Amer. J. Sci., 1930, [v], **19**, 135—146).—Work on refractive indices of mixed crystals is summarised. Mixed crystals of thallous bromide and iodide were prepared and their refractive indices found. The refractive index was plotted against composition, and from the graph thus obtained it was evident that none of the theoretical formulæ hitherto proposed for the optical properties of mixed crystals fits this system. Mixed crystals of silver bromide and silver iodide, with sodium chloride structure, were also investigated, but here, too, deviations from the theoretical formulæ were found. Mixed crystals of $BaO,2SiO_2$ and $2BaO,3SiO_2$ show great deviations. Investigation of the majority of mixed crystals indicates, however, that most of them show proportionality between refraction and composition. It is not possible to tell which of the laws a system obeys. The cause of these deviations is that the refractive power of a mixture depends not only on its density, but also on the nature of the chemical linkings and the degree of deformation of the ions. If the formation of mixed crystals takes place without any deformation of the anions or change of chemical linkings, the refractive indices of the mixtures will vary approximately proportionally to the composition (except for triclinic and partly monoclinic crystals). The application of this to optical mineralogy is considered.
                                              A. J. MEE.

Optical rotation and chemical constitution. W. KUHN (Ber., 1930, **63**, [**B**], 190—207; cf. A., 1929, 981).—The optical activity of a compound must be regarded as the sum of the activity contributions depending on individual bands which can be attributed to definite substituents. The magnitude of the contribution of a band depends on its position in the spectrum and the product of its strength and the so-called anisotropic factor. The circular dichroism of the band depends on the latter factor. The weak and medium strong bands immediately proximate to the visible portion are particularly important, since, for them, the anisotropic factor is unusually great and because they largely eliminate the activity contributions of the bands in the extreme ultraviolet. The bands of substituents placed particularly close to the active carbon atom have a very large anisotropic factor. This anisotropy (" induced anisotropy ") is conferred on these bands by the disturbance (" vicinal action ") which the surrounding substituents exert on the particular group (bands) (cf. Born, A., 1915, ii, 659; 1918, ii, 283). It is shown in a series of examples (simple carbinols, substituted alcohols, vinylcarbinols, derivatives of amyl alcohol) that simple rules apply to vicinal action and, in part, to induced anisotropy. An alkyl group containing halogen, carboxyl, hydroxyl, or a double linking remote from the optically active carbon atom behaves like a larger alkyl group in its vicinal effect.
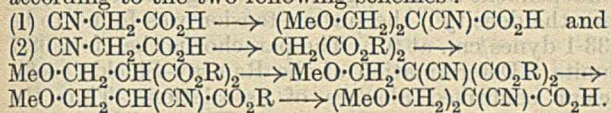   H. WREN.

Co-ordination. I. Ion hydrates. F. J. GARRICK (Phil. Mag., 1930, [vii], **9**, 131—141).—It is assumed that the most stable hydrato-complex ions are those in which the electrostatic energy is a maximum. The electrostatic energies are calculated for a number of such ions and it is found that the co-ordination number is 6 for Na^+, K^+, Mg^{++}, and Ca^{++}, 8 for Cs^+, Sr^{++}, and Ba^{++}, and 4 or 6 for Li^+ and Be^{++}, whilst the co-ordination number 12 is never found. The electrostatic mechanism of the formation of such co-ordination complexes is in satisfactory agreement with observed results.
                                              A. E. MITCHELL.

Experimental test of the theory of geometrical stereochemistry. A. P. SEMENCOV (Ukrain. Chem. J., 1929, **4**, 309—321).—The literature dealing with the configuration of pentaerythritol is reviewed and the possible types of isomerides of a molecule $CR_2R'R''$, assuming the pyramidal configuration, are considered. Two geometrical isomerides may exist, one with the two identical radicals situated at the ends of a side of the quadrilateral formed by the four radicals (cis-isomeride) and the other with these radicals at the ends of a diagonal (trans-isomeride). In the latter case there is a plane of symmetry perpendicular to the line joining the two similar radicals. With the cis-isomeride, the molecule has no plane of symmetry and is thus not identical with its mirror-image, so that there should be optical isomerism. As regards which of these compounds may be assumed to have a pyramidal configuration of the molecule, this should be looked for in cases where Ebert and von Hartel (A., 1928, 462) observed a considerable electrostatic moment, that is, in molecules containing the groups $CH_2·OR$, CO_2R, $CH_2·CO_2R$, and OR combined with

the central atom. Hence, with citric acid there is, according to this hypothesis, justification for expecting optical isomerism. Attempts to prepare optically active citric acids by means of the quinine and brucine salts proved unsuccessful, but this may be because this acid is the *trans*-isomeride. Similar experiments with the monoamide of maleic acid also resulted only in optically inactive compounds. In the hope of obtaining dimethoxycyanoisobutyric acid in *cis*- and *trans*-forms, this acid is now being prepared according to the two following schemes :

(1) $CN \cdot CH_2 \cdot CO_2H \longrightarrow (MeO \cdot CH_2)_2 C(CN) \cdot CO_2H$ and
(2) $CN \cdot CH_2 \cdot CO_2H \longrightarrow CH_2(CO_2R)_2 \longrightarrow$
$MeO \cdot CH_2 \cdot CH(CO_2R)_2 \longrightarrow MeO \cdot CH_2 \cdot C(CN)(CO_2R)_2 \longrightarrow$
$MeO \cdot CH_2 \cdot CH(CN) \cdot CO_2R \longrightarrow (MeO \cdot CH_2)_2 C(CN) \cdot CO_2H.$

T. H. POPE.

Stereochemistry of compounds with quinquevalent nitrogen. A. P. SEMENCOV (Ukrain. Chem. J., 1929, 4, 323—325).—The various hypotheses which have been advanced concerning the stereochemical configuration of compounds containing a quinquevalent nitrogen atom are discussed, the conclusion being reached that the necessary and sufficient condition for the optical isomerism of such compounds is that four radicals combined with the nitrogen atom shall be different. The fifth radical (anion of the acid) exerts no influence on the phenomenon of optical isomerism; thus, the absence of such radical, as in oxides of the form $NabcO$, or its identity with one of the first four radicals, as in $Nabc(OH)_2$, does not interfere with the optical isomerism. Hence, the deciding factor is the structure of the cation quite independently of the anion, this structure being the same as that of methane derivatives and the nitrogen occupying a space-centred position. About the nucleus of the central nitrogen atom eight electrons are distributed at the angles of a cube, the directions of the attractive forces between the central atom and the radicals being perpendicular to four edges of the cube. T. H. POPE.

Distinction between ionic and atomic compounds. E. RABINOWITSCH and E. THILO (Z. physikal. Chem., 1930, B, 6, 284—306).—Calculations of Grimm and Herzfeld (cf. A., 1924, ii, 102) on the existence and stability of various ionic compounds have been extended with the aid of new physical data which permit a wider application of the Born–Haber cycle. The ionic compounds predicted by theory are all known, excepting manganese monochloride and the mono- and di-halides of aluminium, scandium, titanium, yttrium, and lanthanum. The results show definitely that nitrogen and boron trichlorides, and the tetrachlorides of carbon, tin, and lead, among other volatile hydrides and halides, are not ionic compounds, and indicate that cadmium and cuprous iodides, and aurous, mercurous, and mercuric chlorides are typical atomic compounds in the solid state. The solid hydrogen halides are also non-ionic.

F. L. USHER.

Dissociation work of oxygen. G. HERZBERG (Z. physikal. Chem., 1929, B, 4, 223—226).—Theoretical. A re-examination of the experimental data from which the dissociation tension of the oxygen molecule has been calculated leads to the conclusion

that the value of 7 volts hitherto assigned to it is 1—2 volts too high. The corresponding values for carbon monoxide and nitric oxide, which are calculated from the oxygen value, now become approximately 10 and 6·5 volts instead of 11 and 7 volts, respectively. M. S. BURR.

Affinity. T. DE DONDER (Bull. Acad. roy. Belg., 1929, [v], 15, 615—625).—Mathematical. Expressions are derived for the affinity in systems in which the mass is variable. O. J. WALKER.

Diamagnetism of ions. P. WEISS (Compt. rend., 1930, 190, 95—98).—With reference to Reicheneder's assumption (cf. A., 1929, 1370) that the magnetic susceptibility of H^+ ion is nil, thus neglecting the effect of that ion on the diamagnetism of water, it is proposed to deduce this effect from that of H^+ ion on refraction. The changes in refraction and in diamagnetism consequent on the deformation of the ions resulting from the change from solution to crystallisation show that the refraction is almost exactly twice as sensitive to such change as the diamagnetism. This result is shown to be in conformity with theory. The loss of diamagnetism due to, *i.e.*, the apparent paramagnetism of, the H^+ ion is in this way determined as $1 \cdot 1 \times 10^{-6}$. Susceptibilities of several substances calculated on this basis are shown to be in fair agreement with experimental results. C. A. SILBERRAD.

Diamagnetic anomaly in gases. V. Critical examination of methods. I. A. GLASER (Ann. Physik, 1929, [v], 3, 1119—1136).—The diamagnetic anomaly (A., 1925, ii, 82, 642; 1929, 628, 982) is considered by Hammar (A., 1926, 1197) to arise from the adsorption of gases or water vapour at the surface of the material used in the susceptibility measurements, whilst Buchner (A., 1929, 249) ascribes the phenomenon to temperature differences within the apparatus. The actual course of the anomaly is qualitatively different from that consistent with the conjectural adsorption mechanism; it is independent of great differences in the surface condition, etching with hydrofluoric acid and plating with gold, silver, and platinum effecting no change. Exhaustive experiments on drying the gases demonstrate that the presence or adsorption of water vapour cannot account for the anomalous diamagnetism. The presence of traces of oxygen leads to untrustworthy results; in this connexion it is shown that the oxygen pressure corresponding with the reaction $4CuO \longrightarrow 2Cu_2O + O_2$ is negligible only at temperatures distinctly below 800°, at 1000° it is about 100 mm. and at 1100° about 560 mm. Hence, in order to prepare gases free from traces of oxygen, the tube containing heated copper should show a considerable decrease in temperature between the inlet and outlet ends. The presence of oxygen accounts for certain failures to reproduce the author's results. R. A. MORTON.

Interpretation [energetic] of the molecular field and paramagnetism. P. WEISS (J. Phys. Radium, 1930, [viii], 1, 1—10).—The necessary and sufficient condition for a paramagnetic substance to obey the relation $\sigma = CH/(T - \Theta)$ is that the energy $U = -n\sigma^2/2 + f(T)$. It is recommended (with

examples) that $1/\chi T$ (instead of $1/T$) be plotted against T. Theories of the molecular field are discussed, and it is concluded that where the Curie point is independent of concentration the carrier of magnetic moment must be a portion only of the ion.

C. A. SILBERRAD.

Diamagnetic anomaly in gases. VI. Critical examination of methods. II. A. GLASER (Ann. Physik, 1930, [v], **4**, 82—90).—Reconsideration of experimental methods appears to dispose of the view that Buchner's temperature effect (A., 1929, 249) and the magnetic anomaly possess a common origin.

R. A. MORTON.

Magnetic investigations on adsorbed gases. J. AHARONI and F. SIMON (Z. physikal. Chem., 1929, B, **4**, 175—189).—A null method for the measurement of magnetic susceptibility is described. No knowledge of field strength is required and the method is especially suitable for low temperatures. The standardisation curve has been tested by determinations of the magnetic susceptibility of iron ammonium alum at different temperatures, and of solutions of manganous sulphate at different concentrations at 0°. The magnetic susceptibilities of the following systems of adsorbed gases have been measured at different temperatures and gaseous concentrations : chabasite–oxygen; carbon–oxygen; palladium–hydrogen. Oxygen adsorbed by chabasite has a smaller magnetic susceptibility than free oxygen, and a break occurs in the susceptibility–concentration curve when the two components of the system are present in equimolecular proportions. This behaviour confirms the authors' view that the gas molecules are taken up, one by one, into separate cells in the adsorbent (cf. A., 1928, 580). The relationship between concentration and magnetic susceptibility shows a similar discontinuity in the case of the system carbon–oxygen. This may perhaps be ascribed to a transition from a unimolecular to a bimolecular layer. When hydrogen is adsorbed by palladium there is, with increasing concentration, a marked linear diminution of susceptibility which comes to an end at a concentration corresponding with Pd_2H. After this point very little more hydrogen is taken up and the magnetic susceptibility remains constant. The molecular transformation which the ammonium halides are considered to undergo between $-30°$ and $-40°$ has no effect on the magnetic susceptibility of the salts, and similar observations have been made with regard to the transition points of manganous oxide and manganese dioxide at 116° and 92°, respectively.

M. S. BURR.

Determination of the variation with pressure of the force between two plates at different temperatures at low pressures, with a view to the determination of molecular mean free paths. A. E. MARTIN (Phil. Mag., 1930, [vii], **9**, 97—130).—At low pressures the force between two small plane parallel plates at different temperatures is found to be directly proportional to the temperature difference and inversely proportional to the square of the distance between them provided the distance is large compared with their linear dimensions. In both air and hydrogen at low pressures the force is found to be directly proportional to the pressure, but at higher pressures there is a departure from the linear relationship. A maximum is observed in air at a pressure of 0·07 mm., whilst one is predicted in hydrogen at about 0·13 mm. The mean free paths of air and hydrogen molecules have been calculated from these deviations from the linear relationship.

A. E. MITCHELL.

Parachor of chlorine dioxide. G. H. CHEESMAN (J.C.S., 1930, 35—37).—The structure of chlorine dioxide has been deduced from its parachor. Two independent methods gave an average result of 1·642 for the density ; the surface tension was found to be 33·1 dynes/cm. at 0°. The parachor is therefore 98·7 units. Determination of the Ramsay–Shields coefficient confirmed absence of association. Thus the structural parachor is 4·4 units. The possible electron distributions are discussed and three involving singlet linkings are found to have the correct sign. The structure preferred is one having a three-membered ring and a semi-polar singlet linking.

W. R. ANGUS.

Calculation of absorption in X-ray powder photographs and the scattering power of tungsten. A. CLAASSEN (Phil. Mag., 1930, [vii], **9**, 57—65).—The total absorption factor for X-rays of glancing angle θ for a heavy powder is shown to be $A_\theta = \int_0^{2\theta} \sin\phi \sin(2\theta-\phi)/\{\sin\phi + \sin(2\theta-\phi)\}d\phi$, where ϕ is the angle of incidence. The expression is valid under conditions of X-ray powder photography in which the rod of heavy powder is rotated during exposure. The result is applied to the calculation of the scattering power of tungsten on the basis of the Thomas model of the atom. The results obtained are in good agreement with experimental values.

A. E. MITCHELL.

X-Ray investigation of easily deformable crystals. L. CHROBAK (Bull. Acad. Polonaise, 1929, A, 497—505).—The technique of obtaining undeformed specimens of easily deformed crystals for X-ray investigations is given. New apparatus for the work is also described including a simple precision chamber for Laue photographs.

A. J. MEE.

Examination of two technical X-ray tubes for purity of spectra. K. F. JAHR, F. A. SCHNEIDER, and A. WINKEL (Z. physikal. Chem., 1930, B, **6**, 256—260).—Two tubes, with anticathodes of iron and molybdenum respectively, have been examined by means of Seemann's spectrograph (cf. A., 1918, ii, 383) and in each case a pure spectrum has been obtained. Both tubes had been in use for a considerable time, so that no detectable contamination through atomising of metal parts occurs when the tubes are carefully made and properly handled. The result is of importance in the analysis of X-ray structure diagrams for which it is necessary to use only pure spectra.

F. L. USHER.

Reflexion of X-rays. F. JENTZSCH and E. NÄHRING (Naturwiss., 1929, **17**, 980).—A claim for priority against Schön with respect to some of the results published by him (A., 1929, 1355). Experiments by the authors on Schott glasses have shown that the sharpness of the boundary of total reflexion depends largely on the absorption coefficient.

G. E. WENTWORTH.

X-Ray examination of crystal defects. W. BERG (Naturwiss., 1930, **18**, 115).—An image of the crystal face is obtained by reflecting a beam of X-rays from it. Crystals having no defects give an image of uniform darkness; defects are shown by light and dark striations. W. R. ANGUS.

Optical method for demonstrating the results of X-ray analyses. W. L. BRAGG (Z. Krist., 1929, **70**, 475—492; Chem. Zentr., 1929, ii, 969).

Determination of refractive indices for X-rays. K. KELLERMANN (Ann. Physik, 1930, [v], **4**, 185—214).—The substance is made into a plate with a slight curvature, so that a homogeneous small bundle of X-rays is obtained with different angles of refraction. The totally reflected X-rays give on a photographic plate a certain widening of the blackening. For the exposures the curved plates were rotated about an axis in their surface. By finding the change of widening, and knowing the angle of rotation, the angle of total reflexion can be calculated. The method was applied to crown glass and to silver. It can also be used for liquids which are held in a curved plate. Glycerol and concentrated calcium chloride solution were used. The accuracy of the method with the present arrangement is for solids $\pm 4\%$, and for liquids $\pm 7\%$. A. J. MEE.

Crystal structures of the B sub-groups and their connexion with the periodic table and atomic structures. W. HUME-ROTHERY (Phil. Mag., 1930, [vii], **9**, 65—80).—It is held that in the B sub-groups there is a tendency for an element to crystallise so that each atom is surrounded by $(8-N)$ neighbours, where N is the number of the group to which the element belongs. Opposing this tendency there is a tendency to form close-packed structures. For groups IV to VII the first tendency is explained on the basis of co-valency linkings, the atom taking $(8-N)$ neighbours and sharing one electron with each. In group IV the tetrahedral arrangement requires no other forces to ensure the stability, but in groups V to VII the stability can be explained only by the assumption of additional molecular linkings. In groups III and II the presence of simple covalency linkings will not account for each atom having five or six neighbours, there being an insufficient number of electrons for the necessary sharing. The stability in these cases is explained by the existence of a metallic linking. The typical close-packed structures of group I-B elements are attributed wholly to the metallic linkings, since there are not sufficient available electrons for covalency linkings, each electron being shared by more than two atoms. A. E. MITCHELL.

Influence of the symmetry of the medium on the symmetry of crystalline form. G. FRIEDEL and R. WEIL (Compt. rend., 1930, **190**, 243—245; cf. Royer, A., 1929, 750).—Illustrations are provided of the correlation of the symmetry of crystalline forms with the symmetry of the medium. The former may exist in 32 forms, but the latter has only 2, namely, complete spherical symmetry which includes all the elements of symmetry of the crystal, and holoaxial spherical symmetry which is that of isotropic (active) amorphous media. The symmetries of the cubic, quadratic, orthorhombic, and clinorhombic crystal systems are considered, and the apparently new types of merihedry involved are reconciled with existing ideas by considering them as due not to the symmetry of the crystal itself, but to that of one only of its properties, e.g., the external form it assumes under certain conditions. J. GRANT.

Relation between " active centres " and the " attracting places " (Lockerstellen) of crystals. I. N. STRANSKI (Z. Elektrochem., 1930, **36**, 25—26).—Crystal growth is considered to be easier at the " active centres " of a crystal than at the attracting places, e.g., corners, where dissolution occurs more readily. H. T. S. BRITTON.

Orientation of single crystals obtained by recrystallisation. G. SACHS and J. WEERTS (Z. Physik, 1930, **59**, 497—500).—The orientation of aluminium crystals and of crystals of an alloy of aluminium with 5% Cu is investigated. Purity of materials greatly influences the orientation. The cause of this is uncertain, but it may be connected with the ease of preparation of single crystals. With pure materials single crystals are, as a rule, more difficult to prepare than with impure material. It appears that the formation of large crystals by recrystallisation does not in this case, as in other recrystallisation phenomena, depend on the preferential growth of a large number of nuclei. A. J. MEE.

Crystal structures of magnesium, zinc, and cadmium ferrites. E. POSNJAK (Amer. J. Sci., 1930, [v], **19**, 67—70).—Magnesium, zinc, and cadmium ferrites have been prepared by heating equivalent proportions of the carbonates with finely-divided ferric oxide to 800°. Powder diffraction data have been obtained showing that the lengths of the edges of the unit cubes, containing 8 mols., are $8 \cdot 36 \pm 0 \cdot 01$, $8 \cdot 41 \pm 0 \cdot 01$, and $8 \cdot 67 \pm 0 \cdot 01$ Å. respectively (d obs. 4·481, 5·290, 5·764). C. W. GIBBY.

Orientation of single crystals of tin. K. TANAKA (Mem. Coll. Sci. Kyoto, 1929, **12**, 275—379). —The dependence of the crystallographic orientation on the previous history of the crystal is much less than in the case of zinc (A., 1929, 15). The favourable crystallographic direction of growth is found to be roughly parallel to the basal plane of the tetragonal crystal. W. E. DOWNEY.

Crystal structure of iron. R. BACH (Helv. phys. Acta, 1929, **2**, 95—114; Chem. Zentr., 1929, ii, 1131).—α-, β-, and δ-iron have a cubic body-centred, and γ-iron a cubic face-centred lattice. A study of the relation between the lattice constant and the temperature indicates that β- and δ-iron are identical, whilst α- and β-iron differ considerably. A. A. ELDRIDGE.

Crystal structure of barium tungstate. I. I. NAVANO and J. PALACIOS (Anal. Fís. Quím., 1929, **72**, 846—849).—X-Ray investigation demonstrates that barium tungstate belongs to the C_{4h}^6 class, there being 4 molecules in the elementary parallelepiped. H. F. GILLBE.

Crystal structure of glaserite and potassium sulphate. B. GOSSNER (Neues Jahrb. Min., 1927, **57**, 89—116; Chem. Zentr., 1929, ii, 1505—1506).—

The unit cell (a 5·65, c 7·29 Å.) of glaserite, referred to hexagonal axes, contains 2 mols. of $NaK_3(SO_4)_2$; the space-group is D_{3d}^3. The unit cell of potassium sulphate has a 10·06, b 5·85, c 7·33 Å., and contains 4 mols. of K_2SO_4; the space-group is V_h^{13}.   A. A. ELDRIDGE.

Structure of zunyite. B. GOSSNER (Neues Jahrb. Min., 1926, **15**, 319—332; Chem. Zentr., 1929, ii, 1506).—Zunyite, cubic, has a 13·92 Å.; space-group Td^1. The unit cell contains 6 mols. of $3SiO_2,3AlO(F,Cl),4HAlO_2,H_3AlO_3$.   A. A. ELDRIDGE.

Tetrahedral-pyramidal configuration of methane derivatives. F. M. JAEGER (Chem. Weekblad, 1930, **27**, 50—52).—The space configuration of the atoms in molecules of the methane type is discussed with special reference to pentaerythritol, having regard to the X-ray spectrum, the optical and pyroelectric properties, and the structure of certain derivatives.   H. F. GILLBE.

Crystal form of adrenalone hydrochloride. W. FABER (Z. Krist., 1929, **70**, 497—505; Chem. Zentr., 1929, ii, 1157).—Adrenalone hydrochloride, $C_9H_{11}O_3N,HCl,H_2O$, crystallises in rhombic plates, d 1·394, n_a 1·5166, n_β 1·6255, n_γ 1·7605±0·0002, passing into a monoclinic form, d 1·393, n_a 1·5049, n_β 1·6444±0·0003, n_γ 1·7424±0·001.   A. A. ELDRIDGE.

X-Ray diagram of mercerised cellulose. K. R. ANDRESS (Z. physikal. Chem., 1929, **B, 4**, 190—206).—In continuation of previous work on the X-ray diagram of native cellulose (A., 1929, 630), the X-ray diagram of mercerised cellulose has now been interpreted on the basis of a monoclinic unit cell having a 8·1, b 10·3, c 9·1 Å., β 62°. The interference intensities are in agreement with a structure based on glucose residues in a cellobiose combination, the atomic arrangement within the hexoses being very nearly the same as for native cellulose. The difference between mercerised and native cellulose consists in a different orientation of the chief valency chains with respect to one another, and the mercerised lattice appears to represent the more stable configuration.   M. S. BURR.

Structure of gelatin. J. J. TRILLAT (Compt. rend., 1930, **190**, 265—267).—The author's method (A., 1929, 763) has been used for the examination, by means of the copper K-lines, of a sample of gelatin of p_H 6·2 (0·4% ash) in its normal state, dried on a thread, and stretched 200%. As in the case of cellulose (*loc. cit.*) chains of principal valency are formed by elementary groups of length 9·7 Å. joined end on end. A number of these form crystallites, the orientation of which differs for the dried or elongated specimens, and a group of crystallites forms a micelle. The amorphous phase of gelatin has low powers of polymerisation and cannot form long chains, whilst the pseudo-crystalline phase is strongly polymerised.   J. GRANT.

Structure of norbergite. W. H. TAYLOR and J. WEST (Z. Krist., 1929, **70**, 461—474; Chem. Zentr., 1929, ii, 979).—Norbergite, $Mg(F,OH)_2,Mg_2SiO_4$, has a 4·70, b 10·2, c 8·72 Å.; the unit cell contains 4 mols., and the space-group is V_h^{16}.   A. A. ELDRIDGE.

Algodonite and whitneyite. F. MACHATSCHKI (Neues Jahrb. Min., 1929, **A, 59**, 137—158; Chem. Zentr., 1929, ii, 1639).—The minerals are crystallo-graphically inhomogeneous. The regular crystals, apparently metallic copper containing arsenic, have a 3·647—3·651 Å. The hexagonal crystals contain less copper than corresponds with the formula Cu_6As, and have a 2·599, 2·598; c 4·215, 4·213 Å., with d 8·71, 8·72.   A. A. ELDRIDGE.

Is it possible to determine the piezoelectric constant at high temperature by the statical method ? R. D. SCHULWAS-SOROKINA (Physical Rev., 1929, [ii], **34**, 1448—1450; cf. Dawson, *ibid.*, 1927, [ii], **29**, 541).—The relation between the piezoelectric effect in quartz and the temperature was investigated by Dawson's method. It is concluded that his results for quartz, and those of Valasek for Rochelle salt, are untrustworthy because of failure to take into account the effect of the electrical conductivity of the crystals.   N. M. BLIGH.

Thermal and electrical properties of beryllium. E. J. LEWIS (Physical Rev., 1929, [ii], **34**, 1575—1587).—The specific heat of pure beryllium increased rapidly with rise of temperature from 0·0389 at −175·6° to 0·593 at 190°. The thermal conductivity increased with rise of temperature from 0·232 at −176·2° to 0·508 at 190·4°. The specific resistance varies according to the heat treatment; after establishing a steady condition by repeated treatments from liquid-air temperature to 700° the values obtained were 1·56, 6·76, 19·05, and 40·00 microhms at −191°, 22°, 305°, and 690°, respectively. The temperature coefficient of resistance over the above range has been determined, the curve showing three distinct sections; the values obtained were : 0·000371 at −190°, 0·00667 at 20°, 0·008 at 310°, 0·00858 at 500°, and 0·01196 at 685°. The thermoelectric power against lead appears to vary linearly with temperature, but the graph shows a break at −50°, indicating a change in allotropic form. The metal does not obey the Wiedemann–Frantz law.   N. M. BLIGH.

Electrical resistivities and temperature coefficients of lead, tin, zinc, and bismuth in the solid and liquid states. W. B. PIETENPOL and H. A. MILEY (Physical Rev., 1929, [ii], **34**, 1588—1600; cf. A., 1928, 9).—A method of measuring the resistance–temperature coefficients of metals of low m. p. in the solid and liquid states is described, oxide films being employed as containers for the molten metals. Resistivity–temperature curves, and resistance–temperature coefficients at 20° intervals are given for the range 20—460°. The coefficients for zinc above the m. p. are positive; allotropic transformations are indicated at about 180° and 340°. Possible explanations of the high resistivity of non-annealed bismuth below 160° are discussed; in the range 225—275° the negative coefficients are due to a molecular derangement.   N. M. BLIGH.

Electrical conductivity of metallic layers formed by cathodic sputtering. E. PERUCCA (Ann. Physik, 1930, [v], **4**, 252—272).—The electrical properties of thin layers of gold and platinum formed by cathodic sputtering were investigated. The initial phase of the conduction as a function of the duration of projection was especially determined. The conductivity is purely metallic in character, and

the potential gradient is uniform along the length of the layer. The use of these layers as unpolarisable resistances of values up to 10^{12} Ω is mentioned. They have practically no temperature coefficient. An explanation of their electrical properties is given.
A. J. MEE.

Ruthenium a superconductor. J. C. McLennan (Nature, 1930, **125**, 168).—Ruthenium becomes a superconductor at $2\cdot04°$ Abs. The metal was of high purity and it retained its high resistance nearly to $4°$ Abs. L. S. THEOBALD.

Magnetic behaviour of nickel and iron films condensed in vacuum on various metal backings. J. H. HOWEY (Physical Rev., 1929, [ii], **34**, 1440—1447; cf. Edwards, A., 1927, 299; Miller, *ibid.*, 1928, 1314).—Using a high-sensitivity magnetometer and a special arrangement of the magnetising coil, the magnetic nature of evaporated iron and nickel films deposited at various temperatures on backings of aluminium, copper, platinum, and molybdenum was investigated to determine the effect of the two-dimensional strain due to differential thermal contraction imposed by the backing. Special precautions were taken to secure gas-free deposition, and magnetisation curves were obtained. Nickel films under tension were magnetically very hard, and under compression were soft. The magnetic intensity of iron films was practically unchanged by the stresses. All the films were harder than bulk metal, and for high-temperature deposition were more like annealed bulk metal.
N. M. BLIGH.

[Magnetisation of] the mixed oxide of nickel and cobalt and the corresponding ferrite. (MLLE.) S. VEIL (Compt. rend., 1930, **190**, 181—183).—The calcined precipitates produced by sodium hydroxide from solutions containing varying proportions of nickelous and cobaltous sulphates are paramagnetic, and the magnetisation coefficient is a maximum for the mixed oxide NiO,CoO. Mixtures of the corresponding ferrites, containing 68% of ferric sulphate, gave ferromagnetic calcined precipitates, the magnetisation–composition curve rising to sharp maxima for the pure ferrites (Fe_2O_3,NiO and Fe_2O_3,CoO) and for the mixed ferrite (Fe_2O_3)$_2$,NiO,CoO. J. GRANT.

Mechanism of demagnetisation. (FRAU) H. TROSIEN (Ann. Physik, 1930, [v], **4**, 109—120).—Investigation of the relation between magnetisation and the decrease in a strong alternating field superposed on a definite direct-current field, carried out on steel and iron, has provided evidence for a law of corresponding states between the observed magnetisation and the amplitude of the alternating field for different direct-current fields. R. A. MORTON.

Hall effect in permalloy. A. W. SMITH and R. W. SEARS (Physical Rev., 1929, [ii], **34**, 1466—1473).—The Hall effect was studied in nickel–iron permalloys containing 84, 81, and 78% Ni, and was at first positive, becoming negative for larger magnetic fields; for those less than about 11,000 gauss an increase in iron concentration increases the Hall effect. The maximum of the Hall $E.M.F.$–magnetic field curve shifts towards greater magnetic fields, and the magnetic field at which a reversal in the direction of the Hall $E.M.F.$ takes place increases with rise of iron concentration. The interpretation of the Hall $E.M.F.$ curves is discussed. N. M. BLIGH.

Anomalies in the physical properties of the amorphous state. Amorphous sulphur and selenium. P. MONDAIN-MONVAL and P. GALET (Compt. rend., 1930, **190**, 120—122; cf. Samsoen, A., 1928, 354).—Anomalies similar to those in glasses and other amorphous substances are shown to exist in amorphous sulphur and selenium, indicating a new allotropic modification of these elements. Abrupt changes occur in viscosity (in sulphur at $-21°$, in selenium at $45°$), and in density and dilatation (sulphur $-29°$, selenium 30—33°). The change in selenium is accompanied by an absorption of heat at 37°. The temperatures of these changes are slightly below those of softening. C. A. SILBERRAD.

Polymorphism of sodium sulphate. III. Dilatometer investigations. F. C. KRACEK and R. E. GIBSON (J. Physical Chem., 1930, **34**, 188—206; cf. A., 1929, 1221).—Previous results have been confirmed and extended by the use of a dilatometer, designed to study changes in volume under pressure, for the lower inversions of sodium sulphate and by an ordinary dilatometer for the upper inversions. The more accurate transition temperatures now obtained are Na_2SO_4-V $\rightleftharpoons$ IV, 160—180°; IV $\rightleftharpoons$ III, 185°; III—I, 241°; and the respective volume changes are $0\cdot0005$, $-0\cdot0034$, and $0\cdot0070$ cm.^{3}/g. At low pressures, Na_2SO_4-II has no region of stability, but if the change I$\rightarrow$III is inhibited, that of I$\rightarrow$III takes place reversibly at 236° with a decrease in volume of $0\cdot004$ cm.^{3}/g. The changes occur slowly and are accompanied by marked hysteresis when the salt is dry, but in the presence of water or a trace of sulphuric acid inversion is prompt and rapid. L. S. THEOBALD.

Use of effect of pressure on electrical resistance of manganin as a method of measuring pressure. A. MICHELS and M. H. LENSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1379—1385).—The treatment required by the manganin before it can be used for this purpose was investigated. It was found that after heat treatment the variation of the resistance of manganin with pressure for the lower temperatures was sufficiently reproducible to allow of its use for measuring pressure. A. J. MEE.

Change of electrical conductivity in strong magnetic fields. W. MEISSNER and H. SCHEFFERS (Naturwiss., 1929, **18**, 110—113).—A discussion of the results of Kapitza (A., 1929, 632) and of Auwers (cf. this vol., 17). J. FARQUHARSON.

Theory of electrical and thermal conductivity. R. PEIERLS (Ann. Physik, 1930, [v], **4**, 121—148).—Previous theories of electrical and thermal conductivity are considered, and the assumptions made by them are discussed, especially the theory of Bloch (cf. A., 1929, 247). A more strict law is given. For low temperatures there is proportionality between conductivity and T^{-4}, in agreement with the empirical law. The same method is used for the calculation of thermal conductivity. For low temperatures the thermal conductivity is proportional to T^{-2}, and for

high temperatures it is independent of temperature, in agreement with experimental observations.

A. J. MEE.

Electrification and conductivity of liquid hydrocarbons. L. BRÜNINGHAUS (J. Phys. Radium, 1930, [vii], **1**, 11—36).—When petrol or similar oil is passed through an earthed metal tube and collected in an insulated metal vessel connected with an electroscope a considerable negative charge is observed. When a thick film of oil is subjected to a field of about 110 volts there is at first slight conductivity, which gradually disappears; as the thickness of the film diminishes a " semi-conducting " stage is reached in which a large current may pass, the period of such passage increasing with diminution of thickness, until for thicknesses of the order of 10 μ conductivity of metallic order is exhibited, with no visible action on the oil. This explains the use of lubricants to improve sliding contacts and in certain other cases (cf. Watson and Menon, B., 1929, 361). These results are explained as contact phenomena affected by the presence of water.

C. A. SILBERRAD.

Magnetic susceptibility of oxygen as a function of temperature and density. H. R. WOLTJER, C. W. COPPOOLSE, and E. C. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1329—1333).— The formula of Onnes expressing the dependence of magnetic susceptibility (χ) of a paramagnetic substance on the temperature (T), $\chi(T+\Delta)=$const., where Δ is a function of the density, is tested on gaseous oxygen. Deviations from Curie's law are noted, and these cannot be reconciled with Onnes' formula. The deviations become very marked below 175° Abs. Above this they are within the experimental error. There appears to be no systematic difference for the different densities as given by Onnes' formula. If the small deviations from Curie's law between 291° and 175° Abs. are neglected the formula $\chi T=$const. holds, the constant being dependent on density. This implies an atomic volume of oxygen dependent on density.

A. J. MEE.

Anomalous specific heats of solid hydrogen at helium temperatures. F. SIMON, K. MENDELSSOHN, and M. RUHEMANN (Naturwiss., 1930, **18**, 34).—The molecular heat of hydrogen in the region 11—14° Abs. agrees well with a Debye function of characteristic temperature $\phi=91$. If, however, a 50% mixture of ortho- and para-hydrogen is studied at still lower temperatures a marked divergence from the Debye curve becomes increasingly noticeable as the temperature falls. The figures in parentheses denote the number of times the Debye function is exceeded : 10° (1·05), 8° (1·4), 6° (2·7), 5° (4·4), 4° (9), 3° (25). At 3° the anomaly for a 50% mixture attains an absolute value of 0·4 g.-cal./degree. Pure parahydrogen agrees closely with the Debye function $\phi=91$ down to the lowest temperatures, whilst a 75% (ortho-hydrogen) mixture exhibited a much greater anomaly than the 50% mixture. Hence it is likely that a splitting of the ortho-term is responsible for the anomaly.

R. A. MORTON.

Specific heat of nickel. (MME.) E. LAPP (Ann. Physique, 1929, [x], **12**, 442—521).—With the view of investigating reported anomalies in the specific heat of ferromagnetic substances, the specific heat of pure nickel was measured with high precision between —175° and 460°, using an electrical heating method. The specific heat curve shows a region of quantum degeneracy, a rise towards the Curie point, a discontinuity in the region 353·5—360° greater than previously observed, and a paramagnetic region of slowly rising specific heat. The Curie point and the discontinuity are in agreement with the magnetic Curie point and the calculations based on the Weiss molecular field theory. The terms having a known effect on the specific heat (the quantum, expansion, and magnetic terms) were calculated, and the magnetic unknown term was deduced. The latter rises to a constant value at the Curie point, corresponding with the active force of one degree of freedom.

N. M. BLIGH.

Temperature variation of the specific heats of hydrogen and nitrogen. J. H. BRINKWORTH (Proc. Roy. Soc., 1930, **A**, **126**, 204—212).—A new empirical formula is advanced, in which it is proposed to represent the rapidly varying part (quantised) of the specific heat of a gas, S_Q, by a single frequency of the Planck–Einstein expression $S_Q=Rx^2e^x(e^x-1)^2$, but with $x=\beta\nu/(T-X)$, X being a temperature, instead of the usual $x=\beta\nu/T$. The total specific heat at constant volume of any diatomic gas at any temperature is therefore $S_v=3R/2+S_Q+$ (thermodynamic correction)+(term representing increase in specific heat at high temperatures). In the case of hydrogen, where the thermodynamic correction may be neglected, the formula gives excellent agreement with the author's experimental values below 600° (cf. A., 1925, ii, 373). An extension to the case of nitrogen shows that S_v attains the classical value, 4·96, at 50°, but below this temperature S_v decreases rapidly owing to the very high value of the thermodynamical correction. Values are deduced for the moments of inertia of hydrogen and nitrogen which are in good agreement with those deduced from band spectra data.

L. L. BIRCUMSHAW.

Flow method for comparing the specific heats of gases. I. Experimental method. P. M. S. BLACKETT, P. S. H. HENRY, and E. K. RIDEAL. **II. Theory of the method.** P. M. S. BLACKETT and P. S. H. HENRY (Proc. Roy. Soc., 1930, **A**, **126**, 319—332, 333—354).—I. A description is given of a simple method for the direct comparison of the specific heats of gases at constant pressure. The method consists essentially in passing a slow stream (<30 c.c. per minute) of gas through a narrow iron tube along which a temperature gradient has been established. The change of the temperature distribution along the tube depends on the properties of the gas and the rate of flow. A particular form of the method, which yields highly accurate results, consists in keeping the two ends of a narrow tube at the same temperature and heating the central portion by means of an electric current. Thermo-junctions are attached to the tube at two positions symmetrical about the centre of the tube, so that the junctions are initially at the same temperature. On passing a gas at a known slow speed through the tube a temperature difference between the two junctions is established, and this is shown to be

related to the flow speed by a cubic equation of the form $\Theta = C_1\alpha + C_3\alpha^3$, where C_1 is a constant for the tube, C_3 is a constant depending also on the conductivity and other properties of the gas, and $\alpha = Q/2KA$, Q is the heat capacity of the gas passing per sec., K the thermal conductivity of the tube material, and A its area of cross-section. The relative values of the specific heats for carbon dioxide, hydrogen, air, and helium determined by this method with different central temperature differences are tabulated. The mean values $C_p(CO_2)/C_p(air) = 1\cdot264$, $C_p(H_2)/C_p(air) = 0\cdot986$, and $C_p(He)/C_p(air) = 0\cdot717$ at $20°$ are in good agreement with the most trustworthy values hitherto obtained, and serve to establish the practicability of the method.

II. A theory is given of the heat transfer between a tube, along which there is a temperature distribution, and a gas flowing in it, and this theory is applied to the particular form of apparatus (a symmetrically heated tube) described above. The validity of the equation $\Theta = C_1\alpha + C_3\alpha^3$ is proved, and the coefficients C_1 and C_3 are evaluated and found to be in excellent agreement with the experimental values given in Part I. It is shown that the rise in temperature of the centre of the tube should be proportional to the electrical energy dissipated in the tube, and also that the sensitivity (*i.e.*, the temperature change Θ for a given flow) should be proportional to the central temperature. These conclusions are supported by the experimental results. L. L. BIRCUMSHAW.

Kinetic theory of heat conduction in crystals. R. PEIERLS (Ann. Physik, 1929, [v], **3**, 1055—1101).— The mechanism of heat conductivity in the crystal lattice has been studied. The condition for finite conductivity is identical with the condition for an H-theorem. The effect of temperature has been considered from the theoretical point of view. R. A. MORTON.

Ebullioscopic paradox. A. BERTHOUD, E. BRINER, and A. SCHIDLOF (J. Chim. phys., 1929, **26**, 505).—A reply to Verschaffelt (A., 1929, 1136). C. A. SILBERRAD.

Analytical expression of van 't Hoff's rule. A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, **1**, 138—141).— A mathematical expression, of which that obtained by Carneiro is a special case, is derived for van 't Hoff's rule. H. F. GILLBE.

Critical point of water. J. HAVLÍČEK (Engineering, 1930, **129**, 1—3).—A theoretical discussion of the gas equation with special reference to the observations of Callendar (A., 1928, 1179). C. W. GIBBY.

Equation of state of an ionised gas. W. H. McCREA (Proc. Camb. Phil. Soc., 1930, **26**, 107—114). —Theoretical. The pressure is investigated in a gas of given temperature, in which the numbers of atoms per unit volume at the different stages of ionisation are supposed to be known. The validity of treating an atom or ion consisting of several particles with large relative motions as a single particle is examined in computing its contribution to the dynamical pressure. The dynamical correction for free charged particles is calculated, and found to be of the same order of magnitude as the additional electrostatic correction, but of opposite sign; it is evaluated independently

for iron when retaining only two K electrons as $3\cdot1\%$, and appears to reduce the electrostatic correction by about one half. It is concluded that the deviations from perfect gas laws in stellar material may be too small to give observable effects. N. M. BLIGH.

Vapour-pressure curve of liquid helium. II. W. H. KEESOM, S. WEBER, and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1314—1323; cf. this vol., 145).—The results previously obtained are extended for lower pressures. The lowest pressure reached was $0\cdot005$ cm. The correction for thermomolecular pressure difference becomes important, especially in the helium thermometers which were used in which the pressure becomes very small. The size of the effect is known with sufficient accuracy to be used. The method of correcting is indicated. Two empirical formulæ are derived connecting the vapour pressure with the temperature, one for temperatures above $2\cdot19°$ Abs., and the other for temperatures below this. The change of behaviour of helium at this temperature has still to be investigated. A. J. MEE.

Vapour pressure of toluene up to the critical temperature. N. W. KRASE and J. B. GOODMAN (Ind. Eng. Chem., 1930, **22**, 13).—Determinations of the vapour pressure of toluene have been made by a static method from $0°$ to $320\cdot6°$ (the critical temperature). The critical pressure was found to be $41\cdot6$ atm. H. INGLESON.

Vapour density of sodium. W. H. RODEBUSH (Nature, 1930, **125**, 130).—A redetermination of the vapour pressure and vapour density of sodium agrees with an apparent mol. wt. of 25 for the saturated vapour at $706°$. This yields a calculated value of $0\cdot75$ volt, approximately, for the heat of dissociation. L. S. THEOBALD.

Heat of dissociation of the molecule O_4 and Sutherland's constant for oxygen. S. BRESSLER and V. KONDRATJEV (Nature, 1930, **125**, 164—165).— Theoretical. It is shown that the mutual energy of two molecules at the moment of collision is equal to Sutherland's constant. This receives support from the fact that the values of this constant obtained by various workers for oxygen are near to that obtained by Lewis for the molar heat of dissociation of O_4 into $2O_2$. L. S. THEOBALD.

Compressibilities of gases at $0°$ and below 1 atm., and their divergence from Avogadro's law. IV. Carbon monoxide and nitrogen. T. BATUECAS, C. SCHLATTER, and G. MAVERICK (J. Chim. phys., 1929, **26**, 548—555; cf. A., 1925, ii, 497).— The method is that previously described. The mean of 48 determinations for carbon monoxide gives $(1+\lambda) = 1\cdot00048$ and coefficient of compressibility at $0° = 6\cdot3\times10^{-6}$. For nitrogen 45 determinations give as means $(1+\lambda) = 1\cdot00045$ and compressibility $= 5\cdot9\times10^{-6}$. In both cases individual results show such divergence that the figures are regarded as only provisional. C. A. SILBERRAD.

Viscosity of vapours of organic compounds. I. T. TITANI (Bull. Chem. Soc. Japan, 1929, **4**, 277—287).—See A., 1929, 993.

Pressure of gaseous mixtures. III. C. C. TANNER and I. MASSON (Proc. Roy. Soc., 1930, **A**,

126, 248—288).—Previous measurements with helium and hydrogen (Gibby, Tanner, and Masson, A., 1929, 253) are now extended to mixtures of each of these gases with argon. Argon deviates from Boyle's law over the range 25—75° as far in the negative sense as hydrogen and helium do in the positive sense; at 100° it almost follows Boyle's law, and at higher temperatures its deviations become positive. Compressions were made on the three pure gases and 13 binary mixtures of them at temperatures from 25° to 175° and pressures from 30 to 125 atm. As a result of further improvements in the technique, the average deviation of the experimental values of pv from smooth isotherms is now only about 0·02%. The equation $pv = a + bp + cp^2$ is applied to the isotherms of each gas and mixture, and tables are drawn up showing the effect of varying composition and temperatures on the values of a, b, c, and Δ, where Δ is the mean experimental deviation in pv for each isotherm. By plotting b against gas composition it is found that, as with helium–hydrogen mixtures (loc. cit.), Lennard-Jones' partial pressure law (A., 1927, 727) also holds for argon–helium and argon–hydrogen mixtures, and the assumption that the intermolecular fields of force are spherically symmetrical about each molecule appears to be justified. The data for the influence of temperatures on the constants of the isotherms are applied to Lennard-Jones' equations for intermolecular action (loc. cit.). Taking the distance index for the attractive component as —5, the index for the repulsive component is found to be —10 or —11 for pure hydrogen and helium, and —9, —10, —11, or —14½ for pure argon. The force constants are evaluated for each type of encounter according to the different models. Values are also calculated for the " cohesion energy " (a quantity equivalent to the latent heat of separation of a pair of molecules at 0° Abs.), and for the kinetic diameters at various temperatures. The results indicate that the radius of a given gaseous molecule in collision is a function, not only of the kinetic energy of the invading molecule, but also of the nature of this molecule; the argon atom is smaller when it stops another argon atom than when it stops a hydrogen molecule, and in stopping a helium atom is probably larger than when it stops a hydrogen molecule. The special result found with helium and hydrogen is therefore not typical. It is shown that it is not possible to predict the isotherms of mixtures from those of their pure components alone. L. L. BIRCUMSHAW.

Viscosity, heat conductivity, and diffusion in gas mixtures. VII. Relationships with homogeneous gas reactions. M. TRAUTZ (Ann. Physik, 1929, [v], **3**, 1102—1118).—Theoretical. Formal substitutions are made which involve implications which are not self-evident in the physical sense but are capable of experimental test. An expression which may be substituted for the ordinary molecular diameter is suggested; this is less influenced by the special characteristics of models. R. A. MORTON.

Viscosity formula for binary mixtures, taking into consideration association effects. IV. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, **4**, 288—297; cf. A., 1929, 500, 994).—The author's formula is applied to the systems toluene–benzyl benzoate, benzene–benzyl benzoate, benzene–guaiacol, toluene–guaiacol, ethyl alcohol–ether, n-propyl alcohol–ether, chlorobenzene–phenol, and benzene–phenol. Very good agreement exists between the association values obtained experimentally and those calculated from the formula. F. G. TRYHORN.

Viscosity isotherms of binary mixtures. IV. System benzaldehyde–sulphur monochloride. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], **10**, 250—253; cf. this vol., 26).—Viscosity curves for this system at 3°, 9°, 13·2°, and 20° are given. Below 20° mixtures of the two components show a maximum viscosity. The maximum deviation from the value calculated from the mixture rule corresponds with 60% of benzaldehyde, which indicates that the compound $2Ph·CHO,S_2Cl_2$ may be formed in solution.
O. J. WALKER.

Viscosity isotherms of binary mixtures. V. Nitrobenzene–stannic bromide. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], **10**, 372—375; cf. preceding abstract).—Although the thermal diagram for this system is of the simplest type, with a eutectic mixture containing about 53% of stannic bromide, the viscosity isotherms at 32° and 40° suggest the formation of a compound, probably $2PhNO_2,SnBr_4$, which is stable in the liquid state.
F. G. TRYHORN.

X-Ray analysis of system nickel–bismuth. G. HÄGG and G. FUNKE (Z. physikal. Chem., 1930, **B, 6**, 272—283; cf. Voss, A., 1908, ii, 194).—X-Ray and microscopical examination have revealed the existence of two intermediate phases. The β-phase, with 40—50 at.-% Bi, has the nickel arsenide structure, and is composed of an equal number of nickel and bismuth atoms, the excess nickel atoms being distributed in the interspaces. The γ-phase has approximately the composition $NiBi_3$. Its structure could not be determined on account of the complexity of the powder diagram and failure to obtain single crystals. F. L. USHER.

Germanium. XXXII. Alloys of germanium. System lead–germanium. T. R. BRIGGS and W. S. BENEDICT (J. Physical Chem., 1930, **34**, 173—177; cf. A., 1929, 996).—The equilibrium diagram for the system lead–germanium has been determined from thermal data obtained by methods previously described (loc. cit.). Germanium and lead are probably completely miscible as liquids, but form no solid solutions. Cooling the liquid alloys results in the complete separation of the germanium before the lead, and the usual type of eutectic is absent. Photomicrographs (not reproduced) show characteristic crystals of germanium embedded in a matrix of lead. Germanium falls between silicon and tin in its behaviour towards lead, miscibility increasing in the order silicon<germanium<tin; the systems lead–germanium and tin–silicon are similar.
L. S. THEOBALD.

Ternary silver alloys. I. The system silver, copper, zinc. S. UENO (Mem. Coll. Sci. Kyoto, 1929, **12**, 347—374).—The system has been examined thermally and microscopically. No three-phase region was found, but the β-solid solution of the

copper–zinc system unites with the β of the silver–zinc system, and the ε of the copper–zinc system with the ε of the silver–zinc system. This results in two wide homogeneous fields and three heterogeneous fields within the triangular base of the diagram.

W. E. DOWNEY.

Ternary system of Cu–Sn–Sb. M. TASAKI (Mem. Coll. Sci. Kyoto, 1929, **12**, 227—256).—Copper–tin alloys with 60—80% Cu and tin–antimony alloys with 40—60% Sb have been examined. In the ternary equilibrium the γ and δ eutectoids of the Cu–Sn system form ternary mixed crystals with the γ and δ eutectoids of the Cu–Sb system. The ε eutectoid of Cu–Sn gives in the ternary system a compound $Cu_{12}Sb_3Sn_7$. The equilibrium diagram is used in discussing the white metal bearing alloys.

W. E. DOWNEY.

Dependence of some optical properties on temperature in the softening interval of glasses. G. TAMMANN and H. HARTMANN (Z. anorg. Chem., 1930, **185**, 305—323).—Refractive indices of the following substances have been determined at different temperatures above and below the softening temperature : salicin, brucine, sucrose, colophony, and mastic. For the first three substances the refractive index changes linearly with temperature in both the viscous and the vitreous state, and the two straight lines meet at a temperature 2—3·5° higher than the temperature at which brittleness begins. For colophony and mastic, which are mixtures, there is no sharply-defined point of intersection. The refractivities are also given for salicin, brucine, and colophony. For salicin, the refractivity increases with temperature from 5° to 80° by 0·4%, the increase being slightly greater in the liquid state than in the solid. The difference is much more marked in the case of brucine, but still small. The results indicate that molecular changes do not take place on melting. The refractivity of colophony increases in the vitreous state with rising temperature, but falls in the liquid state. The angle of rotation of the plane of polarisation and the specific rotation of colophony decrease linearly with temperature in the liquid state. In the solid state they rise with falling temperature, but the measurements are very difficult to make. For the angle of rotation of salicin there appears to be a maximum and a minimum in the neighbourhood of the temperature at which brittleness sets in, but the results cannot be repeated exactly. Anhydrous dextrose has a maximum angle of rotation at the temperature at which brittleness begins, but with 4% of water the angle of rotation increases linearly as the temperature falls to this point and then increases still more rapidly. The time required for the disappearance of the double refraction produced by distortion under a load has been determined for colophony and salicin at different temperatures. The time increases with falling temperature along a hyperbolic curve of which the asymptote lies near the temperature at which brittleness commences.

M. S. BURR.

B. p. of (ternary) water–alcohol mixtures. P. BRUN (Compt. rend., 1930, **190**, 122—124).—The b. p. of various ternary mixtures of water with ethyl and isoamyl alcohols have been determined with special precautions to ensure uniformity of pressure and homogeneity of imperfectly miscible mixtures. The results are shown by a trilinear graph, on which is also indicated the limit of miscibility at the b. p. The critical b. p. is 88·7—88·8°.

C. A. SILBERRAD.

Steam-distillation of lower volatile fatty acids from a saturated salt solution. W. H. OLMSTED, W. M. WHITAKER, and C. W. DUDEN (J. Biol. Chem., 1929, **85**, 109—114).—The rate of steam-distillation of the lower volatile fatty acids from aqueous solution is much increased by adding to every 100 c.c. of the solution 70 g. of magnesium sulphate and 2 c.c. of 50% sulphuric acid. Characteristic distillation rates are given.

C. R. HARINGTON.

Solubility determinations of U.S.P. chemicals. W. SCHNELLBACH and J. ROSIN (J. Amer. Pharm. Assoc., 1929, **18**, 1230—1235).—The data recorded refer to 25° and 100 parts of solvent. Sodium sulphate decahydrate in glycerol (d_4^{25} 1·246) 7·52 ; sodium nitrite (96·86%) in alcohol (d_4^{25} 0·808) 1·424 ; arsenic trioxide in water about 1·99, in glycerol about 15·88. The determination of sodium by the method of Barber and Kolthoff (A., 1928, 859) is discussed.

E. H. SHARPLES.

Optical detection of the solubility of mercury in water. K. F. BONHOEFFER and H. REICHARDT (Naturwiss., 1929, **17**, 933).—The solubility of mercury in water is demonstrated by the exhibition of ultra-violet absorption bands at approximately 2610, 2510, and 2270 Å. The solubility of the vapour is of the same order as that of an inert gas.

H. F. GILLBE.

Solubility of sulphur in certain saturated hydrocarbons, in the benzene series, and in chloro-substituted benzenes. I. S. TELETOV and N. D. PELICH (Ukrain. Chem. J., 1929, **4**, 387—402).—The solubility of sulphur in saturated paraffin hydrocarbons increases with the specific gravity of these. In any one hydrocarbon it is very low at 20° and increases gradually up to 60°, and rapidly at higher temperatures. In hydrocarbons of the benzene series, the solubility of sulphur is diminished by the introduction of methyl groups but increased by that of chlorine atoms. The benzene hydro-carbons and probably their chloro-derivatives are said to form definite compounds, the character of which is under investigation.

T. H. POPE.

Solubility of benzoquinhydrone in aqueous-alcohol mixtures. M. I. ALFEROV and A. I. BRODSKI (Ukrain. Chem. J., 1929, **4**, 403—404).—See A., 1929, 1302.

Stability of the submicron. II. Dissolution and formation of crystals. W. VON BEHREN and J. TRAUBE (Z. physikal. Chem., 1930, **146**, 1—29; cf. A., 1929, 259).—A continuation of work previously published. Photographs are given showing the ultramicroscopic appearance of various stages observed during the dissolution and formation of crystals. The results are discussed theoretically and shown to support Smekal's theory of "lattice blocks."

F. L. USHER.

Crystalline form in the formation of solid solutions. VI. Thermal and X-ray analyses of

the anhydrous systems $CaCl_2$–$CoCl_2$, $CaCl_2$–$FeCl_2$, $CaCl_2$–$MnCl_2$, and $CaCl_2$–$CdCl_2$. A. FERRARI and A. INGANNI (Atti R. Accad. Lincei, 1929, [vi], **10**, 253—258; cf. A., 1929, 996).—Cobaltous and ferrous chlorides form eutectic mixtures with calcium chloride; the eutectic points at 614° and 592° correspond with 54·3 and 44·5 mol.-% $CaCl_2$, respectively. Manganous and cadmium chlorides form mixed crystals in all proportions with calcium chloride; these decompose into their components at about 475° and 414°, respectively. The behaviour of these systems indicates that calcium chloride is structurally different from the bivalent chlorides of cobalt, iron, manganese, and cadmium. O. J. WALKER.

Fractional precipitation. IV. Influence of the formation of mixed crystals and adsorption compounds. O. RUFF and E. ASCHER (Z. anorg. Chem., 1930, **185**, 369—386).—Fractional precipitation of different pairs of salts, in which the crystal structure makes the formation of mixed crystals possible, has been studied with reference to the conditions necessary for equilibrium and the influence of the size and ratio of the solubility products. Immediately after formation the precipitate always contains more of the more soluble constituent than in the equilibrium state, which can often be reached only after stirring for several hours. The composition of the precipitate depends on the ratio of the concentrations of the constituents in solution. With continued stirring and rise in temperature the proportion of the more soluble constituent of the precipitate at first increases to a maximum and then decreases. When the solubility products are approximately equal, fractional precipitation is impossible, the precipitate always containing a large quantity of the more readily soluble component. This holds until the ratio of solubility products of approximately 10^{-4} is reached, e.g., in the system $PbCrO_4$–$BaCrO_4$. The facility of separation increases from this point as the difference between the solubility products increases. M. S. BURR.

Fractional precipitation. V. Inclusion of foreign matter in the crystal lattice. O. RUFF (Z. anorg. Chem., 1930, **185**, 387—402).—Inclusions in crystals during precipitation depend mainly on two factors : (1) the relation of the affinity between unlike to that between like molecules, (2) failure to attain equilibrium conditions. Electrokinetic phenomena are of minor importance. A small difference in affinity is associated with one or more of the following conditions : similar space relationships, a common ion, and similar solubility products. The following cases have been investigated experimentally : the inclusion of zinc sulphide by copper sulphide, manganese sulphide by zinc sulphide, and potassium permanganate by barium sulphate, and the separation of silver and copper iodides and also of calcium and magnesium oxalates. These phenomena can all be explained, and, at the same time, fractional separation of all these salt pairs can be obtained, by taking into consideration the above conditions. M. S. BURR.

Nature of pyrosols. A. MAGNUS and E. HEYMANN (Naturwiss., 1929, **17**, 931—932).—The partition equilibria of cadmium between bismuth and cadmium chloride at 600° and 700° have been determined, and indicate that the cadmium is in the same molecular state in the two phases. Since the solution in bismuth is monatomic, the pyrosol (metallic fog) formed by cadmium in cadmium chloride is caused by atomic dispersion of the metal. H. F. GILLBE.

Nature of " active carbon." H. H. LOWRY (J. Physical Chem., 1930, **34**, 63—73; cf. B., 1929, 929). —The adsorption of hydrogen, carbon dioxide, and air by charcoal prepared from an anthracite coal has been investigated. The activity of an adsorbent carbon is best defined by the amount of gas adsorbed per unit area and not per unit weight. The pore volume is considered to be a measure of the adsorbing surface. In this case the adsorptive capacity per unit pore volume decreases with a rise in the temperature (above 1000°) to which the material is heated. The data indicate that activity defined as above is independent of the atmosphere in which the charcoal is prepared, but is dependent on the maximum temperature to which it is subjected. At temperatures between 900° and 1300° an increase in adsorptive capacity is probably accompanied by a proportional increase in extent of adsorbing surface. In agreement with previous results on the relation between adsorptive capacity and hydrogen content (loc. cit.), the activity of the charcoal is now found to increase with hydrogen content up to a value of the latter of 0·5%, after which it remains approximately constant. The view that the simultaneous decrease in activity and hydrogen content above 1000° may be due to a gradual crystallisation of the carbon is discussed. L. S. THEOBALD.

Adsorption of air on glass as a function of temperature. A. S. ADAMS (Physical Rev., 1929, [ii], **34**, 1438—1439; cf. Frazer, A., 1929, 503, 1376). —With rise of temperature the thickness of the adsorbed layer decreases at a somewhat slower rate than for rock salt. An " ageing " effect is indicated. The adsorption may be due to some relatively rarer constituent of the atmosphere. N. M. BLIGH.

Adsorption by various silica gels from gaseous mixtures of air, alcohol, and ether. II. L. VON PUTNOKY and G. VON SZELÉNYI (Z. Elektrochem., 1930, **36**, 10—15).—Five different commercial silica gels and one produced by the hydrolysis of silicon tetrachloride were dried in a vacuum and activated by heating at 200°. Three series of adsorption experiments were made with alcohol and ether vapours at 20° under different vapour pressures in an apparatus described by Bachmann and Maier (A., 1928, 119). Curves are given to elucidate the sorption and desorption processes; these show the relationship between p/P (p vapour pressure above the gel, P the initial pressure) and x/m (x mass of vapour adsorbed, and m mass of adsorbent). H. T. S. BRITTON.

Adsorption by active charcoal. E. ENGEL (Z. ges. Schiess- u. Sprengstoffw., 1929, **24**, 495—497).— See A., 1929, 998.

Adsorption of a sodium chloride solution by sand. T. NOMITSU, R. KAMIMOTO, and Y. TOYOHARA (Mem. Coll. Sci. Kyoto, 1929, **12**, 265—274).—

The negative adsorption of five different specimens of sand for sodium chloride has been measured.
                                        W. E. DOWNEY.

Soap solutions. VII. Adsorption of soap on charcoal. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1929, **32**, 178—180B).—The adsorption from alcoholic solution of potassium laurate, myristate, palmitate, stearate, and oleate by charcoal has been investigated. For soaps of the same series Freundlich's adsorption isotherm is valid up to the concentration limit at which the formation of aggregates commences, and Traube's rule also is applicable. For binary mixtures of soaps the component derived from the higher acid is present in excess in the adsorbed layer.
                                        H. F. GILLBE.

Solubility and adsorbability of benzoic acid and salicylic acid in presence of mixed organic solvents. W. HERZ and M. LEVI (Kolloid-Z., 1930, **50**, 21—22).—Measurements of the adsorption of benzoic acid and salicylic acid by carbon from solutions in mixtures of benzene and heptane, heptane and carbon tetrachloride, and benzene and carbon tetrachloride show that solubility varies antibatically with adsorbability.
                                        E. S. HEDGES.

Adsorption processes in precipitates undergoing coagulation. I. Adsorption of lead, bismuth, and thallium on silver and mercurous halides. L. IMRE (Z. physikal. Chem., 1930, **146**, 41—62).—Silver and mercurous halides formed in presence of excess of the halogen ion have been used as adsorbents for lead, bismuth, or thallium, the amount adsorbed being determined by means of the γ-radiation from the radioactive indicators thorium-B, thorium-C, or thorium-C'', respectively. The silver halides are more effective adsorbents than the corresponding mercurous compounds. The values of the exponent $1/n$ in the Freundlich adsorption formula show a gradual drift both with increasing concentration of the solute and, for a given concentration, with time, the effect being most marked when the adsorbent sol is unstable. The observed drift is explicable on the assumption that, along with diminished adsorbing power resulting from the partial neutralisation of the surface charge, molecules of solute become imprisoned in the interstices of the coagulating particles and are thus less easily reached by the external liquid. Adsorption appears to be strictly reversible only in the initial stages and at the surface of particles not undergoing coagulation.
                                        F. L. USHER.

Behaviour of adsorbed electrolytes in direct- or alternating-current electrolysis. S. L. BHATNIA (Kolloid-Z., 1930, **50**, 55—58).—Oxalic acid which has been adsorbed by aluminium hydroxide or silicic acid is obtained therefrom when the adsorbent is placed in water and a direct current is passed. By this process, about 80% of copper sulphate and about 50% of nickel sulphate adsorbed by animal charcoal can be reclaimed. An alternating current obtained from the secondary of an induction coil is not effective in this respect.
                                        E. S. HEDGES.

Surface tension in a vacuum. S. RAY (Kolloid-Z., 1930, **50**, 19—21).—When a flask containing water in which a glass capillary stands is evacuated through a sulphuric acid wash-bottle, the height of the water in the capillary falls. This behaviour is discussed in relation to the author's colloid-chemical theory of surface tension (A., 1928, 702). After the fall of the water column, the inside wall of the capillary was marked by parallel ridges of water, giving the effect of an etched thermometer tube—a phenomenon which is considered to be connected with the Liesegang phenomenon.
                                        E. S. HEDGES.

Surface tension and heat of vaporisation. J. J. VAN LAAR (Z. anorg. Chem., 1930, **185**, 425—427).—Polemical against Herz (A., 1929, 1001).
                                        M. S. BURR.

Surface solutions on mercury. Oleic acid. F. EMIR (Compt. rend., 1930, **190**, 176—178).—Surface solutions of oleic acid on mercury and on water are analogous in behaviour. The former have a surface tension corresponding with saturation of 60 dynes/cm. (approximately double that for water), whilst the thickness of the film is 24 Å. (23 Å. for water). There is therefore evidence that the molecular orientation is the same in both cases. Elaborate attempts to eliminate oxidation of the mercury surface were not completely successful.
                                        J. GRANT.

Surface tension of protein solutions. L. DE CARO and M. LAPORTA (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], **35**, 171).—Dilute solutions of serum- and egg-albumins show a minimum surface tension, whether determined by static or dynamic methods, at the isoelectric point. When the concentration of serum-albumin is greatly reduced a unimolecular surface layer is formed, and the surface tension determined by static methods is again minimal at the isoelectric point. This minimum is the result of the increased power of the individual molecules to reduce surface tension when they are undissociated, in accordance with the conclusions of Bottazzi (A., 1929, 642).
                                        R. K. CALLOW.

Effect of addition of proteins on the surface tension of a solution containing surface-active acid or base. R. SUGINO (J. Biochem. Japan, 1929, **11**, 31—45).—In the p_H region where the added protein exists as an anion the surface tension of a solution of amylamine is affected owing to combination. The isoelectric point of protamine is at p_H 11.
                                        CHEMICAL ABSTRACTS.

Double refraction in cellulose acetate and nitrate films. J. G. MCNALLY and S. E. SHEPPARD (J. Physical Chem., 1930, **34**, 165—172).—An instrument suitable for determining the direction of orientation of micelles in transparent colloidal films is described. Uniaxial, biaxial, or isotropic films can be prepared from a given sample of cellulose acetate or nitrate by varying the tension on the film during drying. Films made by pouring a 2% solution of the ester on to a clean surface of mercury and allowing it to dry slowly were completely isotropic.
                                        L. S. THEOBALD.

Dynamics of amalgamation. C. E. GUYE and (MLLE.) I. ARCHINARD (Arch. Sci. Phys. Nat., 1929, [v], **11**, 312—344).—Measurements have been made of the rate of creep of mercury along wires of silver, copper-gilt, and brass-gilt, and of the rate of spread of mercury drops on copper-gilt plates. Experiments

with silver wire showed a lack of concordance attributable to surface oxidation, which was in some degree improved by making the measurements under petrol. In these latter experiments and in those with gilt wires, the progress of the amalgamation, except in the initial stages, may be satisfactorily represented by means of an equation proposed by Guye (*ibid.*, 1925, **7**, 39) for the rate of ascent of the sap in plants. The rate of ascent of the mercury is accelerated by rise of temperature, which affects both viscosity and the capillary constant of the system. The process of amalgamation is considered to consist in the replacement of the interface air–gold by the interface air–amalgamated gold with the liberation of free energy. The creep of the mercury results from the excess of the energies of amalgamation and of wetting over the work which must be done against gravity and viscosity forces. The rate of spread of a drop of mercury on a gilt plate is proportional to the initial dimensions of the drop provided this is not very small. The process of spreading is analogous to, although not wholly comparable with, that of the ascent of mercury up a wire. After the drop has made contact with the gold it assumes a hemispherical shape and spreading takes place radially from the circumference.

F. G. Tryhorn.

Membrane and osmosis. II. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1024—1031).—The behaviour of ternary liquid mixtures in contact with a membrane is considered. H. F. Gillbe.

Membrane and osmosis. IV. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1305—1313).—Mathematical.

A. J. Mee.

Collodion membranes. IV. Permeability of the membranes to water. E. Mangold and R. Hofmann (Kolloid-Z., 1930, **50**, 22—29; cf. this vol., 154).—A new apparatus for the preparation of collodion membranes having reproducible properties is described. An account is given of the characterisation of the prepared membranes by their thickness, water content, and permeability to water, and of the determination of the size of the pores. The relation previously given, that the product of the permeability to water and the membrane thickness is constant, has been confirmed, and it is found that if this product is multiplied by the viscosity a new constant is obtained which is independent of the temperature and of the nature of the liquid. This constant is termed the specific permeability and is regarded as a constant and characteristic membrane value. The specific permeability may vary as the result of structural changes in the membrane, such as changes in the structure, size, and arrangement of the pores. The specific permeability decreases with the duration of the filtration and this effect has been traced to compression of the capillary structure, and to the substance in suspension stopping up the pores and forming a layer over the membrane surface. Over the range 10—20° no temperature influence on the capillary structure is observed. E. S. Hedges.

Abnormal osmosis at non-swelling membranes. I. K. Söllner (Z. Elektrochem., 1930,

36, 36—47).—The magnitude of the *P.D.* between two solutions of electrolytes separated by a collodion membrane has been found to depend on the previous treatment of the collodion, whereby the size of the pores is affected. Such membranes contain fine pores of widely differing dimensions, thereby causing potentials to be set up which differ from place to place and from pore to pore and in consequence tend to establish closed current circuits within and around the membrane. H. T. S. Britton.

Application of the Donnan effect to nucleic acid compounds. E. Hammarsten (Acta Med. Scand., 1928, **68**, 10 pp.; Chem. Zentr., 1929, ii, 756—757).—Solutions of thymonucleic acid containing hydrogen chloride and sodium chloride were treated with varying amounts of a solution of crystallised egg-albumin and dialysed; the p_H and osmotic pressure are of the same order of magnitude in almost all cases. The means whereby carbon dioxide can produce in the cell nucleus a higher hydrogen-ion concentration than is generally supposed is discussed. The nucleic acid in the cell nucleus has a very small velocity of diffusion. A. A. Eldridge.

Imbibition of some natural colloidal complexes. Cellular exchange. L. Emerique (Ann. Physiol. Physicochim. biol., 1928, 251—296; Chem. Zentr., 1929, ii, 435—436).—The degree of imbibition and change in weight occurring when hen's egg-white or the mucin of frog's eggs is immersed in solutions of sodium, potassium, or calcium chloride was followed. Addition of a non-electrolyte has an effect other than that anticipated according to the osmotic pressure. Imbibition experiments with pig's bladder in sodium chloride solutions in presence of bile acids show that the surface tension is not the only controlling factor.

A. A. Eldridge.

Partition of light between two dissolved absorbents. K. Weber (Z. Elektrochem., 1930, **36**, 26—36).—The absorption constants for $\lambda = 366$ μμ of solutions of æsculin in aqueous alcohol (40% alcohol), quinine sulphate in *N*-sulphuric acid, sodium naphthionate in water, amyl nitrite in aqueous alcohol (40—90% alcohol), sodium nitrite in water, and potassium chromate, have been measured with Plotnikov's fluorometer; for these solutions Beer's law has been found to be obeyed. The variations in the amounts of fluorescence produced in the systems æsculin–amyl nitrite, quinine sulphate–amyl nitrite, sodium naphthionate–sodium nitrite, sodium naphthionate–potassium chromate were also investigated. In some cases fluorescence was entirely suppressed. An exponential formula is derived for the partition phenomena.

H. T. S. Britton.

Absorption of cobalt salts in concentrated solutions. P. Vaillant (Compt. rend., 1930, **190**, 170—172).—By adjusting the thickness (*l*) of the solution measured so that the quantity $nl\beta$ had a maximum value, *n* being the concentration and β the molecular absorption coefficient for a given wavelength (5000—6000 Å.), it is found that the spectral curves obtained for solutions of cobalt chloride (2*N*), sulphate (0·5*N*), and nitrate (2*N*) in water, and for 0·2*N*-cobalt nitrate in concentrated zinc chloride and

sulphate solutions, are superposable. Change of anion, concentration, or solvent therefore modifies the absorption spectrum only by a Kundt displacement and a change in intensity, a conclusion which may be interpreted in terms of the theory of activity if it is assumed that the absorption of the Co'' ion increases when its activity decreases (cf. this vol., 10).

J. GRANT.

Sedimentation of clay suspensions. A. BOU-TARIC and (MLLE.) M. ROY (Compt. rend., 1930, **190**, 272—275).—The rate of sedimentation of kaolin may be followed from the rate of fall (dx/dt) of the surface separating the upper limpid layer and the lower layer of the suspension, and is given by $dx/dt = A/[1 + Bc/(l-x)]$, where l is the initial height, x the height after the time t, and c the concentration. The initial rate of fall (v) varies with c according to the function $v = 1/(\alpha + c)$ whatever the diameter of the containing vessel, and decreases with time. Experiments with acid solutions rendered strictly comparable by control of the p_H values showed that small quantities of camphor, menthol, or isoamyl alcohol do not accelerate the rate of sedimentation, but if anything, slightly retard it. Dubrisay's results (A., 1929, 877) were confirmed.

J. GRANT.

Absorption capacity of some substances for light of various wave-lengths as a function of the particle size. G. P. VORONKOV and G. I. POKROV-SKI (Kolloid-Z., 1930, **50**, 17—19).—The change in light absorption with diminution in the size of the particles (cf. A., 1927, 1138) is discussed theoretically and measurements of the light absorption and size of particles in suspensions of mercuric sulphide and ultramarine in water have been made. With progressive decrease in the particle size Rayleigh's law of absorption is followed more closely, and a marked change in the colour of the suspension occurs when the effective radius of the particles becomes smaller than the wave-length of light.

E. S. HEDGES.

From atom to structure. V. KOHLSCHÜTTER (Kolloid-Z., 1930, **50**, 1—12).—A lecture on the structures produced by chemical growth, such as lead "trees," "hair" silver, silicate growths, etc., particularly in relation to the simulation of living structures. These forms of growth are conditioned mainly by topochemical processes, or the localisation of chemical change, and are in many cases characteristic of the substance.

E. S. HEDGES.

Comparison of silver and lead sols made by the Bredig method. H. Q. WOODARD (J. Physical Chem., 1930, **34**, 138—144).—Silver and lead sols prepared as described for lead (A., 1928, 948) are alike in rising to a maximum concentration during arcing after which silver sols are completely precipitated with further arcing; those of lead decrease with prolonged arcing. In the case of silver, sol formation is determined mainly by the anion present in the arcing solution. No sols could be obtained in solutions of silver or ammonium nitrates, and only transient and dilute sols in solutions of sodium nitrate or acetate, but concentrated and stable sols could be made in solutions of sodium carbonate or potassium hydroxide. Dilute and stable sols resulted in hydrochloric acid, sodium or ammonium chloride, and sodium thiocyanate or sulphide. In the case of lead, the cation chiefly determines the sol formation.

L. S. THEOBALD.

Molybdenum-blue. J. DUCLAUX and R. TITÉICA (Rev. gén. Colloid., 1929, **7**, 289—294).—Molybdenum-blue has a variable chemical composition and its colloid-chemical properties depend on the method of preparation. It may be obtained by chemical or photochemical reduction of molybdic acid by a variety of methods. Molybdenum-blue is considered to be a strong acid, comparable in strength with mineral acids, the colloidal anion of which contains molybdenum in two states of oxidation and is capable of union with metallic ions to form salts. Molybdenum-blue is peculiar in its solubility in a large number of organic solvents, whilst it is insoluble in all liquids of low dielectric constant. When certain organic solvents are shaken with an aqueous solution of molybdenum-blue, the aqueous solution is almost immediately decolorised, the molybdenum compound passing into the organic liquid phase. This is the first example recorded of a colloid passing from one solvent into another; glycerol appears to be the best solvent. The solubility in butyl alcohol provides a rapid means of purifying molybdenum-blue by extraction of the aqueous solution. E. S. HEDGES.

Influence of autoclave treatment on the form of hydroxides and on the nature of colloidal suspension. T. KATSURAI (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1929, **12**, 161—166).—When gelatinous ferric hydroxide is heated with a slight excess of alkali under a pressure of 5—10 atm., a finely powdered form similar to rouge is obtained. The hydroxides of magnesium, aluminium, chromium, and cobalt, prepared by adding a slight excess of either sodium hydroxide or ammonia to salts of these metals, suffered no change under this treatment. Sols of zinc potassium ferrocyanide and of copper ferrocyanide were completely coagulated when heated in an autoclave, and sols of Prussian-blue and of Turnbull's blue deposited rouge: this same deposit was obtained when solutions of potassium ferrocyanide or ferricyanide were treated in this way. An arsenious sulphide sol was not coagulated, but sols of silver halides were coagulated when heated under a pressure of 10 atm. E. S. HEDGES.

Hydrogels. IX. Lead dioxide hydrate. A. SIMON (Z. anorg. Chem., 1930, **185**, 280—299).—Hydrated lead dioxide has been prepared by four different methods : (1) Electrolysis of sodium lead tartrate giving $PbO_2,1\cdot24H_2O$. (2) Hydrolysis of sodium plumbate; three samples contained $0\cdot32$, $0\cdot36$, and $0\cdot44$ H_2O, respectively. (3) Decomposition of sodium plumbate by liquid hydrogen cyanide; three samples contained $0\cdot84$, $0\cdot88$, and $0\cdot82$ H_2O, respectively. (4) Heating sodium plumbate with water under pressure; all samples obtained in this way contained less than $0\cdot3H_2O$ for $1PbO_2$. Isobaric decomposition curves have been obtained from the products of 1, 2, and 3 by a method previously described (cf. A., 1927, 730). At 76° all the samples reached approximately the same composition, $PbO_2,0\cdot3H_2O$. The general form of the curves is that of other colloidal metal oxide hydrates. The

relationship between the vapour pressure of the hydrate and its water content follows the same logarithmic law as observed for other oxide hydrates (A., 1927, 510), i.e., $\log_e p_0/p = kn$, k in this case having a value 1 below 120°. Above this temperature, however, the value falls rapidly, due to the fact that ageing proceeds at a greater rate and the osmotic system splits up into free water and lead dioxide, causing a rise in the vapour pressure, p. The heat of formation of the system lead dioxide–water, calculated from the pressure–concentration diagram, is 19,500 g.-cal., whilst the value for $k=1$ is 20,500 g.-cal. When examined under a polarisation microscope, the colour varied from chocolate or yellowish-brown to black, but there was no crystalline structure or double refraction. Sols were easily prepared in water, alcohol, or ether. Brownian movement was observed in these by the ultramicroscope, the size of the particle varying with the method of preparation of the original oxide. The products obtained by the pressure method (4) did not form sols and were coarsely crystalline. X-Ray diagrams of the products of method 3 were obtained by the Debye method. All the lines obtained were identical with those of crystalline lead dioxide. In all the samples obtained ageing was rapid and consisted in the loss of water, as in the case of other oxides studied. The rate varied with the method of preparation and the final condition was the crystalline anhydrous dioxide. M. S. BURR.

Formation of lyophobic organosols. H. B. WEISER and G. L. MACK (J. Physical Chem., 1930, 34, 86—100).—The methods of formation of organosols stabilised by preferential adsorption of ions have been classified. Details are given of new and improved methods for the preparation of sols of mercuric sulphide in methyl alcohol, acetone, and n-propyl alcohol, of ferric oxide, copper ferrocyanide, zinc ferrocyanide, and Prussian-blue in methyl alcohol, and of ferric, manganic, and chromic oxides in n-propyl alcohol. L. S. THEOBALD.

Refractive indices of hydrosols. II. B. V. DUMANSKI and B. J. PUTSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1301—1307).—See A., 1929, 1142. The formula should read $n = c_1(n_2 - n_1)/d_2 + n_1$.

Viscosity of emulsions. I. J. O. SIBREE (Trans. Faraday Soc., 1930, 26, 26—36).—Using the concentric cylinder viscosimeter, measurements have been made of the viscosities of emulsions of paraffins in sodium oleate solution, bromoform being added to the paraffin in order to obtain an oil of the same density as the oleate solution. The viscosity of such solutions is not constant, but decreases with increasing velocity gradient, becoming nearly constant when the latter reaches a certain value. The viscosity of an emulsion does not depend directly on the viscosity of the disperse phase; thus with disperse phases for which the viscosities in the pure state are in the ratio 38 : 1, the emulsions have viscosities only in the ratio 1·4 : 1 in the constant region ; at very low velocity gradients the viscosities appear to be identical. Difficulty was experienced in testing the validity of Hatschek's equation $\eta_e/\eta_0 = 1/(1 - \sqrt[3]{\phi})$ (A., 1911, ii, 98) owing to the uncertainty of the effect of adsorbed

films on the size of the drops and hence on the apparent concentration of the disperse phase. J. W. SMITH.

Kinetics of formation of colloids. K. JABŁCZYŃSKI and S. KOBRYNER (Rocz. Chem., 1929, 9, 704—722).—The rate of reduction of selenious acid to selenium by hydrazine is found by spectrophotometric measurements to be a linear function of the time; the reduction of gold chloride by white phosphorus follows a similar course; the temperature coefficients are respectively 1·96 and 2·05. The velocity–time curve for the reduction of an ammoniacal solution of silver hydroxide by hydrazine is of the autocatalytic type; the temperature coefficient is 1·85 between 20° and 30° and 1·68 between 30° and 40°. R. TRUSZKOWSKI.

Constitution of colloidal solutions by pectography. P. BARY and J. V. RUBIO (Rev. gén. Colloid., 1929, 7, 308—318).—Further experiments on the production of pectographs of metallic sulphides (cf. A., 1929, 136) by slow evaporation of aqueous colloidal solutions are described. In addition to the periodic formations previously noted, it has been observed that the pectograph is frequently broken by cracks which appear in a characteristic form. These cracks are either vertical or horizontal, or curved in an ellipsoidal form. The pattern is generally horizontal when obtained by the evaporation of dilute solutions and is vertical for solutions above a certain concentration. A relation has been found between the intensity of the Tyndall effect and the complexity of the pectograph. Sols showing little or no Tyndall effect give an almost uniform deposit and the complexity of the periodic deposits increases with the intensity of the Tyndall light and thus with the colloidal instability of the solution. It is deduced that the sols contain two forms of the same chemical substance, lyophilic and lyophobic respectively, one of which protects the suspension of the other. The term " autoprotection " is suggested for this phenomenon. On ageing, the lyophilic component is gradually transformed into the lyophobic and the pectograph becomes more complex. E. S. HEDGES.

Structure and stability of colloid particles. S. LIEPATOV (Kolloid-Z., 1930, 50, 74—76).—Von Weimarn's views of the structure of colloid particles (A., 1921, ii, 324) are further developed. The adsorbed ion giving the charge to the particles is generally the ion of one of the atoms present in the particle. For example, silver iodide particles are negatively charged when formed in presence of excess of potassium iodide because the iodine ion is adsorbed, and are positively charged when formed using excess of silver nitrate because the silver ion is adsorbed. The stability of the particles is considered in this light. E. S. HEDGES.

Stabilising action of capillary-active substances on suspensions of hydrophobic and hydrophilic powders in water and non-aqueous dispersion media. I. P. REHBINDER (Z. physikal. Chem., 1930, 146, 63—78).—The protection of various suspensions by adsorbed layers of capillary-active substances has been investigated. Hydrophilic sub-

stances can be thus stabilised in organic liquids, but not in water, whilst the converse is true of hydrophobic powders. These results can be explained by the author's theory of polarity differences (cf. A., 1927, 1136). The mean size of the particles decreases with increasing concentration of the stabiliser and tends to a minimum value corresponding with the limit of adsorption. The effectiveness of fatty acids in stabilising suspensions of graphite in benzene is in accordance with Traube's rule. Capillary-active substances bring about an increase in the volume of a sedimented powder.   F. L. USHER.

Stability of lyophobic organosols. H. B. WEISER and G. L. MACK (J. Physical Chem., 1930, **34**, 101—121).—The effect of water and organic liquids on the stability of sols of mercuric sulphide in methyl and propyl alcohols and of ferric oxide in propyl alcohol and the effect of organic liquids on mercuric hydrosol has been investigated by determining the precipitation concentration of lithium or calcium chloride necessary as well as the ζ-potential. The precipitation concentration gives a more reliable measure of stability than the ζ-potential. The influence of foreign non-electrolytes on the stability can be accounted for in a qualitative manner by a consideration of their influence on the dielectric constant of the medium, on the ionisation of the electrolytes present, and on the selective adsorption of ions by the colloidal particles. In general, the stability of the hydrosols or organosols towards electrolytes increases or decreases with a corresponding change in dielectric constant.   L. S. THEOBALD.

Effect of dilution and non-electrolytes on the charge of emulsion particles and the mixing of sols. S. S. BHATNAGAR and D. C. BAHL (Kolloid-Z., 1930, **50**, 48—55).—The cataphoretic migration velocity of the particles of mixed sols has been measured, using hydrosols of arsenious sulphide, cadmium sulphide, ferric oxide, and silver, and emulsions of oil in water; curves connecting the migration velocity with composition of the mixture are shown. In a mixture of sols of arsenious sulphide and of silver the migration velocity rises to a higher value than is obtained for either sol singly, indicating that coagulation occurs at a higher potential rather than by reducing the charge below a certain critical value. The supposition of Kruyt and Willigen (A., 1928, 18) that this behaviour is to be explained by the increase in the dielectric constant is not acceptable and it is suggested that larger complexes of particles of similar charge are produced as the result of the chemical affinity of silver atoms in the one sol and of sulphur in the other. When sols of opposite sign precipitate each other the coagulation is influenced by the relative concentrations of the sols, the particle size, and the rate of mixing. The composition of the precipitate is not constant and the remaining sol contains particles of both components. The migration velocity of particles of a sol increases on dilution. Addition of non-electrolytes (ethyl alcohol, acetone, and sucrose) lowers the velocity of cataphoresis and increases the viscosity; the product of these values also decreases, except in the case of alcohol, where a maximum is observed at 20%. This

behaviour is due to the lowering of the dielectric constant of the medium by the non-electrolyte.
    E. S. HEDGES.

Influence of light on the coagulation, electrical conductivity, and the absorption spectra of some colloids. (MISS) S. ROY and N. R. DHAR (J. Physical Chem., 1930, **34**, 122—137; cf. A., 1922, ii, 604).—Sols of ferric, chromium, zirconium, and ceric hydroxides, vanadium pentoxide, Odén sulphur, and manganese dioxide become less stable towards electrolytes on exposure to light, whilst sols of Prussianblue, cupric ferrocyanide, mastic, and gum dammar are stabilised. The specific conductances of sols of ferric, chromium, zirconium, and cerium hydroxides, manganese dioxide, arsenious sulphide, Prussian-blue, and cupric ferrocyanide increase on long exposure to light, but those of vanadium pentoxide, gum dammar, and mastic decrease. More marked absorption is shown in the spectra of exposed sols of ferric hydroxide, arsenious sulphide, and Prussian-blue and less absorption in those of gum dammar and mastic. In most cases, the effect produced by light is an accentuation of the time effect and coagulation by light is considered to be due to decomposition of the stabilising ion and loss of reactivity of the sol particles.
    L. S. THEOBALD.

Temperature coefficient of suspensoids of the second order. K. JABŁCZYŃSKI and A. EMIN (Rocz. Chem., 1929, **9**, 694—697).—The temperature coefficient of the velocity of coagulation of suspensions of silver chloride or bromide is about 2, i.e., equal to that found for suspensoids of the first order, such as ferric hydroxide.   R. TRUSZKOWSKI.

Problems of present-day colloid chemistry. II. Decrease of potential produced by electrolytes. H. R. KRUYT (Chem. Weekblad, 1930, **27**, 54—56).—In the light of published experimental data it appears that the mechanism of the influence of electrolytes on phenomena such as electroendosmosis and cataphoresis and on the stability of sols cannot yet be satisfactorily explained.   H. F. GILLBE.

Structure of jellies. P. THOMAS (Rev. gén. Colloid., 1929, **7**, 295—307).—The conditions of gelation are discussed, and views of the structure of jellies are reviewed. Experiments have been conducted on the crystallisation of l-arabinosazone, which is soluble in hot water and readily crystallises on cooling to form clusters of needles which interpenetrate to give a firm mass. When crystallisation takes place in presence of small amounts of gum, microscopical examination of the units of structure showed them to be intertwining hairs instead of straight needles, and it was found that the flexibility of the hairs as well as their length could be varied by altering the proportion of gum in the mixture. The experiments demonstrate that there is a relation between the flexibility and length of the hairs, their ability to intertwine so as to form a coherent mass, and their power to retain water, and that these factors can be varied by the presence of impurities. Similar, though less striking, results were obtained with lactosazone, rhamnosazone, and xylosazone.
    E. S. HEDGES.

Identity of the colloidal particles in soap sols and jellies. M. E. L. McBain and J. W. McBain (Nature, 1930, **125**, 125).—A defence of the conclusion that the rigid structure of the jelly is built up by progressive linkings of the particles pre-existent in the sols (J.C.S., 1920, **117**, 1506) against recent criticisms. In reply to Krishnamurti (A., 1929, 1379), it is recorded that samples of the same solution of sodium oleate have been prepared which show both in the sol and gel states an identical light-scattering power.　　　　　　　　　　　L. S. Theobald.

Precipitation of soaps, particularly stearolates, from aqueous solution. A. S. C. Lawrence (Kolloid-Z., 1930, **50**, 12—17).—The differences in the physical properties of soaps are greater than is generally supposed. In particular, stearolic acid is more crystalline than any of the other higher fatty acids, and its salts exhibit characteristic forms, the particles being observable in the ordinary microscope. Whilst the other acids crystallise from alcohol in thin microscopic flakes, stearolic acid forms large clusters of needles. In crystallising the soaps from aqueous solution, single crystals of considerable size can be obtained. On cooling a hot 2% aqueous solution of the potassium, sodium, or ammonium salt, thin crystalline leaflets are obtained; the sodium and ammonium soaps change to a more amorphous form when kept. The solutions also contain aggregates of colloidal particles, the sodium salt showing the greatest tendency to exist in the colloidal form. The aggregates are generally in the form of fibres and are generally curved. The fibrous form, which has also been observed in other soap solutions, is a consequence of the long-chain structure of the fatty acid molecule. Stearolic acid and its soaps differ from the higher saturated fatty acids and their salts in the triple linking, which causes the molecules to arrange themselves side by side, thus producing much larger and more crystalline particles. It is argued that since the highly disperse soap solutions exhibit anisotropy, the ultimate particles must have the same structure as the larger crystals of the substance.　E. S. Hedges.

Soaps of fatty acids of the oleic series. III. Sodium oleate. IV. Sodium zoomarate. M. Hirose and T. Shimomura (J. Soc. Chem. Ind. Japan, 1929, **32**, 263—265b, 266—268b).—III. Both the surface tension and the drop number of sodium oleate solution decrease with rise of temperature. With increase in concentration the drop number rises, whilst the surface tension at first falls and subsequently rises. The lathering volume increases with rise of temperature and concentration, but its value is less than that for sodium gadoleate.

IV. The drop number–temperature curve of sodium zoomarate solutions resembles that of sodium gadoleate. The surface tension of sodium zoomarate solution decreases with rise of temperature; with rise of concentration it first decreases and then increases. For soap solutions of the oleic series the power of lowering the surface tension and the drop number decrease in the order C_{18}, C_{20}, C_{16}, C_{22}. The influence of mol. wt. on the lathering properties of members of this series is discussed.
　　　　　　　　　　　　A. A. Goldberg.

Morphology of chemical reactions in colloidal media. II. F. M. Schemjakin (Kolloid-Z., 1930, **50**, 58—65).—See this vol., 33.

Characteristic equation for binary gaseous mixtures. G. van Lerberghe and (Mlle.) G. Schouls (Bull. Acad. roy. Belg., 1929, [v], **15**, 583—589).—The equation $p = p_1 + p_2 + C_1 C_2 \omega_{12}$, where C refers to molar concentrations in the gas phase, and ω to functions dependent solely on temperature, is suggested for the behaviour of gaseous mixtures. For mixtures of methane and nitrogen it is considerably more accurate in application than Dalton's law. It leads to simple expressions for the fugacities of the gaseous components in terms of the fugacities of the pure gases and the new coefficient ω introduced into the characteristic equation. An analogous equation is proposed for ternary gaseous mixtures.
　　　　　　　　　　　　F. G. Tryhorn.

Empirical calculation of the fugacities in gaseous mixtures. II. Its relation to the tangents on certain thermodynamic diagrams. Approximate equations for some important thermodynamic properties of gas mixtures. L. J. Gillespie (Physical Rev., 1929, [ii], **34**, 1605—1614; cf. A., 1929, 1138).—Mainly mathematical. Using the results of previous work, methods are derived for calculating the limiting value of the tangents to curves of functions of the energy, entropy, heat content, and the t–p and t–v thermodynamic potentials; the limiting tangents are found to depend only on the cohesive pressure term of the equation of state, and a group of functions of the fugacity and equilibrium pressure. From these limiting values equations are derived for the change of energy, entropy, heat content, t–p and t–v thermodynamic potentials in the mixing of gases at constant temperature and pressure.　　　　　　　N. M. Bligh.

Methyl alcohol equilibrium. B. F. Dodge (Ind. Eng. Chem., 1930, **22**, 89—90).—The published data concerning the equilibrium $2H_2 + CO = CH_3 \cdot OH$ are discussed and the following reason is given to explain some of the discrepancies. The calculation of the free-energy change for the synthesis, although based on the third law, and therefore requiring a knowledge of absolute entropies, is far more dependent on exact data for the various heats of reaction than on the entropy data. Thus if the value for the heat of combustion of methyl alcohol is in error by 0.1%, the corresponding error in the dissociation constant at 298.1° Abs. is 33%.　　　　　H. Ingleson.

Extended theory of acids and bases. T. M. Lowry (Trans. Faraday Soc., 1930, **26**, 45—46).—A claim for priority over Brönsted (cf. A., 1929, 273).
　　　　　　　　　　　　J. W. Smith.

Apparent dissociation constants of tryptophan and histidine. C. L. A. Schmidt, W. K. Appleman, and P. L. Kirk (J. Biol. Chem., 1929, **85**, 137—140).—Tryptophan has K_a' 4.05×10^{-10}, K_b' 2.4×10^{-12}, the isoelectric point lying at p_H 5.89; histidine has K_a' 6.7×10^{-10}, K_{b_1}' 1.01×10^{-8}, K_{b_2}' 6.6×10^{-13}, the isoelectric point being at p_H 7.7.
　　　　　　　　　　　　C. R. Harington.

Dissociation constants of certain sulphonephthalein indicators. M. Kilpatrick and M.

KILPATRICK, jun. (J. Physical Chem., 1930, **34**, 211—213).—Errors in a paper by Sendroy and Hastings (A., 1929, 765) are pointed out.

L. S. THEOBALD.

Nitrates and the equilibrium law. K. JABŁCZYŃSKI and K. DEMBOWSKI (Rocz. Chem., 1929, **9**, 698—703).—An ebullioscopic study of solutions of the nitrates of cæsium, rubidium, and potassium shows that the ionisation constant is the same in all cases, namely, 1·47. None of the ions present in the above systems is hydrated at 100°. In all cases association of nitrate ions with undissociated molecules takes place; this is most marked in the case of cæsium, and diminishes in extent with rising temperature. R. TRUSZKOWSKI.

Hydrolysis of aluminium salts. E. O. WILSON and R. C. KUAN (J. Amer. Leather Chem. Assoc., 1930, **25**, 15—31).—The p_H value of solutions of aluminium sulphate and potassium alum increases with the dilution. The former show a slight increase on keeping for a week, whilst the latter show a decrease. The p_H value of both solutions is increased by the addition of potassium sulphate and continues to increase on keeping. The p_H is diminished by the addition of sodium chloride, but there is no further alteration on keeping. The p_H value of a solution of aluminium sulphate is much higher than that of an equivalent solution of chromium sulphate.

D. WOODROFFE.

Hydrolysis of solutions of chromic salts. L. MEUNIER and M. LESBRE (Compt. rend., 1930, **190**, 183—185).—The Toussaint photo-electric colorimeter has been used to follow the changes in a 0·445% solution of chromic chloride, $[CrCl_2,(H_2O)_4]Cl,2H_2O$, at 25°, by observing the variations in the transmission of the individual colours of the spectrum. The results confirm those obtained by determinations of the flocculation index (Meunier and Caste, A., 1921, ii, 512) and the electrical resistance, viz., that simultaneous formation of the compounds $[Cr(H_2O)_6]Cl_3$ and $[CrOH(H_2O)_5]Cl_2$ occurs, which is complete after 300 hrs. J. GRANT.

Pseudo-component of hydrogen. A. SMITS (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1118—1123).—The variations of the internal equilibrium with temperature are described: above 170° Abs. the equilibrium constant corresponds with about 25% of α- and 75% of β-hydrogen.

H. F. GILLBE.

Determination of transition point by the vapour-pressure method. M. MATSUI, S. OGURI, S. KAMBARA, and K. KATO (J. Soc. Chem. Ind. Japan, 1929, **32**, 172—174B).—By the differential vapour-pressure method the transition temperature of sodium sulphate is found to be 32·60°, whilst by the absolute vapour-pressure method the value 32·57° is obtained.

H. F. GILLBE.

Transition point of sodium sulphate [decahydrate] by the dynamical vapour-pressure method. S. OGURI and M. NARA (J. Soc. Chem. Ind. Japan, 1929, **32**, 274—276B).—By a slight modification of Partington's method (J.C.S., 1911, **99**, 467) the value 32·4° was found graphically. Combination of the equations representing the vapour pressures above and below the transition leads to 32·57°. S. K. TWEEDY.

Binary systems of certain nitrotoluenes with salicylic acids. H. D. CROCKFORD and F. W. ZURBURG (J. Physical Chem., 1930, **34**, 214—216; cf. Bell and McEwen, A., 1922, i, 726).—F.-p. data for the systems formed by 2 : 4 : 6-trinitrotoluene, p-nitrotoluene, and 2 : 4-dinitrotoluene with salicylic acid are recorded. The eutectic temperatures are 76·3°, 49·4°, and 66·3° at 90, 94·9, and 89·9 mol.-% of the nitro-derivative, respectively.

L. S. THEOBALD.

Points of fusion and of decomposition in the system $KClO_3$-$NaClO_3$. A. P. VITORIA (Anal. Fís. Quím., 1929, **27**, 787—797).—The m. p. of potassium chlorate and sodium chlorate are 356° and 256°, respectively, the corresponding decomposition temperatures being 364° and 350°. The m. p.–composition and decomposition temperature–composition curves exhibit a minimum, which for the former occurs at 25% $KClO_3$ and 237°, and for the latter at 85% $KClO_3$ and 305°. H. F. GILLBE.

Liquid ammonia and calcium nitrate. N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1929, **32**, 242—243B).—The vapour pressure of liquid ammonia saturated with calcium nitrate has been determined at —40° to —10°. The depression caused by calcium nitrate is less than that effected by sodium nitrate. The heat of condensation of ammonia in the saturated solution is 6·32 kg.-cal. per mol. of NH_3 at —20°, and the heat of dissolution of pure liquid ammonia 0·9 kg.-cal. Solid anhydrous calcium nitrate absorbs gaseous ammonia and the compound so formed dissolves in liquid ammonia with precipitation of a less soluble salt, possibly calcium nitrate.

C. IRWIN.

Oxide hydrates. XVIII. System magnesium oxide–water. XIX. System magnesium oxide–carbon dioxide. G. F. HÜTTIG and W. FRANKENSTEIN (Z. anorg. Chem., 1930, **185**, 403—412, 413—416; cf. Hüttig and Kassler, this vol., 162).—XVIII. The dehydration curves at constant pressure, and the Debye spectrograms of the mineral brucite and of twelve other samples of magnesium oxide, prepared by different methods and containing varying quantities of water, have been determined. A hydration experiment was also carried out on one sample after dehydration. The results indicated the presence of the compound MgO,H_2O with a dissociation temperature a little above 300°. In three cases the results appeared to suggest the presence of the compound $MgO,0·5H_2O$, with approximately the same dissociation temperature as the monohydrate. Two different lattice structures were observed, one belonging to brucite and the other to calcined magnesium oxide, and some of the preparations combined both these structures. It seems probable that the only stable hydrate is the monohydrate, and that the so-called hemihydrate is simply a mixture of brucite and magnesium oxide. By different methods of preparation magnesium oxide of different degrees of activity, as measured by the readiness of combination with water, is formed, but there are no indications of these differences in the X-ray spectrograms. The

possibility of the existence of an amorphous magnesium oxide, giving no interference figures, is not excluded. Variations in the activity, or free energy content, of the monohydrate seem to be indicated by changes in the dissociation temperature, and in the breadth of the lines in the X-ray spectrogram when comparing brucite with the freshly-precipitated monohydrate.

XIX. The system magnesium oxide–carbon dioxide has been investigated in a way similar to that previously described for the system calcium oxide–carbon dioxide (Z. angew. Chem., 1928, **41**, 1034). "Dense" magnesite of the Krauparth type and "crystalline" magnesite of the Veitel type formed the starting materials. The times required to reach the equilibrium pressures at different temperatures were extraordinarily long. Debye spectrograms have been obtained of the initial materials and of the products at different stages. Throughout, the system shows a close analogy with that of calcium oxide–carbon dioxide (*loc. cit.*). The results confirm the opinion that composition and previous history of the solid phase must be taken into account when attempting to determine decomposition values in such systems, and that their equilibrium pressures, in the thermodynamic sense, have scarcely ever been measured.

M. S. Burr.

Concentrated solutions. V. P. Schischokin (Z. anorg. Chem., 1930, **185**, 360—368; cf. A., 1929, 995).—The fusion diagrams of the following ternary systems have been investigated by the Alexeiev–Schröder optical method : phenylallylthiocarbamide–*o*-toluidine–*m*-toluidine; *p*-dibromobenzene–nitrobenzene–alyllthiocarbimide ; phenylallylthiocarbamide–acetanilide – aniline ; *p* - dibromobenzene – benzene – aniline ; phenylallylthiocarbamide–acetanilide–allylthiocarbimide. In the first three cases the ternary regions are limited by binary systems of which the fusion curve branches are all represented by the Schröder equation of the form $S = ke^{-a/T}$ (*loc. cit.*). In such cases the isotherms in the crystalline fields of the components are all straight lines, and the eutectic is a simple mixture of the three components. In the last two cases, however, the branches of the binary systems do not satisfy such an equation and the isotherms are curves. By fusion together of the three components chemical combination takes place. It is probable that the Schröder equation can also be applied to more complicated systems.

M. S. Burr.

Heterogeneous equilibria of metal halides with hydrogen and with hydrogen chloride. K. Jellinek and R. Koop (Z. physikal. Chem., 1929, **145**, 305—329; cf. A., 1928, 1191).—The equilibrium concentrations of hydrogen and hydrogen fluoride or chloride have been determined when each of the following metal halides is reduced by hydrogen at temperatures between 200° and 1100° : cobaltic and manganous fluorides, ferric, chromic, and cupric chlorides, the stage of reduction reached being the lower halide except in the case of manganese. From the results the dissociation pressure curves and heats of formation are calculated. The equilibrium between hydrogen chloride and the fluorides of cobalt, cadmium, zinc, manganese, and sodium has been

investigated in a similar manner, and the heats of reaction have been calculated. Vapour pressures of ferric, chromic, and zinc chlorides have been determined. F. L. Usher.

Thiol–disulphide system. I. Complexes of thiol acids with iron. R. K. Cannan and G. M. Richardson (Biochem. J., 1929, **23**, 1242—1262).—The rate of the spontaneous autoreduction and its relation to p_H (8—10·5) of the ferrithiol complex have been studied. The autoxidation of the ferrothiol complex is rapid at p_H 8 and not demonstrable below p_H 6 and is not amenable to direct measurements. The equilibrium potentials of the ferrithiol–ferrothiol reversible oxidation–reduction system have been determined and an electrode equation has been established which defines the electrode behaviour within a limited range of p_H and concentration of thiol acid. Suggestions have been made as to the nature of the complexes. The electrode behaviour of thiol compounds without added iron has also been considered.

S. S. Zilva.

Equilibrium in reduction of antimony trioxide by carbon monoxide. M. Watanabe (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 973—977).—The reaction $Sb_2O_3 + 3CO \rightleftharpoons 2Sb + 3CO_2$ has been studied at 502° and 596°. The change in free energy given by $\Delta F = -33,461 + 34·286T \log T - 0·01110T^2 + 0·00000093T^3 - 88·65T$ agrees with the experimental data. R. A. Morton.

Isotherms of the system $MgSO_4$–Na_2SO_4–H_2O between 0° and 100°. W. Schröder (Z. angew. Chem., 1929, **42**, 1076—1077).—The isotherms have been determined and the results are compared with those of previous observers. H. F. Gillbe.

Reciprocal salt pair $MgSO_4$–$2NaNO_3$–H_2O. VI. W. Schröder (Z. anorg. Chem., 1930, **185**, 267—279; cf. A., 1929, 267).—On the basis of the results of previous investigations a space model showing the behaviour of the system $MgSO_4$–$2NaNO_3$–H_2O for a range of temperature 0—100° has been constructed. The axes are *a*, *b*, and *t*, where *t* is the temperature, *a* the amount of Na_2, and *b* the amount of $(NO_3)_2$. The amount of Mg is then $(100 - a)$ and of SO_4 $(100 - b)$. Plane diagrams have also been drawn indicating the changes in water content with temperature for the binary, ternary, and quaternary systems, respectively. By means of the space model and the diagrams all possible changes in the system, over the range of temperature considered, are quantitatively mapped out.

M. S. Burr.

Reciprocal salt pair $2NH_4NO_3 + K_2SO_4 \rightleftharpoons 2KNO_3 + (NH_4)_2SO_4$, and its aqueous solutions. E. Jänecke (Z. angew. Chem., 1929, **42**, 1169—1172).——Solubilities in the system ammonium nitrate, potassium sulphate, potassium nitrate, ammonium sulphate, water, have been determined from the eutectic points to 50°. In the quaternary systems the solid phases are : (*a*) mixed crystals of potassium sulphate and ammonium sulphate, (*b*) mixed crystals of a known double salt, $(NH_4)_2SO_4,2NH_4NO_3$, with the salt $K_2SO_4,2KNO_3$, which cannot be prepared by itself, (*c*) mixed crystals of potassium nitrate with reltively small amounts of ammonium nitrate, (*d*)

mixed crystals of ammonium nitrate with relatively small amounts of potassium nitrate. There are two quadruple points at which the solid phases a, b, c and a, b, d, respectively, are in equilibrium with the solution. J. A. V. BUTLER.

Heat capacities of real gases and mixtures of real gases. J. A. BEATTIE (Physical Rev., 1929, [ii], 34, 1615—1620).—From Beattie and Bridgeman's equation of state (cf. A., 1927, 819) simple approximate formulæ are derived for the heat capacities of a gas at constant volume (C_v) and at constant pressure (C_p). Values for the latter agree well with the experimental data for air, and fairly well for ammonia. Complete and approximate equations giving C_v and C_p for gas mixtures, in terms of pressure, volume, and temperature, are deduced from the generalised equation of state for gas mixtures (cf. A., 1929, 253), on the assumption that the energies of the gases at very low pressure are additive (cf. A., 1928, 1315; this vol., 292). N. M. BLIGH.

Heat of dissociation of the oxygen molecule and energy of activation of the oxygen atom. V. HENRI (Compt. rend., 1930, 190, 179—181).—The absorption spectrum of gaseous nitrogen peroxide indicates dissociation into nitric oxide and either a normal or an active oxygen atom, the corresponding wave-lengths being 3700 and 2459 Å., and the heats of reaction —77,000 and 116,000 g.-cal., respectively. The value —136,000 g.-cal. (5·5 volts) may then be deduced for the heat of dissociation of the oxygen molecule and —39,000 g.-cal. (1·7 volts) for the energy of activation of the oxygen atom. The first stage of activation of the oxygen atom corresponds with passage from the normal state $^3P_2$ to the metastable state ^1D. The position of the latter term is discussed, with special reference to the green ray of the aurora borealis, which may be due to oxides of nitrogen dissociated by solar electrons into oxygen in the metastable ^1S state, and subsequent passage of oxygen atoms to the metastable ^1D state (cf. McLennan, A., 1928, 1165). J. GRANT.

Thermochemistry of hypochlorous acid. B. NEUMANN and G. MULLER (Z. anorg. Chem., 1930, 185, 428).—A correction (cf. A., 1929, 1238). Recalculated on the basis of a corrected value for the heat of dilution of hypochlorous acid, the mean heat of neutralisation of hypochlorous acid becomes 10,033 g.-cal./mol. The heats of formation of $HOCl,Aq$ from the six hydroxides employed are, in g.-cal., NaOH, 29,300; KOH, 29,250; LiOH, 29,410; $Ca(OH)_2$, 29,210; $Sr(OH)_2$, 29,350; $Ba(OH)_2$, 29,230; mean 29,290. For the complete hydrolysis of gaseous chlorine to form $HCl,Aq+HOCl,Aq$ the corresponding figures are : 230, 180, 340, 140, 280, and 170 g.-cal., mean 220 g.-cal. M. S. BURR.

Thermochemistry of iron, manganese, and nickel. W. A. ROTH (Arch. Eisenhüttenw., 1929—1930, 3, 339—346; Stahl u. Eisen, 1929, 49, 1763—1765).— The following heats of formation have been redetermined (values in kg.-cal./mol.): $MnO + 93·5 (\pm 0·7\%)$; $FeO + 64·3 (\pm 0·7\%)$; $NiO + 58·9 (\pm 1\%)$; $Mn_3O_4 + 345·0 (\pm 0·3\%)$; $Fe_3O_4 + 266·9 (\pm 0·2\%)$; $Fe_2O_3 + 198·5 (\pm 0·4\%)$; $MnCO_3 + 219·1 (\pm 0·4\%)$; $FeCO_3$

$+172·6 (\pm 0·5\%)$, $Mn_3C +23 (\pm 10\%)$; $Fe_3C —5·4 (\pm 30\%)$; $Ni_3C —9·2 (\pm 10\%)$; $Fe(CO)_5 +57·3 (\pm 3\%)$. The heat of formation of manganous carbonate from the oxide and carbon dioxide is $+28·3 (\pm 2—3\%)$ and that of ferrous carbonate from ferrous oxide and carbon dioxide $+14·0 (\pm 11\%)$. A. R. POWELL.

Thermochemistry of the higher oxides of nickel. F. GIORDANI and E. MATTHIAS (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, 35, 172—182).— Measurements have been made of the heat of dissolution in hydrochloric and sulphuric acids of preparations of nickelous hydroxide containing varying amounts of higher oxides. The heat of dissolution of nickelous hydroxide in 2·63N-hydrochloric acid at 26° is 20,652 g.-cal., and in 5·52N-sulphuric acid at 28° is 22,165 g.-cal. When the heats of dissolution in sulphuric acid of the superoxygenated preparations are plotted against the atomic ratio active oxygen/nickel ($=n$) three lines are obtained which are represented respectively by $\Delta H = 22,263 + 70,405n$, $65,483 - 120,960n$, and $9900 + 29,838n$. From these results the existence of the oxides Ni_3O_4 and Ni_4O_5 is indicated. The results, however, are in moderate agreement with those required by the presence of the oxides Ni_2O_3 and Ni_3O_4.

The results are used to calculate the heats of the probable reactions in the Edison cell, viz., $Ni_2O_3 + Fe + 3H_2O = 2Ni(OH)_2 + Fe(OH)_2 + 65,215$ g.-cal., and $Ni_3O_4 + Fe + 4H_2O = 3Ni(OH)_2 + Fe(OH)_2 + 63,950$ g.-cal. The first reaction leads to a value of 1·338 volts and the second to 1·311 volts for the potential of the Edison cell, both of which are rather lower than the measured value of 1·36 volts. F. G. TRYHORN.

Thermochemical revisions. II. W. A. ROTH and G. BECKER (Z. physikal. Chem., 1929, 145, 461—469; cf. A., 1929, 1389).—The following heats of formation have been determined : ZrO_2, $+264·0 \pm 0·3$ kg.-cal.; Cr_2O_3, $+288·0 \pm 1·0$ kg.-cal. (both by combustion in the presence of paraffin in a bomb calorimeter); CrO_3, $+147·1 \pm 0·6$ kg.-cal. by reduction to Cr_2O_3 and $+140·0$ in a few direct determinations. The heat of formation of zirconium dioxide is in good agreement with the relation between heat of formation and atomic number. The calculated heat of formation of zirconium carbide is $+52·5$ kg.-cal. per g.-atom. The following densities have been determined at 21°: ZrO_2, $5·68 \pm 0·02$; Zr, $6·47_3$; Cr_2O_3, $5·20—5·21$; CrO_3, $2·80 \pm 0·01$. J. A. V. BUTLER.

Heat of combustion of camphor, azobenzene, and hydrazobenzene. W. SWIENTOSŁAWSKI and J. BOBIŃSKA (Rocz. Chem., 1929, 9, 723—730).— The heats of combustion of the above three substances are respectively 9260·7, 8483·8, and 8624·3 g.-cal.$_{15}$/g. R. TRUSZKOWSKI.

Limiting heat of dissolution of hydrated manganous chloride. J. PERREU (Compt. rend., 1930, 190, 52—54).—The limiting heat of dissolution of manganous chloride tetrahydrate is found to be —4·57 and —4·56, respectively, by the direct method and by a method which involves the heats of dilution (A., 1929, 1014). A concordant value is obtained by a modified form of the second method (A., 1929, 1238). R. K. CALLOW.

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Thermodynamic data on lead sulphide and the standard potential of sulphur. M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 978—983).—From Jellinek's equilibrium constants (A., 1925, ii, 401) for the reduction of lead sulphide by hydrogen, the values of ΔH and ΔF referred to liquid and solid lead have been calculated. The following data for the reaction $Pb(s)+S(rhombic)=PbS(s)$ are recorded : $\Delta H_{298}=-22,855$ g.-cal., $\Delta F_{298}=-22,224$ g.-cal.; entropy of lead sulphide $S=21.01$ entropy units; standard potential of sulphur $E_{298}(S/S^-)=0.48$ volt. R. A. MORTON.

Thermodynamic data on some metallic sulphates. F. ISHIKAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 965—972).—The following thermodynamic data, based on the standard free energy of formation of aqueous sulphuric acid, are recorded : mercurous sulphate, $\Delta F_{298}=-147,829$ g.-cal., $S=50.13$; lead sulphate, $\Delta F_{298}=-192,607$ g.-cal., $\Delta H_{298}=-217,165$ g.-cal., $S=38.83$; thallous sulphate, $\Delta F_{298}=-196,741$ g.-cal., $\Delta H_{298}=-219,071$ g.-cal., $S=59.93$; silver sulphate, $\Delta F_{298}=-145,951$ g.-cal., $S=54.56$. R. A. MORTON.

Rule for the mechanism of reactions. P. ROBINSON (J. Physical Chem., 1930, **34**, 207—210).—When several reactions are possible in an isothermal system, the one which occurs first is said to be that for which the reaction products have the largest entropy value. The application of the rule to the sulphur and water systems is examined and the rule is considered valid. L. S. THEOBALD.

Stability of crystals and their heats of formation and dissolution. A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, **1**, 17—19).—Endothermic crystals with a negative heat of dissolution become less stable as the size diminishes; for exothermic crystals with a negative heat of dissolution the reverse is true. For crystals with a positive heat of dissolution the relations are reversed. H. F. GILLBE.

Dimensions of crystals formed in a viscous medium. A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, **1**, 1—4).—Theoretical arguments suggest that increase in the viscosity of a crystallising solution should result in the production of smaller crystals when the heat of dissolution of the solid is negative and of larger crystals when the heat of dissolution is positive. H. F. GILLBE.

Electrical conductivity and viscosity of aqueous solutions. M. CHANOZ and G. CLUZET (Compt. rend. Soc. Biol., 1929, **100**, 1205—1207; Chem. Zentr., 1929, ii, 1384).—The electrical conductivities of solutions of potassium chloride, sodium chloride, hydroxide, and sulphate, hydrochloric and sulphuric acid, and cupric chloride are reduced by addition of sucrose, glycerol, agar, or gelatin. A. A. ELDRIDGE.

Electrochemistry of non-aqueous solutions. I. Influence of nature of solvent on equivalent conductivity of typical salts. II. Conception of "strong" binary salts and differences between strong and weak electrolytes. P. WALDEN (Suomen Kem., 1929, **2**, 163—165).—A review. A. I. VOGEL.

Temperature coefficients of the quinhydrone and calomel electrodes. A. I. BRODSKI and S. M. BORUCHOVITSCH (Ukrain. Chem. J., 1929, **4**, 379—386, and J. Chim. phys., 1929, **26**, 542—547).—The $E.M.F.$ of the cell, calomel electrode (KCl 0·1)|KNO$_3$ (satd.)|quinhydrone electrode is given by $E=0.2607-0.00105t$ at p_H 2·15, $E=0.1547-0.00150t$ at p_H 4·155 and $E=0.0413-0.00174t$ at p_H 6·145. The first of these is in good agreement with that obtained by Kolthoff and Tekelenburg (A., 1927, 329). The variation of the temperature coefficient with p_H is given by $dE/dT=+0.00011-0.0001983t$. Similar equations hold for the hydrogen electrode. Since the temperature coefficients of both the quinhydrone and hydrogen electrodes vary with the p_H of the solution it is not permissible to obtain the $E.M.F.$ at 18° from tables of values of dE/dT. If p_{H0} represents the p_H of the standard electrode against which comparison is made, then $p_H=p_{H0}-[(E-E_0)-(A-B)(t-18)]/[0.0577+0.0001983(t-18)]$, where E is the $E.M.F.$ of the cell at $t°$, E_0 the potential of the electrode measured in relation to the standard at $p_H=0$ and $t°$, and A and B are constants, the values of which and of E_0 are given for a number of pairs of electrodes. T. H. POPE.

Temperature measurements at working electrodes. II. B. BRUŽS (Z. physikal. Chem., 1929, **145**, 470—476; cf. this vol., 185).—The temperature changes in the separation of oxygen, hydrogen, and silver at bright platinum electrodes have been determined. For oxygen and silver the effect is independent of the time; for hydrogen it increases exponentially with time. The final values are in the ratio $O_2:H_2:Ag=7.3:4.9:0.6$. J. A. V. BUTLER.

Electrocapillary properties of amalgams. A. FRUMKIN and F. J. CIRVES (J. Physical Chem., 1930, **34**, 74—85; cf. A., 1928, 1193).—Using the null solution method it has been shown that the addition of thallium or cadmium to mercury brings about a shift in the point of zero charge towards higher values of $P.D.$ between solution and metal. The concentration of thallium ions at the zero point varies with the thallium content of the amalgams; this is not the case with cadmium. The data obtained with thallium amalgams agree with the determinations of electrocapillary maxima (loc. cit.), confirming in the case of amalgams the validity of the Lippmann–Helmholtz equation for metals. L. S. THEOBALD.

Methods for the determination of absolute potentials. J. BILLITER (Amer. Electrochem. Soc., May, 1930. Advance copy. 10 pp.).—Methods which have been used in attempts to determine the absolute value of the zero electrode potential on the hydrogen scale are classified and critically examined. Modern methods give values between $+0.4$ and $+0.5$, the most trustworthy being $+0.475\pm0.005$ obtained by Bennewitz using the "scrape method" (A., 1926, 1212). The old value (-0.277) obtained from the electrocapillary curve for mercury and the mercury dropping electrode is regarded as subject to several errors, of which that due to a film of hydrogen on the mercury surface is particularly

important. This view is supported by new experiments in which the surface of a polarised metal wire in an electrolyte solution is increased by stretching and allowed to decrease again on releasing the strain. Wires of various metals were charged to different potentials, either by cathodic or anodic treatment or more frequently by the action of reducing or oxidising agents, and the direction in which the potential changed on stretching or releasing was determined. Critical potentials were found above which the stretching of the wire caused a change of potential in one direction and below which the change was in the opposite direction, these effects being reversed on releasing the tension on the wire. These critical potentials are shown to correspond with the potentials for hydrogen (or oxygen) evolution and the phenomena observed are regarded as due to the stretching of gas films on the metal surface resulting in a reduction of the effective gas pressure.

H. J. T. ELLINGHAM.

Potentiometric study of equilibria in solutions containing quinque- and sexa-valent molybdenum. W. F. JAKÓB and W. TRZEBIATOWSKI (Rocz. Chem., 1929, **9**, 676—693).—Ammonium paramolybdate solutions exhibit on titration with solutions of Klason's salt two potential minima. The colour of the solution at the first minimum is green, due to the formation of a *compound* $[Mo^V(Mo^{VI}O_4)_6](NH_4)_3H_4,5H_2O$; it was not found possible to isolate the complex causing the reddish-brown coloration observed at the second minimum. The reactions taking place may probably be represented by the following equations: $6MoO_4'' + 5H^{\cdot} + MoO(OH_3)_3 \rightleftharpoons [Mo(MoO_4)_6]''''''' + 4H_2O$, and $3MoO_4'' + 2H^{\cdot} + 2MoO(OH)_3 \rightleftharpoons [Mo_2O_2(MoO_4)_6(OH)_4]'''' + 2H_2O$. The potential attains a constant value after the minima have been reached; this is due to the platinum electrode being covered with a layer of inactive molybdenum-blue.

R. TRUSZKOWSKI.

Potential of solutions of carbohydrates. (MLLE.) N. MAYER (J. Chim. phys., 1929, **26**, 565—573).—See A., 1929, 1147.

Behaviour of the quinhydrone electrode in liquid ammonia. E. ZINTL and S. NEUMAYR (Ber., 1930, **63**, [B], 237—243).—Constant and reproducible results are not obtained in the measurement of E.M.F. of concentration chains, $H_2,Pt|NH_4Cl(c_1)$ in liquid ammonia$|NH_4Cl(c_2)$ in liquid ammonia$|Pb,H_2$, in spite of variation in the mode of preparation of the electrodes. Satisfactory results are, however, obtained with the quinhydrone electrode if the concentration of the quinhydrone does not fall below 5×10^{-5}. In ammonium chloride not exceeding $0.002N$, variation in the quinhydrone concentration between 5×10^{-5} and 10^{-3} is without appreciable effect, but in $0.001N$-solution the E.M.F. depends appreciably on the concentration of quinhydrone. The observed potential values can be satisfactorily explained by the Debye–Hückel theory (A., 1923, ii, 459) if complete dissociation of the ammonium chloride is assumed.

H. WREN.

Studies on hydrogen overpotential by the dropping mercury cathode. W. V. LLOYD (Trans. Faraday Soc., 1930, **26**, 12—15).—The hydrogen overpotential w varies logarithmically with the current i, provided that the rate of dropping is constant, and that the current is measured at corresponding periods during the formation of a drop and after the same interval from the beginning of an experiment. Deviations are observed with very low and very high currents; in the latter case concentration effects are pronounced in more dilute solutions. The current varies logarithmically with the time from the beginning of the experiment, so both i and $dw/d \log i$ can be varied considerably by varying the rate of dropping. Related with this is the variation of $dw/d \log i$ with different solutions. These phenomena may account for the discrepancies between the results of Herasymenko (A., 1928, 482) and those of Bowden and Rideal (*ibid.*, 1088). It is suggested that the mechanism of the dropping electrode is too complicated to render it suitable for the study of hydrogen overpotential.

No conclusion regarding the hydrogen overpotential in potassium hydroxide solution could be reached from experiments with the dropping mercury cathode, the latter behaving simply as a potassium electrode.

J. W. SMITH.

Hydrogen overpotential in acid solution. H. J. S. SAND (Trans. Faraday Soc., 1930, **26**, 19—26).—The results of Bowden (*ibid.*, 1928, **24**, 473) on the dependence of hydrogen overpotential on current density in acid solution are explained by postulating the intermediate formation of an ion H_2^+. The process is assumed to take place exclusively at the interface electrode–electrolyte, and the surface concentrations are related to the equilibrium concentrations in the body of the liquid by the Freundlich isotherm, the exponent for both hydrogen atoms and ions being 4. When the concentration of atomic hydrogen on the electrode surface is greater than in Bowden's experiments, overvoltage may be governed by the velocity of direct combination of hydrogen atoms, in which case it is independent of the hydrogen-ion concentration (cf. Bowden and Rideal, A., 1928, 1088; Sand, Grant, and Lloyd, A., 1927, 317; Lloyd, A., 1929, 1241). The double layer is supposed to be capable of existence in two forms. At lower overpotentials a random distribution of ions with respect to electrons in the layer is assumed, whereas at higher overpotentials the ions and electrons are believed to be combined in doublets. In the latter case the hydrogen ions are assumed not to be free for purposes of chemical combination. The double layer must be assumed to behave as a Helmholtz double layer, *i.e.*, to have a constant polarisation capacity and a dielectric constant of unity for the medium. Attention is directed to the significance of the polarisation capacities measured by Bowden and Rideal (*loc. cit.*) which are only one fifth as large as those deduced previously from indirect experiments. Since the polarisation capacity is almost entirely due to the building up of the double layer and the current required for charging the electrode with hydrogen ions is negligible in comparison, the result obtained by Bowden and Rideal, that the polarisation capacity is independent of the material of the electrode, follows immediately. J. W. SMITH.

Overpotential of arsenic and the yields of arsine at an arsenic cathode in acid solutions. W. V. LLOYD (Trans. Faraday Soc., 1930, **26**, 15—18).—The overpotential of arsenic has been measured, using a plane polished surface of a piece of compact arsenic as cathode. A commutator method was used, similar to that previously described (Sand, Grant, and Lloyd, A., 1927, 317). Initial polarisation at low current densities yields a high overpotential which is not maintained at higher current densities. In the latter case a maximum overpotential is attained, as with antimony and bismuth, so long as no arsine is produced. The average commutator overpotential when there is no high degree of supersaturation and no arsine is being evolved is about 0·6 volt in acid solution, corresponding with the average polarisation during an interval of 0·0059 sec. after interruption of the current. Continued electrolysis leads to the production of an " active " form of arsenic, and arsine is evolved. This is accompanied by an appreciable decrease in the overpotential. When the cathode is in an " active " state the percentage of arsine produced at a fixed current density is approximately the same for sulphuric, hydrochloric, phosphoric, and tartaric acids, and does not vary considerably with the concentration. The largest percentage yield of arsine was obtained in $4N$-hydrochloric acid solution by the method of Sand and Lloyd (A., 1927, 38) with anodic and cathodic current densities of 44 and 525 milliamp. per cm.^{2}, respectively, when a yield of 60% was obtained.　　　　　　　J. W. SMITH.

Decomposition potential of solutions of metal bromides in fused zinc bromide. W. ISBEKOV (Z. anorg. Chem., 1930, **185**, 324—332).—The decomposition potentials of a number of metal bromides in fused zinc bromide have been determined and found to stand in the following order, beginning with that of highest potential : Al, Zn, Cd, Pb, Fe, Cu, Ag, Ni, Hg (mercurous), Bi. This is in the same order as the heats of formation of the bromides, with the probable exception of nickel, and, so far as the same metals are included, in the same order as the decomposition potentials of bromides in fused aluminium bromide (A., 1925, ii, 796). Moreover, any metal in this series will displace any subsequent member from a solution of the bromide in zinc bromide. Data have also been obtained for sodium and potassium bromides in zinc bromide, but the decomposition potentials observed in these solutions, and also in that of aluminium bromide, have all the same value and indicate that the ultimate product of electrolysis in these cases is zinc. The relationship of solvent to decomposition potential is discussed and it is considered that the relative positions of the metals will change when a solvent markedly different in chemical character is employed.　　　　　M. S. BURR.

Theory of passivity. VII. Anodic behaviour of copper in electrolyte solutions containing sulphuric acid. VIII. Anodic behaviour of zinc in electrolyte solutions containing sulphuric acid. W. J. MÜLLER and L. HOLLECK. IX. Passivity of lead in sulphuric acid, and theory of forming of the lead anode. X. Variation of autopassivity with time. W. J. MÜLLER and K.

KONOPICKY. XI. Anodic behaviour and passivity of iron in sodium sulphate solutions. W. J. MÜLLER and W. MACHU (Monatsh., 1929, **52**, 409—424, 425—441, 442—462, 463—473, 474—492; cf. A., 1929, 1241).—VII. The anodic passivation of copper in aqueous solutions of sulphuric acid and in mixed solutions of sulphuric acid and copper sulphate is in agreement with the equation $t_p = B(i_o/F_o)^n$ for coating passivation (A., 1928, 713) and examination of the electrode shows a layer of copper sulphate pentahydrate to have been formed on it. At low acid concentrations, this ultimately changes into a basic salt, this transformation occurring the sooner the lower is the acid concentration. Both B and n fall continuously with rise in the acid concentration. The value of B runs approximately parallel with the solubility of copper sulphate in the acid solution, although it is not exactly proportional to it. In pure $10N$-acid solution the temperature coefficient of B is 1·5. The form of the current strength–time curves also accords with the equations developed for rate of growth of surface layers (cf. A., 1929, 146).

VIII. In the anodic passivation of a protected zinc electrode in an aqueous solution of sulphuric acid, the metal first becomes coated with a transparent layer, which appears from the conductivity of the liquid in its pores and from microscopical investigation to be zinc sulphate heptahydrate. This is formed sooner in acid solutions saturated with zinc sulphate than in absence of sulphate. In pure acid solutions or saturated sulphate solutions less than $5N$ in respect of acid, the layer soon becomes opaque, probably as a result of transformation into basic salt. The lower the concentration of acid the sooner this change occurs. The relation between the initial current density and the time of passivation corresponds with that observed for copper, and the form of the current strength–time curves is in accordance with the laws of coating growth, except that the transition to basic salt may interfere with the growth in thickness.

IX. The i_o and t_p data for the anodic passivation of lead in a 25% aqueous solution of sulphuric acid conform to the above equation, the value of n being unity, apparently as a result of the small solubility of lead sulphate. The current strength–time curves also agree with the coating theory of passivation. As the effective applied voltage is increased, both B and the effective current density increase in a linear manner. At 2 volts, however, the effective density assumes a steady value, whilst B increases abruptly and rapidly. If the graph connecting B with the voltage is now extrapolated to zero B, a value of 1·95 volts above the reversible potential of lead is obtained. Corresponding with the change in B there is an abrupt increase in the conductivity of the liquid in the pores of the coating from a value corresponding with a saturated solution of lead sulphate to a value approximating to the conductivity of the acid solution. At an effective applied potential of 2 volts it thus appears that the potential of the metal changes discontinuously from the value corresponding with the dissolution of bivalent lead to that for the dissolution of quadrivalent lead, which then furnishes acid by hydrolysis. The results thus support Elbs' theory of the forming of accumulator plates.

X. Application of the coating theory of passivity to autopassivity leads to the equation $t = M + N \log (e_m - \varepsilon)/(\varepsilon - e_s)$, where e_m is the reversible potential of the metal in the pores, e_s the potential of the coating, and ε the measured potential of the electrode at a time t after immersion in the solution, and M and N are constants. The value of e_s will not be constant, however, until an appreciable coating has been formed, but when this point has been reached the above equation is in satisfactory agreement with experimental results for the autopassivation of aluminium and also with Tammann and Sotter's data for chromium–iron alloys (A., 1923, ii, 825).

XI. In the anodic passivation in aqueous sodium sulphate solutions of iron free from a surface film of oxide the time of passivation and the initial current density are connected by an equation of the above type. The values of B and n vary with the electrolyte concentration in much the same way as they do for sulphuric acid. The results show, in confirmation of those previously obtained (A., 1928, 713), that the actual passivation of the metal occurs in very much less time than would be required for the formation of an oxide film, and that Tronstad's theory of the passivation of iron in acid solutions (A., 1929, 1002) is untenable. The passivation time of nickel is considerably reduced by the presence of a film of oxide.   R. CUTHILL.

Passivity and over-voltage. A. SMITS (Z. Elektrochem., 1930, **36**, 20—25).—The passivity theory of Müller (cf. A., 1929, 886) is criticised, chiefly with reference to the author's theory of allotropy.   H. T. S. BRITTON.

Application of chiolite to the electrolysis of alumina. I. The fusion diagram of the system alumina–cryolite–chiolite. L. WASILEWSKI and S. MANTEL (Przemysł Chem., 1930, **14**, 25—31).—The m. p. of mixtures of alumina and chiolite rise steadily from 735° for 100% chiolite to a constant value of about 890° at 8—20% Al_2O_3; this is due to loss of fluorides by volatilisation. Above 20% Al_2O_3 the m. p. again rises, until at 50% fusion is not achieved at 1300°. No eutectic mixture is formed in this system. The fusion diagram of the system chiolite–cryolite shows a minimum m. p. of 687° at 95% of chiolite. The diagram for the ternary system chiolite–cryolite–alumina shows that the electrolysis of alumina, using chiolite as a flux, can be carried out below 900°, using a mixture containing 10—16% Al_2O_3 and cryolite and chiolite in the proportions from 20 : 80 to 35 : 65, and below 850° with mixtures containing 11—16% Al_2O_3, and 32 parts of chiolite to 68 of cryolite. Electrolysis proceeds smoothly at 850—900° with a current of 6 volts, the efficiency being over 60%, and the aluminium produced falls to the bottom of the electrolyser, no visible vaporisation of metal taking place. Preliminary experiments show that chiolite is a more convenient flux than fluorite.   R. TRUSZKOWSKI.

Experimental basis of the international scale of temperature so far as concerns low temperatures. W. H. KEESOM (Arch. Néerland., 1929, [iiiA], **12**, 115—139).—A critical examination of the bases of the international scale of temperature fixed by the 7th General Conference of Weights and Measures held at Paris in 1927 has been made as far as concerns low temperatures, both as regards reproducibility and agreement with the ideal thermodynamic scale. It is concluded that reproducibility has not been achieved even to the extent ($\pm 0.02°$) to which the various platinum resistance thermometers on which the Conference based its results agree among themselves; for this thermometers of other kinds should also be used. As regards the thermodynamic scale the limit of agreement is $\pm 0.04°$, depending chiefly on Henning's Avogadro scale (1913), whereas the Leyden platinum resistance and a helium thermometer show variations of only $\pm 0.01_4°$, and the helium thermometer is reproducible with an error of only $\pm 0.01_0°$. Leyden is therefore unable to accept the international scale in preference to its own, which corresponds with the thermodynamic scale within $\pm 0.02°$.   C. A. SILBERRAD.

X-Ray oscillography. H. SEEMANN and K. F. SCHOTZKY (Naturwiss., 1930, **18**, 85—86).—A correction and explanation of a previous communication (this vol., 138).   J. W. SMITH.

Ignition limits of the mixtures $2H_2 + O_2$ and $2CO + O_2$. D. KOPP, A. KOVALSKY, A. SAGILUN, and N. ŠEMENOV (Z. physikal. Chem., 1930, **B, 6**, 307—329; cf. A., 1929, 147).—Pressure–temperature diagrams are given to show the regions of explosion and non-explosion for each of the reactions $2H_2 + O_2 = 2H_2O$ and $2CO + O_2 = 2CO_2$. The existence of upper and lower limiting pressures has been confirmed. The upper limit decreases, the lower increases with fall of temperature. The upper limit is defined by the total pressure of the mixture and not by the partial pressure of the explosive constituents. Neither the pressure of inert gas nor change in the dimensions of the reaction vessels affects the shape of the p–t curve. Slight traces of nitrogen peroxide markedly lower the ignition temperature and the residual pressure in the reaction $2H_2 + O_2 = 2H_2O$, but larger quantities, e.g., 0.1%, have less effect than traces. The results are discussed from the point of view of the " chain " theory.   F. L. USHER.

Combustion limits of air–vapour mixtures at high pressures. E. BERL and H. BAUSCH (Z. physikal. Chem., 1929, **145**, 451—460; cf. B., 1927, 546; 1929, 158).—Increasing pressure causes a widening of the range of combustion with mixtures of air with ethyl alcohol, n-hexane, cyclohexane, and cyclohexene. The lower combustion limit of hexane–air mixtures is extended by increase of pressure owing to the separation of hydrogen and the formation of peroxides. With cyclohexane the extension is smaller owing to the greater difficulty of separation of hydrogen. In mixtures of aromatic with aliphatic compounds, the influence of peroxide formation is reduced. Unsaturated hydrocarbons resinify in oxygen under the influence of pressure at low temperatures. They cannot be exploded in air.   J. A. V. BUTLER.

Kinetics of certain simultaneous processes. E. N. GAPON (Ukrain. Chem. J., 1929, **4**, 333—339). —Orlov (Diss., Kinetics of chemical reactions and

catalysis, 1913) deduced kinetic equations of the general form $dx/dt = k_1(A - mx)$, $dx/dt = k_2(A - mx)^2$, etc., and showed their derivation from the differential equations $dx/dt = k(A - x) + k_1 x$, $dx/dt = k(A - x)^2 + k_1\phi(x)$, etc. As a result of numerous calculations Orlov concluded that, if the calculated velocity coefficients k_1, k_2, k_3 do not satisfy the differential equations of the first, second, and third orders but gradually diminish, the differential equation of general type may be applied for calculating the constant. The above equations are applicable either to successive reactions, or when the principal reaction is complicated by a secondary reaction, or to catalytic reactions, m being greater than 1 in the case of negative catalysis.

It is now shown that Orlov's equations of general type are applicable to the case when one substance A reacts simultaneously in independent directions, giving the products M_1, M_2 . . . M_i, the number of which may be 1, 2, 3 . . . i. Three cases are considered, the product M being formed either by unimolecular, or by bimolecular, or partly by unimolecular and partly by bimolecular transformation of A. By means of the results of Lebedev and Mereshkovski (A., 1913, i, 1285) on the polymerisation of isoprene and di*iso*propenyl, it is shown that the kinetics of simultaneous reactions, in particular of polymerisation, proceed according to equations formally identical with those of catalytic reactions.

T. H. Pope.

Rate of reaction in a changing environment. G. Scatchard (J. Amer. Chem. Soc., 1930, **52**, 52—61).—Theoretical. Approximate relationships are developed on the basis of Brönsted's theory to include the effect of changing environment on the velocity of ionic and non-ionic reactions in non-ideal solutions. The principles involved in evaluating the changes of activity coefficients with concentration are applied to the oxidation of ammonia by the persulphate ion in the presence of the silver ion (Yost, A., 1926, 819) and to the reaction between p-nitrobenzoyl chloride and certain alcohols (Ashdown, this vol., 301).   J. G. A. Griffiths.

Temperature coefficient of reactions in solution. F. O. Rice and H. C. Urey (J. Amer. Chem. Soc., 1930, **52**, 95—101).—Theoretical. The reactive complex of Brönsted's theory of acid and basic catalysis is replaced by a series of fugitive molecules differing only in energy content. The distribution of these complexes and their probabilities of reaction do not change with the addition of salts of strong acids and therefore the temperature coefficient is independent of the concentration of salt (cf. Rice and Kilpatrick, A., 1923, ii, 548). In catalysis by weak acids there may be several simultaneous reactions, each with its own characteristic energy of activation. Salts of weak acids therefore affect the temperature coefficient (cf. Rice and Lemkin, A., 1923, ii, 678).   J. G. A. Griffiths.

Velocity of hydrolysis and alcoholysis of acetic anhydride in mixtures of water and ethyl or methyl alcohol. J. F. M. Caudri (Rec. trav. chim., 1930, **49**, 1—16; cf. A., 1929, 655).—The rate of the simultaneous hydrolysis and alcoholysis of acetic anhydride by binary mixtures of water with methyl and ethyl alcohols has been determined at 25°. With increase in the amount of alcohol, the unimolecular velocity coefficient of hydrolysis decreases continuously; but that of alcoholysis first rises and then falls again, the maximum being attained with a solvent containing about 40% by volume of alcohol. The quotient of the former coefficient by the water concentration and also the quotient of the latter coefficient by the alcohol concentration decrease continuously with increase in the alcohol concentration, the alcoholysis being retarded more than the hydrolysis, but both appear to have finite values in pure alcoholic solutions. Methyl alcohol is about 3·5 times as reactive towards the anhydride as is ethyl alcohol.   R. Cuthill.

Kinetics of the interaction of esters with potassium alkyl oxides in alcohol–water mixtures. II. Reaction between potassium ethoxide and ethyl propionate in ethyl alcohol–water mixtures. R. F. W. Selman (Trans. Faraday Soc., 1930, **26**, 7—11).—The reaction between potassium ethoxide and ethyl propionate is similar to that between potassium ethoxide and ethyl acetate (cf. A., 1929, 1018) and can be represented by the equations $EtOK + H_2O \rightleftharpoons EtOH + KOH$ and $CH_3 \cdot CH_2 \cdot CO_2Et + KOH \longrightarrow CH_3 \cdot CH_2 \cdot CO_2K + EtOH$. As in the former case a simple velocity equation is derived, assuming the reaction to be bimolecular and the concentration of water and alcohol to be commensurate with the concentration of ethoxide, the velocity coefficients being composite values involving the concentrations of water and of alcohol and the hydrolysis constant of the ethoxide. It is concluded that the evidence available is insufficient to warrant the inclusion of the possibilities of complex formation between reactants and solvents as part of the mechanism of these reactions. A series of alcohol–water complexes such as have been suggested at various times is inadequate to explain the mechanism of the reaction unless an infinite series of such complexes be postulated.   J. W. Smith.

Velocity of inversion of sucrose. I. N. Taketomi (J. Soc. Chem. Ind. Japan, 1929, **32**, 260—262b).—The inversion velocity, measured polarimetrically, is nearly directly proportional to the hydrogen-ion concentration in the presence of weak organic acids. The proportionality does not obtain in the presence of strong acids. Neutral salts (alkali chlorides, nitrates, and sulphates) are incapable of catalysing the inversion, but chlorides and nitrates accelerate, and sulphates retard, the rate of inversion produced by acids. The cation of the added salt is almost without effect. The anions probably act by influencing the catalytic activity of the hydrogen ions.   S. K. Tweedy.

Velocity of decomposition of diazo-compounds in water. E. Yamamoto.—See this vol., 337.

Velocity of decomposition of diazo-compounds in water. II. E. Yamamoto (J. Soc. Chem. Ind. Japan, 1929, **32**, 308—311b).—The rate of decomposition of phenyldiazonium chloride in water at 0° has been studied. The velocity coefficient becomes constant after 20 hrs. Inorganic acids, neutral salts,

and the concentration of the diazo-compound are without influence on the velocity. Nitrous acid does not affect the stability of the diazo-compound. Sodium carbonate increases the value of the velocity coefficient.   C. W. GIBBY.

Relative rates of reduction of aromatic nitro-compounds [by stannous chloride]. J. R. SAMPEY (J. Amer. Chem. Soc., 1930, **52**, 88—92).— Relative rates of reduction by aqueous-alcoholic acid stannous chloride (cf. A., 1928, 57) of 28 aromatic nitro-compounds to corresponding amines are recorded. The reaction is of the second order with respect to stannous chloride over a tenfold range of concentration and is retarded by water and decrease of acidity. The velocity of reduction of isomeric nitrotoluenes, nitrophenols, chloro-, bromo-, and iodo-nitrobenzenes decreases in the order *o-*, *m-*, *p-*. For the nitrobenzoic acids, this order is reversed. Corresponding chloro-, bromo-, and iodo-nitrobenzenes are reduced at nearly equal rates.   J. G. A. GRIFFITHS.

Rate of reaction of alcohols with *p*-nitro-benzoyl chloride in anhydrous ether. A. A. ASHDOWN (J. Amer. Chem. Soc., 1930, **52**, 268—278).—The reactions between alcohols and *p*-nitrobenzoyl chloride, previously studied by Norris and Ashdown (A., 1925, i, 626) and Norris and Cortese (A., 1927, 1166), are of the third order. The mechanism requires 2 mols. of the alcohol and 1 mol. of the chloride. An equation for calculating the third order constants at infinite dilution has been developed.   H. BURTON.

Kinetics of the reaction of hexaphenylethane with oxygen. R. C. MITHOFF and G. E. K. BRANCH (J. Amer. Chem. Soc., 1930, **52**, 255—268).—The rate of absorption of oxygen by solutions of hexaphenylethane in carbon tetrachloride has been studied at —21° to 5°, using mixtures of oxygen and nitrogen. Varying partial pressures (0·2—0·93 atm.) of oxygen were employed, and the reaction mixture was shaken sufficiently vigorously to permit the transfer of oxygen from the gaseous to the liquid phase to occur at a rate faster than that of oxidation. The absorption of oxygen occurs in three phases : (i) rapidly, due to saturation of the solvent, (ii) less rapidly, representing oxidation of the hexaphenylethane, *i.e.*, dissociation of the ethane into triphenylmethyl, and subsequent rapid oxidation of the free radical, and (iii) very slowly, apparently due to the presence of a small amount of an undissociated but active form of hexaphenylethane. This active form reacts at a slower rate than the free radical, the oxidation of which is a first order reaction.

The rate of oxidation of hexaphenylethane is proportional to the concentration of the ethane, and also to a function of the oxygen pressure, namely, $K_0 - 1/(a + bP_{O_2})$, where K_0, a, and b, are constants. The heats of activation increase with rise of temperature, but are approximately constant to the change in the pressure of oxygen. Little or no energy appears to be needed to activate the oxygen.

Diphenylamine and anthracene have no appreciable effect on the velocity of the reaction, whereas phenol causes an increase in the rate of more than 50%.   H. BURTON.

Hydrolysis and polymerisation of cyanamide in alkaline solutions. G. H. BUCHANAN and G. BARSKY (J. Amer. Chem. Soc., 1930, **52**, 195—206). —The rate of formation of carbamide and dicyanodiamide from cyanamide has been studied in buffer solutions at p_H 6—13 and 50°. At a constant p_H, the polymerisation of cyanamide to dicyanodiamide proceeds as a second order reaction, and up to p_H about 10 dicyanodiamide is the only product formed ; the velocity of formation is a maximum at p_H 9·6. At p_H 12·6—13·6, cyanamide is hydrolysed to carbamide. The reaction is of the first order, and the velocity coefficient is independent of the alkali concentration. Solutions of dicyanodiamide are stable up to p_H 10 ; above this value decomposition occurs, the rate increasing with rise in p_H.   H. BURTON.

β-Glucosidase. II. Hydrolysis of cellobiose. R. WEIDENHAGEN (Z. Ver. deut. Zuckerind., 1930, **80**, 11—24).—The β-glucosidase of emulsin hydrolyses cellobiose at about one eighth the rate of its action on salicin ; the reaction is unimolecular. There is no direct relation between the concentration of the enzyme and the rate of hydrolysis. The optimum is at p_H 5·0. With salicin as substrate the velocity coefficient increases in inverse ratio to decreasing substrate concentration, but with cellobiose this relation only holds even approximately over a narrow range at about 2—3% of substrate. For the dissociation constant of the salicin–enzyme complex the value $K_{sal.} = 0·033$ found is in good agreement with that found by previous workers, but the point of maximum reaction rate is ill defined on the activity-p_S curve for cellobiose–emulsin, and neither of the two values deduced, $K_c = 0·118$ or 0·139, fits the data completely. It is suggested that the application of Langmuir's adsorption isotherm might lead to a better understanding of the discrepancies (see following abstract). The β-glucosidase of malted barley acts more strongly on cellobiose than on salicin, which would seem to point to the existence of two enzymes, a salicinase and a cellobiase. On account, however, of the uncertainty of the value of K_c and the low β-glucoside activity of malt an accurate comparison of the enzymes from the two sources is at present impossible, and the author considers that the identity of all enzymes splitting normal β-linkings is not to be doubted.   F. E. DAY.

Application of the mass action law to the enzymic decomposition of sucrose. R. WEIDENHAGEN and E. LANDT (Z. Ver. deut. Zuckerind., 1930, **80**, 25—27).—It is shown that the velocity of this reaction can be represented equally well by formulæ of the same type derived respectively from the mass action law and from Langmuir's adsorption isotherm, based on the idea of heterogeneous catalysis. The latter is to be preferred as it is broader and allows of conceptions such as explanation of inhibition phenomena as being due to the exclusion of the substrate by foreign substances adsorbed on the enzyme.   F. E. DAY.

Chemical kinetics in mixtures of solvents. VII. Reaction between pyridine and allyl bromide in ethyl benzoate. G. E. MUCHIN and M. I. ZILBERFARB (Ukrain. Chem. J., 1929, **4**, 327—

331; cf. A., 1927, 1149).—Determinations of the velocity of interaction of pyridine and allyl bromide in ethyl benzoate and its mixtures with benzene at 45° and 55° give continuous curves, free from singular points, for the relationship between the constant of the reaction and the composition of the mixed solvents. The observed velocity coefficients are less than those calculated additively and, although the general course of the curves is analogous to that found with mixed nitrobenzene–benzene solvents, the extents of the divergences from additivity and the displacement of the curve caused by change of temperature are less marked in the present case.   T. H. POPE.

First order solid-phase reaction. B. LEWIS and H. J. SCHUMACHER (Nature, 1930, **125**, 129).— The reaction between bromine and ozone (A., 1929, 1395) is regarded as one of the first order which takes place in the solid phase of the crystals. For a given amount of bromine oxide it appears to be of zero order, since any oxide which decomposes is at once reformed by ozone.   L. S. THEOBALD.

Oxidation of copper at higher temperatures. W. FEITKNECHT (Z. Elektrochem., 1930, **36**, 16— 17).—The formula advanced by Wilkins (A., 1929, 1019) to account for the author's data (A., 1929, 517) is shown to be unsatisfactory.
          H. T. S. BRITTON.

Catalysis by nitrous acid of the reaction between oxygen and hydrogen iodide and a method for the determination of oxygen. G. ALSTERBERG (Biochem. Z., 1929, **216**, 278—300).— Nitrogen trioxide when present in amounts greater than 1 mg. per litre causes considerable error in the usual Winkler determination of oxygen dissolved in water. The catalytic effect of nitrogen trioxide on the reaction between hydrogen iodide and oxygen is investigated by titration of the iodine liberated. The reaction is not a true catalysis, since some of the trioxide is irreversibly oxidised to pentoxide. The amount of hydrogen iodide, so long as it is in excess, does not affect the result. Temperature, so long as oxygen is in excess, has little effect, but otherwise rise of temperature accelerates the reaction. With excess of oxygen the extent of reaction is determined by the amount of trioxide, whilst if oxygen is not in excess the reaction proceeds in proportion to the amount of oxygen. The amount of iodine separated at low concentrations of oxygen is greater than theoretical for the amount of oxygen, due to reduction of tri- to di-oxide, and at high concentrations of oxygen is less, due to oxidation of nitrogen tri- to pent-oxide. A method for the determination of oxygen is described.   P. W. CLUTTERBUCK.

Conversion of thiosulphuric acid into polythionic acids with the aid of catalysts. II. A. KURTENACKER and I. A. IVANOV (Z. anorg. Chem., 1930, **185**, 337—359).—In order to follow the course of the reaction between mineral acids and thiosulphates, of which the end-point only had been previously investigated (A., 1928, 1195), sulphurous acid has been employed in place of, or in addition to, hydrochloric acid. In this way, provided the thiosulphate is not too dilute, no sulphur separates, and so it is not necessary to wait for its coagulation

before proceeding with the analysis. The limiting amount of arsenite necessary as catalyst is approximately the same as previously required when hydrochloric acid alone is present. The influence of acidity on the reaction has been investigated by adding different amounts of hydrochloric acid to the sulphurous acid. Even for a high concentration of hydrochloric acid, neither arsenious sulphide nor sulphur separates. The velocity of polythionate formation increases very markedly with the acidity. The influence of the sulphurous acid varies with the acidity. In absence of hydrochloric acid, or in presence of a very small quantity, sulphurous acid has a strong accelerating action, but it has the opposite effect in presence of an excess of hydrochloric acid. The accelerating action is attributed to the hydrogen ion of the sulphurous acid, and the inhibiting action to the formation of a complex ion $[S_2O_3 \cdot SO_2]''$ (cf. Foerster and Vogel, A., 1926, 1016). The kind of polythionate formed depends on the acidity and follows the rule previously observed that, in strongly acid solutions, polythionates with higher sulphur content are formed. In sulphurous acid solution alone, tri- and tetra-thionate are obtained, and practically no pentathionate. At the beginning of the reaction in feebly acid solution, however, appreciable quantities of pentathionate are formed, but this disappears as the reaction proceeds, the time–concentration curve thus possessing a maximum. This maximum is also observed even in the strongly acid solutions where considerable quantities of pentathionate remain at the end of the reaction. Within much narrower limits of concentration of the different reagents similar results are obtained when the arsenite is replaced by antimony trichloride, but sulphur and antimony sulphide or oxysulphide readily separate. The observation that bismuth trichloride exercises a slight catalytic action on the decomposition of thiosulphate has been confirmed, because, throughout the reaction, there is a slightly greater production of polythionate and smaller separation of sulphur in presence than in absence of bismuth. The probable mechanism of the catalysis is discussed.   M. S. BURR.

Oxidation catalysis. H. VON EULER, D. RUNEJHELM, and S. STEFFENBURG (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 7, 6 pp.).—Solutions of hæmin, mesohæmin, and deuterohæmin produce catalytic oxidation of reduced phenolphthalein in presence of small amounts of hydrogen peroxide. The reaction rapidly comes to a standstill, but the colour is intensified on addition of more hydrogen peroxide. Copper sulphate has a similar effect, a maximum intensity of coloration being obtained with a given ratio of copper to hydrogen peroxide. Blood also produces the colour reaction, whether previously heated to 100° or not. Hæmin, mesohæmin, and copper sulphate also cause the evolution of oxygen from solutions of hydrogen peroxide containing phenolphthalein.   K. V. THIMANN.

Active hydrogen. II. Wall-catalysis. H. VON WARTENBERG and G. SCHULTZE. **III. Lead hydride.** G. SCHULTZE and E. MÜLLER (Z. physikal. Chem., 1930, **B**, **6**, 261—271).—II. Washing the glass

walls of the discharge tube with ortho- or meta-phosphoric acid greatly retards the conversion of active into molecular hydrogen. The protective action of oxygen is due to formation of water.

III. A volatile hydride has been produced by the interaction of metallic lead and active hydrogen. The hydride decomposes at a red heat, giving a lead mirror. Attempts to condense it led to spontaneous decomposition, on account of which no chemical analysis was possible. It is considered that active hydrogen rather than the methyl radical is the intermediate product in Paneth's experiments on the decomposition of lead tetramethyl (cf. A., 1929, 788).

F. L. USHER.

Mechanism of oxidation of mercury vapour. I. Equilibrium formula. II. Condensation of oxygen in the molecular or the atomic state. III. Condensation of oxygen in the molecular and atomic states. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1929, **32**, 163—164B, 164—166B, 167—169B).—I. The mechanism of the oxidation of mercury vapour by oxygen in presence of a platinum catalyst has been studied. The equation $a_2 n_2 f = v_2 f_2$, where a_2 is a factor for the condensation of the oxygen molecules on the platinum surface, n_2 the number of molecules impinging on unit area of surface per sec., f_2 the fraction of the total surface which is covered by oxygen molecules, v_2 the number of molecules which evaporate per sec. when $f_2 = 1$ cm.², and f is the fraction of surface uncovered, is a valid expression for the equilibrium even when reaction takes place.

II. The mechanism of the reaction when the oxygen condenses in the atomic or in the molecular state is described and the appropriate equations for the velocity are derived.

III. An equation is derived representing the velocity of the reaction when simultaneous condensation in the molecular and atomic states occurs.

H. F. GILLBE.

Temperature distribution along a heated filament used as a catalyst. E. S. LAMAR and W. E. DEMING (Phil. Mag., 1930, [vii], **9**, 28—36).—An expression has been deduced which gives the temperature gradient at any point along a heated molybdenum filament used as a catalyst in the decomposition of ammonia. Temperatures at any points along the filament are determined by integrating this expression and the temperature distribution so obtained is found to correspond closely with that indicated by the measured resistance of the wire. From the temperature distribution is calculated the effective length of the filament as a catalyst at the maximum temperature. The mean heat of dissociation of ammonia over the range 954—1164° Abs. has been calculated from consideration of the heat losses from the filament. The value 12,067 g.-cal. per mol. so obtained is in fair agreement with the generally accepted value of 13,375 g.-cal. per mol. A. E. MITCHELL.

Catalytic and chemical characteristics of cubic and rhombohedral ferric oxide. P. H. EMMETT and K. S. LOVE (J. Physical Chem., 1930, **34**, 41—62; cf. Welo and Baudisch, A., 1925, ii, 1071).—The catalytic activity, the sorption of water vapour, the rate of reduction by hydrogen, and the effect of alumina on the magnetic permeability and the rate of reduction of the cubic and rhombohedral forms of ferric oxide have been investigated. The cubic form was prepared by heating ferrosoferric oxide in air at 300°, whilst the rhombohedral form was obtained by precipitation with ammonia and drying in air at the same temperature. The catalytic activity of the two oxides with respect to the oxidation of benzidine or of guaiacum resin by hydrogen peroxide is approximately the same and is not a function of crystal structure as was concluded by Welo and Baudisch (loc. cit.). The catalytic activity of both forms is destroyed by heating at 550° for several hours. The catalytic combination of hydrogen and oxygen at 250° is the same for both oxides and is unaffected by heating at 550°. The catalytic decomposition of ozone between −75° and 25° is also the same for the two forms, but is less rapid with the samples which had been heated to 550°. Decomposition in an ozone (2%)-oxygen mixture is practically complete with the most active oxides even at −74°. The decomposition is apparently unimolecular, with a temperature coefficient corresponding with an energy of activation of approx. 2000 g.-cal. Experiments on the sorption of water at 25° and 210° from a stream of nitrogen containing 0·57% of water vapour show that for unit weight of oxide sorption on the cubic form is 10—60% less than that on the rhombohedral form, and that the sorption on samples heated at 550° is less than that on those dried at 300° and is unaffected by activation of the oxide with a mixture of hydrogen and oxygen. The loss of magnetic permeability on heating is quickest with cubic ferric oxide prepared from hydrated ferrosoferric oxide precipitated by ammonia and slowest with cubic ferric oxide prepared from ferrosoferric oxide precipitated by sodium hydroxide; a sample similar to the first but containing 1·5% of alumina is intermediate between the two. The rates of reduction of the cubic and rhombohedral forms are approximately the same, being slightly faster in the former case. Heating at 550° for 2 hrs. reduces the rates of reduction considerably. Co-precipitation of alumina with ferrosoferric oxide has little effect on the rate of reduction of ferric to ferrosoferric oxide, but appears markedly to retard further reduction to metal. The results are discussed and Welo and Baudisch's work (loc. cit.) is adversely criticised. L. S. THEOBALD.

Application of nickel to certain reactions of organic chemistry. A. KORCZYŃSKI, A. REINHOLZ, and E. SCHMIDT (Rocz. Chem., 1929, **9**, 731—740).—The catalytic action of nickel is similar to that of copper in reactions with aromatic hydrocarbons halogenated in the side-chain; thus with benzyl chloride a polymeride of dibenzyl is produced, whilst with benzylidene chloride diphenyltetrachloroethane and diphenyldichloroethylene are obtained. Nickelous cyanide can be substituted for cuprous cyanide in the reaction between aromatic halogen derivatives and potassium cyanide. The action of nickel on the bromination of benzene, nitrobenzene, and naphthal-

ene is analogous to that of iron. Nickel has no catalytic action on the bromination of *s*-tribromophenol. R. TRUSZKOWSKI.

Catalytic oxidation of toluene by air. M. I. KUSNETZOV and M. A. STEPANENKO (Ukrain. Chem. J., 1929, **4**, [Tech.], 153—177).—Results are given of a large number of experiments on the oxidation of toluene in presence of heated basic zinc manganate, vanadium pentoxide on asbestos or pumice, molybdenum trioxide on asbestos, or bismuth vanadate on pumice. With molybdenum trioxide, which gave the best results, of 26·32 g. of toluene oxidised, 7·1 g. were oxidised to benzaldehyde, 0·12 g. to benzoic acid, 7·0 g. to carbon dioxide, and 12·1 g. to carbon monoxide. The carbon monoxide is formed together with benzene by decomposition of benzaldehyde and the carbon dioxide partly by direct oxidation of toluene and partly, along with benzene, by decomposition of benzoic acid. The products obtained were 8·1 g. of benzaldehyde, 0·16 g. of benzoic acid, and 10·3 g. (calculated) of benzene. Of the total quantity of toluene evaporated (89·7 g.), 55·84 g. remained unchanged, and 7·54 g. (8·3%) represented losses and experimental errors. In a further series of experiments in which tin vanadate formed the catalyst and a large excess of air was employed, considerably higher proportions of benzoic acid were obtained.
T. H. POPE.

Chemical action in the glow discharge. II. Further investigation on the synthesis of ammonia. A. K. BREWER and J. W. WESTHAVER (J. Physical Chem., 1930, **34**, 153—164; cf. A., 1929, 891).—The relative reactivity of various portions of the discharge in synthesising ammonia, together with the effect of added gases on the rate of synthesis, have been determined. Maximum synthesis occurs in the negative glow, whilst the positive column, including the anode glow, produces a uniform but smaller synthesis throughout its length, the respective rates being 33 to 1 ; no formation of ammonia occurred in the Crookes or Faraday dark spaces. The effects of the addition of excess of nitrogen or hydrogen, and of helium and argon, have been investigated. The rate of reaction is independent of pressure in these cases so long as the composition of the gas mixture remains constant. The maximum rate of synthesis for hydrogen–nitrogen mixtures occurs in a 2 : 1 rather than in the expected 3 : 1 mixture. Helium added in quantity up to 70% of the total amount of gas present has no effect on the rate of formation of ammonia, but even small amounts of argon decrease the rate considerably. The data indicate that the synthesis is initiated principally by N_2^+ ions, whilst the production of atoms, excited molecules, and H_2^+ ions represents lost energy. The formation of N_2^+ ions is followed by union with hydrogen to form ammonia and the three possible mechanisms for this last step are discussed. L. S. THEOBALD.

Electrolysis of water at high pressure. G. FAUSER.—See B., 1930, 107.

Polarographic studies with the dropping mercury cathode. VIII. Maxima of current due to electro-reduction of oxygen in solutions of strong electrolytes. E. VARASOVA (Coll. Czech.

Chem. Comm., 1930, **2**, 8—30).—A theoretical interpretation of the maxima in current–voltage curves produced in the presence of oxygen with the dropping mercury cathode is given and the influence of various experimental factors studied. In solutions saturated with air at the ordinary temperature, the current maximum is greatest when the specific conductance of the solution is $2·5 \times 10^{-4}$ ohm ; with varying oxygen content the conductance of the solution for the highest maximum is proportional to the oxygen content and is independent of the rate of dropping of the mercury and of the applied external resistance. The magnitude of the maximum is proportional to the oxygen concentration for the same dropping mercury cathode. The shape of the curve is influenced by the rate of dropping. The general character of the current–voltage curves is independent of the valency of the cation ; bivalent ions have a larger suppressive effect on the maxima than the univalent ions, whilst cyanide ions, and to a smaller degree hydroxyl ions, produce an abnormal suppression.
A. I. VOGEL.

Mechanism of electrolytic rectification. M. E. MACGREGOR (Nature, 1930, **125**, 128).—The hypotheses of Burgess and Hambuechen and of Günther-Schulze are only partly correct and, as the result of experiments with a special electrolyte which shows electrolytic reversibility with anodes of aluminium and cathodes of a special passive steel, a combination of the two is now advanced as the true explanation of the mechanism of electrolytic rectification.
L. S. THEOBALD.

Theory of the electro-deposition of chromium from aqueous chromic acid solutions. IV. E. MÜLLER and O. ESSIN (Z. Elektrochem., 1930, **36**, 2—9).—From electrolytic experiments carried out on chromic acid solutions with potentials up to those necessary to cause the evolution of hydrogen, it is concluded that the smallest cathodic polarisation of a perfectly bright electrode is sufficient to bring about the formation of a porous, invisible diaphragm covering the surface of the cathode. This diaphragm is composed of basic chromium chromate, such that the basic part faces the cathode, and the acid radical part the anode. It hinders the passage of chromic acid up to the electrode. By increasing the cathodic polarisation hydrogen ions become able to pass through the pores on account of the enhanced electrostatic attraction, but unless the associated anion is able to follow rapidly, in which case acid is formed within the diaphragm, the diaphragm will remain intact. Hence a greater cathode potential is necessary, it being very great with anions of very large diameter, e.g., $HCrO_4'$, ClO_4', and H_2PO_4'. This explains why a solution of pure chromic acid failed to be reduced. On addition of sodium salts, the anions of which were of small diameter, e.g., F', Cl', NO_3', ClO_3', and HSO_4', the cathode potential becomes smaller than the hydrogen potential and the diaphragm dissolves, and an appreciable reduction of chromic acid ensues. The behaviour at platinised platinum and carbon cathodes was also investigated. Electrodes with rough surfaces caused greater reduction of chromic acid, apparently through the discontinuous nature of the diaphragm, there being a tendency for

chromic acid to gain access to the electrode surface through holes formed at peaks in the surface. As long as such conditions prevail that both hydrogen ions and hydrochromate ions can diffuse quickly through to the electrode, then reduction to the tervalent state occurs and no diaphragm forms. H. T. S. BRITTON.

Electrolysis of metallic oxides dissolved in boric anhydride and in fused borates. Preparation of amorphous boron, borides, and some metals. L. ANDRIEUX (Ann. Chim., 1929, [x], 12, 423—507).—The electrolysis in a carbon resistance furnace of sodium pyroborate at 900° with a carbon cathode and a water-cooled iron anode, of potassium and lithium pyroborates, of calcium, strontium, and barium pyroborates at 1000°, of mixtures of boric anhydride and magnesia either alone or mixed with the fluorides of magnesium, sodium, potassium, lithium, or calcium, of manganese pyroborate, and a mixture of cerium oxide and boric anhydride, is described and the relative yields of boron and borides are determined. Boron of highest purity was obtained from electrolysis of magnesia, boric anhydride, and metallic fluoride mixtures. Electrolysis of calcium, strontium, and barium pyroborates to which the corresponding fluorides had been added, with carbon electrodes, gave the corresponding borides in a state of purity. *Cerium boride*, CeB_6, was obtained from the mixture $CeO_2 + 2B_2O_3 + CeF_3$; the *borides*, XB_6, where $X = La$, Nd, Gd, Y, Er, or Yb, from the oxides of the metal and lithium or magnesium pyroborate and fluoride; thorium boride, ThB_6, from thoria, sodium pyroborate, and sodium fluoride; *zirconium boride*, Zr_3B_4, from zirconia and the magnesium, calcium, or lithium pyroborate and fluoride; *titanium boride*, TiB_2, from titania and magnesium, calcium, or sodium pyroborate and fluoride; *vanadium boride*, VB_2, from vanadium pentoxide and magnesium, calcium, or lithium pyroborate and fluoride; *chromium boride*, Cr_3B_2, from chromium sesquioxide and magnesium or calcium pyroborate and fluoride; *uranium boride*, UB_4, from U_3O_8 and magnesium, calcium, or lithium pyroborate and fluoride; manganese boride, MnB, from manganous oxide and boric anhydride mixed with manganese fluoride, or with the oxide and fluoride of manganese, lithium, or sodium. Electrolysis of zinc oxide in a bath of sodium pyroborate preferably mixed with sodium, potassium, lithium, calcium, barium, or zinc fluoride, with carbon electrodes gave zinc (best yield with $ZnO + 2B_2O_3 + Na_2O + BaF_2$), whilst tungsten and molybdenum were obtained from the trioxides of the metals and the pyroborates and fluorides of sodium, calcium, or magnesium. The maximum yield of tungsten was obtained from a bath with the composition $\frac{1}{4}WO_3 + 2B_2O_3,Na_2O + NaF + ZnO$, and of molybdenum, $\frac{1}{2}MoO_3 + 2B_2O_3,Na_2O + NaF + ZnO$. A. I. VOGEL.

Quantum yield in the photochemical decomposition of azoimide. A. O. BECKMAN and R. G. DICKINSON (J. Amer. Chem. Soc., 1930, 52, 124—132; cf. A., 1928, 970).—Over the pressure range 2—131 mm. and in homogeneous light ($\lambda = 1990$ Å.), $3 \cdot 0 \pm 0 \cdot 5$ mols. of azoimide are decomposed per quantum of light absorbed. In the full radiation

of an aluminium spark, the reaction velocity was directly proportional to pressure for the range 0·06—0·5 mm. It is suggested that the primary reaction process is one of dissociation. J. G. A. GRIFFITHS.

Photochemical dissociation of triatomic molecules. Hydrogen cyanide. D. S. VILLARS (J. Amer. Chem. Soc., 1930, 52, 61—67).—The energies required to dissociate hydrogen cyanide in different modes are calculated, the least (4·3 volts) being for dissociation into hydrogen and cyanogen. The brown colour acquired by hydrogen cyanide is believed to be due to the polymerisation of cyanogen formed in this way. Absorption of light by the gas was not detected between 6593 and 2094 Å. even at 760 mm. and 1000°. Light from the silver arc (>1800 Å.) did not excite fluorescence. J. G. A. GRIFFITHS.

Photolysis of solutions of hydrogen sulphide in hexane and water. E. WARBURG [with RUMP] (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 29, 624—625).—Photolytes may be divided into two classes according to whether reaction between the photolyte and its solvent occurs or not. Hydrogen sulphide in water belongs to the former class, but in hexane it belongs to the second class. The photoequivalence law may be applied satisfactorily only in the second instance. F. G. TRYHORN.

Photochemistry of silver halides. W. LESZYNSKI (Z. wiss. Phot., 1930, 27, 304).—The quantities of silver found in unexposed emulsions by the method of Schmidt and Pretschner (B., 1928, 625) are greater in amount than the photolytic silver determined by Eggert and Noddack (cf. B., 1922, 232) after exposure. This need not imply inaccuracy in the latter work, but only a difference in chemical properties between the two forms of silver. L. V. CHILTON.

Absorption of infra-red radiations and the activation in chemical reactions of molecules. N. R. DHAR and A. K. BHATTACHARYA (Trans. Faraday Soc., 1930, 26, 1—6).—All radiations between 7000 and 4400 Å. have been shown to be absorbed by an aqueous solution of neocyanine and by a mixture of chromic acid and citric acid. Extinction coefficient measurements are much more satisfactory than photographic methods in such cases. Radiation of wave-length greater than 6570 Å. is absorbed completely by a very dilute solution of neocyanine, whilst there is a minimum at about 5200 Å. This agrees approximately with the velocity of reaction in the different regions. Appreciable absorption of all radiations from 7000 to 4400 Å. has also been observed with other reacting mixtures, this being accompanied by acceleration of the reactions. These wave-lengths being much shorter than those which should accelerate the change according to the radiation theory, it is suggested that the latter should be regarded as threshold limits, radiation of wave-length longer than these being ineffective. The relation between intensity of illumination and velocity of reaction is complicated, depending on both the amount of adsorption and on the acceleration of the reaction in the presence of light. The relationship between intensity and velocity of a single reaction can be changed in several cases by changing the

velocity of the dark reaction and the intensity and quality of the incident radiation. The quantum yield of a reaction may vary considerably with experimental conditions. Since chemical reactions involving halogens can be accelerated by radiations of wave-length 7304 Å., it is considered that the theory that halogens are initially converted into atoms on illumination is doubtful. J. W. SMITH.

Photochemical decomposition of nitrosyl chloride. G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, 52, 102—108).—In homogeneous light of various wave-lengths between 6350 and 3650 Å., 2 mols. of nitrosyl chloride are decomposed into nitric oxide and chlorine by each light quantum absorbed (cf. Bowen and Sharp, A., 1925, ii, 695). It is suggested that the reaction proceeds by the excitation of a molecule followed by decomposition on collision with a normal molecule of nitrosyl chloride. Nitrogen has no influence on the quantum efficiency.

The absorption of light commences at 6350 Å. and increases towards the ultra-violet. Maxima occur at 5990, 4690, 3300, and beyond 2500 Å. This spectrum has band structure down to 3300 Å. Fine structure was detected in the bands as far as 4100 Å.
J. G. A. GRIFFITHS.

Combined photographic action of light and α-rays or mesothorium rays. H. ISHIDŌ (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 992—998).—The combined effect of light and α-, β-, and γ-rays from ionium and mesothorium has been studied. For a certain definite exposure to the radioactive emission, the increase in darkening of the photographic plate decreases as the previous exposure to ordinary light is increased; if the plate is exposed first to radioactive radiation and then to ordinary light the increase in density decreases with increasing exposure to ordinary light. An effect similar to the Herschel effect is shown. R. A. MORTON.

Displacement of metals and their oxides from solutions of their salts by hydrogen at high temperatures and pressures. Action of hydrogen on metallic nitrates. V. IPATIEV and B. MUROMTZEV (Ber., 1930, 63, [B], 160—166; cf. A., 1923, ii, 639).—Replacement of metals by hydrogen occurs more readily from nitrates than from solutions of other salts, probably owing to the ready reducibility of the anion. Formation of nitrite in very small amount commences at about 200°. At about 300°, the anion is almost completely reduced to nitrogen, production of ammonia occurring to a very small extent. The solutions are enclosed in quartz or glass tubes and heated in the bomb under an initial pressure of 50—80 atm. of hydrogen, rising to 200—250 atm. during the experiments. Above a certain pressure, the qualitative results are independent of the actual pressure of the gas and the concentration of the solution has little influence. Nickel nitrate in gold tubes at 200° gives the *compound* $Ni(NO_3)_2,4NO,2H_2O$, mixed with nickelous oxide if the temperature rises to 270°; in quartz tubes between 200° and 240° the basic *salt*, $Ni(NO_3)_2,5NiO$, is deposited, whereas at 245° the *compound* $Ni(NO_3)_2,3NiO$ is produced. Between 330° and 360°,

nickelous oxide is produced, accompanied by nickel if the experiment is prolonged. Cobalt nitrate yields the sesquioxide at all temperatures between 200° and 360° in quartz or gold tubes; a basic nitrate could not be obtained. In quartz tubes at 250—300°, manganese nitrate yields trimanganic tetroxide of varying appearance, whereas in gold tubes at 190—240° the *hydrate* Mn_3O_4,H_2O is produced, the anhydrous substance being formed at 250°. Uranyl nitrate in gold tubes at about 300° gives the acid H_2UO_4, accompanied by uranium trioxide when the temperature is raised or the experiment is prolonged; further rise of temperature causes the appearances of the oxide U_3O_8, whilst, finally, at 360° and greatly prolonged time the oxide UO_2 is produced. At about 200°, cadmium nitrate in gold tubes yields cadmium hydroxide monohydrate, which, at 250—350°, becomes admixed with cadmium oxide. At 350° and above, the metallic oxide becomes mixed with the metal when the experiment is prolonged. Zinc nitrate in gold tubes at 250—350° yields zinc hydroxide; at 350° and higher, zinc oxide is precipitated, accompanied by zinc when the experiment is prolonged. Zinc hydroxide does not yield zinc below 380—390°. Crystalline calcium hydroxide is obtained from calcium nitrate at 300° and higher temperatures. H. WREN.

Displacement of metals from solutions of their salts by hydrogen at high temperatures and pressures. Displacement of arsenic from its salts by hydrogen. V. IPATIEV, G. RAZUBAIEV, and V. MALINOVSKI (Ber., 1930, 63, [B], 166—174; cf. A., 1926, 487).—In the author's high-pressure apparatus, arsenic is only slightly oxidised by water, not more than 7% of arsenious acid being obtained at 350°; the formation of arsine could not be detected. In presence of alkali hydroxide the oxidation is more vigorous, arsenious acid, accompanied by arsenic acid in small amount, being formed in quantity. Increase in concentration of the alkali hydroxide facilitates oxidation up to a point beyond which further increase results in marked diminution of the amount of arsenic oxidised. Reaction commences at 200°; the rate increases rapidly up to 350° and then decreases sharply. Quantitative oxidation of arsenic cannot be effected by rise of temperature or prolongation of the experiment. The hypothesis that the reaction is balanced, $2As+3H_2O \rightleftharpoons As_2O_3+3H_2$, is supported by the following evidence. If the hydrogen is removed periodically, the oxidation of arsenic becomes nearly quantitative; if, on the other hand, the apparatus is filled initially with hydrogen at 30 atm. the quantity of arsenic oxidised is diminished to 15%, whereas under similar conditions, but without initial hydrogen pressure, 58% is oxidised. Displacement of arsenic from sodium arsenate solution by hydrogen commences at 300° and increases rapidly with rising temperature (15% at 300°/25 atm., 77% at 350°/25 atm.). The arsenic separates in large, well-defined crystals. The initial pressure of the hydrogen has a very marked influence on the production of arsenic. At 350°, and after 24 hrs., the separation of the element in notable amount occurs at 15 atm. Under lower pressures, arsenic acid is

reduced to arsenious acid. The increase in pressure has no effect at pressures higher than 40 atm.

H. WREN.

Lithium chlorate. L. BERG (J. Russ. Phys. Chem. Soc., 1929, **61**, 1801—1805).—See A., 1929, 1145.

Sodium hydride. I. Preparation and density. II. Heat of formation. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1930, **185**, 239—253, 254—266).—I. Pure sodium hydride has been prepared as fine white needles by bringing together hydrogen and sodium vapour at 400—450° in an apparatus which is described. An exact method for the analysis of sodium hydride is given. By the floating method, using mixtures of benzene and carbon tetrachloride, d^{25} is $1·396±0·005$, in good agreement with the results of Proskurnin and Kasarnovski (A., 1928, 697); d (X-ray), however, is only $1·29$.

II. The mean value of the heat of formation of 1 g.-mol. of sodium hydride from solid sodium and gaseous hydrogen is 12·8 kg.-cal. This is the difference between the heat of dissolution of sodium ($44·38±0·21$ kg.-cal.) and that of sodium hydride ($31·57±0·15$ kg.-cal.) in water as measured in a calorimeter especially designed to obviate errors due to the violence of reaction. M. S. BURR.

Reduction of alkali nitrates by hydrous ferrous oxide. S. H. CARSLEY (J. Physical Chem., 1930, **34**, 178—187).—Hydrous ferrous oxide reduces sodium nitrate quantitatively to ammonia and is itself oxidised to ferrosoferric oxide. In neutral and dilute solutions previously boiled ferrous oxide reduces nitrate more slowly than does the freshly-precipitated oxide owing to agglomeration and dehydration. In dilute alkaline solution ferrous oxide tends to precipitate in a denser and more agglomerated form than in a neutral solution. Boiling with concentrated alkali favours peptisation and hence the speed at which reduction takes place. These results do not agree with Baudisch's conclusions (A., 1924, i, 1141), which are adversely criticised.

L. S. THEOBALD.

Complex alkali copper carbonates. A. COCO-SINSCHI (Bull. Acad. Sci. Roumaine, 1929, **12**, 19—21).—The following complex *salts* were prepared by the use of sodium or potassium hydrogen carbonate : $CuCO_3,Na_2CO_3,H_2O$ and $3H_2O$; $CuCO_3,2Na_2CO_3,2H_2O$; $CuCO_3,3Na_3CO_3,2H_2O$; $2CuCO_3,Na_2CO_3,3H_2O$; $2CuCO_3,3Na_3CO_3,5H_2O$; $CuCO_3,K_2CO_3$; $CuCO_3,2K_2CO_3,H_2O$; $2CuCO_3,K_2CO_3,2H_2O$; $2CuCO_3,2K_2CO_3,H_2O$; $2CuCO_3,3K_2CO_3,3H_2O$. By precipitation with equimolecular proportions of sodium or potassium carbonate and hydrogen carbonate the following *substances* were obtained : $CuCO_3,Cu(OH)_2,Na_2CO_3$; $CuCO_3,2Cu(OH)_2,Na_2CO_3$; $CuCO_3,2Cu(OH)_2,2Na_2CO_3$; $CuCO_3,Cu(OH)_2,2Na_2CO_3$; $2CuCO_3,Cu(OH)_2,Na_2CO_3$; $3CuCO_3,Cu(OH)_2,2Na_2CO_3$; $CuCO_3,Cu(OH)_2,K_2CO_3$; $CuCO_3,Cu(OH)_2,2K_2CO_3,2H_2O$; $2CuCO_3,Cu(OH)_2,K_2CO_3,H_2O$, and $3CuCO_3,Cu(OH)_2,K_2CO_3,H_2O$.

A. I. VOGEL.

Preparation of phosphorescent substances. II. Sulphides of calcium, strontium, and barium. N. F. SHIROV (Ukrain. Chem. J., 1929, **4**, 361—378).—Further details (cf. A., 1929, 1025) of the preparation of phosphorescent materials are given, the subjects considered including improvements in the technique, especially in the heating, the influence of secondary solvents, new fluxes and their combination, investigation of new activators both separately and in combination, determination of the best combinations of all three components to give maximum permanence, stability, friability in relation to the brightness and variation of the colour of the luminescence. When the heating is effected at 900—1000°, the minimum time of heating is 1 hr. for BaS, 1·5 hrs. for CaBaS, 2 hrs. for CaSrS and CaS+BaS, 2·5 hrs. for SrBaS, and 3 hrs. for SrS. Preparations from calcium sulphide alone or mixed with strontium sulphide are soft, those from barium sulphide of medium hardness, and those from strontium sulphide and its mixtures with barium sulphide hard. Magnesium oxide confers softness when added to the extent of 10%, which may be increased to 25% with strontium and barium preparations. Calcium sulphide preparations require no addition of magnesium oxide, which effects slight displacement of the colour of the luminescence towards the violet region of the spectrum. Incorporation of 25% of calcium tungstate with the sulphides lowers the m. p. of the mixtures especially with barium sulphide, increases the hardness of the product, and causes a change in colour towards the violet. Zinc oxide gives no luminophores when added to the extent of 40%, but exhibits triboluminescence. Maximum intensity of luminescence is obtained by using the mixture $Na_2B_4O_9+K_2B_6O_{10}+Li_3PO_4+CaF_2$ as flux, good results being obtained also with $K_2B_6O_{10}+K_2SO_4$ and $Li_3PO_4+Li_2CO_3$. Good luminophores are obtained by using sodium tungstate and, especially, lithium tungstate or sodium pyrophosphate. With calcium sulphide, gold gives greenish dark blue, palladium or cæsium greenish-blue, osmium or thallium greenish-yellow luminescence; with strontium sulphide gold gives greenish-yellow, vanadium yellow, erbium yellowish-green, cæsium yellowish; with barium sulphide, indium gives yellowish luminescence. T. H. POPE.

Action of ammonia on $HgBr_2,2NH_3$. Formation of NH_2HgBr and NHg_2Br. M. FRANÇOIS (Compt. rend., 1930, **190**, 125—126; cf. Gaudechon, A., 1909, ii, 670).—A small amount of ammonia solution (d 0·922) converts the compound $HgBr_2,2NH_3$ into white mercuriammonium bromide, $HgBr_2,2NH_3 \rightleftharpoons NH_2HgBr+NH_4Br$; a larger quantity carries the reaction further, with production of yellow dimercuriammonium bromide, $2HgBr_2,2NH_3 \rightleftharpoons NHg_2Br+3NH_4Br$. Both reactions are reversible. The former continues until the ammonia solution contains 18·92 g. per litre of ammonium bromide, the latter stops when 1·56 g. per litre of ammonium bromide is present. The same equilibrium points are reached when the reactions are carried out in the reverse direction. C. A. SILBERRAD.

Ultramarine problem in the light of recent research. J. HOFFMANN (Chem.-Ztg., 1929, **53**, 953—955, 974—975).—A brief review of recent work

on the constitution of ultramarine, with especial reference to that of Jaeger during 1928—1929.

A. R. POWELL.

Behaviour of amorphous carbon and sulphur compared with that of diamond and of graphite. Ciusa's carbon sulphide. J. P. WIBAUT and E. J. VAN DER KAM (Rec. trav. chim., 1930, **49,** 121—141).—See A., 1929, 896.

Germanium, indium, niobium, titanium, and hydrogen. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1930, **185,** 225—238).—The behaviour of hydrogen towards various metals at different temperatures and pressures has been investigated in an apparatus previously described (A., 1926, 810). Contrary to the results of other investigators, hydrogen appears to be practically insoluble in germanium and indium, since no greater absorption than 1 c.c. of gas in 100—200 g. of metal was observed. Both isotherms and isobars of the system niobium–hydrogen are similar in form to those for vanadium and tantalum hydrides. Exact repetition of the experiments was impossible, owing to increasing inactivity of the niobium as the result of an ageing effect. No formation of gaseous titanium hydride was observed. This is contrary to the results of Renz (A., 1906, ii, 173) and Billy (Ann. Chim. Phys., 1921, [x], **9,** 1), but in agreement with Paneth's rule.

M. S. BURR.

Oxides. V. Preparation, properties, density, and molecular volume of a crystalline lead dioxide. A. SIMON (Z. anorg. Chem., 1930, **185,** 300—304).—Crystalline lead dioxide has been prepared by heating sodium plumbate, with or without water of crystallisation, for three days in an autoclave at 250°, in presence of water (cf. this vol., 289). Violet-black crystals, reddish-brown by transmitted light, and strongly doubly refracting, were formed in interlocking masses. When fractured the crystals displayed blue and red interference colours and dichroism of red with green or blue. X-Ray examination indicates that lead dioxide has a rutile structure. Crystalline lead dioxide is much more stable, both to heat and solvent action, than the amorphous compound. A commercial preparation for analytical purposes had d 8·919, a product consisting of fine crystals admixed with amorphous material, prepared by the autoclave method, had d 9·011, and a coarsely crystalline product, d 9·604, whilst d (X-ray) is 9·5. Calculation of the mol. volume indicates that oxygen must be greatly compressed. The mol. volume of the heaviest sample (24·906) is very little larger than that of lead oxide (24·2). M. S. BURR.

Origin [and extraction] of protoactinium. J. E. WILDISH (J. Amer. Chem. Soc., 1930, **52,** 163—177).—The extraction of protoactinium with tantalum from uranium minerals is described; 90% of the tantalum used was recovered. Difficulties due to barium and moderate quantities of silica were surmounted. Uranium and protoactinium were determined in five minerals. The number of atoms of protoactinium per 100 atoms of uranium was 5·16 in Colorado carnotite, 2·79 and 1·47 in two Bohemian pitchblendes, 3·67 in Belgian Congo soddite, 2·50 in Ceylon thorianite. The results support the view that

the actinium series arises from a source other than uranium II. J. G. A. GRIFFITHS.

Reduction by hydrazine of sexavalent molybdenum derivatives. W. F. JAKÓB and W. KOZŁOWSKI (Rocz. Chem., 1929, **9,** 667—675).—Hydrazine in strongly acid boiling solution reduces sexavalent to quinquevalent molybdenum compounds, being itself oxidised quantitatively to nitrogen. In feebly acid solutions anion complexes containing both quinque- and sexa-valent molybdenum are produced, such as Rammelsberg's salt, $NH_4[Mo_2O(OH)_7MoO_4]$, from ammonium paramolybdate. Solutions of the latter salt containing hydrochloric acid to $2N$ yield on reduction molybdenum-blue, whilst strongly acid solutions, containing 150 c.c. of concentrated acid to 100 g. of molybdate, yield Klason's salt, $(NH_4)_2[MoOCl_5]$. R. TRUSZKOWSKI.

Non-electrolytic compound of polonium. M. GUILLOT (Compt. rend., 1930, **190,** 127—128).—When sodium dithiocarbamate is added to an acid aqueous solution of a heavy metal (e.g., bismuth, cobalt, copper, or nickel) containing polonium, all the polonium is found in the precipitate, which is wholly soluble in chloroform and can be recrystallised therefrom. In dithiocarbamates of copper or nickel the polonium is entirely in the surface layer of the crystals, in those of cobalt or bismuth it is more evenly distributed. The affinity of the polonium compound for the cobaltic, and to a smaller degree the bismuth, dithiocarbamate is markedly greater than for the nickel or copper compound. It is inferred that the polonium is present as dithiocarbamate, with valency 3 and co-ordination number 6, as $Po(S \cdot CS \cdot NR_2)_3$.

C. A. SILBERRAD.

Fluosulphonic acid. E. WILKE-DÖRFURT, G. BALZ, and A. WEINHARDT (Z. anorg. Chem., 1930, **185,** 417—424).—In continuation of previous work (cf. A., 1927, 120, 238) on the similarities between the complex salts of fluoboric, perchloric, permanganic, and fluosulphonic acids, the preparation and properties of a number of fluosulphonates and of some new permanganates and perchlorates are described. These are : *silver tetrapyridineperchlorate,* $[Ag(C_5H_5N)_4]ClO_4$; *nickelous, zinc, cadmium, cobaltous, ferrous,* and *manganous hexamminefluosulphonate,* $[M(NH_3)_6](SO_3F)_2$; *nickelous hexamminopermanganate,* $[Ni(NH_3)_6](MnO_4)_2$; *cobaltic* and *chromic hexammine dinitrate fluosulphonate,* $[M(NH_3)_6](NO_3)_2SO_3F$; *chromic hexammino-perchlorate* and *-permanganate,* $[Cr(NH_3)_6]X_3$; *chromic hexacarbamidofluosulphonate,* $[Cr(CON_2H_4)_6](SO_3F)_3$. M. S. BURR.

Preparation of manganese dioxide. I, II. Y. KATO and T. MATSUHASHI (J. Soc. Chem. Ind. Japan, 1929, **32,** 313—314B, 315—316B).—I. Manganese dioxide may be prepared from any lower oxide by direct oxidation with oxygen, using sodium hydroxide as catalyst. At 400—500° a product containing 50—95% MnO_2 may be obtained.

II. The composition of the air-dried product corresponds with the formula MnO_2, H_2O. It has high values of electrical resistance, oxidation potential, and adsorbing power for gases.

C. W. GIBBY.

Pyrophoric iron. I. Preparation and properties. II. Adsorption of carbon dioxide and ammonia. Use in the ammonia synthesis. T. G. FINZEL (J. Amer. Chem. Soc., 1930, **52**, 142—149, 150—156).—I. Pyrophoric iron, containing 1—2% of impurity, was prepared by reducing with hydrogen at 500° pure ferric oxide of different degrees of dispersion produced by interaction of ammonia and ferric nitrate. Limiting concentrations of oxygen in which this iron was pyrophoric were determined. Reaction occurred in air dried with phosphoric oxide and at −78°. The time of heating at 600° required to inactivate pyrophoric iron is longer for larger grains (estimated by von Weimarn's precipitation law) and is less according as the medium is helium, nitrogen, or hydrogen. Inactivated iron has larger grains than pyrophoric iron, but both are α-iron.

II. The volume of carbon dioxide and ammonia adsorbed per g. of metal was increased in proportion to the grain size of the pyrophoric iron. Fine-grained pyrophoric iron did not catalyse the synthesis of ammonia and adsorbed less gas than coarser, non-pyrophoric iron. Sintering was prevented and catalytic activity was obtained in the fine-grained iron by preparation from a mixture of ferric and aluminium nitrates. It is suggested that the coarser grains of iron, which are catalytically active, had cores of iron oxide which prevented sintering.

J. G. A. GRIFFITHS.

Iron oxide in borate beads. W. D. BANCROFT and G. E. CUNNINGHAM (J. Physical Chem., 1930, **34**, 1—40).—The blue colour of iron compounds is due to an unstable, blue modification of ferric oxide, which is stabilised chiefly by ferrous oxide. In alkali borate ferrous oxide is colourless, ferric oxide is yellow, whilst a certain mixture of ferrous and ferric oxides is blue. Reduction of iron oxide to metal by hydrogen occurs readily when the alkali concentration in the fused mass is low. A higher concentration of alkali prevents the formation of metal but does not favour complete reduction of ferric to ferrous oxide. A ratio $FeO : Fe_2O_3$ equal to 3 : 1 in borate glasses gives a glass free from green and with a ratio 4 : 1 the blue colour becomes more pronounced. Reduction of ferric oxide is easier in a potassium borate bead than in one of sodium borate. The application of these results to fired clays and to iron-bearing minerals is fully discussed. L. S. THEOBALD.

Characterisation of iron carbonyls and their derivatives. W. HIEBER (Naturwiss., 1930, **18**, 33—34).—The carbonyl groups in iron pentacarbonyl can be replaced by pyridine or ethylenediamine, and well-defined carbonyls containing amines can be isolated in which the Fe : CO ratio is 1 : 3, $2\frac{1}{2}$, and 2. With ammonia and ethylenediamine interacting with iron pentacarbonyl (in the presence of pyridine) the molecules $Fe(CO)_3(NH_3)_2$ and $Fe_2(CO)_5$ en$_2$ are formed, whilst pyridine alone leads to $Fe_3(CO)_4(C_5H_5N)_3$, a substance very sensitive to oxygen. The polymeride $[Fe(CO)_4]_6$ appears to decompose according to the simplified equation $2Fe(CO)_4 = Fe(CO)_3 + Fe(CO)_5$. The compounds $Fe(CO)_3(C_5H_5N)$ and $Fe(CO)_3$,MeOH are readily formed. The tricarbonyl compounds are intensely red, soluble in organic solvents, and exceed-

ingly sensitive to oxygen. Acids result in reactions of the type $2Fe(CO)_3$,MeOH$+2H^+ \longrightarrow Fe(CO)_4$ (polymeride $+Fe^{++}+2CO+H_2+2MeOH$. The significance of the results is discussed. R. A. MORTON.

Oxidation of cobalt salts in alkaline medium. R. BERNARD and P. JOB (Compt. rend., 1930, **190**, 186—187).—Spectrophotometric measurements indicate that the oxidation of solutions of cobaltous sulphate in concentrated sodium hydrogen carbonate solution by bromine water or by hydrogen peroxide cannot be expressed by the simple equation $2CoO+O=Co_2O_3$. In both cases there is probably the intermediate reaction $CoO+O \longrightarrow CoO_2$. J. GRANT.

Reaction of nickel carbide, Ni_3C, prepared at a moderate temperature. H. A. BAHR and T. BAHR (Ber., 1930, **63**, [B], 99—102).—Nickel carbide, prepared as described previously (A., 1928, 1336), is strongly pyrophoric, but loses this property when heated in nitrogen at 250°, whereby its reactivity is also diminished. It has d^{18} 7·97. Below 380—400° it is stable, but decomposes more or less rapidly above this temperature with deposition of elementary carbon. With molecular hydrogen at 250°/atm. pressure it gives mainly methane, but slight polymerising power is evidenced by the formation of ethane in small proportion. This tendency is emphasised when hydrogen at 200°/20 atm. is used. Superheated steam at 300° reacts principally according to the equation $C+2H_2O=CO_2+2H_2$; some methane is formed, but its homologues do not appear to be produced. With ammonia at 420° the products are hydrogen and nitrogen with a little methane and ethane; ammonium cyanide is possibly produced. Hydrogen sulphide reacts readily at 240° without apparent formation of methane. Hydrogen chloride gives oily products at 290—300°. Hydrochloric acid yields a clear solution with nickel carbide; the ratio of gaseous to liquid hydrocarbons is 2 : 1. Simple compounds constitute 95% of the gas. Nitric acid appears to afford nitro-derivatives of the hydrocarbons primarily produced. With dilute sulphuric acid a part of the carbide carbon separates in the elementary form from the solution.

H. WREN.

Colorimetric methods. N. SCHOORL (Chem. Weekblad, 1930, **27**, 52—54).—Colorimetric methods of analysis are discussed under the headings of true colorimetry, nephelometry, titrimetric methods, and methods wherein the solution under examination is compared with a graded series of standard solutions. The importance of establishing the validity of Beer's law in the solution under consideration is emphasised in the first and third groups, whilst the velocity of the reaction, the stability of reactants and reaction products, the influence of other substances and of an excess of reagent, and the manner in which the reagent is added have all to be taken into account when considering any particular colorimetric process.

H. F. GILLBE.

Borax and mercuric oxide as standard substances for all methods of volumetric analysis. N. A. LAZARKEVITSCH (Ukrain. Chem. J., 1929, **4**, 405—428).—Mercuric oxide may be employed as the standard substance for all the fundamental methods

of volumetric analysis if no high degree of accuracy is required; where accurate results are desired it cannot be used, especially in iodine and permanganate titrations. Borax, however, may be used as a standard for determining the titre of acids to be employed in measuring the strengths of thiocyanate, thiosulphate, and permanganate solutions, the results thus obtained agreeing well with those given by other methods (cf. Glücksmann, Z. Oesterr. Apoth. Ver. Bel., 1899, **37**, 970; Rosenthaler and Abelmann, A., 1913, ii, 786; Tananaev, A., 1925, ii, 441).
T. H. POPE.

Aid to gravimetric analysis. E. LEHMANN (Chem.-Ztg., 1930, **54**, 62).—After preliminary washing, a filter-paper bearing a precipitate may be folded and washed from the outside.						S. I. LEVY.

Carbon dioxide content of distilled water. W. HOESCH (Chem.-Ztg., 1929, **53**, 956).—Distilled water stored, with free access of air, in the lower part of a building always contains much more carbon dioxide in solution than that stored on an upper floor. This fact is of importance in conducting delicate acidimetric analyses of solutions containing weak acids.
A. R. POWELL.

Conditions for evaporation of mineral waters from the point of view of chemical analysis. P. BRETEAU (J. Pharm. Chim., 1930, [viii], **11**, 5—7).—Evaporation of mineral waters for analysis after acidification with hydrochloric acid in platinum vessels leads to contamination of the solution with platinic chloride (since many waters contain traces of nitric acid) and also renders uncertain the detection of other metals, e.g., iron, copper, zinc, etc., when these are present in traces. Hence waters should be made alkaline preparatory to evaporation.
R. J. W. LE FÈVRE.

Determination of water in micas. K. WISKONT and I. ALIMARIN (Z. anal. Chem., 1929, **79**, 271—286).—The usual methods for the determination of water in silicates give untrustworthy results in the case of the micas, and an improved method, based on a combination of those of Penfield and Kuzirian, has been devised. The mica (0·3 g.) is weighed into a platinum boat, a few crystals of potassium chlorate are added, and the whole is covered with a layer of pure sodium tungstate. The expulsion and determination of the water are then carried out by Penfield's method, the glass tube employed containing a plug of spongy platinum and another of granulated lead oxide wrapped in platinum gauze, which serves to retain volatile constituents such as fluorine. Attention is directed to the importance of distinguishing between the "hygroscopic water" and "inclusion water" in minerals, and further study of the dehydration curves of minerals is recommended.
H. F. HARWOOD.

Method of calculating analyses. III. E. LIESCHE (Z. angew. Chem., 1929, **42**, 1109—1100).—Equations and factors for calculating from the results of indirect analysis the composition of binary mixtures of ammonium and alkali halides are given together with the method of constructing a nomogram for reading directly the composition of a mixture of ammonium chloride and bromide from the number of

c.c. of 0·1N-silver nitrate solution required in the titration of a known weight of the mixture.
A. R. POWELL.

Chlorometric, bromometric, and iodometric determination of available chlorine in hypochlorite solutions and bleaching powder. I. H. DITZ and R. MAY (Z. anal. Chem., 1930, **79**, 333—345).—The various chlorometric and iodometric methods are discussed. A comparison of these showed that the Penot–Lunge method (direct titration with arsenite) gave results which were 0·21% lower than those obtained by the iodometric method of Rupp, this being due to the greater sensitivity of the end-point in the latter case. Rodt's modification of the Penot–Lunge method renders the end-point more sensitive, but the results are still slightly lower than those afforded by the iodometric method. Kolthoff's process (titration of an acidified arsenite solution with the hypochlorite) gave varying results, which were about 0·81% too high.			H. F. HARWOOD.

Determination of halogen by Gasparini's method. III. K. HELLER [with K. WILLINGSHOFER and B. SADRAWETZ] (Z. anal. Chem., 1929, **79**, 256—270; cf. A., 1929, 528, 1158).—The reduction of perchlorates by electrolysis in concentrated sulphuric acid solution, using platinum electrodes, is ascribed to the formation of hyposulphurous acid as intermediary, this substance then catalysing the reduction of the perchlorate. The addition of nitric acid produces the same result, and the reduction is also accelerated by the presence of platinum or its salts. The chlorine in chlorides, chlorates, perchlorates, and many organic chloro-compounds can be determined by Gasparini's method if a mixture of 4 vols. of concentrated sulphuric acid and 1 vol. of concentrated nitric acid is used as electrode liquid; the electrolysis requires 4—6 hrs. In the analysis of chlorates, 1 g. of sodium sulphite must be added to the absorption bulbs containing the acidified silver nitrate before commencing the analysis. Substances which readily sublime cannot be analysed by this method, and it also fails with certain chloro-derivatives of phthalic acid, benzoylbenzoic acid, and anthraquinone.							H. F. HARWOOD.

Iodometric micro-determination of bromides and iodides. R. HOFMANN (Pharm. Zentr., 1930, **71**, 18—21).—Some modifications in the standard apparatus and method of working are described. A mixture of lead peroxide and acetic acid is used in place of chromic acid to oxidise the bromide, and carbon dioxide in place of air to carry the liberated halogen over. The maximum error is 10%, but the determination is very rapid.			S. I. LEVY.

Argentometric studies. III. Determination of bromides and iodides in the presence of a large excess of chlorides. O. TOMÍČEK and A. JÁNSKY (Coll. Czech. Chem. Comm., 1930, **2**, 1—7).—The boiling acid solution is treated with 0·05N-potassium permanganate solution until bromine ceases to pass into the distillate, which is collected in sodium sulphite solution. This treatment with potassium permanganate is repeated with the first distillate and the bromide and iodide in the second distillate are determined argentometrically by potentiometric titra-

tion. The iodate in the two residues is reduced with sodium sulphite in the presence of a very small concentration of bromide ions and the iodide determined potentiometrically. The application of this method to mineral waters and salts is described.

A. I. VOGEL.

Iodine trichloride as a reagent for sulphide minerals, especially pyrites. E. WILKE-DÖRFURT and E. A. WOLFF (Z. anorg. Chem., 1930, **185**, 333—336).—Birk's method (A., 1928, 976) for attacking with iodine trichloride minerals which are difficult of dissolution, has been tested on a pyrites which has also been analysed by two other methods using aqua regia and an ethereal solution of bromine, respectively. For accuracy, the iodine trichloride method is as satisfactory as other methods for bringing sulphides into solution, and it can be employed successfully where all oxidation media hitherto in use react incompletely, or can bring into solution, with the greatest difficulty only, the sulphur separated during the decomposition of the sulphide.

M. S. BURR.

Determination of nitrogen in gaseous mixtures. S. N. BLUMSTEIN (Z. anal. Chem., 1930, **79**, 324—333).—Lidoff's original method for the direct determination of nitrogen in gaseous mixtures (A., 1902, ii, 353) necessitates the employment of a very complex apparatus, and a simpler procedure has now been devised. Two gas burettes connected by a special three-way tap are used; the gas is freed from carbon dioxide and oxygen, dried with sulphuric acid, and passed over heated magnesium contained in a hard glass tube. When absorption of nitrogen is complete the contents of the tube are transferred to a flask, treated with alkali, and the ammonia formed is distilled into standard acid. An analysis can be carried out in 4 hrs., and 99·2% of the nitrogen present can be determined, as compared with 97% by Lidoff's method. Full working details of the method are given.

H. F. HARWOOD.

Determination of carbon monoxide in a gas containing 0·25—0·3%. M. NICLOUX (Compt. rend. Soc. Biol., 1929, **100**, 861—864; Chem. Zentr., 1929, ii, 1182).—The gas is brought into contact with reduced blood in complete absence of oxygen, the determination of carbon monoxide in the blood being made eudiometrically.

A. A. ELDRIDGE.

Detection of the principal anions by separate tests. P. AGOSTINI (Annali Chim. Appl., 1929, **19**, 520—524).—The tests given are made, as far as possible, on the original solid or on its alkaline solution, interaction between oxidising and reducing anions being thus hindered.

T. H. POPE.

Quantitative spectral analysis. I. Determination of potassium, magnesium, and copper in flame spectrum. H. LUNDEGÅRDH (Arkiv Kemi, Min., Geol., 1929, **10**, A, No. 1, 26 pp.).—An apparatus for the quantitative analysis of dissolved compounds by means of absorption spectra is described. A constant stream of the solution is dispersed in minute drops by compressed air with a nozzle spraying apparatus (cf. Gouy, Ann. Chim., 1879, **18**, 5), and brought into a constant acetylene flame. Photographs of the flame spectrum allow the

inclusion of the ultra-violet region, and with 60 sec. exposure eliminate errors due to small variations in the flame and spraying apparatus. The spectral lines of the plate were projected on a thermo-element and the degree of intensity was read accurately from a galvanometer deflexion. Standard solutions for comparison are necessary. The region of suitable measurements depends on the time of exposure and other factors; under the conditions described it was for potassium and magnesium 300^{-1} to 20^{-1}, calcium and copper 2000^{-1} to 50^{-1}, lithium $20,000^{-1}$, and sodium $10,000^{-1}$ mol. The practical and theoretical minimum sensitivities for potassium, magnesium, and copper are 0·36, 0·20, 0·10, and 0·004, 0·002, 0·001 mg., respectively. Experiments are described and results tabulated for these three metals, on the factors, including the presence of impurities, influencing the total error of the analysis. The minimum total error was of the order 2%.

N. M. BLIGH.

Determination of sodium hydroxide in presence of sodium carbonate. W. POETHKE and P. MANICKE (Z. anal. Chem., 1929, **79**, 241—255).—The accuracy of Winkler's method has been investigated, using mixtures of 0·1N-sodium hydroxide and carbonate in varying proportions. The figures obtained for the sodium hydroxide present are invariably slightly too low, but the error is negligible if the precipitation with barium chloride takes place in the cold, and the solution is dilute. The amount of barium chloride employed must be such that the final concentration of barium in the solution after precipitation is 0·1N. The following procedure is recommended. The solution is diluted with water free from carbon dioxide, and the total alkali determined in an aliquot portion by titration with hydrochloric acid and methyl-orange. Another portion is added to an excess of cold N-barium chloride (previously diluted to 25 c.c.), and after shaking, the liquid is titrated with hydrochloric acid in presence of 1 drop of 1% phenolphthalein for every 25 c.c. of solution. An attempt to substitute strontium chloride for barium chloride in the method gave unsatisfactory results.

H. F. HARWOOD.

Employment of sodium thiosulphate in analytical chemistry. E. DONATH (Chem.-Ztg., 1930, **54**, 78—79).—Sodium thiosulphate may be advantageously substituted for the customary mixture of sodium carbonate and sulphur employed for opening up sulphide minerals by fusion, as the precipitation of large quantities of sulphur in the subsequent treatment of the resulting solution is thereby obviated. It may also be employed in place of hydrogen sulphide to precipitate copper and certain other metals from their solutions, and is particularly useful in separating copper from cadmium and zinc. The use of sodium thiosulphate for the determination of aluminium in presence of iron does not, however, offer any advantages over the usual indirect method.

H. F. HARWOOD.

Volumetric determination of potassium with sodium hydrogen tartrate. V. E. TOVARNITZKI and K. I. SLEZAK (Zhur. Sakh. Prom., 1928, **2**, 462—473).—After elimination of ammonium, rubidium, cæsium, and sulphate the neutral solution containing

20—50 mg. of potassium is evaporated to dryness with excess of ammonia solution, the residue is ignited, 15—30 drops of 10% calcium chloride solution and 0·5—1 c.c. of ammonia solution are added, and the mixture is again evaporated and ignited. The residue is dissolved in hot, boiled distilled water, the solution is filtered, and the residue washed with 100—120 c.c. of water. The solution, after neutralisation with barium hydroxide or acetic acid, is evaporated to dryness on the water-bath, 10—12 c.c. of standard sodium hydrogen tartrate solution are added, the mixture is kept over-night, filtered through a dry filter, and 5 c.c. of the filtrate are titrated with 0·15N-barium hydroxide, using phenolphthalein. The standard sodium hydrogen tartrate solution is prepared by dissolving tartaric acid (55 g.) and sodium hydroxide (14 g.) in distilled water (800 c.c.), boiling to remove carbon dioxide, and making up to 1 litre; 5—7 drops of toluene and 6 g. of potassium hydrogen tartrate are then added.   CHEMICAL ABSTRACTS.

Determination of lead peroxide. A. V. PAMFILOV and E. G. IVANČEVA.—See B., 1930, 142.

Determination of non-sulphide lead. H. K. HANSEN.—See B., 1930, 148.

Ceric sulphate as a volumetric oxidising agent. X. Determination of thallium. XI. Oxidation of organic acids. H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1930, 52, 36—42, 132—142).—X. A rapid and accurate volumetric determination of thallium is based on the quantitative oxidation by ceric sulphate of thallous to thallic salts in hydrochloric acid solution. In determining the end-point electrometrically, the solution should be about 2N with respect to hydrochloric acid and at 55°. The visual end-point (A., 1928, 725) is best observed when solutions are of less acidity and at 80—90°. Small quantities of nitric acid, tervalent arsenic and antimony interfere. Many ions, including ferric and chromic (at low temperatures and high acid concentration; cf. A., 1929, 287), are without effect.

XI. The suitability of ceric sulphate for determining organic acids by oxidation in hot sulphuric acid solution has been investigated. After maintaining the solution at 95° for 1 hr., the excess of ceric sulphate was determined by electrometric titration with ferrous sulphate (A., 1928, 725). Formic, acetic, succinic, fumaric, and maleic acids are not oxidised. Tartaric, malonic, malic, glycollic, and citric acids are determined by the respective factors 7·2, 6·66, 9·25, 3·95, 15·85 (g.-equiv. of oxygen per g.-mol. of acid) over an approximately fourfold variation of experimental conditions. Benzoic, phthalic, and salicylic acids give variable results.   J. G. A. GRIFFITHS.

Determination and separation from other metals of rare metals. XVI. Separation of thallium from ter- and quadri-valent metals. L. MOSER and W. REIF. **XVII. Precipitation of tungsten with tannin and antipyrine, and its separation from ter- and quadri-valent metals, from tin, and from silicic acid.** L. MOSER and W. BLAUSTEIN (Monatsh., 1929, 52, 343—350, 351—364).—XVI. The tannic acid method (A., 1928, 148)

cannot be used for the quantitative separation of thallium from aluminium, iron, and chromium, owing to extensive adsorption of the thallous ion by the tannic acid complex, which is little affected by varying the hydrogen-ion concentration. The ammonium nitrite–methyl alcohol method (loc. cit.) can be employed for the separation of thallium–aluminium, –iron, or –chromium mixtures in all proportions. Reprecipitation is generally unnecessary; thallium in the filtrate is determined as chromate by precipitation in boiling ammoniacal solution (cf. A., 1927, 436). The method is recommended on account of its accuracy for the determination of aluminium and chromium, and the metals should preferably be present originally as the sulphates. For determination of small quantities of thallium in the presence of the foregoing metals precipitation as thallous chromate from slightly alkaline solution in the presence of sulphosalicylic acid (A., 1927, 436) is especially advantageous.

The ammonium nitrite is preferably added to the slightly acid thorium solution in the cold, the mixture slowly warmed, and the methyl alcohol added after a part of the precipitate has formed; this method is applicable to the separation of zirconium and titanium. The nitrite method cannot be used to remove cerium. Precipitation of cerium as cerous oxalate can be employed, but the separation is not quantitatively exact. The nitrite method cannot be used to separate molybdenum and tungsten from thallium, but this may be effected by precipitation of thallium as chromate from hot ammoniacal solution. This method cannot be applied to the separation of vanadium and thallium. By taking advantage of the formation of a stable vanadium–tartaric acid complex (Barbieri, A., 1915, i, 380), a quantitative separation may be effected as follows : the precipitate of thallous metavanadate is dissolved in the smallest possible quantity of a concentrated tartaric acid solution at 40°, or below, and ammonia is added in excess to the red solution until the colour is changed to blue or discharged (according to the quantity of vanadium); thallium is determined by precipitation with potassium chromate at the ordinary temperature.

XVII. Tungsten may be determined by use of tannic acid and antipyrine as follows : a dilute, slightly alkaline solution of ammonium tungstate, containing an approximately known amount of tungsten, is treated with sulphuric acid and ammonium sulphate. The boiling liquid is precipitated with tannic acid; after being kept some time on the steambath, the mixture is cooled to 15°, a 10% solution of antipyrine is added with continuous stirring, and the precipitate is washed with a solution containing sulphuric acid, ammonium sulphate, and antipyrine, and ignited to tungsten trioxide.

Quantitative separation of tungsten from iron, aluminium, or chromium may be achieved by the foregoing method; reprecipitation is necessary with iron and chromium. Accurate results are obtained by a single precipitation of tungsten from manganese, zinc, nickel, or cobalt. By adding tartaric acid to a mixture containing tungsten and tin, a soluble tungsten–tartaric acid complex is obtained; tin can then be removed as sulphide. The soluble tungsten

complex is not precipitated with tannic acid and antipyrine, and after removal of hydrogen sulphide by heating, the tartaric acid is removed by oxidation with hydrogen peroxide in the presence of iron (cf. Meigen and Schnerb, A., 1924, ii, 506); the tungsten is now present as tungsten trioxide which does not react with tannic acid, but by addition of ammonium sulphate and tannic acid solution, saturation with ammonia, and boiling, followed by cooling, acidification with sulphuric acid, and reheating, the tungsten–tannic acid complex is completely precipitated, and the determination is completed by addition of antipyrine after cooling.

Separation of tungsten from silicic acid depends on the non-precipitation of colloidal silicic acid with tannic acid and antipyrine; if, however, before adding tannic acid, a solution containing tungstate and silicate is treated for a short time with mineral acid, or is kept for a long time, some silicic acid is adsorbed by the tungsten–tannic acid complex. If more than 0·1 g. of tungsten trioxide is to be determined, a single precipitation with tannic acid and antipyrine effects quantitative separation; with less than 0·05 g., the precipitate contains traces of silicic acid. The precipitate may either be treated with concentrated sulphuric acid and hydrofluoric acid after ignition, or may be collected, redissolved in hot ammonia, filtered, and reprecipitated with tannic acid and antipyrine after acidification with sulphuric acid and addition of ammonium sulphate. C. W. SHOPPEE.

Volumetric determination of copper. A. T. KÜCHLIN (Rec. trav. chim., 1930, **49**, 151—152).— Copper may be determined volumetrically by adding to the solution a known excess of a standard stannous chloride solution in an atmosphere of carbon dioxide and shaking for at least 20 sec. in order to reduce the copper completely to the cuprous state, and then titrating the excess of stannous salt with iodine.

R. CUTHILL.

Potentiometric determination of cerium sulphate. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1929, **18**, 517—523).—See A., 1929, 1032.

Drop method of detecting ferri- and ferrocyanide ions. A. SCHAPOVALENKO (Ukrain. Chem. J., 1929, **4**, 303—307).—In the detection of these ions in low concentrations, it is best to make a spot of the ferrous or ferric salt on the filter-paper and then add a drop of the solution to be tested; the colour is heightened by further addition of a drop of N- or $2N$-hydrochloric acid. In this way ferricyanide is detectable in a concentration of 1 in 10,000 and ferrocyanide in one of 1 in 1000, the actual quantities of the two ions employed in these cases being 0·00007 and 0·00026 mg., respectively. When both ions are present, use may be made of a soluble lead salt, since the ferrocyanide ion is then fixed as an insoluble salt at the centre of the spot, whilst the ferricyanide ion filters through to the edge of the spot and may there be tested. Addition of a lead salt also renders possible the detection of these ions in presence of sulphide, iodide, and thiocyanate ions. T. H. POPE.

Determination of manganese, iron, and aluminium in presence of phosphoric acid. I. S. TELETOV and N. N. ANDRONIKOVA (Ukrain.

Chem. J., 1929, **4**, 341—347).—When the method previously described (A., 1929, 1260) is applied to solutions containing phosphoric acid, this passes entirely into solution on precipitation of the iron and manganese with sodium hydroxide and hydrogen peroxide. Moreover, the precipitate is very easily filtered and washed. Treatment of the alkaline filtrate with barium nitrate results in the total precipitation of the phosphoric acid as barium phosphate, the determination of the aluminium in the filtrate from this being carried out as usual. This procedure gives accurate results except when manganese is present in unduly large proportion.

T. H. POPE.

Sensitive reagent for molybdate ion. E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], **47**, 128).— $2·5 \times 10^{-5}$ part of molybdate ion may be detected by the formation of a red coloration with a reagent consisting of 3 parts of phenylhydrazine, 3 of sulphuric acid, and 65 of water. The test is specific.

C. W. GIBBY.

Spectrophotographic detection of bismuth in the ashes of animal organisms. G. PICCARDI (Atti R. Accad. Lincei, 1929, [vi], **10**, 258—260).— The presence of bismuth is determined by photographing the ultra-violet portion of the spark spectrum formed between two vertical gold electrodes, the lower of which is sealed into a small glass cup containing the solution of the ashes in one drop of concentrated hydrochloric acid solution. The characteristic bismuth lines are obtained with solutions containing as little as $10^{-6}\%$ of bismuth. O. J. WALKER.

Determination of osmium by strychnine sulphate. S. C. OGBURN, jun., and L. F. MILLER (J. Amer. Chem. Soc., 1930, **52**, 42—48).—Solutions of salts of the platinum metals give precipitates with saturated strychnine sulphate. In the absence of all other platinum metals, the osmium in sodium chloroosmate is determined accurately by precipitation of the strychnine compound $(C_{21}H_{22}O_2N_2)_3Os$ (factor 0·1758). It is suggested that in this compound osmium has the co-ordination number 6. A quantitative separation of osmium from ruthenium is effected, since the strychnine compounds of both metals are soluble in boiling 50% aqueous ethyl alcohol, but that of osmium alone is reprecipitated immediately on cooling the liquid.

J. G. A. GRIFFITHS.

Apparatus for the determination of corrected m. p. C. JUNGE (Chem.-Ztg., 1929, **53**, 996).—The apparatus consists of a jacketed heating tube containing a small quantity of heating liquid into which are immersed the thermometer and specimen. The bottom of the jacket is connected externally with the top by means of a narrow circulating tube which can be heated at its lowest part by a small flame. The jacket is filled with sulphuric acid, which, on application of the flame, is caused to circulate, thus ensuring regular even heating of the specimen and keeping the stem of the thermometer at the same temperature as the bulb. A. R. POWELL.

Ebullioscopic apparatus for study of mixtures of liquids. W. SWIENTOSLAWSKI (Rocz. Chem., 1929, **9**, 608—614).—See this vol., 56.

Ebullioscopic and tonometric determinations. W. SWIENTOSLAWSKI (Bull. Acad. Polonaise, 1929, A, 434—486).—See A., 1929, 786.

Arrangement for obtaining a steady flow of gas at constant low pressure. F. G. SLACK (Rev. Sci. Instr., 1930, **1**, 33—35).—The pressure of hydrogen generated electrolytically is transmitted to a mercury manometer which makes and breaks the generating circuit by means of a relay. C. W. GIBBY.

Capillary manometer system for preparing mixtures of gases with a very high ratio between components. E. Q. ADAMS and E. R. H. CHARPENTIER (Rev. Sci. Instr., 1930, **1**, 9—12).—The rate of flow of each gas is measured by the pressure produced in a calibrated manometer when it flows through a capillary tube. C. W. GIBBY.

Growth of single crystals of low-m. p. metals in vacuum. J. H. DILLON (Rev. Sci. Instr., 1930, **1**, 36—38).—The metal is out-gassed at a temperature 60° above the m. p. for 24 hrs. in a pyrex tube, and filtered through a capillary into a limb which is then sealed off and lowered slowly into a furnace kept about 60° above the m. p. C. W. GIBBY.

Platinum contamination of palladium in palladium point determinations. C. L. UTTERBACK (Rev. Sci. Instr., 1930, **1**, 39—44).—Spectral and chemical analyses show that palladium heated in contact with platinum becomes contaminated with the latter, with increasing velocity at temperatures above 1100°. Samples of palladium held by platinum supports close together melt at a higher temperature than if the supports are further apart. C. W. GIBBY.

Methods and apparatus used in the cryogenic laboratory. XXIII. Horizontal cryostat for the measurement of magnetic susceptibilities at low temperatures. E. C. WIERSMA and H. R. WOLTJER (Proc. K. Akad. Wetensch. Amsterdam., 1929, **32**, 1046—1053).—An apparatus employing Weiss' method for the determination of magnetic susceptibility, and a vapour cryostat for use therewith, are described. H. F. GILLBE.

Simple cryostat. E. ZINTL and S. NEUMAYR (Ber., 1930, **63**, [B], 234—236).—An apparatus is figured and described which differs from that of Shinozaki and Hara (A., 1926, 1118) essentially only in the thermoregulator. H. WREN.

Freezing mixture. F. NOACK.—See B., 1930, 124.

Refractometer. E. E. JELLEY (J. Sci. Instr., 1930, **7**, 14—19).—The principle employed is that of grazing incidence, the plate of material under examination being immersed in a liquid of high refractive index, such as 1-bromonaphthalene or carbon tetrachloride. The refractive indices of thin films of aqueous solutions, celluloid, etc. can also be determined by enclosing the film between two glass plates of high refractive index prior to immersion. The apparatus is cheap and easily constructed and yields results which are accurate to 0·0002—0·0003. H. F. HARWOOD.

Scale for determining the refractive indices of liquids under the microscope. G. LINCK and E. KÖHLER (Chem. Erde, 1930, **4**, 458).—A set of eleven powdered glasses ranging in n from 1·5400 to 1·8052, also fluorite n 1·4339, is supplied for checking the values of the liquids used for the determination of the refractive indices of minerals by the immersion method under the microscope. L. J. SPENCER.

Trustworthiness of refractometric tables. A. KARVONEN (Suomen Kem., 1929, **2**, 115—117).—The tables for calculating refractive indices from refractometer readings are not always free from error. R. CUTHILL.

Fallacious determination of the specific heats of gases by the explosion method. O. C. DE C. ELLIS (Nature, 1930, **125**, 165—166).—Determinations of the specific heats of gases by measurements of the maximum pressure developed on explosion are fallacious, since, as is shown by a consideration of the mechanism of such explosions, the constitution of the gas at the moment of maximum pressure is unknown, and the gas cannot be homogeneous, nor can combustion cease before sensible cooling occurs. L. S. THEOBALD.

Small gas-muffle oven. II. F. W. HORST (Chem. Fabr., 1929, 513).—Several minor modifications of the muffles previously described (A., 1929, 1033) are described. A. R. POWELL.

Rapid evaporation. I, II. H. N. NAUMANN (Biochem. Z., 1929, **216**, 136—153, 154—164).—I. The efficiencies of laboratory apparatus and methods for evaporation and distillation of liquids and solutions have been investigated and performances have been compared with calculated values. The distillation, under reduced pressure, of large volumes of liquid can be conveniently and efficiently carried out with the help of a modified form of Liebig condenser having a copper condensation tube.

II. Small volumes of liquid such as those used in micro-analysis may be accurately concentrated to a required volume in a vacuum desiccator containing a heater which warms the liquid from above. A special form of evaporating dish having a small graduated cylindrical attachment at its base is used. W. McCARTNEY.

Reproducibility and constancy of the Weston element accepted as international standard. A. K. KOLOSOV (J. Appl. Chem., Russia, 1929, **2**, 369—388).—The preliminary purification of mercury by electrolysis is described. Crushed crystals of mercurous sulphate gave a higher *E.M.F.* than the original crystals. Elements prepared with electrolytes to which sulphuric acid of a concentration 0·1N or greater is added are characterised by a decrease in *E.M.F.* with time. The *E.M.F.* increases when mercurous sulphate is oxidised in a current of air, but, contrary to the effect of hydrolysis, it remains constant over a long period. The behaviour of the standard elements constructed is described. CHEMICAL ABSTRACTS.

New types of glass filtering apparatus. P. H. PRAUSNITZ (Chem.-Ztg., 1929, **53**, 935—936, 955—956).—Various new types of glass Buchner funnels, Soxhlet tubes, and extraction apparatus in which fused-in filter discs of sintered glass are employed, are illustrated and briefly described. A. R. POWELL.

Apparatus for hot filtration of saturated solutions. S. H. BERTRAM and W. A. VAN MEURS (Chem. Weekblad, 1930, **27**, 7—8).—A simple apparatus for filtering saturated solutions in volatile solvents, in which the filter is heated by means of the vapour of the solvent, is described. S. I. LEVY.

Universal distillation apparatus. R. KATT-WINKEL (Chem. Fabr., 1930, 18—20).—Various forms of apparatus for different purposes, in which the condenser is vertically above the distillation flask, are described. Vapours ascend by a side-tube entering the condenser above the lowest point, the latter being extended to one side to form measuring containers, extraction thimbles, reaction vessels, etc. Several applications are described. S. I. LEVY.

High-frequency field. I. H. RHEINBOLDT and A. HESSEL (Ber., 1930, **63**, [*B*], 84—87).—An apparatus suitable for the examination of substances in a high-frequency field is based on that described by Esau (Elektrotechn. Z., 1926, 321). Only compounds which have a certain electrical conductivity suffer change. Finely-divided metals and active charcoal become incandescent. Pure water, in contrast to tap-water, is almost unchanged, but addition of small amounts of electrolyte causes the liquid to boil more or less rapidly. Moist glass is heated to melting, whereas dry glass is unaffected. Hydrated salts are dehydrated. Moist potassium permanganate, in contrast to the dry salt, becomes decomposed. Organic solvents remain unaffected when absolutely anhydrous. Gases are unchanged at normal pressure, but glow under about 30 mm. pressure. Carbon monoxide and oxygen afford carbon dioxide. Hydrated sulphates of copper, nickel, manganese, and ferrous iron are decomposed in air with production of the metal or its oxide. Mercuric oxide is decomposed thermally. Petroleum and aromatic hydrocarbons in presence of air give tars. Primary alcohols are oxidised to aldehydes in presence of air or oxygen. Iodine combines rapidly with oxygen and sulphur dioxide with chlorine. Ethylenic compounds react with hydrogen.
H. WREN.

Ultra-violet solar radiation and the solarisation of window materials. W. W. COBLENTZ and R. STAIR.—See B., 1930, 103.

Geochemistry.

Ozone in northern and southern hemispheres. F. G. FOWLE (J. Terrest. Mag. Atm. Elec., 1928, **3**, 151—157).—Solar and magnetic observations on Table Mt. are correlated with variations in the ozone content of the atmosphere. CHEMICAL ABSTRACTS.

Iodine content of sea-water. J. F. REITH (Rec. trav. chim., 1930, **49**, 142—150).—The iodine content of sea-water may be satisfactorily determined by Winkler's method (A., 1916, ii, 109), and the alcohol extraction method (cf. von Fellenberg, Biochem. Z., 1923, **139**, 404) is also applicable if the final titration of the iodic acid is carried out in presence of acetic acid, to prevent interference by bromides (cf. A., 1929, 667). Sea-water from various localities has been examined, the results varying only from 43 to 69 γ of iodine per litre, from which it is inferred that the discrepancies in the figures obtained by previous workers are due to analytical errors. No evidence of the presence of organically combined iodine was found, and the iodine content of deep sea-water proved not to differ very much from that of surface water. R. CUTHILL.

Buszite. E. STEINWACHS (Zentr. Min. Geol., 1929, A, 202—205; Chem. Zentr., 1929, ii, 1146).—A crystal of buszite from Khan, S.W. Africa, is ditrigonal-bipyramidal, $a : c = 1 : 1.1792$, H $5\frac{1}{2}$, n 1.72. Silica, neodymium, praseodymium, erbium, and some europium are present. A. A. ELDRIDGE.

South Australian algal limestones in process of formation. D. MAWSON (Quart. J. Geol. Soc., 1929, **85**, 613—623).—Three types of recent limestones from the low-lying land on the south-eastern coast of South Australia are described : (1) Discs ("biscuits") covering the surface of swampy ground, which dries up during the summer. They are encrusted with bluish-green algæ, which evidently caused the precipitation of the calcium carbonate. (2) A reef-formation on the shore of a lake shows algal growths of *Lithothamnion*. Analysis gave MgO 4.73%. (3) Dolomitic lake-marl in the bed of shallow lakes, which dry up during the summer. Analysis shows CaO 28.60, MgO 12.46, SiO_2 5.84, etc.
L. J. SPENCER.

Tourmaline group. F. MACHATSCHKI (Chem. Erde, 1930, **4**, 455—457).—A criticism of the formula of tourmaline proposed by Kunitz (A., 1929, 905).
L. J. SPENCER.

Experimental weathering of felspar. O. TAMM (Chem. Erde, 1930, **4**, 420—430).—Felspar when ground in cold water in a rotating vessel for a long period reduces to particles of 2 to 0.2 μ in size. The water has an alkaline reaction and the fine powder contains about 2% of water. L. J. SPENCER.

Dolomitisation of Middle Devonian [limestone] in the Eifel. P. MÜLLERS (Chem. Erde, 1930, **4**, 431—454).—Many analyses are given of the dolomite-rock in the Gerolstein basin. They show in the majority of cases 80—96% of dolomite ($CaCO_3.MgCO_3$), but in a few streaks only 1—2%. The rock is a coral-reef formation and the dolomitisation took place contemporaneously by the action of the sea-water. The undolomitised streaks represent lagoon deposits.
L. J. SPENCER.

Dehydration and rehydration of kaolin. P. SCHACHTSCHABEL (Chem. Erde, 1930, **4**, 395—419).—Kaolin after being heated at 400—800°, when most of the water is lost, is capable of taking up water again. This is effected very slowly at 110°, but under pressure at 175—205° all the water is restored after 100 hrs. The rehydrated kaolin differs from the

original material by being partly soluble in hydrochloric acid, in its dehydration curve, refractive index, and X-ray pattern, but these differences become less marked after prolonged heating of the material in water at 200°.　　　　L. J. SPENCER.

Rocks of Gomera, Canary Islands. W. MÜLLER (Chem. Erde, 1930, **4**, 369—394).—The Tertiary or post-Tertiary volcanic rocks of the island of Gomera are underlain by a series of extensively weathered rocks which were believed by Gagel (1925) to represent a much older " Grundgebirge." A detailed examination with several analyses of these rocks shows that they are only the weathered equivalents of the ordinary types of volcanic rocks, which include basalts, trachytes, and trachytic phonolites. Analyses are also given of the portions of the weathered rocks soluble in hydrochloric acid.
　　　　　　　　　　L. J. SPENCER.

Geology of Maine. IV. Geology of the Catahdin area. I. A new rhyolite from the State of Maine. E. S. C. SMITH (Amer. J. Sci., 1930, [v], **19**, 6—8).—An analysis of the rhyolite is given.　　　　　　C. W. GIBBY.

Samarskite from Petaca, New Mexico. F. L. HESS and R. C. WELLS (Amer. J. Sci., 1930, [v], **19**, 17—26).—Analyses of the samarskite are given. It consists of two parts, of formulæ approximately Y_2O_3, Nb_2O_5 and $2Y_2O_3, 3Nb_2O_5$. The ages, calculated from the following data, are found to be 1.5×10^8 and 3×10^8 years, respectively: U 4·85, Th 0·97, Pb 0·1%, and U 10·66, Th 1·39, Pb 0·40%.
　　　　　　　　　　C. W. GIBBY.

Minerals of Transylvania. D. GIUŞCĂ (Bull. Acad. Sci. Roumaine, 1929, **12**, 10—17).—Crystallographic descriptions of barytes crystals from Transylvania are given.　　　　C. W. GIBBY.

Sapphirin from Alpe Brasciadega, Val Codera, Italy. H. P. CORNELIUS and E. DITTLER (Neues Jahrb. Min., 1929, **59**, 27—64; Chem. Zentr., 1929, ii, 1640—1641).—The sapphirin, isolated by means

of sulphuric and hydrofluoric acids, contained SiO_2 15·19, TiO_2 0·25, Al_2O_3 61·69, Fe 4·31, MnO 0·12, CaO 0·49, MgO 16·23, $H_2O + 1.60$, $H_2O - 0.19\%$, corresponding with the formula Mg (Fe, Mn, Ca, H_2)$_{11}$Al$_{24}$Si$_5$O$_{57}$.　　　　A. A. ELDRIDGE.

Bohemian clay. G. LINCK and E. KÖHLER (Chem. Erde, 1930, **4**, 459—460).—A clay from the Tertiary lignite beds was analysed in bulk and also the portion soluble in hydrochloric acid after ignition at 600°, and the dehydration curve is plotted. It contains 47·58% of kaolin with 18·94% of amorphous material, 40% of quartz, and some mica, pyrite, and organic matter.　　　　　L. J. SPENCER.

Japanese acid clay. IV. Determination of water. K. KOBAYASHI, K. YAMAMOTO, and K. BITŌ (J. Soc. Chem. Ind. Japan, 1929, **32**, 297—298B).—The water contents of Japanese acid clays, fuller's earth, silica, alumina and aluminium silicate gels, and kaolin have been determined by means of the thermobalance. The heating curves of silica and aluminium silicate gels resemble those of acid clays, but differ from that of kaolin.　　　C. W. GIBBY.

Genesis of Japanese acid clay. K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1929, **32**, 174—175B).—Japanese acidic clay is found exclusively along an intrusion of liparite through pliocene strata; its formation is attributed to the interaction of sodium felspar and sodium silicate under the influence of gases such as carbon dioxide, sulphur dioxide, hydrogen sulphide, and steam. The presence of ferric, calcium, and magnesium oxides is probably due to accidental contamination and also to adsorption by the clay.
　　　　　　　　　H. F. GILLBE.

Brown soils of Crimea and Caucasus. L. I. PRASSOLOV (Chem. Erde, 1930, **4**, 461—474).—A review of Russian papers.　　　L. J. SPENCER.

Chemical composition of peat. S. A. WAKSMAN (Amer. J. Sci., 1930, [v], **19**, 32—54).—A discussion.
　　　　　　　　　　C. W. GIBBY.

Organic Chemistry.

Action of benzoyl peroxide on saturated hydrocarbons. J. BÖESEKEN and A. GASTER (Rec. trav. chim., 1930, **49**, 102—108).—When benzoyl peroxide is boiled with purified petroleum (b. p. 95—100°), carbon dioxide (1 mol.) is evolved and benzene, benzoic acid, heptylbenzene, and probably a *tert.*-heptyl alcohol (isolated after hydrolysis) are formed; small amounts of unidentified acid products are also produced. Reaction appears to occur in the manner formulated by Gelissen and Hermans (A., 1925, i, 545). Using *n*-octane, decomposition begins at about 100°, and carbon dioxide, benzene, and benzoic acid are initial products of the reaction. Hydrolysis of the neutral products formed during the reaction gives benzoic acid, a mixture (?) of *sec.*-octyl alcohols, and resinous products.　　　　H. BURTON.

Polymerisation. XII. Polymeric forms of isobutylene. S. V. LEBEDEV and G. G. KOBLIANSKY

(Ber., 1930, **63**, [*B*], 103—112).—*iso*Butylene, when heated in a hard glass tube at 200° for 14 days, yields 6—8% of polymerised products, from which only tri*iso*butylene could be isolated. The action of sulphuric acid on *iso*butylene affords predominatingly tri*iso*butylene with a very small amount of di*iso*butylene and a less volatile residue which could not be separated into its components by fractional distillation. Butlerov's tri*iso*butylene is, however, separable into two portions, (*a*) b. p. 179—181° (corr.), 56°/10 mm., d_4^{20} 0·7590, n_D^{20} 1·43138, and (*b*) b. p. 195—196° (corr.), 75—77°/12 mm., d_4^{20} 0·7763, n_D^{20} 1·44062. *iso*Butylene readily undergoes polymerisation in presence of Florida earth activated by previous ignition at about 300° (cf. Lebedev and Filonenko, A., 1925, i, 225). Reaction is very marked at —80°. If the gas is passed over the unheated catalyst, the temperature of the latter rises immediately to 110—135° and then slowly falls.

At 200° reaction is very slow, whereas at 290° the *iso*butylene is partly decomposed with deposition of carbon on the catalyst. Prolongation of the period of contact of hydrocarbon and earth leads to an increase in the proportion of more highly polymerised forms. The following polymerides are isolated by fractional distillation of the crude products : di*iso*butylene, $(C_4H_8)_2$, b. p. 101—102°/762 mm., d_4^{20} 0·7195, n_D^{20} 1·41123, the identity of which with Butlerov's product is established by physical constants and by the similarity in the course of hydrogenation of the two products; the substance slowly passes into tetra*iso*butylene when preserved at the atmospheric temperature in contact with Florida earth; tri*iso*butylene, b. p. 178·5—179·5° (corr.), d_4^{20} 0·7600, n_D^{20} 1·43060, apparently identical with the trimeride of lower b. p. (see above), which does not further polymerise in presence of Florida earth and is hydrogenated only slowly; *tetra*isobutylene, $(C_4H_8)_4$, b. p. 106°/7 mm., d_4^{20} 0·7944, n_D^{20} 1·44817; *penta*isobutylene, b. p. 148°/7 mm., d_4^{20} 0·8176, n_D^{20} 1·46006, which appears to be formed also from di- and tri-*iso*butylene in presence of Florida earth; the tetra- and penta-compounds do not polymerise further and can be hydrogenated only with extreme slowness; *hexa*isobutylene, b. p. 158—161°/2·5 mm., d_4^{20} 0·8340, n_D^{20} 1·46841; *hepta*isobutylene, b. p. 183—186°/2 mm., d_4^{20} 0·8455, n_D^{20} 1·47393. The residue remaining after the separation of the heptameride is colourless and very viscous; there appears little prospect of isolating higher polymerides, since the temperature required for distillation under very greatly reduced pressure is sufficiently high to cause depolymerisation. The following changes appear to be established : $C_4H_8 + C_4H_8 \longrightarrow (C_4H_8)_2$; $(C_4H_8)_2 + C_4H_8 \longrightarrow (C_4H_8)_3$; $2(C_4H_8)_2 \longrightarrow (C_4H_8)_4$; $(C_4H_8)_2 + (C_4H_8)_3 \longrightarrow (C_4H_8)_5$. H. WREN.

Illipene, and higher alcohols in commercial illipé butter. M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1929, **32**, 365—367B).—The unsaponifiable matter of illipé butter was treated with 95% alcohol, and the insoluble portion was crystallised from ethyl acetate. So obtained, illipene has m. p. 64°, iodine value 352·0, probable formula $C_{64}H_{106}$ or $C_{65}H_{108}$; it decomposes on attempted distillation at 4·5 mm., and appears to be rather susceptible to atmospheric oxidation. It yields an ether-insoluble *bromide* and by hydrogenation furnishes a white, viscous semisolid, m. p. about 100°, iodine value 56.

The solution of the portion of the unsaponifiable matter dissolved by alcohol yielded when concentrated a higher alcohol, *bassisterol*, $C_{27}H_{46}O$, m. p. 210—211°, iodine value 71·5, $[\alpha]_D^{14} +26·4°$ in ether. Bassisterol does not give a precipitate with digitonin, but affords a pink colour with acetic anhydride and sulphuric acid; the hydroxyl group appears to be difficult to acetylate. C. W. SHOPPEE.

cis-trans-**Ethylenic isomerism. Addition of two atoms of hydrogen to the acetylenic linking.** M. BOURGUEL (Bull. Soc. chim., 1929, [iv], **45**, 1067—1091).—The hydrogenation of tolane, six acetylenic acids, one diacid, one alcohol, one glycol, and one aldehyde in presence of colloidal palladium stabilised by starch (A., 1928, 28) uniformly gives the

cis-ethylenic derivative. The contradictory results obtained by other methods are attributed to the instability of the nascent molecule which is then sensitive to the influence of reagents that normally have little isomerising influence. Support for this view is afforded by the increased rate of formation of the internal oxide of βε-dimethyl-Δγ-hexene-βε-diol in the hydrogenation of βε-dimethyl-Δγ-hexinene-βε-diol in acid medium as compared with the direct dehydration of the hexenediol in acid medium (A., 1928, 989) and the rapid increase in the rate of polymerisation of phenylpropinene under hydrogenation at 20°.

Thus hydrogenation of phenylpropiolic acid in ethyl acetate yields primarily Liebermann's *alloiso*cinnamic acid, m. p. 55—56°, together with its more stable transformation products, Erlenmeyer's *iso*cinnamic acid, m. p. 37—38°, and *allo*cinnamic acid, m. p. 67—68°, but no *trans*-isomeride. Acetylenedicarboxylic acid similarly yields maleic acid and tolane, *iso*stilbene, b. p. 140·5—141°/13 mm., d^{13} 1·023, n_D^{13} 1·620, containing less than 2% of stilbene (formed by isomerisation during distillation). Phenylpropiolic alcohol yields cis-*cinnamyl alcohol*, b. p. 125·5°/13·5 mm., d^{20} 1·044, n_D^{20} 1·582 (*phenylurethane*, m. p. 89·5°), the known alcohol of higher b. p. and density being therefore the *trans*-isomeride. Hydrogenation of methyl Δ$^\alpha$-propinenyl ketone yields a mixture, b. p. 110—130°, of saturated, olefinic, and acetylenic ketones. Methyl phenylethinyl ketone gives a similar mixture containing phenyl styryl ketone and a saturated, b. p. 119—121°/16 mm., and acetylenic ketone, b. p. 126—127°/16 mm. Δ$^\alpha$-Pentinenoic acid affords cis-Δ$^\alpha$-*pentenoic acid*, b. p. 88—88·5°/15 mm., n_D^{21} 1·448, d^{18} 0·988, isomeric with the acid obtained by Auwers (A., 1923, i, 746) which is regarded as the *trans*-isomeride. Similarly, Δ$^\alpha$-hexinenoic acid yields cis-Δ$^\alpha$-*hexenoic acid*, b. p. 100·5—101·5°/15 mm., 201—202°/760 mm., d^{21} 0·962, n^{21} 1·4495, and Δ$^\alpha$-octinenoic acid, cis-Δ$^\alpha$-*octenoic acid*, b. p. 127°/15 mm., d^{10} 0·944, n^{15} 1·456, converted by insolation in presence of iodine into the trans-*isomeride*, m. p. 5—6°, b. p. 143°/15 mm., d^{17} 0·944, n_D^{17} 1·461. Δ$^\alpha$-Noninenoic acid yields cis-Δ$^\alpha$-*nonenoic acid*, b. p. 140°/15 mm., d^{15} 0·9315, n_D^{15} 1·458, similarly converted into the trans-*isomeride*, b. p. 154·5°/15 mm., m. p. 1—2°, d^{15} 0·936, n_D^{15} 1·4635. The structures of the cis- and trans-isomerides of this series of acids are based on the relation between the physical constants and those of crotonic and *iso*crotonic acids.

[With J. YVON.]—Tetrolic acid on hydrogenation similarly yields *iso*crotonic acid, m. p. 14—15°, b. p. 169°, d^{15} 1·028, n_D^{15} 1·446, and no crotonic acid. Phenylpropiolaldehyde when hydrogenated under these conditions is hydrogenated in the aldehydic group, yielding three unsaturated compounds. The diethylacetal, obtained by Moureu and Delange's method (A., 1904, i, 650), undergoes hydrolysis, yielding a mixture containing β-phenylpropaldehyde, but no cinnamaldehyde. Hydrogenation in dimethyl*cyclo*hexane, which has no solvent power for water, yields an acetal, b. p. 130—132°/16 mm., d^{15} 0·966, n_D^{21} 1·492, probably the *diethylacetal* of cis-cinnamaldehyde, hydrolysed to cis-*cinnamaldehyde*, b. p. 111—113°/16 mm., d^{20} 1·032, n_D^{20} 1·565, probably con-

taining some saturated aldehyde, but not the known cinnamacetal, which is regarded as having the *trans*-structure (from the relation of cinnamic acid to cinnamaldehyde).

[With RAMBAUD.]—Hydrogenation of βε-dimethyl-Δγ-hexinene-βε-diol in presence of palladium and starch at p_H 7·1 or in 0·01N-sodium carbonate yields mainly the *cis*-glycol, the proportion of *trans*-isomeride being increased in heterogeneous or acid medium; in the latter case the dehydration of the *cis*-glycol already noted also occurs and tends to mask the formation of the *trans*-isomeride which yields no internal oxide.   R. BRIGHTMAN.

Preparation of alkyl chlorides from the corresponding alcohols. R. H. CLARK and H. R. L. STREIGHT (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 77—89).—Alkyl chlorides have been prepared from methyl and ethyl, the isomeric propyl, butyl, and amyl alcohols, *n*-hexyl, *n*-heptyl, *n*-octyl, "capryl," *n*-nonyl, cetyl, allyl, and cinnamyl alcohols, ethylene, propylene, and trimethylene glycols, benzyl alcohol, phenylmethylcarbinol, and triphenylcarbinol. Four methods have been compared, viz., the action of (*a*) hydrochloric acid in presence of zinc chloride (Norris and Taylor, A., 1924, i, 602), (*b*) phosphorus trichloride and zinc chloride (Dehn and Davis, A., 1907, i, 885), (*c*) phosphorus pentachloride and zinc chloride, and (*d*) thionyl chloride in pyridine or benzene. Method (*a*) is recommended for the preparation of large amounts of aliphatic chlorides and benzyl chloride. Tertiary alcohols give high yields of chloride with hydrochloric acid alone in the cold. Method (*b*) gives yields of 60—80% of primary and secondary and 92—98% of tertiary chlorides. It is inferior to (*a*) only for lower aliphatic chlorides, and is useful for the other chlorides. Method (*c*) gives generally increased yields as compared with the use of phosphorus pentachloride alone. The yields are 70—80% with aliphatic alcohols, with the exception of *n*-hexyl to *n*-nonyl alcohols, with which it is lower; cetyl, cinnamyl, and aromatic alcohols form tars. Method (*d*) is suitable for the preparation of small amounts of pure products. With the lower aliphatic alcohols the use of pyridine is necessary, with the others no solvent, or benzene, is used. The yields are high (80—99%) except with diethylcarbinol (42—44%) and *n*-nonyl alcohol (62%). The relative costs of the methods are in the order (*a*) < (*b*) < (*c*) < (*d*), except when the alcohol is expensive, when (*d*) is cheapest.

The following new or revised data are given for the chlorides : *n*-hexyl, d_{20}^{20} 0·8759, n_D^{20} 1·42364; *n*-heptyl, d_{20}^{20} 0·8741, n_D^{20} 1·42844; *n*-octyl, d_{20}^{20} 0·8745, n_D^{20} 1·43424; *n-nonyl*, b. p. 98—100°/23 mm., d_{20}^{20} 0·8679, n_D^{20} 1·43692; cetyl, d_{20}^{20} 0·8384; methyl-*n*-hexyl, d_{20}^{20} 0·8649, n_D^{20} 1·42954.   R. K. CALLOW.

Tests for *iso*propyl alcohol. H. LEFFMANN and C. C. PINES (Bull. Wagner Inst. Sci., 1929, **4**, 47—50).—Various methods for the detection of *iso*propyl alcohol in the presence of other alcohols are reviewed. Rae's method (Pharm. J., 1926, **116**, 630) slightly modified (10 c.c. of the sample oxidised with 20 c.c. of 1% potassium dichromate solution and 1 c.c. of sulphuric acid, ammonia and a little ammonium chloride added to the first 3 c.c. of the distillate which

is superimposed on a 1% solution of sodium nitroprusside in glycerol, a ring forming at the contact zone if acetone, formed by the oxidation of *iso*propyl alcohol, is present) gives a positive reaction with 10% of *iso*propyl alcohol in 50% alcohol, and negative results with similar concentrations of *n*-propyl, *n*-, *iso*-, and *tert*.-butyl alcohols, and only a faint ring with *sec*.-butyl alcohol. Dale and Simmonds' method (mixture of 1 c.c. of the sample, 1 c.c. of a saturated disodium hydrogen phosphate solution, and 3 c.c. of a saturated solution of potassium permanganate is warmed, left until the permanganate is destroyed, and then 3 c.c. of a 1% sodium hydroxide solution and 1 c.c. of 1% furfuraldehyde solution are added and the mixture is filtered; addition of 1 c.c. of concentrated hydrochloric acid to the filtrate gives a red colour if *iso*propyl alcohol was originally present) gave positive results with both the samples tested. Herstein's test (Pract. Drug., 1922, 38) seems to depend on the presence of some impurity, since not all samples of *iso*propyl alcohol give this test.   J. W. BAKER.

Theory of geometrical stereochemistry. A. P. SEMENCOV.—See this vol., 276.

Benzyl-alcoholic potassium hydroxide and its applications. Determination of halogen. S. SABETAY and J. BLÉGER (Bull. Soc. chim., 1930, [iv], **47**, 114—118).—Halogen in the following substances has been accurately determined with benzyl-alcoholic potassium hydroxide : glycerol mono- and di-chlorohydrins, methylene iodide, iodoform, chloral hydrate, chloro- and trichloro-acetic acid, ethyl α-bromo-α-ethylbutyrate, iodoacetamide, α-bromopropionamide, mono- and di-chloroquinitols, 4-chloro*cyclo*hexanone-semicarbazone, α-bromocamphorsulphonyl chloride, dibromo- and dichloro-styrene. The following method is used : 0·1—0·3 g. of substance is heated for 30—60 min. with 40 c.c. of benzyl alcohol and 10 g. of potassium hydroxide in a pyrex flask, with a long tube attached ; 50 c.c. of water are added after cooling a little, followed by 30 c.c. of ethyl alcohol and 30 c.c. of nitric acid with a known excess of 0·5N-alcoholic silver nitrate solution. The excess of silver nitrate is determined by Volhard's method.
R. BRIGHTMAN.

Ferric ethoxide. R. SUTRA (Bull. Soc. chim., 1930, [iv], **47**, 68—71).—A reply to Thiessen and Koerner (A., 1929, 675). Ferric ethoxide has not been obtained pure, but always contains sodium chloride or magnesium halides, as its instability renders crystallisation impossible. Thus ferric chloride and magnesium ethoxybromide, obtained from magnesium ethyl bromide and alcohol in benzene, in an atmosphere of nitrogen yield a solution of ferric ethoxide, which slowly crystallises after concentration. Addition of alcohol or benzene gives a precipitate containing, *e.g.*, 34·6% of magnesium chlorobromide, 2·2% of ferric ethoxide, and 63·2% of ether. Ferric ethoxide does not give Tischtschenko's reaction with acetaldehyde, polymerisation and aldolisation taking place.
R. BRIGHTMAN.

Reactions of magnesium compounds with ethylene oxide. I. Reaction between trimethylene oxide and magnesium ethyl bromide. L. BERMEJO and V. G. ARANDO (Anal. Fís. Quím., 1929,

27, 798—800).—Treatment of trimethylene oxide with magnesium ethyl bromide in ethereal solution yields a substance which is hydrolysed to *n*-butyl alcohol and trimethylene bromohydrin, both in about 30% yield. If the mixture is not heated at any stage the yield may be raised to 38%. H. F. GILLBE.

Kanyl alcohol, a new alcohol in the liver oil of "Tarabakani," *Paralithodes Camtschatica* (Tilesius). M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 362—364B).—The portion of the unsaponifiable matter of the liver oil soluble in methyl alcohol at 0° was acetylated and distilled; the fractions of higher b. p. were brominated and the portion of the product soluble in light petroleum was debrominated and hydrolysed, thereby yielding *kanyl alcohol*, (?) $C_{10}H_{18}O_2$, b. p. 140—150°/5 mm., d_4^{20} 0·9553, n_D^{20} 1·4740. When hydrogenated, it gives the *compound* $C_{10}H_{20}O_2$, d_4^{20} 0·9314, n_D^{20} 1·4555. C. W. SHOPPEE.

Refractive index of solutions of certain γ-glycols of the acetylenic and saturated series. W. KRESTINSKI and N. PERSSIANZEWA (Ber., 1930, 63, [B], 180—190).—The refractive indices for the α, δ, β, and γ lines of βε-dimethyl-Δγ-hexinene-βε-diol, m. p. 95°, βε-dimethylhexane-βε-diol, m. p. 90°, γζ-diethyl-Δδ-octinene-γζ-diol, m. p. 74°, γζ-diethyl-octane-γζ-diol, m. p. 70°, βι-dimethyl-Δε-decinene-δη-diol, b. p. 159—160°/15 mm., d_4^{20} 0·9188, n_D^{20} 1·45874, γζ-dimethyl-Δδ-octinene-γζ-diol, m. p. 55°, and βββ-trimethylpentane-αγ-diol have been determined in part with the homogeneous material and in part with their solutions in water, amyl alcohol, cyclohexanone, ethyl acetate, and aniline. The mol. refraction of acetylenic γ-glycols in solution is greater than the calculated value when the increment for the triple linking is taken into account; the mean value of the exaltation is 0·4—0·5. The values for the mol. refraction of the corresponding saturated glycols are smaller than the calculated data. With different solvents, somewhat distinct deviations are observed from case to case, but, generally, the effect of the solvent is not very pronounced. In the case of βι-dimethyl-Δε-decinene-δη-diol, for example, the values obtained in amyl alcohol or cyclohexanone solution differ little from those observed with the homogeneous material. H. WREN.

Cyclic acetals. I. Formation of cyclic acetals from Δβζ-octadiene-δε-diol. C. P. BURT and F. HOWLAND (J. Amer. Chem. Soc., 1930, 52, 217—219).—The following *ethers* of Δβζ-octadiene-δε-diol are prepared from the diol and the requisite aldehyde or ketone at about 70°, using a small amount of 40% sulphuric acid as the catalyst (the figures in parentheses are the percentage yields): *ethylidene*, b. p. 88—89°/20 mm. (90), also obtained in 83% yield using paraldehyde; *propylidene*, b. p. 99—100·5°/21 mm. (90); *butylidene*, b. p. 104—105°/15 mm. (92); *heptylidene*, b. p. 129—131°/4 mm. (85), and iso*propylidene*, b. p. 72—75°/8 mm. (71). The length of the aldehyde carbon chain appears to have no appreciable effect on ether formation. Ethers could not be isolated from the diol and chloral, benzaldehyde, cinnamaldehyde, or crotonaldehyde. H. BURTON.

Polymerisation and ring formation. III. Glycol esters of carbonic acid. W. H. CAROTHERS and F. J. VAN NATTA (J. Amer. Chem. Soc., 1930, 52, 314—326).—In agreement with the theory of condensation polymerides previously proposed (A., 1929, 1165), ethylene, b. p. 238°, m. p. 39°, and *trimethylene carbonates*, b. p. 135°/4 mm., m. p. 47—48°, can be obtained in the monomeric form. The latter ester is, however, converted by heating with a small amount of potassium carbonate at 130° into an additive polymeride (cf. loc. cit.), which on distillation in a vacuum regenerates the monomeric ester. When heated at 210°, the polymeride decomposes, yielding some allyl alcohol. Attempts to polymerise ethylene carbonate were unsuccessful. The polymethylene carbonates with a structural unit of 7 or more atoms are all polymeric. *Tetramethylene carbonate* (M=1300—1400), m. p. 55—59°, when heated at 300—325°/0·9 mm., gives about 1% of a dimeric *tetramethylene carbonate*, m. p. 175—176°. *Pentamethylene*, m. p. 44—46°, *hexamethylene*, m. p. 55—60°, *decamethylene*, m. p. 55°, and *diethylene carbonates*, syrupy, are described. p-*Xylylene carbonate* exists in two polymeric forms, m. p. 137—138° and 177—185°, soluble and insoluble in ethylene chloride, respectively. The above carbonates are all prepared from ethyl carbonate and the requisite glycol at 120—170°, in presence of a small amount of sodium; approximately equimolecular quantities are used.

When 2 mols. of ethyl carbonate are heated with 1 mol. of hexamethylene glycol, some OO-*dicarbethoxyhexane*-αζ-*diol*, b. p. 130—140°/0·8 mm., d_{20}^{20} 1·065, n_D^{20} 1·4310, is obtained together with polymerised material. The *di-p-nitrobenzoates* of tetra- and penta-methylene glycols have m. p. 175° and 104—105°, respectively. H. BURTON.

Reactions of sulphurous esters. R. LEVAILLANT (Compt. rend., 1930, 190, 54—57).—αγ-*Dichloropropyl sulphite*, b. p. 149°/1·5 mm., d_0 1·531, n_D^{20} 1·509, is obtained by treatment of αγ-dichloropropyl alcohol with thionyl chloride. In presence of a little iodine the action of chlorine on the solution yields αγ-dichloropropyl chlorosulphonate (Blanchard, A., 1929, 171) and αβγ-trichloropropane. β-Chloroethyl sulphate is obtained in good yield by heating the corresponding chlorosulphonate and sulphite together at 160—180° for 3 hrs.; sulphur dioxide and ethylene dichloride are eliminated. The action of sulphuryl chloride on ethyl sulphite (1 mol.) at a low temperature yields ethyl chlorosulphonate, but when a mixture of sulphuryl chloride and ethyl sulphite (2 mols.) is heated at 150—160° for 2 hrs. ethyl sulphate is obtained in good yield. The interaction of benzoyl chloride and ethyl sulphite at 140—220° yields ethyl benzoate, and the interaction of acetyl chloride and propyl sulphite in presence of a little zinc chloride yields propyl acetate; alkyl chloride and sulphur dioxide are eliminated in each case. Acetic anhydride and ethyl sulphite yield similarly ethyl acetate. The interaction of phthalic anhydride and ethyl sulphite to give ethyl phthalate takes place at 150° only in presence of a little zinc chloride. A convenient method of preparing ethyl sulphate is by heating ethyl chlorosulphonate with ethyl carbonate at 135—160° for 4—5 hrs. or at 110° in presence of zinc chloride. R. K. CALLOW.

Organic compounds of sulphur. XVI. Thermal transformation of thiocarbonic esters into thiolcarbonic esters. A. Schönberg and L. von Vargha (Ber., 1930, 63, [B], 178—180; cf. A., 1929, 1451).—Phenyl thiocarbonate, CS(OPh)₂, m. p. 106°, is isomerised when heated in absence of air at 280° into phenyl phenylthiolformate, m. p. 57°. Similarly, β-naphthylthiocarbonate, m. p. 212°, at 300° affords β-*naphthyl* β-*naphthylthiolformate*, m. p. 136°, hydrolysed by alkali hydroxide to β-naphthol and β-thionaphthol (identified by oxidation to di-β-naphthyl disulphide).   H. Wren.

Dialkyl sulphurdicarbothionates. G. S. Whitby and H. Greenburg (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 21—24).—By a reaction analogous to the conversion of thiuram disulphides into monosulphides (von Braun and Stechele, A., 1903, i, 618), dialkyl disulphurdicarbothionates (xanthogen disulphides) are converted into monosulphurdicarbo-thionates: (RO·CS)₂S₂+KCN=(RO·CS)₂S+KCNS. The disulphides are prepared by the action of iodine (chlorine is unsuitable) on the alkali xanthate in aqueous solution, and treatment with potassium cyanide is carried out in aqueous-alcoholic solution at 0—10°. The following are described : Disulphur-dicarbothionates (xanthogen disulphides): dimethyl, (OMe·CS)₂S₂, m. p. 22—22·5°; *di*-n-*propyl*, b. p. 150—155°/0·5 mm.; *di*iso*propyl*, m. p. 58·5°; *di*-n-*butyl*, d^{22} 1·158, boils with decomposition below 0·5 mm.; *di*iso*butyl*, b. p. 161—164°/0·5 mm., d^{22} 1·1173; sulphurdicarbothionates (xanthogen monosulphides): *dimethyl*, m. p. 55°; diethyl, m. p. 52°; *di*-n-*propyl*, b. p. 135—136°/0·5 mm.; *di*iso*propyl*, m. p. 54°; *di*-n-*butyl*, d^{22} 1·121; *di*iso*butyl*, d^{22} 1·126; *di*iso-*amyl*, an oil.

Diethyl sulphurdicarboxylate, (OEt·CO)₂S, d^{23} 1·158 (Holmberg, A., 1905, i, 323), is obtained in the same way from the monosulphide, and also by the inter-action of potassium ethyl thiolcarbonate with ethyl chloroformate.

Simple aryl and alkyl disulphides, e.g., phenyl di-sulphide, do not react with potassium cyanide, but benzyl tetrasulphide is converted almost quantit-atively into benzyl disulphide.   R. K. Callow.

Synthesis of lengthened sulphur chain com-pounds. P. C. Rây and S. K. Mitra (J. Indian Chem. Soc., 1929, 6, 865—869).—During the prepar-ation of dithiopropylene glycol from trimethylene dibromide and alcoholic potassium hydrogen sulphide (cf. Autenrieth and Wolff, A., 1899, i, 579), some γγ'-*dithioldipropyl disulphide*, b. p. 180°/40 mm., is also produced. Acetylation of dithiopropylene glycol with acetic anhydride and a small amount of pyridine gives the *diacetyl* derivative, b. p. 178°/50 mm., which is hydrolysed by 15% potassium hydroxide solution at 28—30° to the *monoacetyl* derivative, b. p. 115—116°/40 mm. This is converted by iodine in ethereal solution into γγ'-*diacetyldithioldipropyl disul-phide*, which is then hydrolysed to the above disulphide. The *diacetyl* derivative, m. p. 60°, of dithioethylene glycol is converted similarly by way of the *monoacetyl* derivative, b. p. 95—97°/40 mm., into ββ'-*diacetyldi-thioldiethyl disulphide*. This diacetate decomposed on attempted hydrolysis.   H. Burton.

Action of bases on complex compounds derived from organic thio-compounds and platinic chloride. P. C. Rây and P. C. Mukherjee (J. Indian Chem. Soc., 1929, 6, 885—891).—Treatment of an aqueous solution of platinic chloride with an excess of methyl sulphide affords the *compound* PtCl₃,2Me₂S, converted by prolonged boiling with water into the complexes PtCl₂,2Me₂S and PtCl₄,2Me₂S. The last-named compound is practically a non-electrolyte. When treated with ethylamine it furnishes the *sub-stance* PtCl₂,4NH₂Et,2H₂O, m. p. 211° (decomp.); piperidine gives the *compound* PtCl₂,2C₅H₁₁N,2H₂O, whilst pyridine affords the complex PtCl₄,2C₅H₅N (cf. A., 1926, 1023). Diethylamine converts the com-pound PtCl₄,2Et₂S (*loc. cit.*; A., 1927, 444) into the *substances* PtCl₂,Et₂S,NHEt₂ and Pt₂Cl₄,2Et₂S,NHEt₂, whilst with trimethylamine the *complex* PtCl₂,Et₂S,NMe₃ results. The substance PtCl₃,2(CH₂Ph)₂S (A., 1928, 751) yields with propyl-amine and diethylamine, the *compounds* PtCl₂,4NH₂Pr,2H₂O, m. p. 198° (decomp.), and PtCl₂,(CH₂Ph)₂S,NHEt₂, respectively; with methyl-amine, the *complex* [MeNH₂ . . . PtCl₂] results. The majority of the above complexes are postulated as compounds of the Werner type.   H. Burton.

Hydroxymethanetrisulphonic acid. P. Fantl and J. Fisch (J. pr. Chem., 1930, [ii], 124, 159—162). —Potassium and barium hydroxymethanetrisulphon-ates, prepared by Pechmann and Manck's method (A., 1896, i, 14), are salts of methanetrisulphonic acid, m. p. 150° (*silver* salt) (Bagnall, J.C.S., 1899, 75, 278).
                                       A. I. Vogel.

Catalysis in organic chemistry. I. Reactions of ethers with acid chlorides, acids, and anhydrides. H. W. Underwood, jun., and R. L. Wakeman. II. Mechanism of the reactions. H. W. Underwood, jun., and G. C. Toone (J. Amer. Chem. Soc., 1930, 52, 387—391, 391—394).—I. When a mixture of anhydrous ether (1 mol. +10—15%), zinc chloride (about 0·25 mol.), and an acid chloride (1 mol.) is boiled for 2—3 hrs. ethyl esters are often obtained. The chlorides of the following acids all yield ethyl esters, the percentage yield being given in parentheses : acetic (40); chloroacetic (35); prop-ionic (15); n-butyric (21); *iso*valeric (20); benzoic (60); phenylacetic (79); oxalic (4); diphenic (77). Ester formation occurs also with 3 : 5-dinitrobenzoyl and phthalyl chlorides; in the last case some phthalic anhydride is also produced. Benzene- and p-toluene-sulphonyl chlorides do not react with ether under the above conditions. With acetyl, propionyl, and benzoyl chlorides and *iso*propyl, n-butyl, and *iso*amyl ethers varying amounts of the corresponding alkyl esters are produced. Diphenyl ether and anisole do not undergo fission with acetyl or benzoyl chlorides; nuclear acylation takes place.

When the following acids or anhydrides are treated with an ethereal solution of hydrogen bromide, first at the ordinary temperature (10—12 days), and then at the b. p. (3 hrs.), ethyl esters are again obtained (the first figures represent the percentage yields of ester from the acids, those in parentheses the yields from the anhydrides) : acetic, 8 (13); chloroacetic, 30 ; propionic, 34 (23); n-butyric, 41 (38); *iso*valeric,

42 (41); oxalic, 8; malonic, 6; succinic, 16 (13); benzoic, 28 (49); phenylacetic, 56; β-phenylpropionic, 80; *p*-toluic, 23; mandelic, 24; anisic, 5; *p*-chlorobenzoic, 10; *o*-, *m*-, and *p*-nitrobenzoic, 5, 42, and 10, respectively; 3 : 5-dinitrobenzoic, 27; *p*-aminobenzoic, 1; phthalic 9 (13); diphenic, 16 (25). No esters were obtained from stearic, picric, *p*-toluene-sulphonic, and 2 : 4 : 6-trinitrobenzoic acids by the same procedure.

II. When 1 mol. of ethyl, *iso*propyl, *n*-butyl, or *iso*amyl ether is heated with 0·5 mol. of zinc chloride at the b. p. small amounts of the corresponding alcohol and unsaturated hydrocarbon are produced. In presence of an acid chloride, the alcohol affords the alkyl ester and the liberated hydrogen chloride converts some of the alcohol into alkyl chloride. A 77—79% yield of ethyl acetate can be obtained from ether and acetyl chloride, using only a relatively small amount of zinc chloride; the zinc chloride can be used repeatedly. When 1 mol. of the ether is treated with dry hydrogen bromide (about 0·25 mol.) fission into the alcohol and alkyl bromide occurs. Acetic anhydride is converted into acetyl bromide and acetic acid by treatment with hydrogen bromide. Anisole and diphenyl ether are not affected by treating with zinc chloride. H. Burton.

Catalysis in organic chemistry. III. Decomposition of esters by anhydrous zinc chloride. H. W. Underwood, jun., and O. L. Baril (J. Amer. Chem. Soc., 1930, 52, 395—397).—When 1 mol. of methyl benzoate is heated with zinc chloride (0·5 mol.) at the b. p. some decomposition into benzene and benzoic acid occurs; ethyl benzoate affords ethylene in addition. Similarly, ethyl phthalate gives phthalic anhydride and ethylene; ethyl salicylate affords phenol, *o*-ethylphenol, and ethylene; methyl salicylate furnishes *o*-cresol; *iso*amyl acetate, *n*-butyrate, and benzoate yield varying amounts of the corresponding acids, *iso*propylethylene, and polymerised *iso*propylethylene; ethyl cinnamate gives styrene, distyrene, metastyrene, and ethylene; ethyl oxalate furnishes ethyl chloride, saturated hydrocarbons, and a zinc salt (ethyl succinate behaves similarly), and ethyl malonate affords ethyl acetate, ethylene, and *n*-pentane. Ethyl formate, acetate, propionate, and *n*-butyrate are unaffected by heating with zinc chloride.

H. Burton.

Effect of heat on crotonic acid. E. L. Skau and B. Saxton (J. Amer. Chem. Soc., 1930, 52, 335—341). —The mixtures obtained when crotonic acid is heated at 125—175° are not binary as stated by Morrell and Hanson (J.C.S., 1904, 85, 1520), but contain at least three acids, namely, crotonic, *iso*crotonic, and probably β-crotonoxybutyric, CHMe:CH·CO₂·CHMe·CH₂·CO₂H. The last-named acid has not been obtained pure, and its amount is decreased by heating at higher temperatures. The system does not exhibit the phenomenon of false equilibrium as stated by Morrell and Hanson (*loc. cit.*). H. Burton.

Conjugated systems. II. Bromination of β-vinylacrylic acid. I. E. Muskat, B. C. Becker, and J. S. Lowenstein (J. Amer. Chem. Soc., 1930, 52, 326—332).—Treatment of vinylacrylic acid, m. p. 72°

(improved method of preparation given), with 1 mol. of bromine in chloroform affords γδ-dibromo-Δᵅ-pentenoic acid, b. p. 156°/3 mm., which on keeping crystallises partly to a solid, m. p. 47° (cf. Farmer and Healy, A., 1927, 646). Thermal decomposition of the above dibromo-acid (in a vacuum) affords hydrogen bromide and the *lactone*, $\overset{O}{\underset{CH_2:C\cdot CH:CH\cdot CO}{\rule{1.5cm}{0.4pt}}}$ m. p. 143°, resolidifying at 162°, hydrolysed by alkali to aceto-acrylic acid. Treatment of the dibromopentenoic acid with 2 mols. of sodium hydroxide solution at 0° affords the *sodium* salt of γ-*bromovinylacrylic acid*, m. p. about 106°. Addition of bromine to the last-named acid gives γγδ-*tribromo-Δᵅ-pentenoic acid*, b. p. about 172°/10 mm., which on ozonisation affords αⲁβ-tri-bromopropaldehyde. H. Burton.

Synthetic glycerides. II. Refractive indices of glycerides of known constitution. H. P. Averill, J. N. Roche, and C. G. King (J. Amer. Chem. Soc., 1930, 52, 365—367).—An apparatus for the use of an immersion refractometer in a constant-temperature bath is described. The values of *n* at 70° and 75° for five pairs of isomeric mixed triglycerides show that of each pair the symmetrical isomeride has the higher value; equivalent mixtures show intermediate values. The values of n^{70} quoted are : α- and β-stearodilaurin, 1·43986 and 1·44031; α- and β-stearodipalmitin, 1·44289 and 1·44325; α- and β-laurodimyristin, 1·43798 and 1·43901; α- and β-laurodipalmitin, 1·44016 and 1·44044; α- and β-acetodipalmitin, 1·43709 and 1·43749, respectively. H. Burton.

Electrolysis of palmitic acid and preparation of pentadecene. S. Landa and M. Landova (Coll. Czech. Chem. Comm., 1930, 2, 31—35).—Electrolysis of potassium palmitate by Petersen's method (A., 1900, ii, 522) and under reflux furnished two main fractions, b. p. 141—143°/15 mm., and 170—180°/15 mm. The former, after conversion into αβ-dibromo-pentadecane, b. p. 204—205°/17 mm., d_4^{10} 1·2235, n_D^{10} 1·48971 (corresponding diacetate, m. p. 52—53°), and treatment with zinc–copper alloy in the presence of alcohol, yielded *pentadecene*, b. p. 144—145°/15 mm., d_4^{20} 0·7809, $n_D^{12\cdot4}$ 1·44434, heat of combustion at constant volume 2356·8 kg.-cal., oxidised by potassium permanganate to myristic acid, m. p. 50°. The viscosity of pentadecene over the range 0—50° has been determined. The fraction of higher b. p. gave pentadecanol, isolated as the phenylurethane, m. p. 72°. A. I. Vogel.

Sulphonated oils. VI. Reaction mechanism between aqueous solution of sulphuric acid esters of hydroxy-fatty acids and salts. VII. Preparation and properties of pure alkali hydrogen salts of the sulphuric acid ester of ricinoleic acid. K. Nishizawa, K. Winokuti, and T. Kikuti (J. Soc. Chem. Ind. Japan, 1929, 32, 277ᴮ, 278ᴮ) — VI. Addition of inorganic salts to the aqueous solution of the sulphonation product of ricinoleic acid causes precipitation of the acid salt according to the equation $(SO_3H\cdot O)_n\cdot R\cdot CO_2H + nXA \rightleftharpoons (SO_3X\cdot O)_n\cdot R\cdot CO_2H + nHA$, where X and A are metallic and acidic radicals, respectively.

VII. The *hydrogen* salts, $CH_3 \cdot [CH_2]_5 \cdot CH(O \cdot SO_3X) \cdot CH_2 \cdot CH:CH \cdot [CH_2]_7 \cdot CO_2H$ (X=K, Na, and NH_4), have been prepared in the pure state. They are less stable towards precipitation by calcium and magnesium salts than is the normal salt. A. A. GOLDBERG.

Formation of petroleum of the naphthene type. Transformation of fatty acids into hydrocarbons under high pressure. A. D. PETROV (Ber., 1930, **63**, [*B*], 75—84).—When linolenic or myristic acid is heated with water in presence of aluminium oxide at 400° and a maximum pressure of 170 atm. and 250 atm., respectively, a product is obtained of which the fractions of lower b. p. contain a very considerable and similar content of naphthenes. The saturated acid is considered to lose carbon dioxide, giving a saturated hydrocarbon which undergoes cracking with production of unsaturated derivatives or to yield unsaturated acids which undergo cyclisation. Formation of ketones is observed to a minor extent. Support is thus rendered to the hypothesis of the formation of naphthenic petroleum from fatty acids of animal or vegetable origin.

Treatment of lactic acid with water and calcium hydroxide at 360°/130 atm. (maxima) yields an oil identical with those obtained by hydrolysis of cellulose with aqueous alkalis under pressure, and differing from the "synthol" of Fischer mainly in its smaller alcohol content. Treatment of the oil with sulphuric acid affords hydrocarbons identical with the corresponding "synthin" fractions, thus indicating a possible second source of naphthene hydrocarbons.

H. WREN.

Action of peracetic acid on the acetylenic linking. J. BÖESEKEN and G. SLOOFF (Rec. trav. chim., 1930, **49**, 95—99).—Treatment of stearolic acid (containing about 5% of stearic acid) with an acetic acid solution of peracetic acid gives, after 8 days, nonoic, azelaic, and small amounts of keto-stearic acids; more than 30% of the original acid is unaccounted for. Δ^9-Undecinenoic acid affords a mixture of products containing suberic and formic acids; oxidation occurs less readily than with oleic acid. Δ^4-Undecinenoic acid is oxidised even less readily than its isomeride (sebacic acid is isolated after 50 days), indicating that hydrogen attached to the acetylenic linking has a retarding action on the oxidation. When oxidation of the acetylenic linking does occur, the course of the reaction is more complicated than with the double linking.

H. BURTON.

Isolation of erucic acid. W. KIMURA (J. Soc. Chem. Ind. Japan, 1929, **32**, 262—263B).—The various methods for isolating erucic acid from the liquid unsaturated acids contained in rape oil are compared.

A. A. GOLDBERG.

Constitution of arylamides of lævulic acid. Transformation of 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone into lævulanilide. R. LUKEŠ and V. PRELOG (Coll. Czech. Chem. Comm., 1929, i, 617—623; cf. A., 1929, 824).—Of the three theoretically possible constitutions for lævulanilide only the structure $COMe \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$ is in accordance with experimental evidence.

Lævulanilide and *p*-toluidine in hot toluene afford *lævulanilide* p-*tolylimide*, m. p. 153°, decomposed by boiling water into *p*-toluidine and lævulanilide. Similarly, aniline and lævul-*p*-toluidide, m. p. 108—109°, are derived from *lævul*-p-*toluidide anil*, m. p. 142—143°. Hydrogenation of the last-named compound followed by hydrolysis of the product affords 1-phenyl-2-methyl-5-pyrrolidone, m. p. 51—52°, whereas the *p*-tolylimide of lævulanilide affords *p*-toluidine and 1-p-*tolyl-2-methyl-5-pyrrolidone*, m. p. 82·5°. *Lævulanilidephenylhydrazone*, m. p. 107°, prepared from lævulanilide or 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone, is converted by benzaldehyde in boiling alcohol into lævulaldehyde. A. I. VOGEL.

Action of peracetic acid on θι-diketostearic acid, benzil, 1 : 2-naphthaquinone, and o-benzoquinone. J. BÖESEKEN and G. SLOOFF (Rec. trav. chim., 1930, **49**, 91—94).—θι-Diketostearic acid is oxidised by peracetic acid in acetic acid solution to nonoic (90% of theory) and azelaic acids (95% of theory). Whilst diacetyl is oxidised readily, benzil is only slowly converted into benzoic acid. 1 : 2-Naphthaquinone is oxidised readily to 2-carboxy-*allo*cinnamic acid, m. p. 198—203° (anhydride, m. p. 152°), whilst *o*-benzoquinone yields probably cis-cis-*muconic acid*, m. p. 195°. H. BURTON.

Formation of cis-cis-muconic acid from o-benzoquinone with peracetic acid. J. BÖESEKEN and G. SLOOFF (Proc. K. Akad. Wetensch. Amsterdam., 1929, **32**, 1043—1045).—See preceding abstract.

H. F. GILLBE.

Catalytic decomposition of tartronic acid. A. TALVITIE (Suomen Kem., 1929, **2**, 166—168).—The quantity of formic acid produced in the electrolytic oxidation of alkaline tartronate solutions shows that a fission of the molecule occurs in addition to oxidation. A. I. VOGEL.

Preparation and determination of sodium citrate. M. CATULLO.—See B., 1930, 119.

Preparation of γ-d-mannonolactone. W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1930, **52**, 403—405).—γ-d-Mannonolactone is obtained in good yield by oxidising mannose, or the mannose-containing hydrolysate of ivory-nut meal, by Hudson and Isbell's method (A., 1929, 1043).

H. BURTON.

Irreversible oxidation of organic compounds. IV. Oxidation of aldehydes. J. B. CONANT, J. G. ASTON, and C. O. TONGBERG (J. Amer. Chem. Soc., 1930, **52**, 407—419).—The rates of oxidation of acetaldehyde, propaldehyde, *n*- and *iso*-butaldehyde (all unimolecular), and dextrose (bimolecular) have been determined at 80° in presence of *N*-sulphuric acid and varying amounts of ceric sulphate, by the method previously described (A., 1927, 116). Except for dextrose, the rate alters only slightly with change in concentration of the ceric sulphate. The rate decreases considerably when oxidation is carried out at 60°. Oxidation of various aliphatic aldehydes (second order reaction), and dextrose, lævulose, and α- and β-naphthols (all first order reaction) with potassium ferricyanide (cf. *loc. cit.*; A., 1928, 1357), molybdicyanide, and tungsticyanide shows that the

rate is a function of the alkalinity of the solution, and that it increases with rise of p_{H}. The reactions studied can be formulated in terms of "apparent oxidation potentials" (cf. *loc. cit.*).

Oxidation of phenyl *iso*propyl ketone with alkaline potassium ferricyanide at 85—90° affords some phenyl β-amino*iso*propyl ketone (Gabriel, A., 1911, i, 212). Similarly, methyl *iso*propyl ketone furnishes some methyl β-amino*iso*propyl ketone (*benzenesulphonyl* derivative, m. p. 93·5—94°.) H. BURTON.

Romijn's formaldehyde titration. R. SIGNER (Helv. Chim. Acta, 1930, **13**, 43—46).—In the determination of formaldehyde by Romijn's method (A., 1897, ii, 166), the concentrations of both formaldehyde and sodium hypoiodite (*i.e.*, iodine) are important. With relatively concentrated solutions of both reactants, better results are obtained than with dilute solutions containing the same amounts. With a small amount of formaldehyde and a very large excess of iodine, dilution does not cause such differences in the results. In the first of the above cases, transformation of the hypoiodite into iodide and iodate occurs more readily than the oxidation of the aldehyde. H. BURTON.

Aldehydes containing the ether-oxygen group. S. SABETAY (Bull. Soc. chim., 1929, [iv], **45**, 1161—1169).—The following aldehydes containing an ether-oxygen linking have been obtained from the corresponding acetals by hydrolysis with dilute sulphuric acid. The latter were obtained by condensation of chloroacetal with the corresponding alcohol or phenol in presence of potassium hydroxide and copper powder : γ-*phenylpropoxyacetaldehyde*, b. p. 130—131°/6 mm. (*semicarbazone*, m. p. 120° ; *ethylacetal*, b. p. 146—149°/7 mm., d^{19} 0·9785, n_D^{19} 1·4798) ; n-*octoxyacetaldehyde*, b. p. 93—94°/6 mm. (*semicarbazone*; *ethylacetal*, b. p. 121·5—122°/5 mm., $d^{13·5}$ 0·8823, $n_D^{13·5}$ 1·4286) ; o-*methoxyphenoxyacetaldehyde*, b. p. 120—121°/6 mm. (*semicarbazone*, m. p. 153°; *acetal*, b. p. 167—168°/19 mm., d^{20} 1·059, n_D^{20} 1·4937) ; p-*methoxyphenoxyacetaldehyde*, b. p. 143—144°/14 mm., d^{20} 1·176, n_D^{20} 1·5383 (*semicarbazone*, m. p. 168—169°; *acetal*, b. p. 166—168°/15 mm., d^{20} 1·058, n_D^{20} 1·4954) ; *eugenyloxy-* (? *isoeugenyloxy-*)*acetaldehyde* (*semicarbazone*, m. p. 189—189·5°; *acetal*, b. p. 175—176°/6 mm., d^{21} 1·036, n_D^{21} 1·5116) ; 1 : 2 : 3 : 4-*tetrahydro-6-naphthoxyacetaldehyde*, b. p. 150—151°/7 mm. (*semicarbazone*, m. p. 168·5°; *acetal*, b. p. 172—174°/6 mm., d^{20} 1·043, n_D^{20} 1·5114); and p-tert.-*butylphenoxyacetaldehyde*, b. p. 122—123°/5 mm., d^{20} 1·024, n_D^{20} 1·5142 (*semicarbazone*, m. p. 190—191°; *acetal*, b. p. 151—152°/5 mm., d^{15} 0·974, n_D^{15} 1·4866). The acetals of the following aldehydes were obtained by condensation of the alcohol with sodium ethoxide and removal of the ethyl alcohol under reduced pressure (5 mm.) : *citronelloxyacetaldehyde*, b. p. 128—130°/12 mm. (*acetal*, b. p. 147—149°/8 mm., d^{19} 0·8911, n_D^{19} 1·4438) ; *rhodinoxyacetaldehyde*, b. p. 112—116°/5 mm. (*acetal*, 143—147°/8 mm.,) ; *neryloxyacetaldehyde* (*acetal*), *geranoxyacetaldehyde* (acetal), n-*dodecoxyacetaldehyde*, b. p. 155—156°/9 mm., m. p. 16—17°, d^{21} 1·44 (*acetal*, b. p. 176°/8 mm., n_D^{20} 1·4335, d^{20} 0·8697); and *cyclohexoxyacetaldehyde* (*acetal*, b. p. 107—108°/6·5 mm., d^{20} 0·94; n_D^{20} 1·4382). The *acetal* of linaloxyacet-

aldehyde, b. p. 128—130°/5 mm., n_D^{20} 1·4456, is decomposed completely on hydrolysis. Introduction of the ether-oxygen linking, *e.g.*, into myristaldehyde, giving laurinoxyacetaldehyde, definitely increases the strength and persistency of the odour. In compounds of the type $R·O·CH_2·CHO$ this effect is more pronounced when R is alkyl or aralkyl than when R is aryl or a hydroaromatic group. n-Octoxyacetaldehyde possesses a very strong and persistent odour and similarly in geranoxy- and rhodinoxy-acetaldehydes the odour of roses is persistent and slightly piquant. R. BRIGHTMAN.

Action of ammonia on bromoacetaldehyde and preparation of pyrazine. A. E. TSCHITSCHIBABIN and M. N. SCHTSCHUKINA (J. Russ. Phys. Chem. Soc., 1929, **61**, 1645—1650).—See A., 1929, 686.

Formation of glyoxalosazones by the interaction of dichloroacetaldehyde and arylhydrazines. F. D. CHATTAWAY and L. H. FARINHOLT (J.C.S., 1930, 94—98).—When dichloroacetaldehyde (or its alcoholate) is treated with an arylhydrazine in acetic acid solution, the initially formed arylhydrazone loses hydrogen chloride, yielding a crimson solution. The colour is due to the intermediate production of an unstable azo-derivative of chloroethylene, and since this arises from a reversible reaction, $NHAr·N{:}CH·CHCl_2 \rightleftharpoons NAr{:}N·CH{:}CHCl + HCl$, the colour disappears on heating and a glyoxalosazone is obtained : $NHAr·N{:}CH·CHCl_2 \xrightarrow{NHAr·NH_2} (NHAr·N{:}CH)_2$. Thus, dichloroacetaldehyde alcoholate and phenylhydrazine yield glyoxaldiphenylosazone, m. p. 169—171°. Using the requisite arylhydrazine the following are prepared : *glyoxal-di-p-chlorophenylosazone*, m. p. 227° [decomp. ; diacetyl derivative, m. p. about 330° (decomp.)]; -*di-2 : 4-dichlorophenylosazone*, m. p. 253—254° [decomp. ; diacetyl derivative, m. p. 291—292° (decomp.)]; -*di-2 : 4 : 6-trichlorophenylosazone*, m. p. 189° [diacetyl derivative, m. p. about 370° (decomp.)]; -*di-p-bromophenylosazone*, m. p. 215° [decomp. ; diacetyl derivative, m. p. about 340° (decomp.)]; -*di-2 : 4-dibromophenylosazone*, m. p. 243° (decomp.) after darkening at 237° [diacetyl derivative, m. p. 300° (decomp.)], and -*di-2 : 4 : 6-tribromophenylosazone*, m. p. 226—228° [decomp. ; diacetyl derivative, m. p. about 365° (decomp.)].

When glyoxal-diphenyl-, -p-chlorophenyl-, or -2 : 4-dichlorophenyl-osazone is chlorinated in acetic acid solution, *dichloroglyoxaldi-2 : 4-dichlorophenylosazone*, m. p. 248—251° (decomp.) after darkening at about 240°, is produced in each case. *Dichloroglyoxaldi-2 : 4 : 6-trichlorophenylosazone*, m. p. 229—231° (decomp.), is obtained by chlorination of the di-2 : 4 : 6-trichlorophenylosazone. Bromination of the above osazones causes replacement of both nuclear and glyoxal hydrogen atoms. *Dibromoglyoxal-di-2 : 4-dibromophenylosazone*, m. p. 205° (decomp.), -*di-2 : 4 : 6-tribromophenylosazone*, m. p. 230° (decomp.), -*di-2 : 4-dichlorophenylosazone*, m. p. 270—273° (decomp.), and -*di-2 : 4 : 6-trichlorophenylosazone*, m. p. 246° (decomp.), and *dichloroglyoxaldi-2 : 4 : 6-tribromophenylosazone*, m. p. 257° (decomp.), are described. H. BURTON.

Interaction of butyl chloral hydrate and 2 : 4-dihalogenated phenylhydrazines. F. D. CHATTA-WAY and H. IRVING (J.C.S., 1930, 87—94).—Butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride react in aqueous sodium acetate at 75°, yielding an unstable, crimson product, which eliminates hydrogen chloride very readily, forming αβ-*dichlorocrotonaldehyde*-2 : 4-*dichlorophenylhydrazone* (I), m. p. 112°. The colour of the initial product is probably due to the reversible loss of hydrogen chloride from butyl chloral-2 : 4-dichlorophenylhydrazone, giving βγ-dichloro-α-2 : 4-dichlorobenzeneazo-Δ^α-butene. Reduction of I with tin and hydrochloric and acetic acids affords 2 : 4-dichloroaniline, and treatment with bromine in cold acetic acid furnishes αβ-*dichloro*-αβ-*dibromobutaldehyde*-2 : 4-*dichlorophenylhydrazone*, m. p. 126—127° (decomp.). Treatment of I with chlorine in acetic acid suspension affords ααββω-*pentachlorobutaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 84—85° (N-*acetyl* derivative, m. p. 108—109°), which on reduction yields 2 : 4 : 6-trichloroaniline. Carefully regulated addition of chlorine to the N-*acetyl* derivative, m. p. 122·5°, of I furnishes ααββ-*tetrachlorobutaldehyde*-N-*acetyl*-2 : 4-*dichloro-phenylhydrazone*, m. p. 97—98°.

Butyl chloral hydrate and 2 : 4-dichlorophenyl-hydrazine hydrochloride react in boiling alcohol or acetic acid affording β-*chloro*-α-*ketobutaldehyde*-2 : 4-*dichlorophenylhydrazone* (II), m. p. 129° (N-*benzoyl* derivative, m. p. 166·5°). Treatment of this with methyl-alcoholic 2 : 4-dichlorophenylhydrazine hydrochloride gives α-*keto*-β-*methoxybutaldehyde*-2 : 4-*dichlorophenylosazone*, m. p. 196° (decomp.) [the corresponding β-*ethoxy*-compound, m. p. 162° (decomp.), is produced when alcohol is used], which is also formed, together with II, when butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride react in boiling methyl alcohol.

Similar series of reaction with 2-chloro-4-bromo- and 2 : 4-dibromo-phenylhydrazines give rise to the following new compounds : αβ-*dichlorocrotonaldehyde*-2-*chloro*-4-*bromophenylhydrazone*, m. p. 118° (N-*acetyl* derivative, m. p. 134°), and -2 : 4-*dibromophenyl-hydrazone*, m. p. 119·5° (N-*acetyl* derivative, m. p. 141°); αβ-*dichloro*-αβ-*dibromobutaldehyde*-2 : 4-*di-bromophenylhydrazone*, m. p. 132—133° (decomp.); β-*chloro*-α-*ketobutaldehyde*-2-*chloro*-4-*bromophenylhydr-azone*, m. p. 135°, and -2 : 4-*dibromophenylhydrazone*, m. p. 143·5° (N-*benzoyl* derivative, m. p. 183·5°); α-*keto*-β-*methoxy*-, m. p. 194° (decomp.), and α-*keto*-β-*ethoxy-butaldehyde*-2 : 4-*dibromophenylosazone*, m. p. 177° (decomp.). H. BURTON.

Compounds of the citronellic and rhodinol series. J. DŒUVRE (Bull. Soc. chim., 1929, [iv], 45, 1098—1107).—A recapitulation of work already published (this vol., 59). On oxidation with potassium permanganate and chromic oxide, pure, natural *d*-citronellal yields 78% of acetone.

R. BRIGHTMAN.

Bromomalonic dialdehyde. J. GRARD (Compt. rend., 1930, 190, 187—189).—In aqueous solution bromomalonic dialdehyde behaves as a true acid, p_H 2. The *copper*, *zinc*, and *nickel* salts are described. Application of Meyer's method (A., 1911, i, 301)

shows that the keto–enolic equilibrium in alcoholic solution is established only after 48 hrs. and corresponds with 24% of the enol at the ordinary temperature; a rise of temperature raises the concentration of the enol. When heated with alkalis it affords formic acid, methyl alcohol, and the alkali bromide. Sodium ethoxide and bromine yield the *sodium* salt, which is converted by dilute acids into the *compound* OH·CH:C(OEt)·CHO, m. p. 135°. Bromomalonic dialdehyde gives with Grignard's reagent, in poor yield, the *compound* CHO·CHBr·CHMe·OH, *d* 1·5258, *n* 1·5105. Urethane condenses with the dialdehyde to give a *compound*, m. p. 169—171°.

C. C. N. VASS.

Iodometric determination of organic compounds. W. H. HATCHER and W. H. MUELLER (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 35—44).—The determination of acetone, formaldehyde, acetaldehyde, and pyruvic acid in dilute aqueous solutions by the action of iodine and sodium hydroxide solutions followed by determination of the residual iodine after acidification has been studied with reference to the effects of alkalinity and of the order of mixing of the reagents, viz., (*a*) substance, sodium hydroxide, iodine, (*b*) substance, iodine, sodium hydroxide, or (*c*) iodine, sodium hydroxide, substance.

A maximum of 94·5% of acetone was determinable with order (*a*) when the excess of alkali was increased to nine times the theoretical amount. About 45% reaction occurred with order (*b*) and 17% with order (*c*). Increased dilution or time of reaction increased the amount of acetone converted, but complete conversion was not attained. Increasing the time of keeping of acetone and sodium hydroxide before addition of iodine had no effect.

Formaldehyde (Romijn, A., 1897, ii, 166; Borgstrom and Horsch, A., 1923, ii, 590) is determined practically quantitatively with orders (*a*) or (*b*), and 40% excess of alkali. Order (*c*) gives very incomplete reaction.

The reaction of acetaldehyde (Wieland, A., 1924, i, 606) is only about 60% complete with order (*a*) and less with (*b*) and (*c*), even with seven times the theoretical amount of alkali.

The reaction of pyruvic acid is 94·5% complete with order (*a*), less with (*b*) and (*c*), with six times the theoretical amount of alkali (cf. Wieland, *loc. cit.*). Increasing the dilution or time of reaction has little effect.

In general, it is concluded that a large excess of hydroxyl ion must be present, and the effect of this is particularly marked where iodination is the principal reaction. R. K. CALLOW.

Allyl and propenyl ketones. L. COPPENS (Bull. Soc. chim. Belg., 1929, 38, 310—316).—By Blaise's method (A., 1904, i, 290) the following unsaturated ketones are prepared, a mixture of the allyl and propenyl ketones being obtained directly by the action of zinc and allyl or propenyl iodide on the nitrile, and their ultra-violet absorption spectra are plotted (with CASTILLE) : ethyl allyl ketone, b. p. 124—124·2°, d_4^{20} 0·84976, n_D^{20} 1·42443 (absorption spectrum, maximum λ 2824, ε 58·3; minimum λ 2529,

ε 23·3); ethyl propenyl ketone, b. p. 140·4—140·6°, d_4^{20} 0·85587, n_D^{20} 1·43911 (maximum, λ 3247, ε 28; minimum λ 2598, ε 4·6); *cyclo*propyl allyl ketone, b. p. 157—157·4°/761 mm., d_4^{20} 0·91721, n_D^{20} 1·45846 (maximum λ 2824, ε 58; minimum λ 2620, ε 2·7); and *cyclo*propyl propenyl ketone, b. p. 173—173·5°/761 mm., d_4^{20} 0·93476, n_D^{20} 1·47616 (maximum, λ 3129, ε 28; minimum λ 2703, ε 7).　　J. W. BAKER.

Semicarbazones of *iso*butylidene- and *iso*amylidene-acetones. R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], **45**, 1126—1132).— When treated with the theoretical amount of semicarbazide in aqueous alcohol *iso*butylideneacetone affords no precipitate even on dilution; with 2 mols. of semicarbazide, the *semicarbazidosemicarbazone*, m. p. 188—189°, is obtained. If the *iso*butylideneacetone is previously boiled for a few minutes with 20% sulphuric acid, a *semicarbazone*, m. p. 126°, is obtained together with the isomeric compound, m. p. 164—165°, described by Kishner (A., 1913, i, 1165). The latter compound is also obtained by hydrolysis of the residues, b. p. 130—150°/15 mm., obtained in the preparation of 3-methyl-5-*iso*propylpyrazoline (this vol., 94) and is the semicarbazone of β-*methyl-Δ^β-hexen-ε-one*, b. p. 152—153°/745 mm., d_4^{11} 0·8643, n_D^{11} 1·4417, and not of *iso*butylideneacetone, as Kishner supposed. With sodium hypobromite β-methyl-Δ^β-hexen-ε-one yields bromoform and an acid which with 20% sulphuric acid yields a tar and not *iso*hexolactone. Attempts to synthesise this ketone by the action of magnesium methyl iodide on acetonylacetone yielded almost exclusively $\beta\varepsilon$-dimethylhexane-$\beta\varepsilon$-diol, b. p. 92—93°, with only traces of β-methyl-Δ^β-hexen-ε-one and a little β-methylhexan-β-ol-ε-one (semicarbazone, m. p. 135°). With phenylmethylhydrazine acetonylacetone yields in place of the expected monophenylhydrazone (cf. Diels and Johlin, A., 1911, i, 254) N-*methylanilino*-2 : 5-*dimethylpyrrole*, b. p. 145—146°/17 mm. The indefinite b. p. of *iso*butylideneacetone and the sticky deposits obtained by the action of semicarbazide are regarded as indicating the existence of this ketone and its semicarbazones in stereoisomeric forms. *iso*Amylideneacetone when similarly boiled with 20% sulphuric acid before treatment with semicarbazide yields the two semicarbazones, m. p. 100° and 113—114°, described by Léser (A., 1898, i, 512), the latter when kept at 90—100° for 24 hrs. having m. p. 118—120°. With 2 mols. of semicarbazide in aqueous alcohol, *iso*amylideneacetone yields the semicarbazidosemicarbazone, m. p. 205° (decomp. 185° when slowly heated; cf. Tiemann, A., 1900, i, 275).　　R. BRIGHTMAN.

Identification of stereoisomeric ethylenic ketones. R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], **45**, 1112—1124).—Largely a recapitulation of published results (A., 1928, 509). The property of unsaturated ketones containing an $\alpha\beta$-ethylenic linking of yielding pyrazolines with hydrazine (A., 1929, 1183), whereas other unsaturated ketones yield hydrazones or azines, is applied to the determination of the structure of the methyl α-ethyl-Δ^α-propenyl ketones and methyl α-*n*-propyl-Δ^α-butenyl ketones. The methyl α-ethyl-Δ^α-propenyl ketones both yield 3 : 5-dimethyl-4-ethyl-

pyrazoline, b. p. 72—73°/10 mm., and hence must be stereoisomeric $\alpha\beta$-unsaturated ketones. This similarity of constitution is supported by the similarity of the absorption curves, both curves showing maxima at 3240 and 3000 Å., due to the carbonyl group and the conjugated double linking, respectively. Similarly, the methyl α-*n*-propyl-Δ^α-butenyl ketones yield the same 3-methyl-5-ethyl-4-*n*-propylpyrazoline, b. p. 100°/11 mm., d_4^{11} 0·9055, n_D^{11} 1·4692, and accordingly the ketones are $\alpha\beta$-unsaturated stereoisomerides. Hydroxyketones of the type $(R{\cdot}CH_2)_2{\cdot}C(OH){\cdot}CO{\cdot}Me$ thus yield stereoisomeric $\alpha\beta$-unsaturated ketones on dehydration.

Oxidation of the ketones with alkali hypochlorite or hypoiodite did not yield substituted acrylic acids, $CHR{:}C(CH_2R){\cdot}CO_2H$ (cf. Colonge, A., 1927, 449), but a lachrymatory oil, stable to sodium hydroxide, and traces of chloroform. Ozonisation similarly afforded little evidence regarding the constitution of these ketones. Methyl α-ethyl-Δ^α-propenyl ketone yields much acetic acid, a small quantity of an oil, probably pentane-$\beta\gamma$-dione, giving a dioxime, m. p. 170—171° (cf. Fileti and Ponzio, A., 1897, i, 317), but no propionic acid, and methyl α-*n*-propyl-Δ^α-butenyl ketone yields a trace of hexane-$\beta\gamma$-dione (dioxime, m. p. 165—166°; cf. Fileti and Ponzio, A., 1895, i, 499), a little acetic and propionic acids, but no butyric acid.

R. BRIGHTMAN.

Dehydration of α-hydroxyketones. R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], **45**, 1107—1112).—Dehydration of γ-ethylpentan-γ-ol-δ-one with sulphuric acid containing the theoretical amount of sulphuric anhydride for the dehydration, at 0° yields 65% of an oil, $C_7H_{14}O_2$, b. p. 150—155°, from which two *ketones*, b. p. 150°/747 mm., d_4^{12} 0·8718, n_D^{12} 1·4593 (*semicarbazone*, m. p. 201°), and b. p. 153—154°/747 mm., d_4^{11} 0·8789, n_D^{11} 1·4554 (*semicarbazone*, m. p. 161°), are separated by means of their semicarbazones. Similarly, δ-propylhexan-δ-ol-ε-one yields 80—85% of an oil, $C_9H_{16}O$, b. p. 68—74°/10 mm., composed of a mixture of two *ketones*, b. p. 71°/11 mm., $d_4^{11\cdot5}$ 0·8620, $n_D^{11\cdot5}$ 1·4563 (*semicarbazone*, m. p. 142°), and b. p. 74°/11 mm., d_4^{11} 0·8668, n_D^{11} 1·4573 (*semicarbazone*, m. p. 110°, and then 120—121° after resolidifying).

R. BRIGHTMAN.

Colorimetric determination of rhamnose. R. A. McCANCE (Biochem. J., 1929, **23**, 1172—1174). —The sugar is determined as methylfurfuraldehyde obtained by heating rhamnose with hydrochloric acid and extracting the compound with benzene.

S. S. ZILVA.

Fucose (*l*-galactomethylose) and *epi*fucose (*l*-talomethylose) series. E. VOTOČEK and V. KUČERENKO (Coll. Czech. Chem. Comm., 1930, **2**, 47—53).—Treatment of fuconolactone with aqueous pyridine for 3 hrs. at 145° gave *epi*fuconic acid, separated from the attendant fuconic acid by precipitation of the aqueous solution of the barium salts with alcohol, converted into *epi*fuconophenylhydrazide, m. p. 178°, $[\alpha]_D^{20}$ +17·6° in water, which yielded *epi*fuconolactone, m. p. 126—127°, $[\alpha]_D^{20}$ +36·7° in water, with aqueous baryta at 100°. Reduction of the latter with sodium amalgam gave epi*fucose*, $[\alpha]_D$ —36·9° in water (*phenylmethylhydrazone*, m. p.

137°; p-bromophenylosazone, m. p. 203—203·5°); further reduction in acid solution yielded epifucitol, m. p. 104°, $[\alpha]_\text{D}$ —2·3° in water (benzylidene derivative, m. p. 183°, $[\alpha]_\text{D}$ +39·7° in chloroform). The rotatory powers are in agreement with the views of Hudson. A. I. Vogel.

Rhodeose (d-galactomethylose) and epirhodeose (d-talomethylose) series. E. Votoček and F. Valentin (Coll. Czech. Chem. Comm., 1930, 2, 36—46).—The rotatory powers of some rhodeose and epirhodeose derivatives have been determined and are in agreement with Hudson's rules. Tadokoro and Nakamura's methylfucoside, $[\alpha]_\text{D}$ —122°, is optically impure, the pure d-compound having $[\alpha]_\text{D}$ +189·9° (Hudson predicted 189°). The mutarotation of rhodeose, $[\alpha]_\text{D}^{18-19}$ +127·0° to +76·0° in water, follows a unimolecular law. Methylrhodeose, $[\alpha]_\text{D}$ +189·9° in water (phenylbenzylhydrazone, $[\alpha]_\text{D}$ —14·9° in methyl alcohol), is prepared by the action of methyl-alcoholic hydrogen chloride on rhodeose at 100° for 50 hrs. in a closed vessel. Rhodeosephenylbenzylhydrazone has m. p. 178—179°, $[\alpha]_\text{D}$ —14·9° in methyl alcohol; rhodionophenylhydrazide, from rhodionolactone, m. p. 106°, has m. p. 205°, $[\alpha]_\text{D}$ +12° in water. epiRhodionolactone, m. p. 128°, $[\alpha]_\text{D}$ —28·6° in water (corresponding phenylhydrazide, m. p. 170°, $[\alpha]_\text{D}$ —17·7° in water), was prepared by oxidising rhodeose with bromine water, and fractionally crystallising the barium salts; rhodeotetronolactone, $[\alpha]_\text{D}$ +44·2° in water, was similarly prepared. Rhodeotetrose, $[\alpha]_\text{D}$ +32·4° in water, was obtained by the Wohl degradation of rhodeose. Reduction of epirhodionolactone with sodium amalgam gave epirhodeose (phenylmethylhydrazone, m. p. 136°), converted by a further quantity of sodium amalgam in acid solution into epirhoditol, m. p. 104°, $[\alpha]_\text{D}$ +2° in water, purified through the benzylideneacetal derivative, m. p. 184°, $[\alpha]_\text{D}$ —40·9° in chloroform.
A. I. Vogel.

Sugar carbonates. IV. Dicarbonates of dextrose, lævulose, mannose, galactose, and arabinose. W. N. Haworth and C. R. Porter (J.C.S., 1930, 151—157).—Dicarbonates are prepared from the sugars mentioned in the title by treatment with carbonyl chloride in cold pyridine solution; amorphous by-products are usually formed. The esters are hydrolysed rapidly by dilute alkali in the cold, but less readily by dilute acids. Dextrose dicarbonate, m. p. 224° (decomp.) after sintering at 200°, $[\alpha]_\text{D}$ —29° in acetone containing 25% of water, galactose dicarbonate, m. p. 212° (decomp.) after slight sintering at 190°, $[\alpha]_{5780}^{21-23}$ —86·5° in acetone containing 25% of water, lævulose dicarbonate, m. p. 173—174° (decomp.), $[\alpha]_{5780}^{16}$ —143° in 50% aqueous acetone, and arabinose dicarbonate, m. p. 200—202° (decomp.), $[\alpha]_{5780}^{25}$ +61·3° in acetone containing 33% of water, do not exhibit mutarotation in aqueous acetone, even after the addition of a trace of hydrochloric acid. Mannose dicarbonate, m. p. 122—123° (decomp.) after slight sintering at 118°, $[\alpha]_{5780}^{21}$ +26° in acetone, when heated with alcoholic aniline yields an anilide, $C_{14}H_{13}O_7N$, m. p. 174—175°, $[\alpha]_{5780}^{20}$ —70° after 5 min., —32° after 18 hrs. (in alcohol). The amorphous by-product formed during the preparation of lævulose

dicarbonate decomposes between 150° and 180° without melting, and has $[\alpha]_{5780}^{16}$ —58° in acetone. The mol. wt. is intermediate between the values for 3 and 4 condensed dicarbonate molecules. Fractions differing in their solubilities were obtained by fractional precipitation of an acetone solution with ether.

Constitutional formulæ, based on the similarity in properties to the diisopropylidene derivatives, are given for the five dicarbonates. H. Burton.

Conversion of simple sugars into derivatives of 4-pyrone and preparation of further unsaturated anhydro-sugars. III. K. Maurer (Ber., 1930, 63, [B], 25—34; cf. A., 1927, 751; 1929, 428).—2-Hydroxyglucal tetra-acetate [formerly designated tetra-acetylglucoseen (loc. cit.)] is converted by chlorine in anhydrous ether into the unstable dichloride, m. p. (indef.) 46—70°, $[\alpha]_\text{D}^{20}$ +48·57° to +43·98° (not equilibrium value) in chloroform in 3 hrs., which, with silver carbonate and aqueous ether, affords 2 : 3 : 4 : 6 - tetra - acetylglucosone hydrate, $C_{14}H_{20}O_{11}$, m. p. 112°, $[\alpha]_\text{D}^{12}$ +14·69 to +53·66° in aqueous alcohol. If crystallisation of the dichloride cannot be induced, conversion into the hydrate is effected by aqueous ether. Hydrolysis of the last-named compound by 0·1N-sodium hydroxide and treatment of the product with phenylhydrazine acetate affords glucosazone, m. p. 213°. 2 : 3 : 4 : 6-Tetra-acetylglucosone hydrate is converted by acetic anhydride and pyridine into diacetylkojic acid, $C_{10}H_{10}O_6$, m. p. 102°, transformed by methyl-alcoholic ammonia successively into acetylkojic acid, m. p. 136°, and kojic acid [5-hydroxy-2-hydroxymethyl-4-pyrone], m. p. 152° (dibenzoyl compound, m. p. 136°).

Treatment of acetobromolactose with diethylamine in chloroform affords 2-hydroxylactal hepta-acetate, m. p. 166—167°, $[\alpha]_\text{D}^{21}$ —17·07° in chloroform; hydroxycellobial hepta-acetate, m. p. 125°, $[\alpha]_\text{D}^{20}$ —21·47° in chloroform, is similarly prepared. Neither anhydride affords an osazone with phenylhydrazine.
H. Wren.

Mechanism of carbohydrate oxidation. XI. Action of potassium hydroxide on maltose. W. L. Evans and M. P. Benoy (J. Amer. Chem. Soc., 1930, 52, 294—307).—The action of aqueous potassium hydroxide on maltose has been studied at 25° and 50° by the methods previously described for other sugars (A., 1926, 149, 1228; 1928, 397, 741, 1222). Maltose yields larger amounts of formic acid than does dextrose under the same conditions, but affords smaller amounts of pyruvaldehyde, mannose, lactic and acetic acids. The explanation advanced to account for these differences is that maltose is converted into both 1 : 2- and 2 : 3-dienols, with subsequent oxidative degradation of the former into formic acid, dextrose, and erythrose, and the latter into glycollaldehyde, dextrose, and erythrose. The lactic acid and pyruvaldehyde are then formed from the dextrose, the total amount being approximately half of the amount from dextrose alone. Mannose-phenylhydrazone is formed slowly from maltose by treatment with 0·05—0·42N-potassium hydroxide and phenylhydrazine at 25°. It is produced either from dextrose or 4-glucosidomannose. H. Burton.

Walden inversion in glucoside fission. W. Schneider and M. Becker (Naturwiss., 1930, **18**, 133).—Scission of sinigrin by aqueous silver nitrate in the presence of silver carbonate to remove the free nitric acid formed in accordance with the equation

$C_3H_5N:C(O \cdot SO_3K) \cdot S \cdot C_6H_{11}O_5 + 2AgNO_3 + H_2O =$
$C_3H_5N:C(O \cdot SO_3Ag) \cdot SAg + C_6H_{12}O_6 + HNO_3 + KNO_3$

yields a sugar solution which has a higher dextro-rotation (mutarotation ultimately the equilibrium value) than that required for the total liberated β-dextrose, showing that the product of hydrolysis is α-dextrose. Conversely, enzymic hydrolysis of the same glucoside gives a small lævorotation, converted by addition of a few drops of ammonia into a dextro-rotation of ten times this value (corresponding with 55% hydrolysis). Since sinigrin is a β-glucoside the silver nitrate scission must involve a Walden inversion about the terminal carbon atom of dextrose.

J. W. Baker.

Natural glucosides. I. Constitution of phloridzin. F. R. Johnson and A. Robertson (J.C.S., 1930, 21—26).—Methylation of phloridzin by prolonged treatment with methyl iodide and potassium carbonate in dry acetone or with ethereal methyl-alcoholic diazomethane affords *trimethylphloridzin* (*monohydrate*, m. p. 63—65° after softening at 60°), This is hydrolysed by aqueous methyl-alcoholic sulphuric acid to 6-*hydroxy*-2 : 4-*dimethoxyphenyl* β-*p*-*methoxyphenylethyl ketone*, m. p. 110° (*acetate*, m. p. 62—63°), which on treatment with acetic anhydride and sodium acetate at 180° yields 5 : 7 : 4′-*trimethoxy*-3-*benzyl*-2-*methyl*-1 : 4-*benzopyrone*, m. p. 165—166°. Phloridzin is, therefore, 4 : 6-dihydroxy-2-glucosidoxyphenyl β-*p*-hydroxyphenylethyl ketone. Dehydration of β-*p*-methoxyphenylpropionamide with thionyl chloride gives β-*p*-*methoxyphenylpropionitrile*, b. p. 172—173°/17 mm., which condenses with phloroglucinol dimethyl ether in presence of zinc chloride and ethereal hydrogen chloride, yielding a mixture of ketimine hydrochlorides, hydrolysed to the above ketone and the isomeric 4-*hydroxy*-2 : 6-*dimethoxyphenyl* β-*p*-*methoxyphenylethyl ketone*, m. p. 142°. H. Burton.

Formation of bases from carbonyl compounds. V. N-Alkylation of secondary amines; diastereoisomeric amino-alcohols. A. Skita and F. Keil [with H. Havemann and K. P. Lavrovski] (Ber., 1930, **63**, [*B*], 34—50; cf. A., 1928, 1228; 1929, 441, 808, 1436).—Ethyl*iso*amylamine is converted by formaldehyde and hydrogen in presence of colloidal platinum into methylethyl*iso*amylamine, b. p. 133—137° (*picrate*, m. p. 101—102°). When similarly treated with acetaldehyde, propaldehyde, and *iso*butaldehyde, the secondary amine affords diethyl*iso*amylamine, b. p. 153—157° (*picrate*, m. p. 74—75°), *ethyl*-n-*propyliso amylamine*, b. p. 167—168°/atm. press., 52—53°/14 mm. (*picrate*, m. p. 82°), and *ethyl*-*isobutyliso amylamine*, b. p. 56—57°/40 mm. (*picrate*, m. p. 60·5—61°), respectively, with compounds of higher b. p. Since ethyl*iso*amylamine and *iso*-valeraldehyde yield the secondary *amine*, $C_{12}H_{27}N$, b. p. 74—76°/13 mm. (*picrate*, m. p. 96·5—97·5°; *methiodide*, $C_{14}H_{32}NI$, m. p. 148·5—149·5°), the production of tertiary amine appears to cease in this

instance with *iso*butaldehyde. With the simpler dimethylamine, aldehydes of higher mol. wt. can, however, be used, thus leading to the following compounds : *dimethyl*-γη-*dimethyloctylamine*, b. p. 94—95° (*hydrogen oxalate*, m. p. 159°), from citral; dimethyl*iso*amylamine, b. p. 110—116° (picrate, m. p. 135°), from *iso*valeraldehyde; *dimethylbenzylamine*, b. p. 66—67°/15 mm. (very hygroscopic *hydrochloride*; *picrolonate*, m. p. 151°), from benzaldehyde; *dimethyl*-α-*phenylethylamine*, b. p. 73·5°/14 mm. (*picrate*, m. p. 138°), from acetophenone. *cyclo*Hexylethylamine and acetaldehyde afford *cyclo*hexyldiethylamine, b. p. 193—195°/760 mm. (*picrolonate*, m. p. 147°).

Acetylacetone when reduced in presence of di-methylamine affords δ-dimethylaminopentan-β-ol, b. p. 63—65°/16 mm. (*picrolonate*, m. p. 120—121°), in good yield, but it is preferable to hydrogenate the ketone in presence of methylamine to δ-*methylaminopentan*-β-*ol*, b. p. 80—82°/17 mm. (*picrolonate*, m. p. 170°), and to hydrogenate the last-named compound in presence of formaldehyde. A limit to the production of tertiary compounds exists, since γ-*ethylamino*-α-*phenylbutan*-α-*ol*, b. p. 156—160°/12 mm. (*picrate*, m. p. 158°), from benzoylacetone and ethyl-amine, is transformed by reduction in presence of acetaldehyde into γ-*diethylamino*-α-*phenylbutan*-α-*ol*, b. p. 163—165°/14 mm. (*benzoate*, b. p. 230—234°/20 mm.), whereas γ-*iso*amylamino-α-phenylbutan-α-ol, b. p. 182°/16 mm. (*picrolonate*, m. p. 201°), from benzoylacetone and *iso*amylamine, is unchanged by hydrogenation in presence of *iso*valeraldehyde.

Hydrogenation of a mixture of acetylbenzoyl and ethylamine leads to β-*ethylamino*-α-*phenylpropan*-α-*ol*, b. p. 138°/18 mm., m. p. 47—48° (*hydrochloride*, m. p. 196—197°; *benzoyl* derivative, $C_{18}H_{21}O_2N$, b. p. 205—207°/16 mm.), converted by reduction in presence of formaldehyde into β-*methylethylamino*-α-*phenylpropan*-α-*ol*, b. p. 135—136°/15 mm. (*hydrochloride*, m. p. 171—172°). The following compounds are prepared from acetylbenzoyl and the requisite base : β-β′-*hydroxyethylamino*-α-*phenylpropan*-α-*ol*, m. p. 109° (*hydrochloride*, m. p. 166°); β-*iso*amyl-amino-α-phenylpropan-α-ol, b. p. 162°/13 mm., m. p. 75—77° (*hydrochloride*, m. p. 210—212°); β-*heptyl*-*amino*-α-*phenylpropan*-α-*ol hydrochloride*, m. p. 223—225°. The products in every case consist of only one of the two possible forms.

Catalytic reduction of benzoylacetone in presence of dimethylamine yields the two diastereoisomeric γ-*dimethylamino*-α-*phenylbutan*-α-*ols*, the main product being the crystalline *base*, m. p. 74° (*picrate*, m. p. 126°); the non-crystalline *modification*, b. p. 144°/10 mm., yields a *picrate*, m. p. 139—140°. The solid variety is obtained by reduction of γ-methylamino-α-phenylbutan-α-ol (picrate, m. p. 193°) in presence of formaldehyde, whereas the diastereoisomeric mono-methyl compound (picrate, m. p. 119°) gives the liquid modification.

Catalytic reduction of acetylacetone in presence of ethylamine yields δ-ethylaminopentan-β-ol, b. p. 70—72°/10 mm., separable into two *picrolonates*, m. p. 260° and 159°, respectively, the *base* from the last-named salt having b. p. 74°/11 mm. The existence of pure aliphatic, diastereoisomeric amino-alcohols is thus established. δ-*Diethylaminopentan*-β-*ol*, b. p. 78°/10

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mm. (*picrolonate*, m. p. 137°; *benzoate*, b. p. 195—200°/ 16 mm.), is obtained from δ-ethylaminopentan-β-ol and acetaldehyde, from acetylacetone, ethylamine, and acetaldehyde in a single operation, or from acetyl-acetone and diethylamine.   H. WREN.

Additive compounds of halides of bivalent metals with organic bases. VII. G. SCAGLIARINI and G. TARTARINI (Atti R. Accad. Lincei, 1929, [vi], **10**, 267—270).—By mixing cold saturated solutions of hexamethylenetetramine and the metallic halide, both in 95% alcohol, the following crystalline compounds are obtained : $2MgCl_2,16H_2O,5C_6H_{12}N_4$; $2MgI_2,16H_2O,5C_6H_{12}N_4$; $2MgBr_2,16H_2O,5C_6H_{12}N_4$; $2CaCl_2,8H_2O,5C_6H_{12}N_4$.   T. H. POPE.

Acetylcholine chloride. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1930, **52**, 307—310).— Acetylation of β-dimethylaminoethyl alcohol with acetyl chloride in ether gives β-dimethylaminoethyl acetate, b. p. 86—88°/80 mm. (*hydrochloride*, m. p. 129—130°), which with methyl iodide affords *acetyl-choline iodide*, m. p. 160—162°. This is converted by treatment with silver chloride in warm alcohol into the hygroscopic acetylcholine chloride, m. p. 151° [chloroaurate, m. p. 168—169° (lit. 154—155°); chloroplatinate, m. p. 227° (decomp.; lit. 223—224° and 256—257°)].   H. BURTON.

Guanidoethyl alcohol. E. FROMM, P. FANTL, and J. FISCH (J. pr. Chem., 1930, [ii], **124**, 163—167).— Interaction of β-aminoethyl benzoate hydrobromide (I) (*allylthiocarbamide*, m. p. 92°; *phenylthiocarbamide*, m. p. 108°) and cyanamide in the presence of alcohol for 5 hrs. at 115° gives β-*guanidoethyl benzoate* (*picrate*, m. p. 186°), in which the presence of an open chain is beyond question ; this yields the *tribenzoyl* derivative of *guanidoethyl alcohol*, m. p. 156° (also prepared from I, S-ethyl-ψ-thiocarbamide hydrobromide, and alcoholic potassium hydroxide, on benzoylation of the product). Fromm and Honold's guanidoethyl alcohol (A., 1922, i, 531) therefore has an open chain and not a ring structure as Fromm and others (A., 1925, i, 595) supposed. Fromm and Frieder's 2-amino-2-methyl-amino-oxazolidine (A., 1925, i, 596) is accordingly methylguanidoethyl alcohol. *Guanidoethyl alcohol picrate* has m. p. 147°.   A. I. VOGEL.

[**Action of nitrosyl bromide on amino-acids.**] G. ZEMPLÉN and Z. CSÜRÖS (Ber., 1930, **63**, [B], 98).— In their previous communication (A., 1929, 1283), the authors have overlooked the work of Karrer (A., 1927, 55).   H. WREN.

Conversion of β-ketonic esters into β-amino-esters. J. DÉCOMBE (Compt. rend., 1930, **190**, 268—270).—The oximes and azines of β-ketonic esters are not reduced by hydrogen in the presence of platinum-black or of colloidal palladium, or by aluminium amalgam. The acetyl- and benzoyl-hydrazones are reduced by aluminium amalgam (three times the theoretical quantity) to the corre-sponding β-amino-esters, the latter being obtained in yields of 50—100%.
Ethyl acetoacetate acetylhydrazone, m. p. 90° (from acetylhydrazine and the ester in alcohol), is reduced to ethyl β-aminobutyrate, b. p. 82°/20 mm. (*chloro-platinate*; normal *oxalate*, m. p. 88—90°; *phenyl-*

carbamide, m. p. 110°). *Ethyl β-ketovalerate acetyl-hydrazone* has m. p. 93°. The acetylhydrazones of the higher ketonic esters are not obtained pure ; the only crystalline compound, $C_6H_{10}ON_2$, m. p. 206°, isolated from ethyl β-ketohexoate and acetylhydrazine is possibly propylpyrazolone (cf. Curtius, A., 1895, i, 33), but *ethyl β-aminohexoate*, b. p. 102—104°/25 mm. (*chloroplatinate*; normal *oxalate*; *phenylcarbamide*, m. p. 76°), is readily obtained by reduction of the crude reaction product.
The benzoylhydrazones are similarly not isolated (cf. Struve, A., 1895, i, 35), but the crude products are directly reduced. The resulting amino-esters are less pure than when obtained from the acetylhydrazones and are best purified through the oxalate.
Ethyl β-amino-octoate has b. p. 132—133°/25 mm. (*chloroplatinate*; normal *oxalate*; *phenylcarbamide*, m. p. 114°).   R. CHILD.

Preparation of glycerol esters of amino-acids. L. HASKELBERG (Compt. rend., 1930, **190**, 270—272 ; cf. A., 1929, 1048, 1269).—The reaction of glycerol and pyruvic acid leads to (i) the crystalline product "pyruvin," m. p. 83·5° (*phenylhydrazine* derivative, m. p. 156°) (α-lactone of Brigl, Schütze, and Hartung, this vol., 193); (ii) an oil, b. p. 118—119°/10 mm. (*oxime*, m. p. 119·5°, and its *tribenzoyl* derivative, m. p. 110°; *phenylhydrazone*, m. p. 114°), described as glycide pyruvic ester, and (iii) a residue insoluble in water and in ether.
iso*Propylideneglyceryl α-bromopropionate*, b. p. 138°/ 10 mm., is converted into the α-*oximinopropionate*, m. p. 43°, which on careful hydrolysis yields *glyceryl α-oximinopropionate*, m. p. 118—118·5° (not identical with the above-mentioned oxime ; *tribenzoyl* deriv-ative, m. p. 79°). The latter on reduction gives the α-monoglyceride of *dl*-alanine, isolated as the *picrate*, m. p. 265° (decomp.).   R. CHILD.

Kolbe's synthesis with cyanoacetic acid. F. FICHTER and A. SCHNIDER (Helv. Chim. Acta, 1930, **13**, 103—107 ; cf. Moore, A., 1871, 701).—When solutions of potassium cyanoacetate containing some of the free acid are electrolysed, a small amount of ethylene dicyanide, m. p. 54·5°, is formed ; the amount increases with rise in the current density. The main reaction occurring is, however, the oxidation of cyano-acetic acid to hydrogen cyanide, carbon dioxide, and formaldehyde: $CN\cdot CH_2\cdot CO_2H+O=HCN+CO_2+ CH_2O$. This occurs by way of the intermediate percyanoacetic acid, which decomposes at the anode into the three products.
Barium peroxide and cyanoacetyl chloride in ether give some cyanoacetyl peroxide, which is converted by water into percyanoacetic acid. The acid is also formed from cyanoacetyl chloride and hydrogen peroxide in ether at the ordinary temperature. Percyanoacetic acid decomposes when warmed into hydrogen cyanide, carbon dioxide, and formaldehyde.
                H. BURTON.

Pellitorine, the pungent principle of *Anacyclus pyrethrum*. J. M. GULLAND and G. U. HOPTON (J.C.S., 1930, 6—11).—The residue from the alcoholic extract of the powdered root of *Anacyclus pyrethrum* (pellitory root) is extracted with ether, and the acid-free solution evaporated. Distillation of the syrup

obtained gives an oil, b. p. 150—275°/0·3 mm., which when fractionated yields *pellitorine*, $C_{14}H_{25}ON$, b. p. 162—165°/0·3 mm., m. p. 72° (corr.) (0·04% yield) (cf. Buchheim, A., 1876, i, 195, who calls the active principle pyrethrin; Dunstan and Garnett, J.C.S., 1895, 67, 100; Schneegans, A., 1897, i, 485). Hydrolysis of pellitorine with 2N-hydrochloric acid at 150° gives *iso*butylamine (p-*toluenesulphonyl* derivative, m. p. 75—76°), neutral nitrogenous material, and an oily, unsaturated acid (amide, m. p. 35°). Catalytic reduction of pellitorine, using palladised charcoal and methyl alcohol, affords *tetrahydropellitorine*, m. p. 35° (corr.), which is identical with n-*deco*iso*butylamide*. Pellitorine is, therefore, the *iso*butylamide of a n-nonadienecarboxylic acid. It is not identical with piperovatine (Dunstan and Garnett, J.C.S., 1895, 67, 94), but is closely related to spilanthol (n-deceno*iso*butylamide) (Asahina and Asano, A., 1920, i, 654; 1922, i, 505). Pellitorine is one fifth as pungent as piperine. H. BURTON.

Synthesis of dioxypyramidone [α-acetyl-β-dimethyloxamyl-β-phenyl-α-methylhydrazine]. R. DELABY and R. CHARONNAT (Compt. rend., 1930, 190, 59—61).—The constitution assigned to "dioxypyramidone," obtained by oxidation of pyramidone (Charonnat and Delaby, this vol., 223) has been confirmed by synthesis. Dimethyloxamic acid yields with thionyl chloride the *acid chloride*, b. p. 86·5—89·5°/14 mm., which reacts with α-acetyl-β-phenyl-α-methylhydrazine to give α-acetyl-β-dimethyloxamyl-β-phenyl-α-methylhydrazine, identical with "dioxypyramidone." The mechanism of the oxidation of pyramidone is discussed. Formation of a diamine oxide and subsequent migration of oxygen to carbon is preferred to direct rupture of the 3 : 4-double linking by addition of hydrogen peroxide and oxidation, but this cannot be supported by the isolation of any intermediate compound. R. K. CALLOW.

***iso*Carbamides and *iso*ureides. II. Condensation of *iso*carbamides with diketones and ketonic esters.** S. BASTERFIELD and E. C. POWELL (Canad. J. Res., 1929, 1, 285—291).—Ethyl*iso*carbamide and acetylacetone interact when mixed without a solvent to give *ethyl*iso*ureidoacetylacetone*, $NH:C(OEt)\cdot NH\cdot CMe:CH\cdot CO\cdot Me$, m. p. 49—50°, which is unstable, and yields at the ordinary temperature 2-*ethoxy*-4 : 6-*dimethylpyrimidine*, m. p. 162° (decomp.), which gives a 5-*bromo*-derivative, m. p. 196°. The condensation of ethyl*iso*carbamide with impure ethyl oxalacetate under similar conditions yields a gum, but with fractions of redistilled ester two *substances*, $C_9H_{12}O_4N_2$, m. p. 154° and 149°, have been obtained. The product from ethyl*iso*carbamide and ethyl acetylpyruvate has not been obtained crystalline. Ethyl*iso*carbamide and ethyl acetonedicarboxylate yield *ethyl* 2-*ethoxyuracil*-4-*acetate*, m. p. 112·5°, which forms the 4 : 5-*dibromide*, m. p. 175°, and is hydrolysed by alkali to the *acid*, which loses carbon dioxide above 150° to yield 2-ethoxy-3-methyluracil.
R. K. CALLOW.

Guanylthiocarbamides. I. K. H. SLOTTA, R. TSCHESCHE, and H. DRESSLER (Ber., 1930, 63, [B], 208—222).—Treatment of methylthiocarbimide with a boiling alcoholic solution of sodium ethoxide and guanidine thiocyanate followed by passage of carbon dioxide through the solution yields N^1-*methyl*-N^2-*guanylthiocarbamide carbonate*, m. p. 103—104°, in 77% yield. Boiling water transforms the salt into the free *base*, $NHMe\cdot CS\cdot NH\cdot C(:NH)\cdot NH_2$, m. p. 159°. The following compounds are analogously prepared : N^1-*ethyl*-N^2-*guanylthiocarbamide* (*carbonate*, m. p. 94° ; *chloride*, m. p. 158° ; *nitrate*, decomp. 204°) ; N'-*n-propyl*-N^2-*guanylthiocarbamide* (*carbonate* ; *chloride*, m. p. 133°) ; N^1-iso*butyl*-N^2-*guanylthiocarbamide* (*carbonate*, decomp. 91° ; non-crystalline *chloride* ; *sulphate*, m. p. 120° ; *nitrate*, m. p. 179° ; *picrate*, m. p. 203°) ; N^1-*allyl*-N^2-*guanylthiocarbamide* (*carbonate*, m. p. 95° ; non-crystalline *chloride* ; *sulphate*, m. p. 143° ; *nitrate*, m. p. 187° ; *picrate*, decomp. 213°) in the preparation of which N^1-*allyl*-N^2-*allylthiocarbamylguanylthiocarbamide*, $NH:C(NH\cdot CS\cdot NH\cdot CH_2\cdot CH:CH_2)_2$, softening at 240°, is obtained as by-product when an excess of allylthiocarbimide is employed ; N^1-iso*amyl*-N^2-*guanylthiocarbamide* (*carbonate*, m. p. 82° ; *nitrate*, m. p. 176° after softening at 170° ; *picrate*, m. p. 205° ; *sulphate*, m. p. 96° after softening at 92°), also obtained by treatment of guanidine thiocyanate with aqueous potassium hydroxide, removal of water, and addition of *iso*amylthiocarbimide in acetone to the residue (N^1-iso*amyl*-N^2-iso*amylthiocarbamylguanylthiocarbamide hydrochloride*, m. p. 95—100°, is obtained as by-product) ; N^1-β-*phenylethyl*-N^2-*guanylthiocarbamide picrate*, decomp. 215° after darkening at 200°. The preparation·of arylguanylthiocarbamides from guanidine thiocyanate, arylthiocarbimide, and alcoholic sodium ethoxide is less satisfactory, owing to the readiness of the reaction of the thiocarbimide with the solvent to form arylthiourethanes. Unsatisfactory results are also obtained when the guanidine is liberated from its salts by potassium hydroxide, since ammonia is readily liberated and combines with the carbimide more readily than does guanidine, so that the product contains arylthiocarbamide in considerable amount. The best results are obtained by use of the pasty mixture formed by the action of sodium on acetone which has been shaken with potassium carbonate and distilled over phosphoric oxide. Addition of guanidine thiocyanate gives a dark red solution in which the arylguanylthiocarbamide is almost instantaneously produced after addition of arylcarbimide. The following compounds are thus obtained : N^1-phenyl-N^2-guanylthiocarbamide, m. p. 178° (hydrochloride, decomp. 178° ; sulphate, decomp. 282° after darkening at 210° ; picrate, decomp. 250° after darkening at 232°) ; N^1-p-*anisyl*-N^2-*guanylthiocarbamide hydrochloride*, m. p. 181° ; N^1-p-*ethoxyphenyl*-N^2-*guanylthiocarbamide*, m. p. 148° (*hydrochloride*, m. p. 188° after softening at 182° ; *salicylate*, decomp. 139° ; *formate*, m. p. 164°) ; p-*phenylene*-N^2N^1-*di*-N^2-*guanylthiocarbamide hydrochloride*, $C_6H_4[NH\cdot CS\cdot NH\cdot C(:NH)\cdot NH_2]_2$,HCl, decomp. 212° ; N^1-3 : 4 : 5-*trimethoxyphenyl*-N^2-*guanylthiocarbamide picrate*, decomp. 270° ; N^1-p-*carbethoxyphenyl*-N^2-*guanylthiocarbamide*, m. p. 178° (*picrate*, decomp. 250°) ; N^1-m-*hydroxymethylphenyl*-N^2-*guanylthiocarbamide picrate*, decomp. 240° ; N^1-p-*acetoxyphenyl*-N^2-*guanylthiocarbamide*, m. p. 305° ; N^1-p-*hydroxyphenyl*-N^2-*guanylthiocarbamide hydrochloride*, m. p. 199° ;

N^1- 3 - *bromo* -p- *ethoxyphenyl* - N^2- *guanylthiocarbamide hydrochloride*, decomp. 178°; N^1-p-*carbo*-β-*diethylaminoethoxyphenyl* - N^2 - *guanylthiocarbamide hydrochloride*, m. p. 213°; N^1-p-*dimethylaminophenyl*-N^2-*guanylthiocarbamide*, m. p. 196° (*hydrochloride*; *sulphate*, decomp. 200°); N^1-*phenyl*-N^2-*phenylguanylthiocarbamide*, NHPh·CS·NH·C(:NH)·NHPh, decomp. 188°, from the sodium salt of phenylcyanothiocarbamide and aniline hydrochloride in boiling alcohol.

Phenylcarbimide and guanidine thiocyanate are converted by the sodium–absolute acetone method into N^1N^2-diphenylcarbamylguanidine, NH:C(NH·CO·NHPh)$_2$, m. p. 176°, in 76% yield, whereas p-anisylcarbimide yields p-anisylcarbamide, m. p. 172°, in presence of technical acetone. N^1N^2-*Di*-p-*ethoxyphenylcarbamylguanidine* has m. p. 196°   H. WREN.

Molecular compounds of ethyl diazoacetate with inorganic salts and oxides. K. LOREY (J. pr. Chem., 1930, [ii], **124**, 185—190).—The following *compounds* were prepared by interaction of ethyl diazoacetate with the appropriate inorganic substance in the correct proportions : $CHN_2·CO_2Et$,1 and $2CaCl_2$; $CHN_2·CO_2Et$,2, 3, and $6CaSO_4$; $CHN_2·CO_2Et$,6CaO; $CHN_2·CO_2Et$,6CaCO$_3$; $CHN_2·CO_2Et$,MgO. Calcium sulphate hemihydrate and ethyl diazoacetate yield the compound $3CHN_2·CO_2Et$,2CaSO$_4$. The ester is catalytically decomposed in ethereal solution by anhydrous copper sulphate to ethyl fumarate.   A. I. VOGEL.

Diethylarsine. E. GRISCHKIEWITCH-TROCHIMOVSKI and A. SPORZYŃSKI (Rocz. Chem., 1929, **9**, 741—746).—Diethylarsine, b. p. 96·5—97°, $d_4^{23·7}$ 1·1338, n_D 1·4709, is prepared by the reduction by means of zinc and hydrochloric acid of diethylarsine chloride in alcoholic solution. Diethylarsine forms with mercuric chloride a compound, $AsEt_2Cl,2HgCl_2$, which is not identical with that obtained from " Gosio-gas "; the formula has been wrongly given by Wigren (A., 1924, i, 888).   R. TRUSZKOWSKI.

Reaction between alkali alkyls and quaternary arsonium compounds. M. E. P. FRIEDRICH and C. S. MARVEL (J. Amer. Chem. Soc., 1930, **52**, 376—384).—Triethylarsine is oxidised by atmospheric oxygen to diethylarsinic acid, m. p. 136—137° (lit. 134°). Similarly, *diethyl*-n-*butylarsine*, b. p. 78°/28 mm., d_{20}^{20} 1·0306, n_D^{20} 1·4745, gives *ethyl*-n-*butylarsinic acid*, m. p. 93—96°, also obtained from dichloro-n-butylarsine and ethyl bromide by Quick and Adams' method (A., 1922, i, 600). Lithium n-butyl and *tetraethylarsonium bromide*, m. p. 298—300°, react in light petroleum, forming triethylarsine and a mixture of hydrocarbons containing a small amount of ethylene; ethylene is polymerised by lithium alkyls, affording non-gaseous products. Lithium ethyl and *triethyl*-n-*butylarsonium bromide*, m. p. 227°, give diethyl-n-butylarsine and hydrocarbons. Similar results are obtained with triethylarsine dibromide and the lithium alkyls. *Tetramethylarsonium iodide*, sublimes at 320—328°, and sodium triphenylmethyl react in dry ether, affording a coloured solid, which is unaffected by treatment with carbon dioxide and decomposed by pyridine to triphenylmethane. No evidence of the formation of a stable penta-alkyl arsenic compound has been obtained.   H. BURTON.

Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid. II. B. ENGLUND (J. pr. Chem., 1930, [ii], **124**, 191—208).—Measurements of the solubility of arsinoacetic acid and of arsenic trioxide in 99% acetic acid in the presence of various glycols have been made, and the constant L has been evaluated in each case (cf. A., 1929, 52, 945). The glycols studied were ethylene glycol, propane-αβ- and -αγ-diols, *meso*- and *r*-butane-αβ- and -βγ-diols, β-methylpropane-αβ-diol, butane-αγ-diol, hexane-βε-diol, decane-ακ-diol, and pinacol. α-Glycols have a greater influence on the solubility than other glycols ; the effect is increased by the introduction of alkyl groups, but this depends on the number and nature of the substituents ; stereoisomerides exert different effects. The bearing of these results on the relative ease of formation and on the configuration of rings is discussed. The method has also been applied to phenol, 2 : 4- and 2 : 6-dinitrophenols, pyrocatechol, 3- and 4-nitropyrocatechols, and to δ-keto-β-methylpentane-βγ-diol. Abnormal results were obtained for the 3- and 4-nitropyrocatechols, these being attributed to the presence of the tautomeric *aci*-form ; the results for δ-keto-β-methylpentane-βγ-diol are not in agreement with those obtained by the boric acid and acetone method of Böeseken. A modification of the method involving the dissolution of arsenic trioxide in water is described and is applied to a number of hydroxy-compounds. The results are in qualitative accord with those obtained by the original method.

The action of arsenious oxide on pentaerythritol and pinacol gives the *compounds* $C_5H_9O_4As$, m. p. 102—103°, and $C_{12}H_{25}O_4As$, m. p. 110° ; erythritol yields a *substance* containing 37·5% As.   A. I. VOGEL.

Effect of prolonged ebullition on magnesium organo-halides. H. GILMAN and (MISS) E. L. ST. JOHN (Bull. Soc. chim., 1929, [iv], **45**, 1091—1095).—The rate of decomposition of magnesium organo-halides in boiling solvents has been determined with the colour reaction previously described (A., 1925, ii, 1011; 1928, 160; 1929, 303). Magnesium n-butyl bromide is decomposed by 135 hrs.' boiling in ether, 66 hrs.' in ether–benzene, 60 hrs.' in ether–toluene. Similarly, magnesium benzyl chloride is decomposed in 134 hrs. in boiling ether and in 82 hrs. in ether–benzene, and magnesium phenyl bromide by 84 hrs. in ether–benzene and 40 hrs. in boiling ether–toluene. Since after 9 hrs.' boiling in ether–benzene magnesium phenyl bromide gives practically the same yield (70·1%) of benzoic acid as is obtained without refluxing, the decomposition is not due to heat alone and is attributed to the action of diffused oxygen. Accordingly, reactions which necessitate prolonged boiling at high temperatures should be effected in an inert atmosphere.   R. BRIGHTMAN.

Action of ultra-violet light on magnesium *iso*butyl bromide and *tert*.-butyl chloride. H. GILMAN and L. L. BECK (Bull. Soc. chim., 1929, [iv], **45**, 1095—1098).—No appreciable isomerisation of the

organic radical occurs when ethereal solutions of magnesium *iso*butyl bromide and magnesium *tert.*-butyl chloride are exposed for 63 hrs. to ultra-violet light. With magnesium *iso*butyl bromide 47% of *iso*valeric acid is subsequently obtainable by the usual method; magnesium *tert.*-butyl chloride similarly gives 58% of trimethylacetic acid containing up to 5% of *iso*valeric acid (cf. A., 1928, 255; 1929, 433).

R. BRIGHTMAN.

cycloPropene and some of its derivatives. N. J. DEMJANOV and M. N. DOJARENKO (Bull. Acad. Sci. U.S.S.R., 1929, 653—665; cf. A., 1923, i, 1188).— The total yield of hydrocarbons and that of allene obtained on heating the quaternary base (*loc. cit.*) increase as the temperature is raised, but the yield of *cyclo*propene diminishes. When heated with water in a sealed tube, dibromo*cyclo*propane remains virtually unchanged at 100—105°, but at 150—155° about 77·5% and at 160—165° almost the whole of the bromo-compound reacts, yielding acraldehyde and a mixture of products of its condensation with loss of water. Similar results are obtained if the reaction takes place in presence of silver carbonate or lead oxide, no formation of the glycol corresponding with *cyclo*propene occurring. When treated with a concentrated absolute alcoholic solution of iodine, *cyclo*propene yields di-iodo*cyclo*propane, $C_3H_4I_2$, m. p. below $-5°$, d_4^{14} 2·725, n_D^{14} 1·6765. Among the products formed by the action of potassium permanganate on *cyclo*propene at a low temperature (snow), only formic acid was identified. When heated at 245—255° in presence of aluminium oxide, *cyclo*propene undergoes polymerisation to some extent.

T. H. POPE.

Cracking of cyclic hydrocarbons with hydrogen at high pressures. V. N. IPATIEV, N. ORLOV, and N. LICHATSCHEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1339—1343, and Ber., 1930, 63, [B], 156—160).— The behaviour of the hydrides of aromatic hydrocarbons under conditions of pressure hydrogenation was investigated, with the view of elucidating the mechanism of the cracking of petroleum and primary coal tars in which the compounds selected occur. Di*cyclo*hexyl, di*cyclo*hexylmethane, αβ-di*cyclo*hexylethane, and αε-di*cyclo*hexylpentane were hydrogenated at 440—450° and 75 atm. in the presence of iron and alumina as catalysts. Besides these di*cyclo*hexylparaffins, decahydronaphthalene, αδ-diphenylbutane, αγ-diphenylpropane, 1 : 3 : 5-triphenylbenzene, pentamethyldihydroxytetrahydroxanthen, and a primary tar were also investigated under similar conditions. The di*cyclo*paraffins and diphenylparaffins gave only mono-substituted *cyclo*hexanes and benzene homologues. Decahydronaphthalene gave a mixture of naphthenes, 1 : 3 : 5-diphenylbenzene was unaffected, whilst pentamethyldihydroxytetrahydroxanthen gave both naphthenes and aromatic hydrocarbons. The primary tar, which was anhydrous and contained 40% of phenols, yielded a considerable quantity of benzene hydrocarbons, which were, in part, due to the reduction of phenols, since water was also obtained. M. ZVEGINTZOV.

Thermal decomposition of perhydro-fluorene and -acenaphthene in presence of hydro-

gen under pressure. N. A. ORLOV and M. A. BELOPOLSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1267—1277).—The behaviour of the perhydro-derivatives of the condensed nuclei hydrocarbons in the presence of hydrogen under pressure was investigated, since they occur in the products of coal distillation, and their reactions with hydrogen should throw light on the mechanism of that process. Fluorene was hydrogenated at 210—230°/60—75 atm. in the presence of nickel, silver, manganese, copper, and cobalt oxides as catalysts, and the perhydrofluorene, b. p. 254—258°, d^{22} 0·9203, isolated from the liquid product by fractionation. It was hydrogenated at 380°/70—75 atm. with alumina and other oxides as catalysts, yielding a liquid product containing a mixture of mono- and di-cyclic naphthenes, among which perhydrindene and *cyclo*pentadiene were isolated. When fluorene was distilled with anhydrous aluminium chloride, diphenyl and its hydrides were obtained.

Hydrogenation of acenaphthene under the same conditions gave perhydroacenaphthene, b. p. 232—239°, d_0^{25} 0·9329, n_D^{14} 1·5200, which, on further hydrogenation at 450°, yielded a mixture of benzene homologues, indene and its homologues, diphenylfulvene, and other cyclic hydrocarbons. The isolation of indene in these reactions is considered to explain the mechanism of its formation during the carbonisation of coal to yield a primary tar. M. ZVEGINTZOV.

Polarities and orienting influence of substituents in the benzene ring. W. M. LATIMER and C. W. PORTER (J. Amer. Chem. Soc., 1930, 52, 206—211).—The residual charge on an atom attached to a benzene ring is calculated from a consideration of the electronic configuration of the group in which the atom occurs. It is assumed that the electrons are quantised with respect to the field between the atoms (except for hydrogen), the effects being distributed between the atoms in the ratio of the positive charges on the nuclei. The residual charge, calculated for 30 groups, varies from $-0·4$ (·OR) to $+2·1$ (NO_2). A positive residual charge generally indicates a *m*-orienting substituent, but the division is not sharp. Groups with values of 0·1—0·6 usually give mixtures of *o*-, *m*-, and *p*-derivatives.

An electronic configuration for benzene is postulated, in which alternate carbon atoms possess, or share, six and eight electrons, respectively. Three pairs of electrons are assumed to be quantised with respect to the field of the molecule as a whole. H. BURTON.

1 : 3 : 4 : 5-Tetranitrobenzene. A. F. HOLLEMAN (Rec. trav. chim., 1930, 49, 112—120).—When picramide is suspended in cold nitric acid (d 1·4) and then treated repeatedly with nitrous fumes, 1 : 3 : 4 : 5-*tetranitrobenzene*, m. p. 129—130°, is formed, probably through the intermediate 2 : 4 : 6-trinitrobenzenediazonium nitrite. Some picric acid and hexanitrodiphenylamine are also produced; the latter is probably formed by interaction of the diazonium hydroxide with picramide. The tetranitrobenzene is purified by dissolution in benzene, washing the solution with sulphuric acid until pale yellow, and subsequently washing with cold water, drying, and evaporating; the tetranitrobenzene crystallises with 1 mol. of

benzene, which is lost at 60°. 1 : 3 : 4 : 5-Tetranitro-benzene is decomposed rapidly with boiling water, and slowly with cold water, to picric and nitrous acids : decomposition also occurs with any solvent containing oxygen. The ease of conversion of the tetranitro-benzene into picramide by dilute aqueous ammonia (97% yield) is used for the determination of the tetranitrobenzene in mixtures containing picric acid. 1 : 3 : 4 : 5-Tetranitrobenzene is a more powerful explosive than picric acid.

Details are given for the preparation of picramide from *p*-nitroaniline and acetanilide (cf. Witt, A., 1908, i, 874).   H. BURTON.

Nitration of aromatic thiocyanates. F. CHAL-LENGER, C. HIGGINBOTTOM, and A. HUNTINGTON (J.C.S., 1930, 26—34).—Phenyl and substituted phenyl thiocyanates are prepared, generally by Korczyński's method (A., 1923, i, 159). The mixture of *o*- and *p*-nitro-derivatives obtained in 94% yield when phenyl thiocyanate is nitrated with nitric (*d* 1·41) and sulphuric acids at 0—5° contains 20% of the *o*-, and 80% of the *p*-derivative (cf. A., 1924, i, 953). *o*-Chlorophenyl thiocyanate, b. p. 160—160·5°/42—47 mm., is converted by nitric acid (*d* 1·5), first at −6° and then at the ordinary temperature, mainly into 2-*chloro*-4-*nitrophenyl* thiocyanate, m. p. 85° ; a small amount of the 5-*nitro*-isomeride, m. p. 107°, is also produced. o-*Bromophenyl* thiocyanate, b. p. 161—165°/10—12 mm., m. p. about 24°, yields, similarly, 2-*bromo*-4-, m. p. 93° (main), and 2-*bromo*-5-*nitrophenyl* thiocyanate, m. p. 126° (trace). m-*Chlorophenyl* thiocyanate, b. p. 135°/12·5 mm., affords 3-*chloro*-4-, m. p. 59° (main), and 3-*chloro*-6-*nitro*-*phenyl* thiocyanate, m. p. 104—105° (trace). These results show the strong *para*-directing influence of the thiocyano-group. *p*-Aminophenyl thiocyanate is con-verted by the usual method into p-*iodophenyl thio-cyanate*, m. p. 53°, which is unaffected by nitric acid (*d* 1·41) at −10° or 15°, or by the acid of *d* 1·5 in acetic anhydride solution. With nitric and sulphuric acids at −14 to 5°, *p*-nitrophenyl thiocyanate is produced. Treatment of the iodo-compound with chlorine in cold chloroform affords a *dichloride*, m. p. 111°, which on thermal decomposition regenerates the original iodo-derivative. Attempts to decompose this dichloride under various conditions so as to induce nuclear chlorination failed (cf. Werner, J.C.S., 1907, 91, 240, 529) ; *p*-iodophenyl thiocyanate was regenerated in most cases. When decomposed by sunlight, the dichloride gives 4 : 4′-di-iododiphenyl disulphide.

     H. BURTON.

Action of selenium bromide on aromatic hydro-carbons. J. LOEVENICH and K. SIPMANN (J. pr. Chem., 1930, [ii], 124, 127—132).—Interaction of benzene, aluminium bromide, and selenium bromide gives bromobenzene and a 22—27% yield of diphenyl selenide ; in dilute carbon disulphide solution diphenyl diselenide, m. p. 62° (2% yield), is also obtained. Aluminium bromide and selenium bromide react with toluene to give chiefly *o*-bromotoluene and a small quantity of oo′-*ditolyl selenide*, b. p. 174—180°/13 mm. ; mesitylene yields bromomesitylene and dimesityl, naphthalene affords 1-bromonaphthalene and 1 : 1′-di-naphthyl, whilst no well-defined products could be

isolated with anthracene. The bearing of these results on the constitution of selenium bromide is discussed.

     A. I. VOGEL.

Catalytic oxidation of toluene by air. M. I. KUZNETZOV and M. A. STEPANENKO.—See this vol., 304.

Thermal decomposition of coal-tar con-stituents. V. Reaction products of the thermal decomposition of toluene. VI. Reaction mechanism of the thermal decomposition of toluene. Y. KOSAKA (J. Soc. Chem. Ind. Japan, 1929, 32, 298—299B, 299—300B).—V. Pyrolysis of toluene at 700° and 800°, employing various contact materials, and at 900° without a tube-filling, indicates that the decomposition is independent of the filling material (silica or coke), and the main reaction products consist of benzene, diphenyl, diphenyl-benzene, and their homologues, minute quantities (1—2%) of naphthalene, anthracene, and phenanthr-ene, together with ethylene, methane, hydrogen, and free carbon. The amount of toluene undecom-posed at 700° is 86—88%, at 800° 54—57%, and at 900° 3%. The formation of benzene increases from 3·5% at 700° to 26% at 900°. The yield of diphenyl and its homologues reaches a maximum (8%) at 800°, whilst the production of diphenylbenzene and its homologues rises from 1% at 700° to 11% at 900°. The amounts of methane, hydrogen, and free carbon produced increase with rising temperature, 27% of carbon being formed at 900°.

VI. Twelve reactions are proposed to express completely the exact nature of the pyrolysis of toluene, and their distribution at 700°, 800°, and 900° is traced by calculation.   C. W. SHOPPEE.

Separation of xylenes. I. Fusion curves of the systems *o*-xylene–*m*-xylene and *o*-xylene-*p*-xylene. II. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1929, 32, 333—335B, 335—336B).—I. *p*-Xylene, m. p. 13·19°, *m*-xylene, m. p. −49·0°, and *o*-xylene, m. p. −25·74°, were employed. The points found for the systems lie on a smooth two-branch curve in each case. The heats of fusion of the xylenes have been calculated thermodynamically and are : *o*-, 3100, *m*-, 2800, and *p*-xylene, 4100 g.-cal.

II. Fractional distillation of a mixture of xylenes tends to concentrate *m*-xylene in the highest fraction, whereas the distribution of *p*-xylene is not appreciably affected. Selective sulphonation is more effective, since the chief component of the unsulphonated material is *p*-xylene ; dissolution of the unsulphonated material in concentrated sulphuric acid at 95° affords crystalline *p*-xylenesulphonic acid, which by hydro-lysis with 50% sulphuric acid furnishes pure *p*-xylene. The relation between the composition of hydrocarbon mixtures liberated by hydrolysis of sulphonic acids and the hydrolysis temperature is given in tabular form, and it is concluded that Patterson's process (A., 1925, i, 124) for the separation of *m*-xylene has no value for large-scale operations. It is found that in the Friedel–Crafts reaction *p*-xylene combines less readily than either isomeride with unsaturated hydro-carbons, *e.g.*, *iso*butylene, and it is stated that 94% of the total *p*-xylene may be separated in this manner.

     C. W. SHOPPEE.

Highly-polymerised compounds. XXXIII. Relationships between viscosity and mol. wt. among polystyrenes. H. STAUDINGER and W. HEUER (Ber., 1930, **63**, [*B*], 222—234; cf. this vol., 78).—Examination of the viscosity of polystyrenes of differing concentration shows that the expression η_{sp}/C is not constant, but increases with increasing concentration. Only in very dilute solution is the deviation from $K = \eta_{sp}/C$ relatively slight; at higher concentration the specific viscosity increases much more rapidly than the concentration. Association cannot entirely account for these observations, since the relative viscosity of hemicolloids in molar solution at 60° is only slightly less than at 20°. The deviation from the Einstein expression is attributed to the non-spherical form of the polystyrene molecule. On the assumption that the latter has a cylindrical form and is free to rotate around its centre, the modified expression, $\eta_{sp}/C = K_m M$ is deduced. Preliminary determinations of the constant K_m for purified fractions of hemicolloidal polystyrenes in 0·25M-solution in benzene give the value $K \times 10^3 = 0·20$, the individual variations being slight. Application of the method to the determination of the mol. wt. of more highly-polymerised products gives values of the order 100,000. The constant K_m is valid only in one and the same polymeric-homologous series and for a single solvent. H. WREN.

Compounds between metallic chlorides and polyenes. H. VON EULER and H. WILLSTAEDT (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 9, 6 pp.).—It was shown by Karrer, Euler, and Euler (this vol., 379) that the Carr and Price reaction is given by substances of the carotenoid group. The compounds between these substances and metallic chlorides were therefore studied. By mixing chloroform solutions of stilbene and antimony trichloride, colourless crystals, $C_{14}H_{12},2SbCl_3$, m. p. 106—107°, were obtained. With *iso*stilbene, the same product seems to be obtained. With ferric chloride, yellow crystals, $C_{14}H_{12},2FeCl_3$, decomp. 326°, are obtained. In the same way, diphenylbutadiene gives a colourless substance, $C_{16}H_{14},2FeCl_3$. Dimethylfulvene produces with antimony trichloride a resinous substance, and in dilute solutions a deep violet colour, but the product could not be isolated without decomposition. Carotene gives rise to a blue product of approximate formula $C_{40}H_{56},2SbCl_3$. The cause of the colour reaction is believed to lie in the formation of readily dissociated compounds of the carotenoid and the metallic chloride. K. V. THIMANN.

Substitution of bromine by chlorine in organic halogen compounds. P. PFEIFFER and B. EISTERT (J. pr. Chem., 1930, [ii], **124**, 168—184).—The influence of substituent groups on the replacement of bromine by chlorine in compounds of the stilbene type has been investigated by the interaction of the stilbene dibromides with tin tetrachloride in anhydrous thiophen-free benzene solution. α-Stilbene dibromide, m. p. 237° (decomp.), gives *stilbene chlorobromide*, m. p. 225° (decomp.), after 5 min. at the ordinary temperature, and stilbene dichloride on boiling for 30 min. 4-Nitrostilbene dibromide, m. p. 205—206° (decomp.), yields only 4-*nitro-α-bromo-α'-chlorostilbene*,

$NO_2 \cdot C_6H_4 \cdot CHBr \cdot CHClPh$, m. p. 180—181°, on prolonged boiling, whilst 4 : 4'-dinitrostilbene dibromide, m. p. 288° (decomp.) (4 : 4'-dinitrostilbene has m. p. 286°), is unaffected. 2 : 4-Dinitrostilbene dibromide, (α-form, m. p. 185°, β-variety, m. p. 145—146°), yields a mixture of α- and β-2 : 4-*dinitrostilbene chlorobromides* (m. p. 161° and 145—146°, respectively). 4-Methoxystilbene dibromide, m. p. 183—184° (decomp.), converted at 170—180° into 4-*methoxy-μ'-bromostilbene*, m. p. 53—54°, yielded the corresponding *dichloride*, m. p. 150—151° (slight decomp.); this change is more facile in the conversion of 4 : 4'-*dimethoxystilbene dibromide*, m. p. 172° (decomp.), into the corresponding *dichloride*, m. p. 184° (decomp.). 4-*Nitro-*4'-*methoxystilbene dibromide*, m. p. 166° (decomp.), converted at 150—170° into the *monobromostilbene*, m. p. 93°, yielded a *substance*, m. p. 200°. Under similar conditions, benzyl bromide gave diphenylmethane, p-nitrobenzyl bromide was unaffected, diphenylmethyl bromide, m. p. 42—43°, yielded triphenylmethane, and triphenylmethyl bromide afforded an additive *compound*, $CPh_3Br,SnCl_4$. A. I. VOGEL.

Molecular compounds and colour reactions of conjugated unsaturated hydrocarbons. II. R. KUHN and T. WAGNER-JAUREGG (Helv. Chim. Acta, 1930, **13**, 9—13; cf. A., 1928, 281).—The colorations obtained when the previously described unsaturated hydrocarbons (*loc. cit.*) are treated with benzoquinone, chloroanil, maleic, phthalic, and tetrachlorophthalic anhydrides, and oxalyl, fumaryl, phthalyl, thionyl, and sulphuryl chlorides are given. Diphenyl is used for comparison. The coloration increases in intensity with rise in the number of double linkings in the hydrocarbon molecule. Methylbixin gives deep reddish-brown and greenish-blue colours with fumaryl and thionyl chlorides, respectively. The f.-p. diagram of αδ-diphenylbutadiene and methyl fumarate shows that no compound formation occurs. Picryl chloride and αδ-diphenylbutadiene give a compound containing 2 mols. of the former and 1 mol. of the latter substance. H. BURTON.

Plant colouring matters. XVII. Carotenoids in fæces of sheep and cow. P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1930, **13**, 86—87).— The coloured compound isolated by Fischer (A., 1916, i, 574) from sheep's fæces has been investigated. It is essentially a xanthophyll, $C_{40}H_{56}O_2,MeOH$, m. p. 190—191°, $[\alpha]_G +90°$ in chloroform. The same substance is also isolated from fresh cow's fæces. Lutein from egg-yolk has $[\alpha]_G^{20} +7·17°$ in chloroform. H. BURTON.

Plant colouring matters. XVIII. Constitution of carotenoids. P. KARRER, A. HELFENSTEIN, and H. WEHRLI (Helv. Chim. Acta, 1930, **13**, 87—88). —Succinic acid is obtained in small amount when lycopene is oxidised with potassium permanganate; it is formed by further oxidation of lævulic acid, which must be a primary oxidation product, if the previously assigned formula (A., 1929, 569) is correct. It is possible that the group $CMe_2:CH \cdot [CH_2]_2 \cdot CMe:CH \cdot$, which is present in lycopene, becomes cyclicised in carotene (cf. this vol., 76). Xanthophyll contains two hydroxyl groups (Zerevitinov), and is probably a di-

hydroxycarotene. Zeaxanthin (A., 1929, 1077) also contains two hydroxyl groups. H. BURTON.

Action of peracetic acid on naphthalene. J. BÖESEKEN and G. SLOOFF (Rec. trav. chim., 1930, **49**, 100—101).—Naphthalene is slowly oxidised by per-acetic acid in acetic acid solution, yielding 2-carboxy-*allo*cinnamic acid. H. BURTON.

New class of coloured hydrocarbons. N. MAXIM (Bull. Soc. chim., 1929, [iv], **45**, 1137—1148).— The dehydration of 9 : 10-diethylacenaphthene-9 : 10-glycol to the coloured hydrocarbon, 9 : 10-diethyl-ideneacenaphthene (A., 1928, 1137), is now shown to be characteristic of ditertiary acenaphthene glycols when treated with hydrochloric acid in glacial acetic acid. Only traces of the α-pinacolins, resulting by loss of 1 mol. of water, obtained by Zincke and Tropp in the phenanthrene series (A., 1908, i, 786) are formed, but no β-pinacolin. The formation of a β-pinacolin in the dehydration of 9 : 10-diphenylacenaphthene-9 : 10-glycol (Beschke, A., 1909, i, 917) is due to pinacolin transformation of the α-pinacolin first formed. Oxidation of these hydrocarbons with acetic and chromic acids yields a mixture of acenaphthene-quinone and naphthalic anhydride. The ditertiary acenaphthene glycols are obtained by the action of Grignard reagents on acenaphthenequinone, magnes-ium methyl iodide alone yielding two stereoisomeric compounds. cis-9 : 10-*Dimethylacenaphthene*-9 : 10-*glycol* has m. p. 158°; the trans-*isomeride*, m. p. 184°. On dehydration, both isomerides yield 9 : 10-*dimethyl-eneacenaphthene*, orange-yellow, together with a little α-pinacolin, $C_{10}H_6 <^{CMe}_{CMe}> O$, in the case of the *cis*-isomeride. 9 : 10-*Dipropylacenaphthene*-9 : 10-*glycol* has m. p. 173°; 9 : 10-*dipropylideneacenaphthene*, m. p. 101°, orange; 9 : 10-*diisobutylacenaphthene*-9 : 10-*glycol*, m. p. 132° (yield 50%); 9 : 10-*diiso-butylideneacenaphthene*, b. p. 215°/15 mm., reddish-orange; 9 : 10-*diisoamylacenaphthene*-9 : 10-*glycol*, m. p. 155° (yield 30%); 9 : 10-*dibenzylacenaphthene*-9 : 10-*glycol*, m. p. 174° (yield 80%), and 9 : 10-*di-benzylideneacenaphthene*, yellowish-orange, m. p. 142°. 9 : 10-Di*iso*amylideneacenaphthene was only obtained crude as an orange liquid. R. BRIGHTMAN.

Polynuclear aromatic hydrocarbons and their derivatives. VI. Syntheses of 1 : 2 : 3 : 4-di-benzpyrene and its derivatives. E. CLAR (Ber., 1930, **63**, [B], 112—120; cf. A., 1929, 435, 689, 922; this vol., 203).—o-1-Naphthoylbenzoic acid is con-verted by benzene in presence of 1 mol. of aluminium chloride at the atmospheric temperature into phenyl-1-naphthylphthalide, m. p. 225·5—227° (cf. McMullen, A., 1922, i, 1025); p-*tolyl*-1-*naphthylphthalide*, m. p. 235—236°, and m-*xylyl*-1-*naphthylphthalide*, m. p. 205—207·5°, are similarly prepared. o-Benzoyl-benzoyl chloride and 2- and 1-methylnaphthalene under like conditions but in presence of carbon disulphide and benzene, respectively, afford *phenyl*-2-*methylnaphthylphthalide*, m. p. 207—208°, and *phenyl*-4-*methyl*-1-*naphthylphthalide*, m. p. 203—204°. If 2 mols. of aluminium chloride are used and the mixture is heated, the green colour of the additive compounds characteristic of all these phthalides becomes changed to reddish-brown, blue, or violet and acids are

produced of which o-*benzanthran*-10-*ylbenzoic acid*, m. p. 267—268° (*sodium* salt), is described in detail. If phenyl-1-naphthylphthalide is acted on by alumin-ium chloride in absence of solvent at 130—165° it yields 1 : 2 : 3 : 4-*dibenzpyrene* (I), m. p. 226—227° (*picrate*, m. p. 231°). The substance is more conveniently prepared by the distillation of o-benzanthran-10-yl-benzoic acid with zinc dust; as by-product, a colourless *hydrocarbon*, $C_{24}H_{16}$, which cannot be dehydrogen-ated catalytically, is produced. Sup-port of the structure assigned to the dibenzpyrene is obtained by the following synthesis. 1 : 2-Benz-anthraquinone is converted by magnesium phenyl bromide in ether–benzene into 9 : 10-*dihydroxy*-9 : 10-*diphenyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m. p. 246—248° (decomp.), transformed by aluminium chloride and benzene at the atmospheric temperature into 5-*phenyl*-1 : 2 : 3 : 4-*dibenzpyrene*, m. p. 242—243°, frequently accompanied by its dihydro-deriv-ative from which it cannot be separated readily. More advantageously, the diol is reduced by glacial acetic acid and potassium iodide to 9 : 10-*diphenyl*-1 : 2-*benzanthracene*, m. p. 192°, which with aluminium chloride in boiling benzene yields 5-*phenyl*-1 : 2 : 3 : 4-*dibenzdihydropyrene*, m. p. 257—258°, dehydrogen-ated by platinised charcoal at 300° to 5-phenyl-1 : 2 : 3 : 4-dibenzpyrene. The absorption curves of 1 : 2 : 3 : 4-dibenzpyrene and its phenyl derivatives are very closely similar. H. WREN.
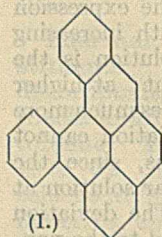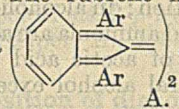
Rubrenes. A. WILLEMART (Ann. Chim., 1929, [x], **12**, 345—422).—*Diphenylheptinenylcarbinol*, b. p. 184—185°/2 mm., d^{20} 1·0228, n_D^{20} 1·5599, obtained in 43% yield by the successive action of Δα-heptinene and benzophenone on magnesium ethyl bromide, is con-verted by phosphorus tri- or penta-chloride into a *compound*, $C_{20}H_{21}Cl$ (I), b. p. 172—175°/2 mm. (not the corresponding chloro-compound), and isomerised by warm alcoholic sulphuric acid to ββ-*diphenylvinyl* n-*amyl ketone*, b. p. 173°/1 mm., m. p. 7—8° (*dibromide*; *semicarbazone*, m. p. 129—130°; *oxime*, m. p. 83—84°), oxidised by potassium permanganate in acetone to benzophenone and hexoic acid. Dimethylphenyl-ethinylcarbinol, m. p. 55—56°, similarly prepared from phenylacetylene, magnesium ethyl bromide, and acetone, gave an impure *substance*, $C_{11}H_{11}Cl$ (II), b. p. 76—79°/1·2 mm., with phosphorus trichloride. No rubrene was obtained by heating I or II. *Diphenyl*-β-p-*tolylethinylcarbinol* (III), m. p. 68—69°, prepared in 62% yield from p-tolylacetylene, magnesium ethyl bromide, and benzophenone, gives αα-*diphenyl*-γ-p-*tolyl*-Δβ-*propenyl chloride* (IV), m. p. 130—131°, in 88% yield, with phosphorus trichloride in light petroleum, which on heating at 15 mm., best in the presence of a little quinoline, afforded dimethyl-rubrene, $C_{44}H_{32}$, m. p. 315° (cf. Moureu and others, A., 1928, 996). p-*Tolyl* ββ-*diphenylvinyl ketone*, m. p. 74—75°, is produced by heating III with alcoholic sulphuric acid or IV with alcohol. Interaction of magnesium phenylacetylenyl bromide and phenyl α-naphthyl ketone or of magnesium α-naphthyl bromide and phenyl β-phenylethinyl ketone gives

phenyl-α-naphthyl-β-phenylethinylcarbinol (V), m. p. 137—138°, converted by phosphorus trichloride in ether into the corresponding *chloride* (VI), m. p. 130—131° (decomp.), and yielding no rubrene on heating. *Phenyl* β-*phenyl*-β-1-*naphthylvinyl ketone*, m. p. 107—108°, is obtained by boiling V with alcoholic sulphuric acid or VI with alcohol.

1 : 1-*Dinaphthyl-β-phenylethinylcarbinol* (+Et$_2$O), m. p. 70—71° (decomp.), prepared from magnesium phenylacetylenyl bromide and 1 : 1-dinaphthyl ketone in 90% yield, gave the corresponding *chloride*, m. p. 122—123° (decomp.), with phosphorus trichloride, converted into a coloured resin on heating. *Phenyl* ββ-*di*-1-*naphthylvinyl ketone* has m. p. 170—171°. *Dibenzorubrene*, C$_{50}$H$_{32}$, m. p. 80° (cf. A., 1928, 996), was prepared from *diphenyl-β-naphthylethinylcarbinol*, m. p. 99—100° (obtained from magnesium ethyl bromide, β-naphthylacetylene, and benzophenone in 50% yield), through the *chloride*, m. p. 116—117° (decomp.), and heating the latter to 200° in the presence of quinoline. Dimethyl- and dibenzo-rubrene form *peroxides*, C$_{44}$H$_{32}$·O$_2$·C$_6$H$_6$ and C$_{50}$H$_{32}$·O$_2$·C$_6$H$_6$, respectively, when exposed to sunlight in benzene solution. The new rubrenes resemble closely those described previously in absorption spectrum. The mechanism of the formation of rubrenes by elimination of hydrogen chloride from the chloro-compounds CR‴:C·CR′R″Cl is discussed; the three methods of Moureu and others (A., 1927, 355) are considered to be improbable and two alternative mechanisms suggested. The rubrene hydrocarbons have the general formula

A. I. VOGEL.

Luminescence phenomena of the satellites of rubrene. Two phosphorescent hydrocarbons ; the so-called " brown " and the yellow substance. C. MOUREU, C. DUFRAISSE, and P. LOTTE (Compt. rend., 1930, **190**, 148—149 ; cf. A., 1929, 922, 1166).—The luminescence phenomena of these two substances, both of which have the probable formula C$_{42}$H$_{30}$, are closely analogous, and it is suggested that the substances are identical, and that differences in properties (*e.g.*, in colour) are due to impurities, probably mineral in nature, which in the case of the brown substance are partly or completely destroyed by light. Both substances luminesce if exposed to light and warmed, but in the case of the yellow substance, irradiation activates only the solid substance and not its solutions. J. GRANT.

Chlorination of anilides. VI. Rates of N-chlorination of acetanilides and acetobenzyl-amides and effects of substituents on side-chain reactivity. G. WILLIAMS (J.C.S., 1930, 37—46).—It is shown that, in accordance with the electronic theory, side-chain reactions may be classified into two main groups according as they are accelerated by the nitro- and retarded by the methyl group and *vice versa* ; out of 36 such reactions only 5 cannot be allocated with certainty to either group. The velocities of chlorination in 40% acetic acid at 18° are tabulated for acetanilide, acetobenzylamide, and their *o*-, *m*-, and *p*-nitro-, -chloro-, and -methyl derivatives

(excepting aceto-*o*- and -*m*-methylbenzylamides), and also for aceto-β-phenylethylamide and acetamide. The velocities of N-chlorination are given and compared with those of C-chlorination where the latter are not too slow to be determined, and it is shown that the former fall into these two groups. The experiments include new rates of C-chlorination for *m*-chloroacet-anilide (k_c=3140) and aceto-*m*-toluidide (k_c=50,000), and a description of *aceto*-p-*chlorobenzylamide*, m. p. 109·5°, and *aceto*-m-*chlorobenzylamide*, m. p. 38°.
H. A. PIGGOTT.

Conversion of N-chloroacetanilide into p-chloroacetanilide by hydrogen and chlorine ions. J. W. BELTON (J.C.S., 1930, 116—124).—The velocity of conversion of N- into p-chloroacetanilide in relation to the concentrations of hydrogen and chlorine ions, on both of which it is dependent (Orton and Jones, Brit. Assoc. Rep., 1910, 85), was measured at 25°. The reaction was followed volumetrically : chlorination of the p-chloroacetanilide (Soper, A., 1927, 837) and hydrolysis of the N-chloroacetanilide known to occur as side reactions were considered negligible. In hydrochloric acid–sodium chloride solutions the rate bears no relation to the activities of the reactants, and reaction mechanisms involving intermediate formation of a charged complex (cf. Brönsted, A., 1922, ii, 699 ; 1925, ii, 681) do not agree with experimental data. In mixtures of hydrochloric and perchloric acids the rate is proportional to the product of the molecular proportions of hydrogen and chlorine ions. H. A. PIGGOTT.

Additive compounds of organic bases with salts of heavy metals. J. V. DUBSKÝ and A. RABAS (Publ. Fac. Sci. Univ. Masaryk, 1929, No. 112, 1—12).—The following double *compounds* have been prepared : ZnCl$_2$,2C$_5$H$_5$N, m. p. 210° ; ZnCl$_2$,2NH$_3$Ph,decomp. 266° ; ZnCl$_2$,2*o*-toluidine, m. p. 234° ; ZnCl$_2$,2*p*-toluidine, m. p. 267° ; ZnCl$_2$,3glycine, decomp. 235°. These results are in disagreement with those of Lachowicz and Bandrowski (A., 1888, 1281). R. TRUSZKOWSKI.

Electrolytic reduction of nitriles. I. K. OGURA (Mem. Coll. Sci. Kyōtō, 1929, **A, 12**, 339—342).—Optimum yields of the corresponding amines are obtained when benzonitrile, p-toluonitrile, and phenylacetonitrile are reduced electrolytically in aqueous alcoholic solution containing ammonium sulphate and a small amount of ammonia, with a lead cathode. The yields are 49·5, 57, and 13%, respectively. With more alkaline or acid cathode solutions, hydrolysis of the nitrile occurs to varying extents, especially with phenylacetonitrile. H. BURTON.

dl-β-**Phenyl*iso*propylamine and related compounds.** D. H. HEY (J.C.S., 1930, 18—21).—Benzyl methyl ketoxime, described for the first time as a crystalline solid, m. p. 70°, is readily reduced in aqueous acetic acid to dl-p-*phenyl*iso*propylamine*, b. p. 205° ; the *acetyl* derivative, freshly crystallised from aqueous alcohol, has m. p. 64°, rising on vacuum drying to 93° ; *picrate*, m. p. 143° ; *hydrochloride*, m. p. 145—147°. The action of phosphoric oxide on the acetyl compound gave 1 : 3-*dimethyl*-3 : 4-*diyhdro*iso*-quinoline*, isolated as the *picrate*, m. p. 136°. Com-

plexes of oximinopropiophenone with *iron* (blue, soluble in benzene), *cobalt*, $(C_9H_8O_2N)_3Co$, and *copper*, $C_9H_8O_2N \cdot CuOH$ are described. H. A. PIGGOTT.

Diphenylamine derivatives. K. DZIEWOŃSKI and M. RUSSOCKI (Bull. Acad. Polonaise, 1929, **A**, 506—527).—The conclusions of Merz and Weith (A., 1873, 74) concerning the proportion of mono- and di-sulphonic acids formed by the action of concentrated sulphuric acid on diphenylamine are confirmed. With chlorosulphonic acid in nitrobenzene solution below 90°, however, the initial product is the unstable, crystalline, diphenylammonium chlorosulphonate which at higher temperatures readily decomposes, giving nuclear substitution products in accordance with the scheme $Ph_2NH_2 \cdot SO_3Cl \longrightarrow NPh_2 \cdot SO_3H \longrightarrow NHPh \cdot C_6H_4 \cdot SO_3H$, the proportion of mono- and di-sulphonic acids produced depending on the molecular proportion of chlorosulphonic acid used. Thus with 0·5, 1·0, 1·5, and 2·0 mols. of chlorosulphonic acid for each mol. of diphenylamine the proportions of mono- and di-sulphonic acids and of unchanged diphenylamine are, respectively, 25, 5, 70; 38, 22, 40; 34, 50, 16; and 0, 99—100, 0 mols. %. Hence with 0·5 mol. of the reagent diphenylamine-4-sulphonic acid (*aniline* salt, m. p. 206·5°) is readily separated from the reaction mixture as its *magnesium* salt. Nitration of sodium diphenylamine-4-sulphonate with 1 mol. of nitric acid (*d* 1·48) in acetic acid gives the *4-nitro*-derivative (*magnesium* salt) converted by hydrolysis with concentrated hydrochloric acid in a sealed tube at 190° into 4-nitrodiphenylamine (Goldberg, A., 1907, i, 1027), and further nitrated to *sodium 2 : 4-dinitrodiphenylamine-4'-sulphonate.* Excess of nitric acid converts sodium diphenylamine-4-sulphonate into the 2 : 4 : 6-trinitro-derivative identical with a specimen obtained by the condensation of 2 : 4 : 6-trinitrochlorobenzene and sulphanilic acid (Turpin, J.C.S., 1891, **59**, 717) and hydrolysed by concentrated hydrochloric acid at 180—200° to 2 : 4 : 6-trinitrodiphenylamine. The action of bromine (2 mols.) on a suspension of sodium diphenylamine-4-sulphonate in carbon tetrachloride at 45—50° converts it into its *4-bromo*-derivative, whilst with 6 mols. of bromine at 60—70° the product is *sodium 2 : 4 : 2'-tribromodiphenylamine-4-sulphonate* (magnesium salt), converted by excess of hydrobromic acid at 60° into 2 : 4 : 2' : 4'-tetrabromodiphenylamine and by dilute hydrochloric acid at 190° into 2 : 4 : 2'-*tribromodiphenylamine*, m. p. 94°, whilst the action of nitric acid (*d* 1·48) in acetic acid at 165—190° yields 2 : 4 : 2'-*tribromo-6'-nitrodiphenylamine*, m. p. 215°, together with the corresponding 4' : 6'-*dinitro*-derivative, m. p. 179°, and *sodium 2 : 4 : 2'-tribromo-6'-nitrodiphenylamine-4-sulphonate.* Diphenylamine-4 : 4'-disulphonic acid (*magnesium*, $+2 \cdot 5H_2O$, and *aniline*, m. p. 239°, salts) is best obtained by the action of an excess of chlorosulphonic acid on diphenylamine in nitrobenzene at 110—115°. By reactions similar into those described in the case of the monosulphonic acid, its sodium salt is converted into the 2-*nitro*- and 2 : 2'-*dinitro-diphenylaminedisulphonic acids* (converted into 2 : 2'-dinitrodiphenylamine), 2 : 4 : 2'-*trinitro-diphenylaminesulphonic acid*, and 2 : 4 : 2' : 4'-*tetra-nitrodiphenylamine*, small quantities of the 2 : 4 : 6 : 2' : 4'-pentanitro- and 2 : 4 : 6 : 2' : 4' : 6'-

hexanitro-derivatives being formed as by-products of the nitrations. Similarly, bromination of barium diphenylamine-4 : 4'-disulphonate converts it into the 2 : 2'-*dibromo*-, $+0 \cdot 5H_2O$, together with some 2-*bromo*-derivatives, and, ultimately, into 2 : 4 : 2' : 4'-tetrabromodiphenylamine. J. W. BAKER.

Catalytic reduction of nitrosoamines. C. PAAL and W. N. YAO (Ber., 1930, **63**, [*B*], 57—66).—Reduction of diphenylnitrosoamine in alcoholic solution in presence of palladised calcium carbonate or barium sulphate gives, almost quantitatively, nitrogen and diphenylamine; *as*-diphenylhydrazine or ammonia is not produced. Reaction proceeds according to the following scheme : $2NPh_2 \cdot NO \xrightarrow{+2H} 2H_2O + NPh_2 \cdot N:N \cdot NPh_2 \xrightarrow{+2H} NPh_2 \cdot NH \cdot NH \cdot NPh_2 \longrightarrow 2NHPh_2 + N_2$. The intermediate condensation of unchanged nitrosoamine with *as*-diphenylhydrazine is improbable, since these substances react only slowly in alcoholic solution and do not form the tetrazene. The last-named compound is reduced catalytically or by zinc dust and hydrochloric acid to nitrogen and diphenylamine without formation of *as*-diphenyl-hydrazine or ammonia. Conversion of diphenyl-nitrosoamine into diphenylamine and nitrogen occurs more rapidly in alkaline solution, whereas in presence of acetic acid hydrogenation is slow and incomplete, giving diphenylamine and a little *as*-diphenylhydrazine. Phenylethylnitrosoamine is quantitatively converted into ethylaniline and nitrogen only in alcoholic-alkaline solution ; in alcoholic solution *as*-phenylethyl-hydrazine and ammonia are also formed to some extent. In presence of acetic acid the change is similar to that in neutral alcohol except that ammonia is not formed.

Nitrosopiperidine in alcoholic solution undergoes slow catalytic reduction to nitrogen, piperidine, and piperylhydrazine ; ammonia is also produced in acetic acid solution. Similarly, in alcoholic solution di-*n*-propylnitrosoamine affords nitrogen, di-*n*-propylamine, and di-*n*-propylhydrazine.

p-Nitrosodimethylaniline is smoothly hydrogenated to *p*-aminodimethylaniline. H. WREN.

1-Methylnaphthalene derivatives. K. DZIE-WOŃSKI and T. WASZKOWSKI (Bull. Acad. Polonaise, 1929, **A**, 604—610).—Sulphonation of 1-methyl-naphthalene with concentrated sulphuric acid at 150—170° gives 1-*methylnaphthalene-7-sulphonic acid* (*sodium* and *aniline*, m. p. 248—250°, salts ; *chloride*, m. p. 120—122° ; *amide*, m. p. 188—189°), isolated as its crystalline *barium* salt, and converted by fusion with moist potassium hydroxide at 180° into 7-*hydroxy-1-methylnaphthalene* (*benzoyl* derivative, m. p. 107—108° ; *azo*-compound with benzenediazonium chloride, m. p. 137° ; *azo*-compound with *p*-nitro-benzenediazonium chloride, m. p. 258—260°). This is converted by heating with a solution of ammonium sulphite and concentrated ammonia in a sealed tube at 150—170° into 7-*amino-1-methylnaphthalene*, b. p. 170—180°/8 mm., m. p. 46—47° [*acetyl* derivative, m. p. 146°], that of m. p. 158—160° described by Veselý and others (A., 1929, 1288) probably not being obtained from the pure base]. The configuration of these derivatives is based on the fact that the new amino-

derivative is different from the other six isomerides, all of which are known. J. W. Baker.

Diphenyl and its derivatives. V. L. Mascarelli and D. Gatti (Atti R. Accad. Lincei, 1929, [vi], **10**, 441—446).—See this vol., 205.

Azobisazoxybenzene and its oxidation product. D. McIntosh, H. E. Bigelow, and W. H. McNevin (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 119—123).—*Azobisazoxybenzene,* m. p. 214·7° (corr.), is formed, accompanied by *p*-nitroazobenzene, when *p*-nitroazoxybenzene is boiled for 6 hrs. with excess of sodium arsenite solution. It is unattacked by bromine, and probably has the structure [Ph·NO:N·C$_6$H$_4$·N:]$_2$. Prolonged boiling with benzene and peracetic acid yields azoxybisazoxybenzene, Ph·NO:N·C$_6$H$_4$·NO:N·C$_6$H$_4$·N:NO·Ph, m. p. 242°. Doubt is cast on the work of Passerini (A., 1921, i, 624), who records m. p. 223° for a compound for which this structure is claimed, prepared from *p*-acetamidoazobenzene, m. p. 157° (lit. and present authors, 146°).
R. K. Callow.

Electrolytic reduction of 2-nitro-4'-hydroxyazobenzene. H. Itomi (Mem. Coll. Sci. Kyōtō, 1929, **A**, **12**, 343—346).—2-Amino-4'-hydroxyazobenzene is obtained in 75% yield when 2-nitro-4'-hydroxyazobenzene is reduced electrolytically at 50—60°, using a lead cathode, and a cathode solution of alcohol containing 10% sulphuric acid and a small amount of stannous chloride. During many of the reductions tried, using a lead or copper cathode, and acid or alkaline cathode solutions, 2-*p*-hydroxyphenylbenztriazole (Elbs and Keiper, A., 1903, i, 662) was formed. H. Burton.

Velocity of decomposition of diazo-compounds in water. I. E. Yamamoto (J. Soc. Chem. Ind. Japan, 1929, **32**, 279—282b).—A method of titrating diazo-compounds is described in which the potassium α-naphthol-5-sulphonate is mixed in solution with rather less than the equivalent quantity of the diazo-compound, an experimentally determined quantity of alkali then being added. The titration is finished by addition of the diazo-compound until an end-point is reached. By working thus the dye is precipitated before the diazo-compound can be affected by the alkali and phenol. The velocity coefficient for the decomposition of diazobenzene chloride at 0° was determined. (See also this vol., 300.)
S. K. Tweedy.

Condensation products of phenols and aldehydes. XIV. Intermediate products containing nitrogen. I. T. Shono (J. Soc. Chem. Ind. Japan, 1929, **32**, 212—214b).—When an aqueous solution of hexamethylenetetramine-triphenol is shaken with ether, the phenol is quantitatively extracted, leaving an aqueous solution of hexamethylenetetramine. A mixture of phenol (200 g.), formaldehyde (168 c.c.), and ammonia (29% ; 147 c.c.), kept at 37° for 24 hrs., acidified, and extracted with ether, yielded a nitrogenous *compound,* m. p. 137—138°. At 50° this reaction yields 2 : 2'-dihydroxydibenzylamine.
A. A. Goldberg.

Dimorphism of 2 : 4-dinitroanisole. J. van Alphen (Ber., 1930, **63**, [*B*], 94—95).—2 : 4-Dinitroanisole is dimorphous. The labile form, m. p. 86·9°,

has the greater rate of crystallisation and, hitherto, has been almost exclusively described. The stable variety, m. p. 94·55°, can be obtained only from technical preparations or from very old specimens. Once prepared, it infects the whole working space, so that the labile form can be again isolated only under particular conditions. H. Wren.

Manufacture of alkyl*iso*propylphenols and their hydrogenation products [thymol, menthol]. Chem. Fabr. auf Actien vorm. E. Schering.—See B., 1930, 136.

Electrometric studies on β-naphtholsulphonic acids. I. Preparation of β-naphthol-6-sulphonic acid. K. H. Engel and A. W. Hutchison (J. Amer. Chem. Soc., 1930, **52**, 211—217).—β-Naphthol-6-sulphonic acid, m. p. 167° (corr.) [monohydrate, m. p. 129° (corr.) ; dihydrate, m. p. 118° (corr.)], is obtained pure by repeatedly saturating an aqueous solution of the crude acid with hydrogen chloride. The acid is then kept over potassium hydroxide until free from chloride. Electrometric titration of potassium β-naphthol-1- and -6-sulphonates gives values of $1·1 \times 10^{-11}$ and 1×10^{-9}, respectively, for the dissociation constants of the hydroxyl groups. The first dissociation constant of β-naphthol-6-sulphonic acid is $3·3 \times 10^{-2}$; the break occurring in the curve for this acid makes possible its determination in presence of the 1-acid or neutral salts. H. Burton.

2'-Nitro-2- and -4-aminodiphenyl sulphides and 4'-nitro-2- and 4-aminodiphenyl sulphides. H. H. Hodgson and W. Rosenberg (J.C.S., 1930, 180—181).—The following derivatives of diphenyl sulphide were prepared by reaction of the appropriate " diaminodiphenyl sulphides " (apparently diaminodiphenyl disulphides) with sodium in alcohol followed by *o*- or *p*-chloronitrobenzene in slight excess : 2'-*nitro*-2-*amino*-, m. p. 81·5° ; 2'-*nitro*-4-*amino*-, m. p. 102° ; 4'-*nitro*-2-*amino*-, m. p. 93° ; 4'-nitro-4-amino-, m. p. 143° (cf. Kehrmann and Bauer, A., 1897, i, 27). Constitutions were confirmed by reduction to the known diaminodiphenyl sulphides.
H. A. Piggott.

Thermochemical studies of *cyclo*paraffins and their derivatives. Experimental data for 5- and 6-membered cyclic diacetates, XVII, and dibenzoates, XIX. P. E. Verkade, J. Coops, (Frau) A. Verkade-Sandbergen, and C. J. Maan (Annalen, 1930, **477**, 279—297).—XVII. The molecular heats of combustion (kg.-cal. at 15° at constant volume, Q_V, and, in parentheses, at constant pressure, Q_P) of the acetates (prepared by acetylation of the corresponding alcohol with acetic anhydride and a few drops of concentrated sulphuric acid) of the various *cis*- and *trans*-diols previously investigated (A., 1929, 142) have been determined. The configuration of both the acetates and benzoates (below) was confirmed in several cases by hydrolysis to the original diol. The following data are given : cis-cyclo*pentane*-1 : 2-*diol diacetate,* b. p. 80—80·5°/2 mm., setting point —5·0°, 1113·9 (1114·7) ; trans-cyclo*pentane*-1 : 2-*diol diacetate,* b. p. 85·5—86·5°/ 3·5 mm., setting pt. —3·9°, 1113·1 (1114·0) ; cis-, m. p. 50·8—51·6°, 1514·9 (1515·7), and *trans*-1 : 2-dihydroxyhydrindene diacetate, b. p. 160·0—160·2°/10 mm., 1518·4 (1519·3) ; *cis*-, m. p. 78·6—79·4°, 1667·9
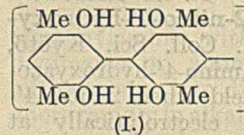
(1669·1), and *trans*-1 : 2-dihydroxy-1 : 2 : 3 : 4-tetra-hydronaphthalene diacetate, m. p. 84—84·5°, 1664·4 (1667·5); cis-, b. p. 113·8—114°/12 mm., 1260·9 (1262·1), and *trans*-*cyclo*hexane-1 : 2-diol diacetate, b. p. 113—113·2°/11·5 mm., 1262·5 (1263·7) (Brunel, A., 1905, i, 869, erroneously assigned the *cis*-configuration); cis-1-*phenylcyclohexane*-1 : 2-*diol diacetate*, m. p. 136·4—137·8°, 1982·5 (1984·3). Berner's method for the determination of the heat of combustion of super-cooled diethyl *anti*tartrate (Archiv Math. Naturvi-denskab, 1926, 39, 116, 129) is shown to be invalid, since the value calculated for supercooled *cis*-1 : 2-di-hydroxyhydrindene diacetate from a determination of the heat of combustion of a mixture of 32% *trans*- and 68% *cis*-isomerides is nearly 100 kg.-cal. below that obtained with the pure solid *cis*-diacetate.

XIX. Similar data for the corresponding dibenzo-ates (prepared by the action of benzoyl chloride and pyridine on the appropriate diol) are recorded : cis-, m. p. 46·5—47·5°, 2240·9 (2242·3), and *trans*-*cyclo*pentane-1 : 2-diol dibenzoate, m. p. 62·2—63·2°, 2239·0 (2240·5); trans-1-*methylcyclopentane*-1 : 2-*diol dibenzo-ate*, m. p. 60·2—61·2°, 2394·5 (2396·2) (*cis*-isomeride could not be obtained crystalline); cis-, m. p. 109·5—110·5°, 2643·8 (2645·3), and *trans*-1 : 2-dihydroxy-hydrindene dibenzoate, m. p. 77·5—78·5°, 2645·8 (2647·3); cis-, m. p. 123—124°, 2797·7 (2799·4), and *trans*-1 : 2-dihydroxy-1 : 2 : 3 : 4-tetrahydronaphth-alene dibenzoate, m. p. 137·2—137·8°, 2796·2 (2797·9); cis-, m. p. 128·8—129·8°, 2796·1 (2797·8) (erroneously described as *trans*- by Leroux, A., 1910, ii, 828, who gave m. p. 127°), and *trans*-2 : 3-dihydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene dibenzoate, m. p. 91·6—92·0°, 2798·3 (2800·1); cis-, m. p. 62·6—63·6° (71·5° on remelting), 2390·7 (2392·5) (Brunel, *loc. cit.* erroneously described this as the *trans*-isomeride), and *trans*-*cyclo*hexane-1 : 2-diol dibenzoate, m. p. 93·0—93·5°, 2386·9 (2388·7) (Brunel, *loc. cit.*, erroneously described as *cis*-isomeride); trans-1-*methylcyclo-hexane*-1 : 2-*diol dibenzoate*, m. p. 101·8—102·6°, 2543·2 (2545·2) (*cis*-isomeride could not be obtained crystalline). J. W. BAKER.

Replacement of a nitro-group in 4 : 5-dinitro-methylenedioxybenzene and 4 : 5-dinitrovera-trole by other groups. A. H. PARIJS (Rec. trav. chim., 1930, 49, 45—56).—The following derivatives of 4-nitromethylenedioxybenzene are prepared from 4 : 5-dinitromethylenedioxybenzene and the requisite amine in alcoholic solution at 100° : 5-amino-, m. p. 197° (lit. 195—199°); 5-*methylamino*-, m. p. 171°; 5-*ethylamino*-, m. p. 133°; 5-n-*propylamino*-, m. p. 115°; 5-n-*butylamino*-, m. p. 137°; 5-n-*amylamino*-, m. p. 95°; 5-n-*heptylamino*-, m. p. 79°, and 5-*di-methylamino*-, m. p. 98°. 6 : 6'-*Dinitro*-3 : 4 : 3' : 4'-*di(methylenedioxy)diphenyl sulphide*, m. p. 234°, yellow and orange modifications, and disulphide, m. p. 267° (decomp.) after darkening at 260°, are formed from the above dinitro-derivative and alcoholic sodium sulphide and disulphide, respectively. The following deriv-atives of 4-nitroveratrole are prepared from 4 : 5-di-nitroveratrole and the requisite amine : 5-*methyl-amino*-, m. p. 146°; 5-*ethylamino*-, m. p. 174—175°; 5-n-*propylamino*-, m. p. 141—142°; 5-n-*butylamino*-, m. p. 114°; 5-n-*amylamino*-, m. p. 90·5°; 5-n-*heptyl-*

amino-, m. p. 84°, and 5-*dimethylamino*-, m. p. 130—131°. 4 : 5-Dinitroveratrole is converted by methyl-alcoholic sodium methoxide into 4-nitro-1 : 2 : 5-tri-methoxybenzene; with aqueous methyl-alcoholic sodium sulphide, 6 : 6'-*dinitro*-3 : 4 : 3' : 4'-*tetrameth-oxydiphenyl sulphide*, m. p. 220—220·5°, is produced. The 6-nitroveratryl-4 : 5-thiotriazoveratrole of Jones and Robinson (J.C.S., 1917, 111, 910, 925) is identical with the above sulphide. 6 : 6'-*Dinitro*-3 : 4 : 3' : 4'-tetramethoxydiphenyl disulphide has m. p. 212° (decomp.). H. BURTON.

Oxidation of *m*-xylorcinol [4 : 6-dihydroxy-*m*-xylene]. T. L. DAVIES and J. F. WALKER (J. Amer. Chem. Soc., 1930, 52, 358—365).—4 : 6-Di-hydroxy-*m*-xylene, m. p. 124·5—125·2° (obtained by the usual method from 4-amino-6-hydroxy-*m*-xylene, using copper sulphate as a catalyst), is oxidised by ferric chloride solution to a mixture of 2 : 6 : 2' : 6'-tetrahydroxy-3 : 5 : 3' : 5'-tetramethyldiphenyl, m. p. 242—243° (*tetra-acetate*, m. p. 158—159°), and the *ether* (I), chars gradually above 250°; I is formed by further oxidation of the diphenyl derivative, which is obtained in optimum yield when the oxidation is carried out in presence of ether. Bromination of 4 : 6-dihydroxy-*m*-xylene in chloroform affords a bromo-derivative, m. p. 119—119·5°, which is oxidised by ferric bromide solution to a mixture of a *compound*, $C_{20}H_{19}O_4Br_2$(?), chars gradually between 265° and 278°, and an amorphous substance, m. p. 128—135°. Bromination of the above tetrahydroxytetramethyl-diphenyl in boiling chloroform affords a *compound*, $C_{16}H_{16}O_2Br_2$, m. p. 274—277° (decomp.). An excess of bromine water converts 4 : 6-dihydroxy-*m*-xylene into small amounts of three substances, m. p. 71—72°, 173°, and 194°, respectively. H. BURTON.

Me OH　HO Me

Me OH　HO Me
(I.)

Constitution of cholesterol. X. Action of persulphuric acid. E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], 47, 93—95).—With persulphuric acid in light petroleum cholesterol yields an *oxide*, m. p. 141°, which does not combine with bromine in chloroform and yields an acetate, m. p. 98° (cf. Westphalen, A., 1915, i, 884). The constitution (I) is suggested. With xanthydrol in acetic acid at 100°, cholesterol yields *xanthyl-cholesterol*, m. p. 141·5—142°, [α]$_D$ —53° (*bromide*, m. p. 103°). R. BRIGHTMAN.

$C_{18}H_{34}$
(I.)
CH
HO·CH　CH·O
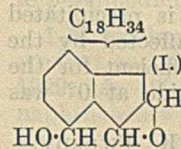
Dehydroergosterol and ergosterol. A. WIND-AUS, W. BERGMANN, and H. BUTTE (Annalen, 1930, 477, 268—278).—Reduction of dehydroergosterol (Windaus and Linsert, A., 1928, 1372) with sodium and alcohol converts it into *dihydrodehydroergosterol* (*ergosterol*-F), m. p. 150—151°, [α]$_D$ —20° (*acetyl* derivative, m. p. 152—153°, [α]$_D^{15}$ —23·5°; *phenyl-urethane*, m. p. 167°, [α]$_D$ —18·4°, depressing the m. p. of the *phenylurethane*, m. p. 178°, [α]$_D$ —16°, of dihydroergosterol), which has characteristic bands in the spectrum at 252 and 235 μμ, and is reduced by platinum and hydrogen in acetic acid to *allo*-α-ergosterol acetate. Reduction of dehydroergosterol (or its peroxide) with sodium and boiling propyl

alcohol, however, yields *dihydroergosterol*-II, m. p. 158—159°, $[\alpha]_D^{18}$ —6·6° (*acetyl* derivative, m. p. 157°, $[\alpha]_D^{18}$ —7·27°; *phenylurethane*, m. p. 177—178°) (band at 240 μμ), isomeric with dihydroergosterol and also reduced at *allo*-α-ergostanol. Reduction of dehydroergosterol peroxide with zinc dust and boiling alcoholic potassium hydroxide yields an *ergostatrienediol*, $C_{27}H_{42}O_2$, m. p. 220—221°, $[\alpha]_D^{19}$ +48·3° (*monoacetyl* derivative, m. p. 216°, $[\alpha]_D^{20}$ +48·05°) (band at 240 μμ), reduced catalytically to *allo*-α-ergostanol, but converted by sodium and alcohol into an ergostenediol, probably identical with that obtained by Windaus, Bergmann, and Lüttringhaus (A., 1929, 1065) from ergosterol peroxide. When ergosterol is heated with alcoholic sodium ethoxide in a sealed tube at 175° it is converted into two isomeric alcohols, $C_{27}H_{44}O$ (two double linkings), dihydroergosterol II (above), separated by its insoluble digitonin compound from *epidihydroergosterol*, m. p. 208°, $[\alpha]_D^{19}$ —20·4°, the *acetate*, m. p. 148—149°, of which is reduced by hydrogen and a platinum catalyst to the acetate, m. p. 144°, $[\alpha]_D^{18}$ +20·5°, of epiergostanol characterised by Reindel and Detzel (A., 1929, 61). Similar treatment of the ketone of dihydroergosterol with sodium ethoxide gives mainly dihydroergosterol and only a small amount of epidihydroergosterol.   J. W. BAKER.

Three homologues of ephedrine. E. FOURNEAU and C. E. BARRELET (Bull. Soc. chim., 1930, [iv], **47**, 72—86).—See this vol., 85.

Grignard compounds of certain polyhalogenated benzene derivatives and their condensation products with aromatic aldehydes and ketones. M. A. MIHĂILESCU and S. P. CARAGEA (Bull. Acad. Sci. Roumaine, 1929, **12**, 7—18).—Decomposition of the Grignard reagents prepared from *p*-chloroiodo- and *p*-chlorobromo-benzene, respectively, with water yielded, in both cases, chlorobenzene and traces of 4 : 4'-dichlorodiphenyl; *p*-dibromobenzene gave bromobenzene and a small quantity of 4 : 4'-dibromodiphenyl. The following compounds were obtained by condensation of magnesium *p*-chlorophenyl iodide and the under-mentioned aldehydes and ketones : 4-chlorobenzhydrol, m. p. 62°, from benzaldehyde; 4-*chloro*-4'-*methoxybenzhydrol*, m. p. 60°, from anisaldehyde; 4-*chloro*-4'-*dimethylaminobenzhydrol*, m. p. 103—104°, from *p*-dimethylaminobenzaldehyde; *p*-chlorotriphenylcarbinol, m. p. 85°, from benzophenone; p-*chlorophenylbenzoin*, m. p. 84°, or s-4 : 4'-*dichlorotetraphenyl glycol*, m. p. 169°, depending on the experimental conditions, from benzil. Using magnesium *p*-bromophenyl bromide, the following substances were prepared : *p*-bromobenzhydrol, m. p. 65°, 4-*bromo*-4'-*dimethylaminobenzhydrol*, m. p. 107°, 4-*bromo*-4'-*methoxybenzhydrol*, m. p. 75°, *p*-bromotriphenylcarbinol, p-*bromophenylbenzoin*, m. p. 88°, and 4 : 4'-*dibromotetraphenyl glycol*, m. p. 178°.
    A. I. VOGEL.

Optically active diphenylethylene oxide. J. READ and I. G. M. CAMPBELL (Nature, 1930, **125**, 16—17).—*s*-Diphenylethylene oxide has been prepared from *d*-diphenyl- and *l*-*iso*diphenyl-hydroxyethylamine; the optically active and externally compensated forms of the *iso*-base yielded an identical optically inactive diphenylethylene oxide (I), whilst

the former gave a strongly lævorotatory oxide (II); hence the configurations allocated to the bases by Erlenmeyer must be reversed.
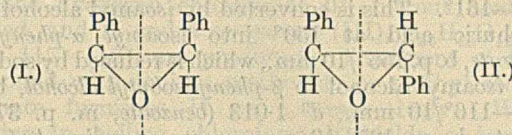
The specific rotatory power of the *l*-oxide (for sodium light in absolute alcohol) exceeds —300°, whilst that for l-*iso*hydrobenzoin is only —92°, whence the optical effect of the three-membered ring is apparent.   A. A. ELDRIDGE.

Configuration of *l*-phenylalanine, *l*-tyrosine, and *l*-dihydroxyphenylalanine. P. KARRER and W. KEHL (Helv. Chim. Acta, 1930, **13**, 50—63).—The rotatory powers of a series of *N*-acyl derivatives of *l*-leucine (and its methyl ester) are similar in sign and magnitude to the corresponding series from *l*-hexahydrophenylalanine (and its methyl ester), indicating that the amino-acids have the same stereochemical configuration. The results also show that *l*-phenylalanine, *l*-tyrosine, and *l*-dihydroxyphenylalanine have the same configuration as *d*-alanine and the other acids in group 1 of Karrer, Escher, and Widmer's classification (A., 1926, 505).

The N-*benzoyl* derivative, m. p. 102°, $[\alpha]$ —21·14° (all rotatory powers are at 20° for the *D* line in alcoholic solution), of *l*-leucine methyl ester is hydrolysed by aqueous-alcoholic sodium hydroxide to N-*benzoyl*-l-*leucine*, $[\alpha]$ —10·82°, purified through the *quinidine* salt, m. p. 148°. The following *N*-acyl derivatives of *l*-leucine are also described : p-*nitrobenzoyl*, m. p. 219—220°, $[\alpha]$ —8·87° (*methyl* ester, m. p. 103·5°, $[\alpha]$ —16·92°); benzenesulphonyl, m. p. 119°, $[\alpha]$ —4·36° (*methyl* ester, m. p. 64°, $[\alpha]$ —20·75°); *toluenesulphonyl*, m. p. 113·5°, $[\alpha]$ —4·05° (*methyl* ester, m. p. 55°, $[\alpha]$ —15·95°), and β-*naphthalenesulphonyl*, m. p. 117·5—118°, $[\alpha]$ +1·72° (*methyl* ester, m. p. 91·5—92°, $[\alpha]$ —31·09°).

l-Hexahydrophenylalanine, $[\alpha]$ —11·37° (hydrochloride, $[\alpha]$ +13·4°), is conveniently prepared by the catalytic reduction (platinum) of *l*-tyrosine in presence of dilute hydrochloric acid (cf. Waser and Brauchli, A., 1924, i, 1068). The following *N*-acyl derivatives of *l*-hexahydrophenylalanine are described : *benzoyl*, m. p. 124·5—125°, $[\alpha]$ —12·68° (cf. *loc. cit.*) (*methyl* ester, m. p. 104·5—105°, $[\alpha]$ —26·66°, prepared by esterification with ethereal-alcoholic diazomethane); p-*nitrobenzoyl*, m. p. 158·5—159°, $[\alpha]$ —5·04° (the *methyl* ester, m. p. 72°, $[\alpha]$ —21·2°, is accompanied by a small amount of by-product); *benzenesulphonyl*, m. p. 147·5°, $[\alpha]$ —2·33° (*methyl* ester, m. p. 61—61·5° after sintering at 56°, $[\alpha]$ —21·92°); *toluenesulphonyl*, m. p. 160·5°, $[\alpha]$ +1·14° (the *methyl* ester, m. p. 114°, $[\alpha]$ —17·13°, is accompanied by a by-product, m. p. 59°), and β-*naphthalenesulphonyl*, m. p. 185°, $[\alpha]$ +11·24° (*methyl* ester, m. p. 99° after sintering at 95°, $[\alpha]$ —22·77°).   H. BURTON.

β-Phenyl*iso*butyl alcohol and derivatives. G. DARZENS and A. LÉVY (Compt. rend., 1929, **189**, 1287—1289).—Phenylacetonitrile is methylated by Bodroux and Taboury's method (A., 1910, i, 257) to

α-*phenylisobutyronitrile*, b. p. 115—116°/14 mm., which is hydrolysed by 90% sulphuric acid, first in the cold and then at 70°, to α-*phenylisobutyramide*, m. p. 160—161°. This is converted by *iso*amyl alcohol and sulphuric acid at 150° into *iso*amyl α-*phenyliso-butyrate*, b. p. 155°/10 mm., which is reduced by sodium and *iso*amyl alcohol to β-*phenyl*iso*butyl alcohol*, b. p. 115—116°/10 mm., d^0 1·013 (*benzoate*, m. p. 37·5°; *acetate*, b. p. 127°/13 mm.; corresponding *bromide*, b. p. 103°/12 mm.; *ethyl ether*, b. p. 72°/12 mm.).

H. BURTON.

Fatty acid derivatives. II. Solid derivative of phenylstearic acid. T. MAZUME and K. KINO (J. Soc. Chem. Ind. Japan, 1929, **32**, 338—339B).— Phenylstearic acid, obtained by hydrolysing the methyl ester, b. p. 228°/4 mm., reacts with *p*-aminoazobenz-ene to give *phenylstearyl*-p-*aminoazobenzene*, m. p. 82—82·5°. An analogous azo-derivative from β-naphthylamine could not be isolated.

C. W. SHOPPEE.

Autocatalysis in oxidation. I. Auto-oxid-ation of abietic acid. G. DUPONT and J. LÉVY (Bull. Soc. chim., 1930, [iv], **47**, 60—68).—See this vol., 86.

Carbithioic acids. I. *p*-Tolylcarbithioic [di-thio-*p*-toluic] acid and derivatives. R. W. BOST and W. J. MATTOX (J. Amer. Chem. Soc., 1930, **52**, 332—335).—Magnesium *p*-tolyl bromide and carbon disulphide react at 0° forming dithio-*p*-toluic acid, which solidifies at 27° (cf. Sakurada, A., 1927, 134) [*zinc*, m. p. 180°, and *lead*, m. p. 200° (decomp.), salts ; *methyl*, b. p. 130°/3 mm., ethyl, b. p. 132°/3 mm., d^3 1·1173 (cf. *loc. cit.*), n-*butyl*, b. p. 169°/5 mm., d^{30} 1·070, and p-*nitrobenzyl* esters, m. p. 70·5° (all prepared from the sodium salt and the corresponding alkyl halide or sulphate); *amide*, m. p. 155°; p-*toluidide*, m. p. 170·5°]. The acid decomposes on attempted distill-ation, does not furnish an acid chloride, and when treated with nitric acid in ethereal solution is oxidised to *p*-toluic acid.

H. BURTON.

Nitrosation of salicylic acid by copper nitrite. V. G. GULINOV (Ukrain. Chem. J., 1929, **4**, [Tech.], 215—225).—The yield of nitroso-compound obtained when sodium salicylate is treated with copper nitrite reaches 95%, but the separation of the nitroso-salt,

Cu<CO₂—⟩NO, from the mother-liquor is diffi-cult. This separation occurs more readily at 22—23° than at 7—8° or at 14—15°, a 93·2% yield being obtained from the reacting solution after 80 hrs., with a lower proportion of sodium sulphite in the precipitate. An experiment on a larger scale with commercial salicylic acid (560 g.) gave a yield of 86·2%.

T. H. POPE.

Preparation of aminosulphosalicylic acid from nitrososalicylic acid. V. G. GULINOV (Ukrain. Chem. J., 1929, **4**, [Tech.], 227—239).—Reduction of copper nitrososalicylate by means of sulphite results in the formation of 3-amino-6-hydroxy-2 : 4-disulphobenzoic acid. The best results are obtained by using normal sodium sulphite as reducing agent. When either a mixture of sodium and ammonium sulphites, or ammonium sulphite alone, or sodium hydrogen sul-phite is employed, the yield is low, the product is diffi-

cult to separate, and it is impossible to remove copper salts which largely remain in solution with the amino-compound. The acid obtained always contains admixed 3 : 6-dihydroxy-4-sulphobenzoic acid.

T. H. POPE.

Stereoisomerism of disulphoxides and related substances. V. Dioxides of 3 : 5-dimethyl-thiolbenzoic acid. E. V. BELL and G. M. BENNETT (J.C.S., 1930, 1—6).—3 : 5-Dimethylthiolbenzoic acid dioxide exists in two forms, α- or *meso*-, and β-, which is potentially active and has been resolved by means of brucine. 3 : 5-*Dimethylthiolbenzoic acid*, m. p. 153° [*sodium* salt, m. p. 283° (decomp.)], was synthesised as follows : carboxybenzene-3 : 5-disulphonyl chloride (preparation by improved method described) was reduced by zinc and hydrochloric acid in acetic acid to 3 : 5-dithiolbenzoic acid, not isolated as such, but oxidised in solution to 3 : 5-*disulphidobenzoic acid*, m. p. 195—200° (decomp.), which was then reduced with dextrose in alkaline solution and treated with methyl sulphate. On oxidation with hydrogen peroxide it gave α- and β-*dimethylthiolbenzoic acid dioxides*, m. p. 251° (decomp.) and 209° (decomp.), separated by crystallisation from alcohol. The *brucine* salts, when freed from chloroform of crystallis-ation, melted at 170—175° (decomp.) and 130°, respectively. The former was unchanged on re-crystallisation from chloroform, consequently the α-dioxide is the *meso*-form; the brucine salt of the β-dioxide after seven recrystallisations from chloro-form had $[\alpha]_D$ −59·7° and m. p. 184°, but was not optically pure. The 1-3 : 5 -*dimethylthiolbenzoic acid dioxide* isolated from this had $[\alpha]_D$ −99·65° in water, m. p. 200—202° (after recrystallisation). d-3 : 5-*Di-methylthiolbenzoic acid dioxide* was isolated from the mother-liquors in an optically impure form, m. p. 190—205°, $[\alpha]_D$ +22·7° in water.

s-*Diphenylthiolethane-mm′-dicarboxylic acid*, m. p. 265°, obtained by reduction of *m*-dithiobenzoic acid with dextrose in alkaline solution and condensing the product with ethylene dibromide, did not give a pure product on oxidation with hydrogen peroxide. Its *methyl* ester, m. p. 73°, however, gave a mixture of α- and β-*dioxides*, m. p. 195° (decomp.) and 126—129° (decomp.), respectively. Both yielded the parent sulphide on reduction, but on hydrolysis suffered disruption. Consequently resolution could not be effected.

H. A. PIGGOTT.

Bromination of 2 : 4-dimethoxycinnamic acid. M. REIMER and E. TOBIN (J. Amer. Chem. Soc., 1930, **52**, 341—347).—Treatment of 2 : 4-dimethoxy-cinnamic acid with bromine in presence of chloro-form affords 5 : αβ-*tribromo*-2 : 4-*dimethoxy*-β-*phenyl-propionic acid* (I), m. p. 228—229° (decomp.) [the *methyl* (II), m. p. 142° (decomp.), and *ethyl* esters (III), m. p. 158° (decomp.), can be obtained only by esterification with ethereal diazomethane and diazo-ethane, respectively]; addition of bromine could not be accomplished without nuclear bromination. Attempted esterification of I with methyl-alcoholic hydrogen chloride gives the *methyl* ester, m. p. 149°, of α : 5-*dibromo*-β : 2 : 4-*trimethoxy*-β-*phenylpropionic acid*, m. p. 171° (decomp.) (the *ethyl* ester, m. p. 109°, is prepared from the acid and diazoethane or by

dissolution of III in methyl alcohol), also formed together with the methyl ester by dissolution of I in methyl alcohol. The *ethyl* ester, m. p. 105—107°, of α : 5-*dibromo*-2 : 4-*dimethoxy*-β-*ethoxy*-β-*phenylpropionic acid*, m. p. 161—162° (decomp.) (*methyl* ester, m. p. 138° after softening at 134°, is also prepared from the acid and diazomethane or from II and ethyl alcohol), is obtained similarly. Treatment of I with methyl-alcoholic potassium hydroxide solution, affords ω : 5-*dibromo*-2 : 4-*dimethoxystyrene*, m. p. 67—68°, readily decomposed by light. The *dibromide*, m. p. 146° (slight decomp.), of this styrene is converted by dissolution in methyl alcohol into αα : 5 - *tribromo* - β : 2 : 4 - *trimethoxy* - β - *phenylethane*, m. p. 138—139° (the corresponding β-*ethoxy*-derivative, m. p. 117—120°, is prepared similarly). Addition of bromine to methyl 2 : 4-dimethoxycinnamate affords II, but attempted addition to ethyl 2 : 4-dimethoxycinnamate, m. p. 68—69°, results in the formation of 5-*bromo*-2 : 4-*dimethoxybenzaldehyde*, m. p. 134—138° (*semicarbazone*, decomp. about 275°). Distillation of the ethyl ester, m. p. 68—69°, gives an isomeric *ethyl* 2 : 4-*dimethoxycinnamate*, b. p. 219°/ 22 mm., m. p. 61°, which when treated with bromine affords III. H. BURTON.

*cyclo*Propane series. XII. Nitro*cyclo*propanes. E. P. KOHLER and S. F. DARLING (J. Amer. Chem. Soc., 1930, **52**, 424—432).—*Methyl* m- and *p*-*nitrobenzylidenemalonates*, m. p. 98—99° and 133— 134°, respectively, are converted by short treatment with sodium methoxide and subsequent acidification with acetic acid into *methyl* β-m- and -p-*nitrophenyl*-β-*methoxyethane*-αα-*dicarboxylates*, m. p. 66° and 116°, respectively. These are brominated in chloroform solution to the corresponding α-*bromo*-derivatives, m. p. 78—80° and 133°, respectively. *Methyl* α-*cyano*-m-*nitrocinnamate* has m. p. 135— 137°. Addition of nitromethane to the above nitrobenzylidenemalonates and bromination of the products formed in chloroform affords α-bromo-esters, whilst bromination in presence of sodium methoxide gives γ-bromo-esters. The following are described : *ethyl* α-*bromo*-γ-*nitro*-β-m-*nitrophenylpropane*-αα-*dicarboxylate*, m. p. 85·5° (*methyl* ester, m. p. 123°) ; *ethyl* α-*bromo*-γ-*nitro*-β-p-*nitrophenylpropane*-αα-*dicarboxylate*, m. p. 88°; *methyl* α- and γ-*bromo*-γ-*nitro*-β-*phenylpropane*-αα-*dicarboxylates*, m. p. 107—109° and 81·5—83°, respectively, and *methyl* γ-*bromo*-γ-*nitro*-β-m-*nitrophenylpropane*-αα-*dicarboxylate*, m. p. 147—148°. Treatment of the last-named ester with methyl-alcoholic potassium acetate affords *methyl* 3-*nitro*-2-m-*nitrophenyl*cyclopropane - 1 : 1 - *dicarboxylate*, m. p. 122—123·5°. This is converted by treatment with methyl sodiomalonate into *methyl* β-m-*nitrobenzylidenepropane* - αα γγ - *tetracarboxylate* (I), m. p. 92—94° (ozonolysis product m-nitrobenzaldehyde), and by boiling methyl-alcoholic potassium acetate into *methyl* β-*methoxy*-γ-m-*nitrophenyl*-Δ^β-*propene*-αα-*dicarboxylate* (II), m. p. 104—105°, which is hydrolysed by methyl-alcoholic hydrochloric acid to *methyl* m-*nitrophenacylmalonate*, m. p. 64—66° [*copper* derivative, m. p. 195—200° (decomp.)]. Treatment of this ketonic ester with semicarbazide gives a *compound*, $C_{26}H_{11}O_6N_4$, m. p. 177—179°.

When the above *cyclo*propane ester is treated with methyl-alcoholic sodium methoxide, a red *sodium* salt is first produced. When this is added to methyl-alcoholic hydrogen chloride at 0°, nitrous acid is evolved, and II and a *compound* (III), $C_{26}H_{22}O_{12}N_2$, m. p. 115—116°, are produced. Treatment of this compound with sodium methoxide or methyl sodiomalonate furnishes II or I, respectively. With bromine in boiling chloroform it yields a *bromo*-derivative, m. p. 154—155°, and with sulphuric acid at the ordinary temperature yields two *substances*, $C_{22}H_{18}O_8N_2$, m. p. 140° after softening at 135°, and $C_{24}H_{20}O_{11}N_2,H_2O$, m. p. 122° (with loss of water), m. p. (anhydrous) 157°. The compound III is readily oxidised with cold potassium permanganate solution but it is relatively inert to acidic reagents. The following constitution is assigned to III :

$$\left[NO_2 \cdot C_6H_4 \cdot CH \underset{C}{\overline{\qquad}} C(CO_2Me)_2 \right]_2$$
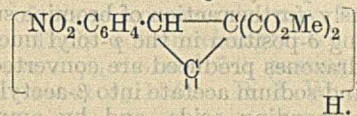
H. BURTON.

Synthesis of dimethoxyphthalimidineacetic acid. W. M. RODIONOV and A. M. FEDOROVA (J. Amer. Chem. Soc., 1930, **52**, 368—371).—Opianic and malonic acids react in presence of 10% alcoholic ammonia at 100°, yielding a mixture of meconine-acetic acid, m. p. 165—167°, and β-*amino*-β-3 : 4-*dimethoxy*-2-*carboxyphenylpropionic acid*, m. p. 132— 134° with loss of water. Dehydration of this amino-acid at 140—150° gives 3 : 4-*dimethoxyphthalimidineacetic acid* (I), m. p. 174—

MeO ⟨ ⟩ $\overset{CH \cdot CH_2 \cdot CO_2H}{\underset{CO}{>}NH}$ OMe (I.)

175° [*methyl* ester, m. p. 141—143°; nitroso-derivative, m. p. 167° (decomp.)]. Methyl opianate and malonic acid condense similarly, forming I, whilst opianic acid and ethyl malonate afford *ethyl meconinemalonate*, m. p. 74—75°. H. BURTON.

Action of sodium ethoxide on ethyl *cyclo*-hexane - 2 : 3 - dione - 1 : 4 - dicarboxylate. L. S. DEDUSENKO (Acta Univ. Asiae Med., 1928, [vi], No. 1, 3—16).—With excess of alcohol, ethyl *cyclo*-hexane-2 : 3-dione-1 : 4-dicarboxylate is converted by sodium ethoxide into ethyl *cyclo*pentan-2-ol-1 : 2 : 3-tricarboxylate, the reverse change taking place in the absence of alcohol under the influence of sodium and sodium ethoxide. In the condensation of adipic with oxalic ester, only ethyl oxaladipate, in addition to *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate, *cyclo*-pentenetricarboxylate, and *cyclo*pentan-2-ol-1 : 2 : 3-tricarboxylate, was identified. Probably the last-named compound is a primary transformation product of the oxaladipate, which may eliminate water to form the *cyclo*pentenetricarboxylate, or alcohol to form ethyl *cyclo*hexane-2 : 3-dione-1 : 4-dicarboxylate. The hypothesis that the conversions ·CO·CO·+ EtOH ⇌ >C(OH)·CO₂Et constitute a reversible process is supported. CHEMICAL ABSTRACTS.

Oxidation of benzaldehyde. W. P. JORISSEN and P. A. A. VAN DER BEEK (Rec. trav. chim., 1930, **49**, 138—141).—The various theories of autoxidation of benzaldehyde are reviewed. When benzaldehyde is kept in sealed tubes in the dark (a small quantity

of air being present), the product gives a peroxide reaction (liberation of iodine from potassium iodide). This cannot be due to the formation of benzoyl hydrogen peroxide, which would have reacted with the benzaldehyde (cf. A., 1926, 519; 1928, 413). Exposure of the stored material to sunlight for a short time causes the disappearance of the peroxide reaction. The autoxidation process is not yet satisfactorily explained.　　　　　　H. BURTON.

Action of bromine on the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes. F. D. CHATTAWAY and A. B. ADAMSON (J.C.S., 1930, 157—163).—Bromination of the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes occurs first in the *o*-position with respect to the nitrogen atom of the *p*-tolyl nucleus and the ω-position simultaneously, further action of bromine substituting the remaining *o*-position in the *p*-tolyl nucleus. The ω-bromohydrazones produced are converted by acetic anhydride and sodium acetate into β-acetylhydrazides of the corresponding acids, and by ammonia into hydrazidines of the general formula NHR'·N:C(NH₂)R, highly coloured weak bases yielding colourless hydrochlorides. In the case of *o*-nitrobenzaldehyde these ω-bromo-compounds on crystallisation from alcohol yield the violently explosive keto*endo*aryliminodihydrobenz*iso*diazole oxides (the so-called *iso*diazo-compounds; cf. A., 1926, 169), which on long boiling with the same solvent are reduced to the corresponding *iso*diazoles (A., 1927, 353).

By the action of 2 mols. of bromine in acetic acid on *m*-nitrobenzaldehyde-*p*-tolylhydrazone, ω-*bromo*-*m*-*nitrobenzaldehyde-3-bromo*-p-*tolylhydrazone*, m. p. 145·5°, is obtained (β-*acetyl* derivative not obtained crystalline); further bromination gave ω-*bromo*-*m*-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, m. p. 154·5° (β-*acetyl* compound, m. p. 170°), also obtained by brominating *m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone. Similarly prepared are : ω-*bromo*-p-*nitrobenzaldehyde-3-bromo*-p-*tolylhydrazone*, m. p. 176° (β-*acetyl* compound, m. p. 173°), ω-*bromo*-p-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, m. p. 161° (β-*acetyl* compound, m. p. 183°); ω-*bromobenzaldehyde-3-bromo*-p-*tolylhydrazone*, m. p. 74°, and ω-*bromobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, m. p. 106° (β-*acetyl* compound, m. p. 190°). In every case the acetyl compounds of the dibromohydrazones gave on hydrolysis the corresponding benzoic acid, 3-bromo-*p*-tolylhydrazine, and acetic acid, whilst those of the tribromohydrazones gave the corresponding benzoic acid, and α-acetyl-3 : 5-dibromo-*p*-tolylhydrazine. 3-*Bromo*-p-*tolyl*-m-*nitrobenzhydrazidine*, red, has m. p. 136°, [*hydrochloride*, m. p. 230° (decomp.)] ; 3 : 5-*dibromo*-p-*tolyl*-m-*nitrobenzhydrazidine*, m. p. 151°; 3-*bromo*-p-*tolyl*-p-*nitrobenzhydrazidine*, deep purple, m. p. 155°; 3 : 5-*dibromo*-p-*tolyl*-p-*nitrobenzhydrazidine*, orange-yellow, m. p. 145°. ω-*Bromo*-o-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*, m.p. 105°, yields, when crystallised from alcohol, the highly explosive 3-*keto*-1 : 2-endo-3'-*bromo*-p-*tolyl*-*imino*-2 : 3-*dihydrobenzisodiazole* 1-*oxide*, explosion point 139°, which, when boiled for 2 hrs. with alcohol, gives 3-*keto*-1 : 2-endo-3'-*bromo*-p-*tolylimino*-2 : 3-*dihydrobenzisodiazole*, m. p. 166°. *o*-Nitrobenzaldehyde-

p-tolylhydrazone yields with excess of bromine in the cold 3 : 5-*dibromo*-p-*toluidine perbromide*, m. p. 134° (decomp.). ω-*Bromo*-o-*nitrobenzaldehyde*-3 : 5-*dibromo*-p-*tolylhydrazone*, obtained by brominating *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, has m. p. 123° (decomp.). The benz*iso*diazole oxide, obtained by crystallisation from alcohol, had explosion point 167°, and the benz*iso*diazole, m. p. 190° (decomp.). *o*-Nitrobenzaldehyde-*p*-tolylhydrazone with bromine in acetic acid in presence of sodium acetate yields 3-*keto*-1 : 2-endo-p-*tolylimino*-2 : 3-*dihydrobenzisodiazole* 1-*oxide*, explodes at 143°; even with excess of bromine the product remains halogen-free.
　　　　　　　　　　　　H. A. PIGGOTT.

Structure and tautomerism of *o*-nitrobenzaldehyde. Interference of nitro-groups with the Zerevitinov method for the determination of active hydrogen. H. GILMAN and R. E. FOTHERGILL (Bull. Soc. chim., 1929, [iv], **45**, 1132—1136).—With nitrobenzene and *o*-nitrotoluene in *n*-butyl ether, magnesium methyl iodide yields from 1·13 to 1·57 equivalents of hydrogen. In pyridine the reaction is slower and the results were less accurate, but nitrobenzene gave 1·49 equivalents of hydrogen in 10 min. *n*-Butyl ether and pyridine thus give higher results (cf. A., 1928, 64, 536) than ether as solvent. The gas evolved contains unsaturated compounds, and even with 1 : 2 : 4 : 6-tetrachloro-3 : 5-dinitrobenzene and tribromonitromethane in *n*-butyl ether or with trichloronitromethane in *iso*amyl ether, which contain no hydrogen, gas is liberated on treatment with magnesium methyl iodide, 1 : 2 : 4 : 6-tetrachloro-3 : 5-dinitrobenzene affording 1·96—2·24 equivalents, containing very little methyl chloride. Accordingly, the quantitative liberation of methane by Zerevitinov's method cannot be adduced as evidence for Tanasescu's cyclic hydroxy-formula for *o*-nitrobenzaldehyde (A., 1926, 726).　　　R. BRIGHTMAN.

Isomerisation of hydroxyaldehydes. II. Transformation of bromodi*cyclo*hexylacetaldehyde and di*cyclo*hexylglycollaldehyde. S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1929, **61**, 1661—1682).—See A., 1929, 1448.

Replacement of the aldehyde group in piperonal and its derivatives. A. H. PARIJS (Rec. trav. chim., 1930, **49**, 17—32).—Nitration of piperonal in acetic acid suspension gives 4-nitromethylenedioxybenzene and 6-nitropiperonal (*azine*, decomp. about 257°; *phenylhydrazone*, m. p. 218·5° with blackening and evolution of gas; p-*nitrophenylhydrazone*, decomp. 245—248°; *semicarbazone*, decomp. 272·5—278°; *semioxamazone*, m. p. 325° with blackening and evolution of gas). The acetic acid appears to exert some protective influence on the aldehyde group, since the yield of the former nitro-compound is only 15—18% (cf. Salway, J.C.S., 1909, **95**, 1163). Chlorination of piperonal, using a slight modification of the method of Robinson and others (J.C.S., 1917, **111**, 948), affords a small amount of 4 : 5-dichloromethylenedioxybenzene in addition to 6-chloropiperonal [*diacetate*, m. p. 133°; *azine*, m. p. 303° (decomp.) after darkening at 300°; *phenylhydrazone*, m. p. 117—118°; p-*nitrophenylhydrazone*, m. p. 281—282° (decomp.); *semicarbazone*, m. p. 280° (violent decomp.) after

darkening at 278°; *semioxamazone*, m. p. 299° (decomp.) after darkening at 291°]. 5-Chloro-4-nitromethylenedioxybenzene (from 6-chloropiperonal by nitration) is reduced by stannous chloride and alcoholic hydrochloric acid to the corresponding *amino*-derivative, m. p. 99° [*hydrochloride*, m. p. 254—255° (decomp.) after becoming yellow at 189° and blackening at 247°]. Treatment of the chloronitro-derivative with alcoholic methylamine at 135° gives 4-nitro-5-methylaminomethylenedioxybenzene, also obtained by similar treatment of 4 : 5-dinitromethylenedioxybenzene. Similar treatment of the chloro-derivative with alcoholic ammonia affords only a small amount of the 5-amino-derivative, but the 5-ethylamino-, 5-*n*-propylamino-, and 5-dimethylamino-compounds are readily produced with the appropriate amine. Treatment of 5-chloro-4-nitromethylenedioxybenzene with alcoholic sodium sulphide or disulphide gives 6 : 6′-*dinitro*-3 : 4 : 3′ : 4′-*di*(*methylenedioxy*)*diphenyl disulphide*, m. p. 267° (decomp.) after darkening at 260°.

Bromination of piperonal in acetic acid furnishes 6-bromopiperonal [*azine*, m. p. 252° (decomp.) after darkening at 249°; p-*nitrophenylhydrazone*, m. p. 253° (decomp.); *semicarbazone*, m. p. 230° (decomp.); *semioxamazone*, m. p. 278—279° (decomp.)], and some 4 : 5-dibromomethylenedioxybenzene. 5-Bromo-4-nitromethylenedioxybenzene is converted by alcoholic sodium disulphide into the above disulphide (also obtained by similar treatment of 4 : 5-dinitromethylenedioxybenzene); reaction is much slower than with the corresponding chloro-compound. 5-Bromo-3 : 4-dinitromethylenedioxybenzene (prepared by nitration of 6-bromopiperonal) is converted by alcoholic methylamine at 100° into 5-*bromo*-3-*nitro*-4-*methylaminomethylenedioxybenzene*, m. p. 167° (decomp.).

H. BURTON.

Opening of the methylenedioxy-ring. A. H. PARIJS (Rec. trav. chim., 1930, **49**, 33—44).—Attempted nitration of 6-*nitropiperonylidene diacetate*, m. p. 142°, with a mixture of 100% nitric acid and acetic anhydride at —5° affords 6-*nitroprotocatechualdehyde*, m. p. 203° (decomp.) [*azine*, darkens at 241° and becomes black at 278°; *semicarbazone*, m. p. 254° (decomp.); *phenylhydrazone*, m. p. 203° (decomp.); p-*nitrophenylhydrazone*, m. p. 290° (decomp.)], fission of the methylenedioxy-ring having occurred. Similarly, 6-*bromopiperonylidene diacetate*, m. p. 128°, yields 6-*bromoprotocatechualdehyde*, m. p. 220° [*azine*, m. p. 251° (decomp.); *semicarbazone*, m. p. 239° (decomp.); p-*nitrophenylhydrazone*, m. p. 243° (decomp.)].

4 : 5-Dinitromethylenedioxybenzene is converted by methyl-alcoholic sodium methoxide solution into 4 : 5-dinitroguaiacol, m. p. 177° (lit. 172°) (corresponding 2-*ethoxy*-derivative, m. p. 113°), methylated to 4 : 5-dinitroveratrole. Under similar conditions piperonal undergoes the Cannizzaro reaction, whilst 4 : 5-dibromomethylenedioxybenzene is unaffected.

Other methods (lit.) of opening the methylenedioxy-ring are reviewed. H. BURTON.

Derivatives of *cyclo*hexanone including several new indicators. B. SAMDAHL (J. Pharm. Chim., 1930, [viii], **11**, 8—19).—The following compounds

were prepared by treatment of 1 mol. of the required *cyclo*hexanone with 2 mols. of the appropriate aldehyde dissolved in hot acetic acid through which a current of hydrogen chloride was passing : *di*-5-*bromovanillylidenecyclohexanone*, m. p. 222—224° (decomp.); *di*-5-*bromovanillylidene*-m- and -p-*methylcyclohexanones*, m. p. 171° [+EtOH, m. p. 120° (decomp.)] and 189°, respectively; *di*-5-*nitrovanillylidenecyclohexanone*, m. p. 241—242° (decomp.); *di*-4-*hydroxy*-3-*ethoxybenzylidenecyclohexanone*, m. p. 158° (corresponding *derivatives* of m- and p-methyl-*cyclo*hexanones have m. p. 153° and 148—149°, respectively); *di* - 3 : 4 - *dihydroxybenzylidenecyclohexanone*, m. p. 242—245° (decomp.), and *di*-3 : 4-*dihydroxybenzylidene*-m- and -p-*methylcyclohexanones*, m. p. 242—245° (decomp.) and 221—223° (decomp.), respectively.

Several of these compounds may be of use as indicators. Their colour changes from yellow to orange between p_H 6·8 and 7·0, passing through red to violet at about p_H 11·7. R. J. W. LE FÈVRE.

Constitution of so-called tetrahydropyrone compounds. R. CORNUBERT (Compt. rend., 1930, **190**, 308—309).—Reduction of benzylidene-2 : 2-dimethyl*cyclo*hexanone with hydrogen and a nickel catalyst gives 6-*benzyl*-2 : 2-*dimethylcyclohexanone*, b. p. 179°/29 mm., d^{13} 1·005, n_D^{13} 1·5251 (*oxime*, m. p. 145°; *semicarbazone*, m. p. 201—202° in 41% yield), whilst similar reduction of *benzylidene*-2-*methyl*cyclo*hexanone* affords 6-benzyl-2-methyl*cyclo*hexanone (*oxime*, m. p. 115°; *semicarbazone*, m. p. 163—164° in 58% yield). Benzylation of 2 : 6-dimethyl*cyclo*hexanone gives 6-*benzyl*-2 : 6-*dimethylcyclohexanone*, b. p. 174°/22 mm., $d^{18.3}$ 1·014, $n_D^{18.3}$ 1·5297 (*oxime*, m. p. 155—156°; gives only a trace of semicarbazone with great difficulty), together with a small quantity of the 2 : 6-*dibenzyl* derivative, m. p. 78°, as a by-product. Of the above *cyclo*hexanones only the 2 : 6-dimethyl and 6-benzyl-2-methyl derivatives give so-called tetrahydropyrone condensation products with 2 mols. of benzaldehyde in the presence of hydrochloric acid. This condensation probably involves the hydrogen atoms in the α-positions to the carbonyl group.

J. W. BAKER.

Benzylpinacolones and their reduction products. I. G. A. HILL and W. F. BRUCE (J. Amer. Chem. Soc., 1930, **52**, 347—351).—Treatment of the sodium derivative of methyl *tert.*-butyl ketone (prepared by the action of sodamide in dry ether) with benzyl chloride gives a mixture of β-phenylethyl *tert.*-butyl ketone, b. p. 132°/10 mm., d_4^{20} 0·9483, n_D^{20} 1·4999 (cf. A., 1923, i, 789), and *dibenzylmethyl* tert.-*butyl ketone*, m. p. 49° (crystallographic data given). *Tribenzylmethyl* tert.-*butyl ketone*, b. p. 268·9° (corr.)/8 mm., m. p. 161·5° (corr.) (crystallographic data given), is obtained similarly, using toluene as the solvent. Reduction of the above ketones with sodium and alcohol affords β-*phenylethyl*-tert.-*butylcarbinol*, b. p. 145·5° (corr.)/15·5 mm., d_4^{20} 0·9578, n_D^{20} 1·5097 (cf. *loc. cit.*) [*phenylcarbimide* derivative, m. p. 88·1° (corr.)], *dibenzylmethyl*-tert.-*butylcarbinol*, b. p. 206—208°/15 mm., d_{20}^{20} 1·005 (*phenylcarbimide* derivative, m. p. 148°), and *tribenzylmethyl*-tert.-*butylcarbinol*, m. p. 156·5° (crystallographic data given),

respectively. Reduction of β-phenylethyl *tert.*-butyl ketone with red phosphorus and 57% hydriodic acid at 180—190°, with subsequent treatment of the mixture with zinc and dilute sulphuric acid, furnishes *α-phenyl-δδ-dimethylpentane*, b. p. 115°/9 mm., d_4^{20} 0·9443, n_D^{20} 1·5281.   H. BURTON.

Electrolytic reduction of ketones. I. αβ-Unsaturated ketones. G. SHIMA (Mem. Coll. Sci. Kyōtō, 1929, **A**, **12**, 327—337).—Electrolytic reduction of styryl methyl ketone to β-phenylethyl methyl ketone is best carried out at 30—35°, using a lead or platinum anode, a mercury cathode, an aqueous-alcoholic solution of sodium hydrogen carbonate as the cathode solution, 5% sodium hydroxide as the anode solution, and a current density of 6—8 amp./100 cm.² The yield is about 90%. With aqueous-alcoholic sodium hydroxide as the cathode solution, benzylacetone, dibenzyldiacetone, m. p. 161°, *αζ-diphenyl-γδ-dimethyl-Δ^{αε}-hexadiene-γδ-diol*, b. p. 194—195°/3 mm., d^{20} 1·0842, and resinous material are obtained. With cathode materials other than mercury, the formation of dimeric products is favoured.

Reduction of phenyl styryl ketone in ethereal-alcoholic solution containing sodium hydrogen carbonate at 20—25°, gives a 70—75% yield of phenyl β-phenylethyl ketone; at 35—40°, *αδ-dibenzoyl-βγ-diphenylbutane* and *αγδζ-tetraphenyl-Δ^{αε}-hexadien-γδ-ol*, m. p. 194—195°, are also produced. The last-named substance, contrary to the statement of Harries and Hübner (A., 1897, i, 549), is also produced when phenyl styryl ketone is reduced with sodium amalgam and acidified alcohol. If the electrolytic reduction is carried out in absence of the ether, resinous products are formed in large amount.

H. BURTON.

Action of alcoholic hydrochloric acid on unsaturated ketones. B. COFFEY and H. RYAN (Proc. Roy. Irish Acad., 1929, **39**, **B**, 107—113).—Styryl ethyl ketones are converted by the action of cold alcoholic hydrogen chloride, or alcoholic stannic chloride, into dimerides to which, in accordance with the structures assigned by Staudinger and Breusch (A., 1929, 434) to the dimerides of α-methylstyrene derivatives, the constitution $\begin{array}{c}\text{CHR·CH·COEt}\\\text{CHR·CH·COEt}\end{array}$ is assigned. Thus styryl ethyl ketone gives the *substance* $C_{22}H_{24}O_2$ (I) (R=Ph), m. p. 195—196°, which does not form a phenylhydrazone or a semicarbazone, will not condense further with piperonal or methyl ethyl ketone, is stable to potassium permanganate in acetone, is not reduced either by sodium amalgam in alkaline solution or by phosphorus and hydrogen iodide in acetic acid, but reacts with bromine in acetic acid to give the *substance* $C_{22}H_{24}O_2Br_3$, m. p. 171—172°. With hydroxylamine hydrochloride in aqueous-alcoholic sodium carbonate solution, I is converted into a *substance*, m. p. 242—243°, which by treatment with phosphoric oxide in boiling benzene gives another *substance*, m. p. 249°. Similar condensation of *p*-methoxystyryl and 3 : 4-methylene-dioxystyryl ethyl ketones gives the *substances* $C_{24}H_{28}O_4$ (R=MeO·C_6H_4), m. p. 199—200°, and $C_{24}H_{24}O_6$ (R=CH_2O_2:C_6H_3), m. p. 202°, respectively.

J. W. BAKER.

Mechanism and application of the Fries reaction. E. H. COX (J. Amer. Chem. Soc., 1930, **52**, 352—358).—When *m*-tolyl butyrate is treated with aluminium chloride in presence of diphenyl ether and carbon disulphide, the carbon disulphide removed after a short time by distillation, and the residue then heated at from 100° to 175°, 4-*butyryldiphenyl ether*, m. p. 50°, and 6-*butyryl-m-cresol*, m. p. 88°, are obtained. Similarly, *o*-tolyl acetate furnishes 4-acetyldiphenyl ether and 5-acetyl-*o*-cresol; *p*-tolyl acetate yields 4-acetyldiphenyl ether and 3-acetyl-*p*-cresol, and *o*-tolyl benzoate gives 4-benzoyldiphenyl ether and 5-benzoyl-*o*-cresol. The results support Skraup and Poller's conclusion (A., 1925, i, 143) that an acid chloride is an intermediate product in the Fries reaction.

Treatment of methyl 2-acyloxybenzoates with aluminium chloride in presence of carbon disulphide, and subsequent short heating of the solvent-free residue, affords methyl 5-acylsalicylates. These are hydrolysed to the free acids, of which the following are described: 5-*propionyl*-, m. p. 177—179° (*methyl* ester, m. p. 64—65°); 5-*butyryl*-, m. p. 152—153° (*methyl* ester, m. p. 73°); 5-*isohexoyl*-, m. p. 132—133·5° (*methyl* ester, b. p. 195—198°/15 mm.), and 5-*hexoyl-salicylic acids*, m. p. 117° (*methyl* ester, m. p. 50—51°). Reduction of these acyl derivatives by Clemmensen's method gives 5-*propyl*-, m. p. 99—100°; 5-*butyl*-, m. p. 84—86°; 5-*isohexyl*-, m. p. 104—105°, and 5-*hexyl-salicylic acids*, m. p. 83—84°, respectively. These acids are more toxic than salicylic acid, but possess higher phenol coefficients.

H. BURTON.

Derivatives of *p*-methoxy-α-methylstyryl methyl ketone. H. RYAN, P. M'GEOWN, and J. KEANE (Proc. Roy. Irish Acad., 1929, **39**, **B**, 132—141).—By the action of various aromatic aldehydes (1 mol.) on *p*-methoxy-α-methylstyryl methyl ketone (Iwamoto, A., 1927, 566) in the presence of aqueous-alcoholic potassium hydroxide, various *cyclo*pentenone derivatives of the type CO$<\begin{array}{c}\text{CH=CR}\\\text{CMe·CH·}C_6H_4\text{·OMe}\end{array}$ (I) have been prepared. Thus with the appropriate aldehyde are obtained 4-*phenyl-3-anisyl-2-methyl*- (R=Ph), m. p. 57—59°; 3 : 4-*dianisyl-2-methyl*- (R=C_6H_4·OMe), m. p. 88·5—90° (which could not be converted into a crystalline isomeride by the action of alcoholic hydrogen chloride), and 3-*anisyl-4-piperonyl-2-methyl*- (R=C_6H_3:O_2CH_2), m. p. 113—114°, -Δ⁴-cyclo*pentenones*. When *p*-methoxy-α-methylstyryl methyl ketone is condensed with 2 mols. of the aldehyde in the presence of alcoholic hydrogen chloride or when a further mol. of the aldehyde reacts with the above condensation products, the following are obtained: 4-*phenyl-3-anisyl-5-benzylidene-2-methyl*-, m. p. 150—151°; 3 : 4-*dianisyl-5-anisylidene-2-methyl*-, m. p. 158—160°, and 3-*anisyl-4-piperonyl-5-piperonylidene-2-methyl*-, m. p. 172—174°, -Δ³-cyclo*pentenones*.

J. W. BAKER.

Condensation of aldehydes with ethyl benzylacetoacetate. H. RYAN, W. B. CORNELIA, and P. HURLEY (Proc. Roy. Irish Acad., 1929, **39**, **B**, 142—145).—Anisaldehyde condenses with ethyl benzylacetoacetate in cold aqueous-alcoholic sodium

hydroxide to give, initially, α-p-*methoxycinnamoyl-β-phenylpropionic acid*,
$MeO \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot CH(CH_2Ph) \cdot CO_2H$, m. p. 147°
(decomp.), which is converted on keeping in the reaction mixture into p-*methoxystyryl β-phenylethyl ketone*, m. p. 89° (*phenylhydrazone*, m. p. 119—120°). Similar condensation with piperonal gives 3 : 4-*methylenedioxystyryl β-phenylethyl ketone*, m. p. 137°, the intermediate derivative, m. p. 150° (decomp.), not being investigated. J. W. BAKER.

Reaction of aniline and benzoin. C. N. CAMERON (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 53—60).—So-called benzoinanil (desylaniline), m. p. 99°, is obtained either by interaction of desyl chloride with aniline (Bischler and Fireman, A., 1893, i, 519), or by the condensation of benzoin and aniline (Voigt, A., 1886, 887), preferably in boiling dilute alcoholic acetic acid. Bromination yields successively *p*-bromodesylaniline, m. p. 171° (lit. 168°), and *tri-bromodesylaniline*, m. p. 157°, identical with the products obtained synthetically. *Benzil-p-bromoanil* has m. p. 97°. Methylation of desylaniline with methyl iodide alone (silver oxide causes oxidation) gives the N-*methyl* derivative, m. p. 100°, also obtained from desyl chloride and methylaniline. The N-acetyl derivative is obtained in poor yield by acetylation or by condensation of benzoin with acetanilide or sodio-acetanilide. These reactions establish that desyl-aniline is not an anil.
Phenyl anilinodiphenylmethyl ketone (α-phenyl-desylaniline), m. p. 182°, obtained by interaction of aniline and α-phenyldesyl chloride, is, on the other hand, distinct from *phenylbenzoinanil*, m. p. 168°. The latter is not obtainable by condensation of phenyl-benzoin with aniline, but is obtained in poor yield by the action of magnesium phenyl bromide on benzilanil. In this case the replacement of the mobile hydrogen has made the transformation of anil to anilide impossible. *Phenyl α-anilino-α-phenylethyl ketone* (α-methyldesylaniline), m. p. 105—106°, is obtained from methylbenzoin by interaction of the chloro-compound (not isolated) with aniline. Methylbenzoin-anil could not be prepared. R. K. CALLOW.

Mixed benzoins. I. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1930, **52**, 220—224).—Aldehydes forming simple benzoins possess both a reactive carbonyl group and a mobile hydrogen atom (cf. Staudinger, A., 1913, i, 1354) and are termed type 1; the rate of formation of the benzoin is a qualitative measure of either carbonyl reactivity or hydrogen mobility. Aldehydes not forming simple benzoins have either a reactive carbonyl group or a mobile hydrogen atom; these are designated type 2. By the regulated addition of an aldehyde of type 1 (benzoin formation normally rapid) to an aqueous-alcoholic solution of an aldehyde of type 1 (slow benzoin formation) or type 2, containing potassium cyanide it is possible to synthesise mixed benzoins. The following are described: *furfuroyl-p-dimethyl-aminophenylcarbinol*, m. p. 168°; o-*chlorobenzoyl-p-dimethylaminophenyl-*, m. p. 166°; m-*bromobenzoyl-p-dimethylaminophenyl-*, m. p. 145°; *benzoyl-3 : 4-methylenedioxyphenyl-*, m. p. 120°; 3 : 4-*methylene-dioxybenzoylphenyl-*, m. p. 112°; *benzoyl-m-bromo-*

phenyl- (?), m. p. 129—130°; 3 : 4-*methylenedioxy-benzoyl-m-bromophenyl-* (?), m. p. 106°, and 3 : 4-*methylenedioxybenzoyl - o - chlorophenyl - carbinol* (?), m. p. 115°. H. BURTON.

Dioximes. LVII. G. PONZIO and M. TORRES (Gazzetta, 1929, **59**, 718—723).—The conditions of formation of several dioximes from oximinoketones, $R \cdot CO \cdot C(N \cdot OH) \cdot R'$, are investigated with special reference to the yields of the two forms at different hydrogen-ion concentrations. The α- and β-forms are separated as the copper and nickel salts, respectively. Oximinoacetophenone yields dioximes in acid solution only. Phenyl oximinoethyl ketone yields no dioxime in neutral solution, mixtures in acid solution, and only the β-form in alkaline solution. Oximinobenzyl methyl ketone yields only the β-form in acid, neutral, or alkaline solution. Oximino-benzoylacetone yields mixtures in acid solution, the β-form only in neutral solution, and no dioxime in alkaline solution. The proportions of α- and β-forms, when both are obtained, vary with the hydrogen-ion concentration. In no case is the α-form obtained exclusively. The variation in behaviour is assigned to the influence of hydrogen-ion concentration on the configuration of either the existent or entrant oximino-group. The different behaviour of the oximino-groups of isomeric oximinoketones to certain reagents has previously been noted (Gazzetta, 1901, **31**, 133). The behaviour is similar, however, on methylation. β-*Phenylmethylglyoxime methyl ether*, $CPh(N \cdot OMe) \cdot CMe:N \cdot OH$, m. p. 162°, is prepared by treating oximinobenzyl methyl ketone with methyl sulphate and alkali, and heating the oily product with hydroxylamine hydrochloride. It is converted into the dimethyl ether (Avogadro and Tavola, A., 1925, i, 1040) when methylated. An improved method of preparing α-phenylmethylglyoxime (Avogadro, A., 1924, i, 1202) is described, in which the β-compound is removed by crystallisation and precipitation of the nickel salt from the mixture obtained from hydroxyl-amine and phenyl oximinoethyl ketone.
R. K. CALLOW.

Benzilic acid rearrangement. T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, **52**, 252—254).—When benzil is treated with an equimolecular quantity of solid potassium hydroxide in dry ether at the ordinary temperature for 4 days, potassium benzilate is obtained; water is not necessary for the reaction. An additive compound is first formed, which undergoes molecular rearrangement in the solid phase. Similar results are obtained using furil. H. BURTON.

Inner complex salts of α-benziloxime. P. PFEIFFER and H. BUCHHOLZ (J. pr. Chem., 1930, [ii], **124**, 133—143).—*cis* - Hydroxyaquo - diethylene - diaminecobaltic bromide, $[en_2Co(OH_2)(OH)]Br_2$, condenses with α-benzilmonoxime in alcoholic solution to the orange-coloured complex *bromide*, $[en_2Co(C_{14}H_{10}O_2N)]Br_2 + 3H_2O$ (*iodide* $+xH_2O$; *thiocyanate*; *perchlorate* $+H_2O$; *dichromate*; *hexanitro-cobaltiate* $+8H_2O$). This salt is formulated as $\left[en_2Co \underset{O=CPh}{\overset{NO:CPh}{<}} \right] Br_2$, the oxime residue occupying two co-ordination positions. Analogous constitutions

are assigned to the cobalt salt of nitroso-β-naphthol, the nickel salt of dimethylglyoxime, and to Tschugaev's dioxime cobaltic salts. α-Benzilmonoxime and sodium cobaltinitrite in warm alcoholic solution give the *compound* [Co(C$_{14}$H$_{10}$O$_2$N)$_3$].

A. I. VOGEL.

Diacylstyrenes. II. C. F. H. ALLEN and J. R. HUBBARD (J. Amer. Chem. Soc., 1930, **52**, 384—386).—Benzil condenses with 2-acetylthiophen, 2-acetylfuran, β-naphthyl methyl ketone, 4-acetyldiphenyl, *p*-ethylacetophenone, and 3 : 4-dichloroacetophenone under the conditions previously described (A., 1927, 971), yielding 2-*thiophenyl β-benzoylstyryl ketone*, m. p. 152°, 2-*furyl β-benzoylstyryl ketone*, m. p. 168°, α-*benzoyl-β-naphthoylstyrene*, m. p. 152°, α-*benzoyl-β-p-phenylbenzoylstyrene*, m. p. 132°, α-*benzoyl-β-p-ethylbenzoylstyrene*, m. p. 117°, and α-*benzoyl-β-3 : 4-dichlorobenzoylstyrene*, m. p. 199°, respectively. α-Naphthyl methyl ketone and 2 : 4-dihydroxyacetophenone do not condense with benzil, nor does acetophenone condense with 2 : 2'-dimethoxybenzil. Groups in the *o*-position of either component appear to prevent condensation (cf. *loc. cit.*).

H. BURTON.

Influence of substituents on the benzoin reaction. H. H. HODGSON and W. ROSENBERG (J.C.S., 1930, 14—18).—The effect of substituents on the benzoin reaction is considered from the point of view both of the intermediate mandelonitrile and of the hypothetical intermediate benzoin cyanohydrin (cf. Lapworth, J.C.S., 1903, **83**, 1004). On the first consideration it is shown that the electronic influences on the activity of the labile hydrogen atom of the mandelonitrile and the carbonyl group of the benzaldehyde are in opposite direction, with the net result of inhibition to a greater or smaller degree of the formation of benzoin. The following are described : 2 : 2'-*dichlorobenzoin*, m. p. 56—57° ; 2 : 2'-*dichlorobenzil*, m. p. 128° ; 3 : 3'-*dimethoxybenzoin*, m. p. 41—42° ; 2 : 2'-*dichloro-3 : 3'-dimethoxybenzoin*, m. p. 133—134° (p-*nitrophenylhydrazone*, m. p. 129°) ; 2 : 2'-*dichloro-3 : 3'-dimethoxybenzil*, m. p. 200° ; 2 : 2'-*dichloro-3 : 3'-dimethoxybenzilic acid*, m. p. 182—185° ; 2-*chloro-3-methoxybenzoic acid*, m. p. 161·5°.

H. A. PIGGOTT.

Action of phenylhydrazine on substituted anilinoquinones. M. COVELLO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], **35**, 86—89).—By the interaction of an alcoholic solution of phenylhydrazine with concentrated solutions of tetra-substituted *p*-benzoquinones, or the powdered solids, *phenylhydrazides* [*monophenylhydrazones*] of the following have been prepared : 3 : 5-*ditoluidino*-2 : 6-*diphthalimidobenzoquinone*, decomp. about 275° ; 3 : 5-*dianisidino*-2 : 6-*diphthalimidobenzoquinone*, decomp. about 290° ; 3 : 5-*ditoluidino*-2 : 6-*disuccinimidobenzoquinone*, m. p. 202—203° ; 3 : 5-*dianisidino*-2 : 6-*disuccinimidobenzoquinone*, m. p. 256—259°. The usual red colorations are given with nitric or sulphuric acid.

R. K. CALLOW.

Action of hydroxylamine on substituted anilinoquinones. M. COVELLO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], **35**, 90—95).—By the interaction of hydroxylamine hydrochloride (2 mols.)

with tetra-substituted *p*-benzoquinones in boiling alcoholic solution *dioximes* of the following have been prepared : 3 : 5 - *ditoluidino* - 2 : 6 - *diphthalimido*-, m. p. 232—235° ; 3 : 5-*dianisidino*-2 : 6-*diphthalimido*-, m. p. 247—248° ; 3 : 5-*ditoluidino*-2 : 6-*disuccinimido*-, m. p. 208—210° ; and 3 : 5-*dianisidino*-2 : 6-*disuccinimido-benzoquinone*, m. p. 155—156°. Characteristic colorations are given with Liebermann's reagent. Treatment of the quinones with hydroxylamine in alkaline solution merely brings about reduction to the quinols.

R. K. CALLOW.

Action of alkali on 2-aminoanthraquinone at 150°. T. MAKI (J. Soc. Chem. Ind. Japan, 1929, **32**, 303—305B).—The product obtained by heating 2-aminoanthraquinone with potassium hydroxide (75%) at 150° for 2 hrs., after treatment with water and aëration has the following composition. (i) Soluble in water 5%, mainly benzoic acid ; (ii) soluble in ammonia, 22·5%, chiefly alizarin ; (iii) soluble in potassium hydroxide, 17·5%, 2-amino-1-hydroxyanthraquinone (acetyl derivative, m. p. 247°, uncorr. 242°, cf. lit.) ; (iv) soluble in hot nitrobenzene, unchanged 2-aminoanthraquinone, 42% ; (v) insoluble in hot nitrobenzene, 13%, pure indanthrone. The maximum yield of indanthrone (19%), or allowing for recovered 2-aminoanthraquinone, 27%) is obtained after heating for 4 hrs.

When 2-aminoanthraquinone is added to molten alkali at 150°, a dark violet colour appears ; if a specimen of the mass be removed immediately and treated with water, 2-aminoanthraquinone is regenerated without formation of detectable quantities of alkali-soluble products ; with increasing time the latter appear in increasing quantity. It is suggested that the violet colour is to be associated with the compound (I), which is probably the active intermediate in the formation of indanthrene and 2-amino-1-hydroxyanthraquinone.

C. W. SHOPPEE.

Formation-curve of 2-aminoanthraquinone in the presence of sodium dichromate. T. MAKI (J. Soc. Chem. Ind. Japan, 1929, **32**, 344—347B).—Conditions for the production of 2-aminoanthraquinone from sodium anthraquinone-2-sulphonate and aqueous ammonia at 200° in the presence of sodium dichromate (cf. G.P. 256515) have been systematically investigated. If the reaction period is prolonged above 20 hrs., a blackish-brown by-product is produced, with consequent decrease in the yield of 2-aminoanthraquinone. The optimum period at 200° is about 15 hrs. The highest yield of 2-aminoanthraquinone is obtained using 0·50 mol. of dichromate (theory requires 0·33 mol.). The yield of 2-aminoanthraquinone increases with increasing concentration of ammonia up to 16%, but not with higher concentration. The highest yield obtained, at 200° in 15 hrs., using excess of 16·13% ammonia, is 63% of theory.

C. W. SHOPPEE.

Anthraquinoneazo-compounds. I. Some anthraquinoneazo-β-naphthols. T. MAKI (J. Soc. Chem. Ind. Japan, 1929, **32**, 347—352B).—2-Aminoanthraquinone is diazotised in cold concentrated

sulphuric acid, the diazo-compound filtered and coupled with an alkaline solution of β-naphthol. Anthraquinone-2-azo-β-naphthol (I) is readily soluble in acetylene tetrachloride, and crystallises therefrom in scarlet needles, m. p. 267·8° (corr.). It is slowly sulphonated by concentrated sulphuric acid in the cold, more rapidly on heating; the azo-group is reduced by sodium hyposulphite, whilst molten potash furnishes some indanthrone. 1-Aminoanthraquinone similarly affords *anthraquinone*-1-*azo*-β-*naphthol* (II), m. p. 305·8° (corr.), and 1 : 5-diamino-anthraquinone yields *anthraquinone*-1 : 5-*bisazo*-β-*naphthol* (III), m. p. 389° (corr.; decomp.); II and III are readily sulphonated. All three dyes colour acetate silk when used in colloidal suspension or emulsion. Their water-soluble sulphonic acids behave as acid dyes, whilst that from III exhibits, to some degree, a substantive nature and dyes cotton rose.
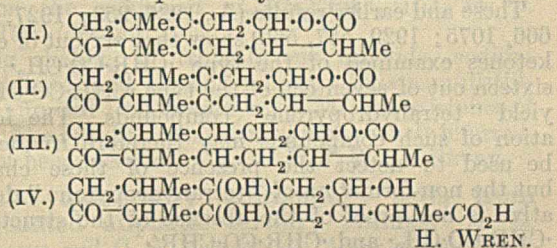
The absorption curves and extinction coefficients of I, II, and III, in acetylene tetrachloride and sulphuric acid (concentrated) solution have been determined; in the first-named solvent, the absorption maxima (Å.) and maximal extinction coefficients are : I, 5100, 0·348; II, 5180, 0·335; III, 5490, 0·465. In concentrated sulphuric acid, 1—2 hrs. after preparation of the solution the corresponding figures are : I, 6480, 0·330; II, 5880, 0·255; III, 5960, 0·615. As sulphonation gradually occurs, the absorption maxima change with time, finally having the values, 6140, 5640, and 5700, respectively. C. W. SHOPPEE.

Velocity of decomposition of indanthrone by molten alkali. T. MAKI (J. Soc. Chem. Ind. Japan, 1929, **32**, 300—303B).—Contrary to the general assumption that indanthrone is not decomposed by alkali below 300° (cf. Scholl, A., 1904, i, 109, 110; "Das Anthracen u. die Anthrachinone," Leipzig, 1929), it is found that extensive decomposition occurs at a much lower temperature. From the alkali-soluble decomposition products, benzoic acid and a water- and ether-insoluble brown, amorphous powder containing about 10% N were isolated. Finely-powdered indanthrone (1 mol.) was treated with potassium hydroxide (36 mols.) and water (37 mols.) in a nickel vessel with continuous stirring (a) for 1 hr. at temperatures from 150° to 290°, and (b) at 250° for varying periods. (a) Decomposition occurs to the extent of 8% at 150°, 16% at 180°, 25% at 200°, 61% at 250°, and 85% at 290°. (b) Decomposition takes place rapidly, 36% and 48% of indanthrone being destroyed in 15 and 30 min., respectively. The time–decomposition curve appears to correspond closely with a reaction of the third order (mean velocity coefficient $K=0·047$ min.$^{-1}$), but from the decomposition products isolated, the main phase of the reaction must be of the fifth order at least. It is concluded that the usual temperature (about 250°) employed for the production of indanthrone is dangerously high. C. W. SHOPPEE.

2 : 4 - Dichloro - 1 - aminoanthraquinone. I. GUBELMANN, H. J. WIELAND, and O. STALLMANN.— See B., 1930, 94.

Santonin. XIV. Dihydrosantonin. E. WEDEKIND, T. GOOST, and I. JÄCKH (Ber., 1930, **63**, [B],

50—56; cf. A., 1915, i, 705).—Reduction of santonin according to the method of Wedekind and Beniers (A., 1913, i, 476) yields a mixture of tetrahydrosantonin and an oil from which, after treatment with hydroxylamine, dihydrosantoninoxime, m. p. 230°, [α]$_D^{18}$ +118° in methyl alcohol, is obtained (cf. Cusmano, A., 1913, i, 864). Decomposition of the oxime with cold hydrochloric acid in presence of formaldehyde yields dihydrosantonin (II), m. p. 105°, [α]$_D^{18}$ +75·3° in ethyl alcohol (cf. Cusmano, *loc. cit.*). The dihydro-compound absorbs 2 atoms of hydrogen per mol. in methyl alcohol in presence of palladised charcoal, giving tetrahydrosantonin (III). Dihydrosantonin is readily converted by ozone into a mixture of acids which could not be separated into its components. Potassium permanganate in acetone transforms it into a *dihydroxydihydrosantoninic acid* (IV), m. p. 198°, [α]$_D^{18}$ +448° in ethyl alcohol, which, when distilled in a vacuum, loses carbon dioxide and yields a mixture of compounds. The relationships of santonin (I) to its derivatives are expressed by the formulæ :

(I.) $\begin{array}{l}CH_2 \cdot CMe \vdots C \cdot CH_2 \cdot CH \cdot O \cdot CO \\ CO \quad CMe \vdots C \cdot CH_2 \cdot CH \quad CHMe\end{array}$

(II.) $\begin{array}{l}CH_2 \cdot CHMe \cdot C \cdot CH_2 \cdot CH \cdot O \cdot CO \\ CO \quad CHMe \cdot C \cdot CH_2 \cdot CH \quad CHMe\end{array}$

(III.) $\begin{array}{l}CH_2 \cdot CHMe \cdot CH \cdot CH_2 \cdot CH \cdot O \cdot CO \\ CO \quad CHMe \cdot CH \cdot CH_2 \cdot CH \quad CHMe\end{array}$

(IV.) $\begin{array}{l}CH_2 \cdot CHMe \cdot C(OH) \cdot CH_2 \cdot CH \cdot OH \\ CO \quad CHMe \cdot C(OH) \cdot CH_2 \cdot CH \cdot CHMe \cdot CO_2H\end{array}$

H. WREN.

Constitution of cyclanones. I. R. CORNUBERT and C. H. R. BORREL (Bull. Soc. chim., 1929, [iv], **45**, 1148—1161).—In presence of hydrogen chloride at −15°, benzaldehyde and *l*-menthone, [α]$_D^{12}$ −28·67°, give 65% of benzylidenementhone hydrochloride, m. p. 140° (cf. Martine, A., 1904, i, 903), but no "tetrahydropyrone" compound. Thujone after 24 hrs. gives benzylidenethujone, b. p. 190—210°/17 mm., and a "tetrahydropyrone" *compound*, m. p. 115—115·5°, converted in benzene solution or by fusion into an isomeric *compound*, m. p. 147—147·5°, from which the original compound, m. p. 115°, could not be regenerated. 1-Methyl*cyclo*pentanone similarly gives an oil, b. p. 153—154°/12 mm., forming a *semicarbazone*, m. p. 180—181° (decomp.) (*benzylidene*-1-*methyl*cyclopentanone has m. p. 57°, b. p. 187—188°/23 mm.; *semicarbazone*, m. p. 205°), and a tetrahydropyrone *compound*, m. p. 105—105·5°, b. p. 230—240°/13 mm., which by evaporation of its solution in benzene is converted into an *isomeride*, m. p. 125°. The latter is obtained direct when hydrogen bromide is used for the condensation, and could not be converted into the isomeride of lower m. p. The structures

m. p. 125°.   m. p. 105°.
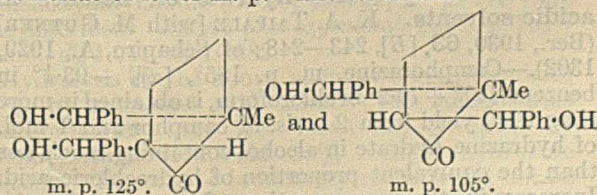
are suggested, but the possibility of isomerism in the pyrone ring is admitted.

1:5-Dimethyl-Δ^1-*cyclo*hexen-3-one, b. p. 94°/17 mm.,

134°/80 mm., 1:5:5-trimethyl-Δ^1-*cyclo*hexen-3-one (*isoacetophorone*), b. p. 95°/16 mm., 137°/90 mm. (*benzylidene* derivative, m. p. 78·5—79°), and 1-methyl-5-*isopropyl*-Δ^1-*cyclo*hexen-3-one, b. p. 121°/16 mm. (*benzylidene* derivative, m. p. 91—92°), when condensed with benzaldehyde in presence of hydrogen chloride or sodium ethoxide give the corresponding benzylidene derivatives, but no pyrone derivative, although traces of viscous oils of high b. p. are formed in each case. 2-*Benzyl*-6-*methyl*cyclohexanone, b. p. 167°/20 mm., obtained (yield 90%) by catalytic hydrogenation of benzylidene-2-methyl*cyclo*hexanone in presence of platinum or nickel reacts with benzaldehyde to give a theoretical yield of a *substance*, $C_{28}H_{28}O_2$, m. p. 196°. 2:6-Dibenzyl*cyclo*hexanone, m. p. 121—122°, similarly obtained by hydrogenation in presence of nickel, does not condense with benzaldehyde. When obtained by hydrogenation in presence of platinum, an oil, b. p. 235—240°/17 mm., is also obtained, and in one experiment the product $C_{20}H_{22}O$ had m. p. 103° (? an isomeric dibenzyl*cyclo*hexanone).

These and earlier results (A., 1926, 953; 1927, 152, 666, 1075; 1929, 557, 560) show that six out of eight ketones examined of the type ·CHR·CO·CH₂· and sixteen out of seventeen of the type ·CHR·CO·CHR'· yield "tetrahydropyrone" compounds. The formation of such compounds may therefore frequently be used to detect the presence of these chains, but the non-formation of "tetrahydropyrone" derivative is not proof of the absence of the structures ·CHR·CO·CH₂· and ·CHR·CO·CHR'·.
R. BRIGHTMAN.

Formation of cis-, cis-trans-derivatives in the terpene group. K. SŁAWIŃSKI and S. HOFSZAJN (Rocz. Chem., 1929, 9, 747—753).—Terpineol acetate *cis*-dibromide and sodium acetate give sobrerol and pinol. This result confirms Wagner's theory (A., 1899, i, 766) that Wurtz's method for the introduction of hydroxyl groups leads to the formation of *cis*-derivatives, whilst direct introduction by permanganate oxidation gives the *cis-trans*-isomerides.
R. TRUSZKOWSKI.

Action of Japanese acid clay on terpenes. I. Isomerisation of d-α-pinene. T. KUWATA (J. Fac. Eng. Tokyo, 1929, 18, 117—124, and J. Soc. Chem. Ind. Japan, 1929, 32, 372—373B).—When *d*-α-pinene, d_4^{20} 0·8585, n_D^{20} 1·4657, from American turpentine, is treated with 40% by weight of dry Japanese acid clay for 2 hrs., *d*-camphene (converted into *iso*borneol and its phenylurethane), *d*-limonene (tetrabromide and nitrosochloride), a small quantity of terpinene (?), and dipentene are produced.
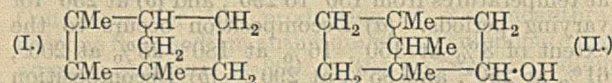A. I. VOGEL.

Action of hydrazine hydrate on ketones in acidic solvents. K. A. TAIPALE [with M. GUTNER] (Ber., 1930, 63, [B], 243—248; cf. Schapiro, A., 1929, 1302).—Camphorazine, m. p. 185°, $[\alpha]_D^5$ −93·1° in benzene, $[\alpha]_D^{20}$ +79·2° in chloroform, is obtained in more than 90% yield from 2 mols. of camphor and 1 mol. of hydrazine hydrate in alcohol containing much less than the equivalent proportion of hydrochloric acid. Increase in the concentration of the acid to the equivalent amount diminishes the yield to 50%. The azine is readily hydrogenated to s-*dibornylhydrazine*. In hot glacial acetic acid, camphor and hydrazine

hydrate afford camphoracetylhydrazone, m. p. 210°, $[\alpha]_D^{19}$ −35·5° in chloroform, catalytically reduced to *bornylacetylhydrazine*, m. p. 95°, $[\alpha]_D^{19}$ −53·1° in chloroform. The last-named substance is stable towards boiling water and alkalis, but is transformed by hydrochloric acid into *bornylhydrazine hydrochloride*, m. p. about 225° (decomp.). The hydrochloride is converted by potassium cyanate into *bornylsemicarbazide*, m. p. 191° (decomp.), and by benzoyl chloride and anhydrous sodium carbonate in benzene into *dibenzoylbornylhydrazine*, m. p. 199—200°. *Benzaldehydebornylhydrazone hydrochloride* has m. p. 116—117°. Fenchone in alcoholic hydrochloric acid solution gives a *ketazine*, m. p. 106°. Even with an excess of hydrazine hydrate in glacial acetic acid acetophenone affords exclusively the ketazine, m. p. 121—121·5°, whereas benzophenone gives the ketazine, m. p. 162—163°, and the acetyl derivative of benzophenonehydrazone.
H. WREN.

Lanthanum, cerous, neodymium, and samarium camphorates. L. CONIGLIO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 40—43).—The following *camphorates*, of the general formula $M_2[C_8H_{14}(CO_2)_2]_3,20H_2O$, have been prepared from solutions of the acetates and camphoric acid. The solubilities in water at 25° are given in parentheses: *lanthanum* (0·21%); *cerous* (0·29%) (cf. Morgan and Cahen, A., 1907, i, 1021); *neodymium* (0·24%); *samarium* (0·26%). All the salts lose water of crystallisation at moderate temperatures, but dehydration is complete only at 110°.
R. K. CALLOW.

Phenyl-substituted camphor and its derivatives. S. NAMETKIN, A. KITSCHKIN, and D. KURSANOV (J. pr. Chem., 1930, [ii], 124, 144—158).—See this vol., 216.

Catalytic dehydrogenation of fenchyl alcohol by aluminium phosphate; a new series of terpene and camphor compounds. N. J. TOIVONEN and E. TIKKANEN (Suomen Kem., 1929, 2, 169—176).—Dehydration of fenchyl alcohol at 190° with aluminium phosphate gives *mesantene* [α-*methylsantene*] (I), undergoing a Wagner rearrangement on hydration by the Bertram–Walbaum method to *mesantenol* (II) (*acetate*). This is oxidised by alkaline

$$
\text{(I.)}\quad
\begin{array}{c}
\text{CMe}\text{—CH}\text{—CH}_2 \\
| \quad\quad | \\
\text{CH}_2 \quad\quad | \\
| \quad\quad | \\
\text{CMe}\text{—CMe}\text{—CH}_2
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2\text{—CMe}\text{—CH}_2 \\
| \quad\quad | \\
\text{CHMe} \quad | \\
| \quad\quad | \\
\text{CH}_2\text{—CMe}\text{—CH·OH}
\end{array}
\quad\text{(II.)}
$$

potassium permanganate to *mesantenic acid*, m. p. 240° (decomp.) (*anhydride*, m. p. 93—94°), probably 1:2:3-*trimethylcyclopentane*-1:3-*dicarboxylic acid*, presumably by way of mesantenone, isomeric with camphor. The acid could not be resolved with cinchonidine.
A. I. VOGEL.

3′:4′-Dimethoxybenzyl-3:5-dimethoxycoumaranone. J. J. DRUMM, S. M. MAQUIRE, and H. RYAN (Proc. Roy. Irish Acad., 1929, 39, B, 121—123).—In the reduction of veratrylidene-3:5-dimethoxycoumaranone (Drumm and others, *ibid.*, 1924, 36, B, 152) to the dihydro-compound the carbonyl group remains unaffected, since the dihydrocompound (3′:4′:3:5-tetramethoxybenzoylcoumaranone) reacts with magnesium phenyl bromide in

benzene at 40—50° to give the corresponding *phenyl-carbinol*, m. p. 82·2—82·8°, converted by bromine in glacial acetic acid into a *monobromo*-derivative, m. p. 115°.　　　　　　　　　　　　J. W. BAKER.

Constitution of *isocatechin* tetramethyl ether.

J. J. DRUMM, R. J. P. CAROLAN, and H. RYAN (Proc. Roy. Irish Acad., 1929, **39**, B, 114—120).—On the basis of the results of Freudenberg (A., 1926, 73) and of the different properties of the chloride of catechin tetramethyl ether (Drumm, A., 1923, i, 1221) from those of the pyrylium chloride synthesised by Robinson (A., 1924, i, 306) the structure assigned to dehydrocatechin tetramethyl ether by the second author is corrected to I, with corresponding alterations in the structure of the pyrylium salt. Thus the action of

(I.)　MeO ⟨ring⟩ CH ⟨ring⟩ OMe
　　　　　O　　　　OMe
　　　OMe CH₂　　　C OMe
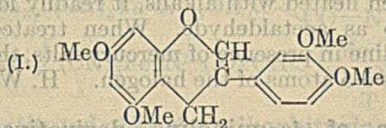
phosphorus pentachloride on catechin tetramethyl ether involves a wandering of the veratryl group. The following results are considered to be in agreement with this view. The substance previously called ethylcatechin tetramethyl ether (Drumm, *loc. cit.*) is renamed B-*catechin tetramethyl ethyl ether*, $[\alpha]_D^{16}$ +119° (all rotations in tetrachloroethane), the corresponding B-*catechin pentamethyl ether*, m. p. 80—81°, $[\alpha]_D^{16}$ +42°, being obtained similarly by the action of boiling methyl alcohol on the chloride of catechin tetramethyl ether. Cold acetic acid converts the last-named substance into the *acetate*, m. p. 154—155°, $[\alpha]_D^{20}$ +171°, of B-catechin tetramethyl ether, hydrolysed by boiling alcoholic hydrogen chloride to B-*catechin tetramethyl ether*, m. p. 121—122°. Methyl alcohol converts the pyrylium monobromide (Drumm, *loc. cit.*) into the methoxy-colour *base*, m. p. 116—117°, to which the structure II (alternative positions of ethoxy-group

(II.)　MeO ⟨ring⟩ CH·OEt ⟨ring⟩ OMe
　　　　　O　　　　　OMe
　　　OMe CH　　　C OMe
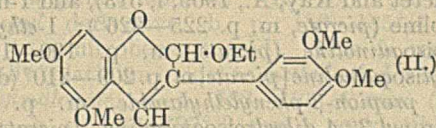
and the double linking) is now assigned. The base is converted by reduction with hydrogen and platinum-black into deoxycatechin tetramethyl ether (Drumm and others, Proc. Roy. Irish Acad., 1924, **36**, B, 152).
　　　　　　　　　　　　J. W. BAKER.

Preparation and oxidation of flavindogenides.

H. RYAN and G. CREUSS-CALLAGHAN (Proc. Roy. Irish Acad., 1929, **39**, B, 124—131).—Various arylidene-flavanones have been prepared by the action of the appropriate aldehyde on the flavanone in alcoholic hydrogen chloride, the experimental conditions varying slightly from case to case. Thus are obtained : 3-*benzylidene*-, m. p. 103—104° (oxidised by potassium permanganate to a *substance*, m. p. 163—164°); 3-*anisylidene*-, m. p. 148—149°; 3-*piperonylidene*-, m. p. 155—156°; and 3-*vanillylidene*-, m. p. 92—94°, *flavanone* : 3-*anisylidene*-, m. p. 136—137°, and 3-*piperonylidene*-, m. p. 145—147°, -4'-*methoxy-flavanone*; and 3-*piperonylidene*-, m. p. 183—185°,

and 3-*benzylidene*-, m. p. 161—163°, -3' : 4'-*methylene-dioxyflavanone*.　　　　　　　J. W. BAKER.

1 : 3-Dithiolan.

D. T. GIBSON (J.C.S., 1930, 12—14).—Addition of ethylene dimercaptan (prepared by boiling the product of reaction of ethylene dibromide, water, sodium thiosulphate, and alcohol with hydrochloric acid) to formaldehyde solution containing a trace of hydrochloric acid led to 1 : 3-*di-thiolan*, b. p. 175°/760 mm., 61°/11 mm., d^{17} 1·259, n_D^{15} 1·5975 (*mercurichloride*, m. p. 119°; *disulphone*, m. p. 224°), accompanied by a voluminous *polymeride*, m. p. 105—110°. 1 : 3-Dithiolan was more conveniently prepared by treating sodium ethylene thiosulphate with hydrochloric acid and twice the calculated amount of formaldehyde; with hydrogen peroxide in acetic acid solution it formed a *monoxide*, b. p. 115—120°/1 mm., decomposed by warm hydrochloric acid into dithiolan and a *dioxide*, m. p. 134°. With methyl iodide dithiolan monoxide gives a *methiodide*, m. p. 96°; and with platinic chloride solution the *compound* $(C_3H_5S_2)_2, PtCl_3, H_2O$, m. p. 146—150° (decomp.).

Long shaking of trimethylene bromide, sodium thiosulphate, and alcohol, followed by steam-distillation, afforded 1 : 3-*dithian*, m. p. 54°, the existence of which, like 1 : 3-dithiolan, although previously inferred, has not been recorded.　　R. J. W. LE FÈVRE.

Cyclic quaternary ammonium salts from halogenated aliphatic tertiary amines.

E. R. LITTMANN and C. S. MARVEL (J. Amer. Chem. Soc., 1930, **52**, 287—294).—Dimethyl-ω-bromoalkylamines, $Br \cdot [CH_2]_n \cdot NMe_2$, where $n = 4$—7, have been prepared by the action of hydrogen bromide on the corresponding ω-phenoxy-derivatives and their ease of conversion into the cyclic bromides, $[CH_2]_n > NMe_2Br$, has been studied. *Ethyl ε-phenoxyhexoate*, b. p. 157—159°/3 mm., d_{20}^{20} 1·031, n_D^{20} 1·4928 (the free acid is prepared from ethyl δ-phenoxybutylmalonate), is reduced by sodium and alcohol to ζ-phenoxyhexyl alcohol, b. p. 152—154°/3 mm., m. p. 31°. The *bromide*, b. p. 155—156°/3 mm., d_{20}^{20} 1·248, n_D^{20} 1·5361, from this reacts with dimethylamine, forming *dimethyl-ζ-phenoxy-hexylamine*, b. p. 132—134°/3 mm., d_{20}^{20} 0·942, n_D^{20} 1·4988 (*chloroplatinate*, m. p. 126°). *Ethyl ζ-phenoxy-heptoate*, b. p. 161—163°/3 mm., d_{20}^{20} 1·015, n_D^{20} 1·4932, is reduced similarly to η-*phenoxyheptyl alcohol*, b. p. 157—158°/3 mm., m. p. 34°, the *bromide*, b. p. 154—157°/3 mm., d_{20}^{20} 1·199, n_D^{20} 1·5240, of which reacts with dimethylamine, forming *dimethyl-η-phenoxyheptylamine*, b. p. 158—160°/6 mm., d_{20}^{20} 0·939, n_D^{20} 1·4980 (*chloroplatinate*, m. p. 162°). Dimethyl-δ-phenoxybutylamine (*chloroplatinate*, m. p. 104°) and dimethyl-ε-phenoxyamylamine (*chloroplatinate*, m. p. 112°) are also described. *Ethyl δ-phenoxyvalerate* has b. p. 151°/6 mm., d_{20}^{20} 1·041, n_D^{20} 1·4982.

Hydrolysis of the above phenoxy-derivatives with 48% hydrobromic acid affords the bromoamine hydrobromides; the free bases are obtained by decomposition with cold 28% sodium hydroxide solution. Dimethyl-δ-bromobutylamine could not be isolated owing to the ease with which it undergoes transformation into NN-*dimethylpyrrolidinium bromide*, not melted at 325° (76% yield). Evaporation of the freshly-prepared ethereal solution of dimethyl-

ε-bromoamylamine (*chloroaurate*, m. p. 57°) affords 63% of NN-*dimethylpiperidinium bromide*, m. p. 324° [the corresponding chloride chloroplatinate has m. p. 243° (lit. 209—210°)]. *Dimethyl-ζ-bromohexylamine*, b. p. 78—80°/6 mm. (*chloroaurate*, m. p. 111°), on keeping gives 56% of NN-*dimethylhexamethyleneiminium bromide*, m. p. 289°, whilst *dimethyl-η-bromoheptylamine*, b. p. 85—87°/7 mm., d_{20}^{20} 1·029, n_D^{20} 1·4695 (*chloroaurate*, m. p. 126°), yields similarly 37% of NN-*dimethylheptamethyleneiminium bromide*, m. p. 268°. H. BURTON.

Nitration of 2′- and 4′-nitro-1-phenylpiperidines. R. J. W. LE FÈVRE (J.C.S., 1930, 147—151). —Whereas 2′-nitro-1-phenylpiperidine cannot be further nitrated by the ordinary reagents, 4′-nitro-1-phenylpiperidine quantitatively yields 2′ : 4′-dinitrophenylpiperidine with nitric acid (d 1·4) at 0°. Similar, but less pronounced, differences are noticed in the nitration of 1 : 4-*di*-(2′- and 4′-*nitrophenyl*)*piperazines*, m. p. 193—194° and 263—264°, respectively (both prepared directly from piperazine and the appropriate chloronitrobenzene). The following derivatives of 2′-nitrophenylpiperidine are also described : *ferrichloride*, m. p. 147—148°; *mercurichloride*, m. p. 170—175°; *perchlorate*, m. p. 240—243° (decomp.). The *ferrichloride* and *mercurichloride* of 4′-nitro-1-phenylpiperidine have m. p. 130—135° and 70—80°, respectively. R. J. W. LE FÈVRE.

Local anæsthetics in the pyrrole series. I. F. F. BLICKE and E. S. BLAKE (J. Amer. Chem. Soc., 1930, **52**, 235—240).—Methyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, *iso*amyl, and ethyl pyrrole-2-carboxylates (*tribromo*-derivative, m. p. 195—196°) are prepared by the silver salt–alkyl iodide method. These esters possess marked local anæsthetic action on the tongue. *Phenyl pyrrole-2-carboxylate*, m. p. 44—45°, is prepared from the acid chloride and sodium phenoxide in ether.

Phenyl β-piperidinoethyl ketone (Mannich and Lammering, A., 1923, i, 43) [hydrochloride, m. p. 187—188° (lit. 192—193°)] is obtained from piperidine and ω-*bromopropiophenone*, m. p. 59—60° (prepared from β-bromopropionyl chloride and benzene) in ether. The ketone is reduced catalytically (platinum oxide) to the corresponding carbinol, m. p. 64—65° (lit. 68—69°). Phenacyl bromide and piperidine afford N-*phenacylpiperidine* (I) (*hydrochloride*, m. p. 210—211°), reduced catalytically to the corresponding *carbinol* (II), m. p. 69—70° (*benzoate hydrochloride*, m. p. 193—194°). 2-Acetylpyrrole, piperidine hydrochloride, and paraformaldehyde react in alcohol, yielding 2-*pyrryl β-piperidinoethyl ketone* (III) (cf. Mannich and Lammering, *loc. cit.*). Anæsthetic action is shown by I, II, and III.

Further details for the preparation of pyrrole (cf. B., 1928, 82) are given. H. BURTON.

Aromatic alkylvinylamines. H. STACH and W. KÖNIG (Ber., 1930, **63**, [B], 88—93).—Methyl-β-hydroxyethylaniline is heated at 130—135° with hydrobromic acid saturated at 0°, whereby methyl-β-bromoethylaniline, b. p. 122°/1 mm. (picrate, m. p. 125°), is prepared in 73·2% yield. With trimethylamine in alcohol at the ordinary temperature it slowly affords trimethyl-β-methylanilinoethylammonium

bromide quantitatively (cf. von Braun, A., 1918, i, 107). 2-Methyldihydroindole when heated with ethylene chlorohydrin and ignited potassium carbonate yields 2-*methyl*-1-β-*hydroxyethylindoline*, b. p. 123°/2 mm. [corresponding *methiodide*, m. p. 160° decomp.)], converted by hydrobromic acid into 2-*methyl*-1-β-*bromoethyl*-2 : 3-*dihydroindole*, b. p. 130°/2 mm., which readily undergoes change when preserved. Trimethylamine in alcohol converts the bromo-compound into *trimethyl*-β-2-*methylindolinoethylammonium bromide*, from which the corresponding, very hygroscopic *hydroxide* and its *perchlorate*, m. p. 186°, are derived. Not too rapid distillation of the hydroxide in a vacuum affords 2-*methyl*-1-*vinyl*-2 : 3-*dihydroindole*, b. p. 100—103°/6 mm. The base readily polymerises under the influence of heat or acids. When heated with alkalis, it readily loses the vinyl group as acetaldehyde. When treated with alcoholic iodine in presence of mercury salts, the vinyl base absorbs 5·5 atoms of the halogen. H. WREN.

Synthesis of *isoquinoline* derivatives. E. SPÄTH, F. BERGER, and W. KUNTARA (Ber., 1930, **63**, [B], 134—141).—The general procedure consists in the conversion of an amine of the type of β-phenylethylamine into its acyl derivative by heating with a 10—20% excess of the appropriate acid at 170° and removal of the product in a high vacuum. The product is treated with three times its weight of phosphoric oxide in 20—50 times its weight of gently boiling tetrahydronaphthalene for 15 min., and ebullition continued for a like period after addition of a further equal quantity of the dihydrating agent. The free base is isolated by distillation and purified through the picrate. It is dehydrogenated by spongy palladium at 190°. The following compounds are thus prepared : 3 : 4-dihydro*iso*quinoline (picrate, m. p. 175—176°), and thence *iso*quinoline from form-β-phenylethylamide; 1-methyl-3 : 4-*dihydroisoquinoline*, b. p. 130°/10 mm.* (picrate, m. p. 188—190°; cf. Pictet and Kay, A., 1909, i, 513), and 1-methyl*iso*quinoline (*picrate*, m. p. 225—226°); 1-*ethyl*-3 : 4-*dihydroisoquinoline* (*picrate*, m. p. 190—192°) and 1-*ethylisoquinoline* [*picrate*, m. p. 209—210° (decomp.)], from *propion-β-phenylethylamide*, m. p. 50—51°; 1-*n-propyl*-3 : 4-*dihydroisoquinoline* (*picrate*, m. p. 173—174°) and 1-*n-propylisoquinoline* (*picrate*, m. p. 200—201°) from *n-butyr-β-phenylethylamide*, m. p. 49—50°); 1-*n-butyl*-3 : 4-*dihydroisoquinoline*, b. p. 170—180°/10 mm.* (picrate, m. p. 153—154°), and 1-*n-butylisoquinoline* (*picrate*, m. p. 185—186°) from n-*valer-β-phenylethylamide*, m. p. 44—46°; 1-phenyl-3 : 4-dihydro*iso*quinoline, b. p. 190—200°/12 mm. (picrate, m. p. 173—175°), and 1-phenyl*iso*quinoline, m. p. 95—96° (picrate, m. p. 165—166°), from benz-β-phenylethylamide; 1-*benzyl*-3 : 4-*dihydroisoquinoline*, b. p. 220°/12 mm.* (picrate, m. p. 173—175°), and 1-*benzylisoquinoline*, b. p. 140—150°/1 mm.* (*picrate*, m. p. 182°), from phenylacet-β-phenylethylamide; 4-methyl-3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 132—133°) and 4-methyl*iso*quinoline (*picrate*, m. p. 202—203°) from *form*-β-*phenylpropylamide*, b. p. 140—160°/0·35 mm.*; 1 : 4-dimethyl-3 : 4-dihydro-*iso*quinoline (*picrate*, m. p. 167—168°) and 1 : 4-*di*-*methylisoquinoline*, b. p. 140—160°/12 mm.* (*picrate*,

m. p. 221—222°), from *acet-β-phenylpropylamide*, b. p. 160—180°/0·4 mm.; 5-methyl-3 : 4-dihydro*iso*quinoline [*picrate*, m. p. 182—183° (decomp.)] and 5-methyl-*iso*quinoline (*picrate*, m. p. 235—236°) from *form-β-o-tolylethylamide*, b. p. 160—180°/0·25 mm.*; 1 : 5-dimethyl-3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 182—184° after softening) and 1 : 5-*dimethylisoquinoline*, m. p. 97—98° [*picrate*, m. p. 230—231° (decomp.)], from *acet-β-o-tolylethylamide*. The temperatures marked * are measured in the bath. H. WREN.

Colour reaction between sodium nitroprusside and creatinine. G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1929, [vi], **10**, 261—266).—The red compound formed in this reaction in alkaline solution may have either of the two formulæ,

$$Na_3\left[(CN)_5Fe^{II}N^{III}(OH):C \begin{matrix} NMe \cdot C:NH \\ CO—NH \end{matrix} \right] \text{ or}$$

$$Na_3\left[(CN)_5Fe^{II}N^{III}(:O)\cdot CH \begin{matrix} NMe\cdot C:NH \\ CO—NH \end{matrix} \right].$$
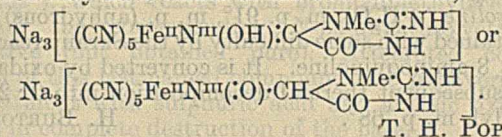
T. H. POPE.

Substituted phenylethylbarbituric acids. E. W. BOUSQUET and R. ADAMS (J. Amer. Chem. Soc., 1930, **52**, 224—229).—Nitration of 5-phenyl-5-ethyl-barbituric acid with nitric (d 1·5) and sulphuric acids at —10° to 3° affords 5-*p-nitrophenyl-5-ethyl-barbituric acid*, m. p. 276—277°, reduced catalytically (platinum oxide) to the corresponding 5-*p-amino-phenyl* derivative, m. p. 205—206°. Bromination of 5-*p-acetamidophenyl-5-ethylbarbituric acid*, m. p. 147—148°, affords a 5-*bromo-p-acetamidophenyl* derivative, m. p. 291—292° (the *bromoamino*-compound has m. p. 253—255°), whilst nitration furnishes 5-*nitro-p-acetamidophenyl-5-ethylbarbituric acid*, m. p. 295—296° (*nitroamino*-derivative, m. p. above 320°). 5-*p-Chlorophenyl-5-ethylbarbituric acid*, decomp. 243—245°, has about the same hypnotic power as the original compound but is slightly more toxic. The other derivatives have no hypnotic action.

Nitration of methyl ethyl phenylethylmalonate with nitric and sulphuric acids at —10° to 0° gives the *p-nitrophenyl* derivative, b. p. 180—185°/4 mm. (oxidised to *p*-nitrobenzoic acid). This is reduced catalytically (platinum oxide) to *methyl ethyl p-amino-phenylethylmalonate*, b. p. 182—185°/4 mm. (*acetyl* derivative, b. p. 192—197°/3 mm.), convertible by the usual method into *methyl ethyl p-hydroxyphenyl-ethylmalonate*, b. p. 180—185°/4 mm. (*methyl ether*, b. p. 152—156°/4 mm.). Condensation of these esters with carbamide could not be effected. H. BURTON.

Constitution of " dioxypyramidone." R. CHARONNAT and R. DELABY (Compt. rend., 1929, **189**, 1285—1286).—The compound, $C_{13}H_{17}O_3N_3$, b. p. 194—201°/2 mm., m. p. 105·5°, previously described (this vol., 223) as dioxypyramidone, is unaffected by the usual reducing agents, acetic anhydride, and iodine, indicating that it is not a pyramidone. On complete hydrolysis with concentrated sodium hydr-oxide solution at 100°, dimethylamine, β-phenyl-α-methylhydrazine, sodium acetate, and sodium oxalate are obtained, whilst partial hydrolysis affords α-acetyl-β-phenyl-α-methylhydrazine and sodium NN-di-methyloxamate. The above compound is, therefore, α-*acetyl-β-NN-dimethyloxamyl-β-phenyl-α-methylhydraz-ine*, NMeAc·NPh·CO·CO·NMe₂. H. BURTON.

Local anæsthetics derived from piperazine. E. FOURNEAU and C. E. BARRELET (Bull. Soc. chim., 1929, [iv], **45**, 1172—1189).—Monosubstituted deriv-atives of piperazine are obtained in 50—70% of the theoretical yield by refluxing ethylene oxides with excess of piperazine hydrate (cf. Moore and others, A., 1929, 331). Mixed disubstituted derivatives are obtained in theoretical yield by treating a mono-substituted piperazine (1 mol.) with 1 mol. of a halogen compound in benzene. The *s*-disubstituted amino-alcohol derivatives of piperazine are obtained quantitatively from molecular quantities of piper-azine and ethylene oxide. They give no additive products with carbon disulphide and when of high mol. wt. have a strong anæsthetic action. Attempts to obtain compounds of the stovaine or amino-stovaine type failed, benzoylation of the amino-alcohol taking place on the free piperazyl imino-group. If the latter position was first blocked with a carbethoxyl group, subsequent benzoylation gave products similar to those obtained by Moore (*loc. cit.*) and on hydrolysis the benzoyl group is also removed. The following are described : 1-*β-hydroxy-β-methyl-n-butylpiperazine*, m. p. 77—78°, b. p. 133°/20 mm. (yield, 60%, from methylethylethylene oxide) [*hydro-chloride*; *dihydrochloride*, m. p. 136° (decomp.); *picrate*, m. p. 230° (decomp.); N-*benzoate*, a neutral oil, b. p. 247°/17 mm. (*monohydrochloride*, m. p. 190°, anæsthetic powers)], giving with ethyl chloroacetate *ethyl 1-β-hydroxy-β-methyl-n-butylpiperazine-4-acetate*, b. p. 183°/17 mm. (*hydrochloride*, m. p. 119°; *picrate*, 178°); m-*nitrobenzoate dihydrochloride*, m. p. 172° (*picrate*, m. p. 175°), m-*aminobenzoate trihydrochloride*, m. p. 173—174° (anæsthetic powers) [*picrate*, m. p. 169° (decomp.)], and with carbon disulphide the *di-thiocarbamate*,

$$OH\cdot CMeEt\cdot CH_2\cdot N \begin{matrix} [CH_2]_2 \\ [CH_2]_2 \end{matrix} N\cdot CS\cdot SH,$$

m. p. 137° [sodium *salt*, m. p. 225—226° (decomp.)]; 1 : 4-*bis-β-hydroxy-β-methyl-n-butylpiperazine*, m. p. 33°, b. p. 183—186°/19 mm. [*hydrochloride*; *dihydro-chloride*, m. p. 218° (decomp.); *picrate*, m. p. 221° (decomp.); *dibenzoate*, m. p. 86—87° (*dihydrochloride*, m. p. 199°, weak anæsthetic powers; *picrate*, m. p. 195°)]; γ-*butoxy-β-hydroxy-n-propylpiperazine*, b. p. 185—188°/30 mm. (*dihydrochloride*, m. p. 108—109°; *picrate*, m. p. 204°; *dithiocarbamate*, m. p. 113°); β-*hydroxy-γ-phenyl-n-propylpiperazine* (*piperazyl-phenylmethylcarbinol*), b. p. 203—208°/18 mm., m. p. 63—64° (*dihydrochloride*, m. p. 147—148°; *picrate*, m. p. 209°; *dithiocarbamate*, m. p. 91°); 1 : 4-*bis-β-hydroxy-γ-phenyl-n-propylpiperazine*, m. p. 136° [*mono-hydrochloride*, m. p. 167° (0·5% solution p_H 6·1—6·2 has complete anæsthetic action by intradermic injection into the arm); *dihydrochloride*, m. p. 229° (toxic for mice in doses of 0·01 g. per 20 g.-wt. by subcutaneous injection); *picrate*, m. p. 228—230° (decomp.)], obtained in the preparation of piperazyl-phenylmethylcarbinol, together with an isomeric *base*, m. p. 110°, resulting from the alternative rupture of the ethylene oxide ring; 1-*β-hydroxy-γ-phenoxy-n-propylpiperazine*, m. p. 58—59°, b. p. 220—225°/16 mm. [*monohydrochloride*; *dihydrochloride*, m. p. 156°; *picrate*, m. p. 210°(decomp.); *dithiocarbonate*, m. p. 124°]; and 1 : 4-*bis-β-hydroxy-γ-phenoxy-n-propylpiperazine*, m. p. 135° [*hydrochloride*, m. p. 231° (decomp.) after

darkening at 220° (anæsthetic powers); *picrate*, m. p. 223° (decomp.)]. Piperazine hydrate and 2-chloroquinoline in alcohol at 140° yield N-2-*quinolylpiperazine*, solid [*monohydrochloride*; *dihydrochloride*, m. p. 229—231° (decomp.); *picrate*, m. p. 243—245° (decomp.)]. 2-Chloroquinoline and N-β-hydroxy-β-methyl-*n*-butylpiperazine in benzene at 130° similarly yield 1-(2'-*quinolyl*)-4-β-*hydroxy*-β-*methyl*-n-*butylpiperazine* [*dihydrochloride*, m. p. 247° (decomp.) (slight anæsthetic action); *picrate*, sinters at 140°, m. p. 168—169°]. N-β-Hydroxy-β-methyl-*n*-butylpiperazine and ethylchloroformate yield the N'-*carbethoxy*-derivative, b. p. 184°/16 mm. [*hydrochloride*, m. p. 171° (decomp.)]. The m-*nitrobenzoate* [*hydrochloride*, sinters at 133°, m. p. 145° (decomp.) (strong anæsthetic action)] of this substance affords on hydrolysis with sodium hydroxide, *m*-nitrobenzoic acid and a viscous brown mass giving a hydrochloride, sinters at 143°, m. p. 161° (decomp.), and on reduction a brown solid from which the carbethoxyl group has been eliminated. The o- and p-*nitrobenzoates* behave similarly, the o-nitrobenzoate being the least stable. None of the anæsthetics obtained showed any advantage over those already known.   R. BRIGHTMAN.

Pyrimidines. CX. Condensation of Claisen's ethyl ethoxymethylenemalonate with ψ-ethylthiocarbamide. T. B. JOHNSON and Y. F. CHI (Rec. trav. chim., 1930, **49**, 86—90; cf. Wheeler, Johnson, and Johns, A., 1907, i, 559).—Condensation of ethyl ethoxymethylenemalonate with ψ-ethylthiocarbamide in presence of excess (3·25 mols.) of potassium hydroxide solution, gives the *potassium salt*, m. p. 285—288° (decomp.), of ethyl 6-hydroxy-2-ethylthiolpyrimidine-5-carboxylate. In presence of 1 mol. of potassium hydroxide solution the additive *compound*, m. p. 190—195° (decomp.), of 1 mol. of the above potassium salt and 1 mol. of the corresponding ψ-ethylcarbamide salt is produced. Both of the above salts yield the corresponding *hydroxypyrimidine*, m. p. 131° (*ethyl 2-ethylthiol-6-keto-*1 : 6-*dihydropyrimidine-5-carboxylate*), on acidification.   H. BURTON.

2-Thiol-4(5)-β-aminoethylglyoxaline (2-thiolhistamine). F. L. PYMAN (J.C.S., 1930, 98—100).— Hydrolysis of αδ-dibenzamido-β-ketobutane, m. p. 158—159° (corr.) (lit. 151°), with alcoholic hydrochloric acid at 150° gave αδ-*diamino*-β-*ketobutane dihydrochloride*, m. p. 221° (decomp.; corr.) [corresponding *picrate*, m. p. 212° (decomp.; corr.)], which, by interaction with aqueous sodium thiocyanate, formed 2-*thiol*-4(5)-β-*aminoethylglyoxaline hydrochloride*, m. p. 248—249° (corr.) [corresponding *picrate*, m. p. 225° (decomp.; corr.)]. This compound underwent oxidation when boiled with aqueous ferric chloride with formation of histamine; physiological tests showed it to possess no significant histamine-like action.   R. J. W. LE FÈVRE.

Skraup's reaction applied to phenylenediamines. Preparation of phenanthrolines and related dipyridyls. C. R. SMITH (J. Amer. Chem. Soc., 1930, **52**, 397—403).—Details are given for the preparation of m- and p-phenanthrolines from m- and p-phenylenediamines, by the Skraup reaction, in 40—60% yield. Oxidation of p-phenanthroline with

alkaline potassium permanganate affords 3 : 3'-dipyridyl-2 : 2'-dicarboxylic acid, which on thermal decomposition in glycerol suspension yields 3 : 3'-dipyridyl, b. p. 300—301° (corr.). Similarly, m-phenanthroline furnishes 2 : 3'-dipyridyl-3 : 2'-dicarboxylic acid, which when heated at 190—200° gives two 2 : 3'-dipyridylmonocarboxylic acids (the *acid* formed in smaller amount has m. p. 152—154°, and is new). Both monocarboxylic acids are decomposed at about 290° to 2 : 3'-dipyridyl, b. p. 298°. The Skraup reaction with o-phenylenediamine furnishes a small amount of a *compound*, $C_{12}H_8ON_2$, m. p. 253° (corr.), oxidised by alkaline potassium permanganate to a *dicarboxylic acid*, m. p. 167°. This undergoes thermal decomposition to a *substance*, m. p. 113°. o-*Phenanthroline* ($+H_2O$), m. p. 91°, m. p. (anhydrous) 97°, is obtained with some difficulty by the Skraup reaction with 8-aminoquinoline. It is converted by oxidation and subsequent thermal decomposition into 2 : 2'-dipyridyl, m. p. 68°.   H. BURTON.

Picolide of Scholtz and acetyl derivatives of indolizine and 2-methylindolizine. A. E. TSCHITSCHIBABIN and F. N. STEPANOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1635—1644).—See A., 1929, 704.

Anserine. F. L. PYMAN (J.C.S., 1930, 183—184). —The author points out that in consequence of previous work by himself and collaborators the dimethylglyoxaline isolated by Linneweh, Keil, and Hoppe-Seyler (A., 1929, 944) by distillation of anserine with soda-lime must be the 1 : 5-compound; consequently their methylhistidine (hydrolysis product of anserine) is *dl*-β-(1-methylglyoxalinyl-5)-α-aminopropionic acid, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot C{<}^{NMe\cdot CH}_{CH-N}$, and the relative positions of the side-chains and the N-methyl groups are the same in anserine and pilocarpine.   R. J. W. LE FÈVRE.

Components of the Chinese drug " Ma Huang." VII. *l*-Norephedrine. S. KANAO (Ber., 1930, **63**, [*B*], 95—98).—The concentrated aqueous extract of the drug is rendered alkaline and extracted with benzene. The neutralised solution of the bases deposits *l*-ephedrine hydrochloride, m. p. 216—217°. The mother-liquor, after addition of potassium hydroxide, yields *d*-*iso*ephedrine, m. p. 118°. The remaining bases are neutralised with alcoholic oxalic acid, thereby giving crystals mainly of *l*-methylephedrine oxalate, m. p. 187°. The mixture of bases still remaining is distilled under diminished pressure. The distillate affords *l*-methylephedrine, m. p. 87°, and the remainder is converted by absolute ethylalcoholic sulphuric acid into a mixture of sulphates. The bases derived from the last-named mixture are heated with aqueous *l*-tartaric acid, thereby giving successively *d*-nor*iso*ephedrine hydrogen *l*-tartrate, m. p. 202°, and *l*-norephedrine hydrogen *l*-tartrate, (also +1EtOH), m. p. about 160° after softening at 130°, $[\alpha]_D^{13}$ −34·64° in water [corresponding hydrochloride, m. p. 171—172°, $[\alpha]_D^{14}$ −33·74° in water; chloroplatinate, m. p. 221° (decomp.); chloroaurate, m. p. 188°]. The identity of the natural and synthetic product (A., 1929, 807) is further established by the conversion of the N-p-nitrobenzoyl derivative,

m. p. 175—176°, into *d*-nor*iso*ephedrine *p*-nitro-benzoate. H. WREN.

Papaverine. Attempted Rügheimer synthesis. I. ALLEN, jun., and J. S. BUCK (J. Amer. Chem. Soc., 1930, **52**, 310—314).—Reduction of veratril with tin and alcoholic hydrochloric acid containing copper sulphate, or treatment of veratrole with homoveratryl chloride in presence of aluminium chloride and carbon disulphide, affords *deoxyveratroin*, m. p. 107°. The *oxime*, m. p. 128°, of this is reduced by sodium amalgam and alcoholic acetic acid to 3 : 4 : 3′ : 4′-*tetramethoxystilbylamine* [αβ-*di*-(3 : 4-*dimethoxyphenyl*)-*ethylamine*], m. p. 107° (*hydrochloride*, m. p. 195°; *hydrobromide*, m. p. 241°; *acetyl* derivative, m. p. 160—162°), which reacts with bromodimethylacetal to form the corresponding *N*-ββ-dimethoxyethyl derivative (not obtained pure). Attempted conversion of this last-named compound into papaverine by treatment with sulphuric acid and arsenic oxide results in complete destruction of the base.

The *oxime*, m. p. 158°, of *deoxypiperoin*, m. p. 114° (obtained by reduction of piperoin), is reduced as above to 3 : 4 : 3′ : 4′-*dimethylenedioxystilbylamine* [αβ-*di*-(3 : 4-*methylenedioxyphenyl*)*ethylamine*], m. p. 111° (*hydrochloride*, m. p. 245°; *acetyl* derivative, m. p. 141°). The *N*-ββ-dimethoxyethyl derivative of this base is decomposed by treatment with arsenic oxide and cold 75% sulphuric acid. H. BURTON.

Constitution of conessine. E. SPÄTH and O. HROMATKA (Ber., 1930, **63**, [B], 126—133).—Determination of the methyl alcohol evolved shows that the main decomposition of conessine dimethyl hydroxide does not follow the course $C_{24}H_{40}N_2Me_2(OH)_2 = C_{22}H_{33}N + NMe_3 + MeOH + H_2O$ (cf. Kanga, Ayyar, and Simonsen, A., 1926, 1047), but proceeds according to the equation $C_{24}H_{40}N_2Me_2(OH)_2 = C_{23}H_{35}N + NMe_3 + 2H_2O$. Confirmation of the consequently modified formula, $C_{23}H_{35}N$, for *apo*conessine is found in the observation that it contains two methyl groups attached to nitrogen. Further, conessine contains one double linking, since it is hydrogenated in presence of palladised charcoal to *dihydroconessine*, m. p. 105—105·5° (*hydrochloride*). On the authors' hypothesis, therefore, *apo*conessine contains three double linkings, as is proved by its conversion into *hexahydro*apo*conessine*, m. p. 69—70° [a by-product yielding a picrate, m. p. 255—256° (decomp.), is also obtained]. Analysis of *apo*conessine hydrochloride [corresponding picrate, m. p. 234° (decomp.)], confirms the composition $C_{23}H_{35}N,HCl$. Attempts to apply the Hofmann degradation to the quaternary base from *apo*conessine and methyl iodide do not yield a nitrogen-free product. The methiodide is therefore converted into the corresponding *methochloride*, which is transformed by sodium amalgam into trimethylamine and a *hydrocarbon*, $C_{21}H_{30}$, m. p. 74—76°, $[\alpha]_D^{15} -183·7°$ in pyridine. Hydrogenation of the last-named substance in presence of palladised charcoal yields the *compound* $C_{21}H_{36}$, m. p. 56—58°, d^{22} 0·9547, n_D^{32} 1·50664, $[\alpha]_D^{15} +14·5°$ in benzene. The non-production of a more highly hydrogenated compound under conditions which cause the hydrogenation of unpurified mesitylene appears to imply the absence of a benzene nucleus from conessine. On the assumption that the number of hydrogen atoms as previously determined in the alkaloid is correct, conessine appears to be a combination of four hydrogenated, carbocyclic rings to which a ring with one nitrogen atom is attached. In the ring complex or in a side-chain thereof, a difficultly reducible double linking is placed. H. WREN.

Harmala alkaloids : harmaline, harmine, and harman. E. SPÄTH and E. LEDERER (Ber., 1930, **63**, [B], 120—125).—3-β-Aminoethylindole is converted by acetic anhydride at the ordinary temperature into its *acetyl* derivative, which, when treated with phosphoric oxide in boiling xylene, affords dihydroharman, m. p. 182°, in 56% yield (cf. Manske, Perkin, and Robinson, A., 1927, 265). Dehydrogenation of the compound to harman, m. p. 237°, is effected with spongy palladium at 200° (yield 89%). 3-Methoxyphenylhydrazine and γ-amino-*n*-butaldehydediethylacetal in presence of anhydrous zinc chloride at 130—150° appear to yield a mixture of 4- and 6-methoxy-3-β-aminoethylindoles, from which, by treatment with acetic anhydride followed by ether, 6-*methoxy*-3-β-*acetamidoethylindole*, m. p. 136°, is isolated in 30% yield. The compound is transformed by phosphoric oxide in boiling xylene into harmaline, m. p. 250—251°, from which harmine, m. p. 264—265°, is obtained by the action of spongy palladium at 200°. H. WREN.

Sinomenine and disinomenine. XII. Sino-menine hydrate. K. GOTO and H. SUDZUKI (Bull. Chem. Soc. Japan, 1929, **4**, 271—277).—Treatment of sinomenine at 100° with dilute hydrochloric acid, followed by sodium carbonate, gives *sinomenine hydrate*, m. p. 139°, $[\alpha]_D^{26} +40·8°$ in chloroform [*methiodide*, m. p. 264° (decomp.); *disemicarbazone*, m. p. 191° (decomp.); *dioxime*, m. p. 231° (decomp.)], reduced by sodium amalgam to α-demethoxysinomenine hydrate, m. p. 128° (40% yield), and by palladium and hydrogen to α- [*oxime*, m. p. 170° (decomp.); *semicarbazone*, m. p. 191° (decomp.); *phenylhydrazone*, m. p. 140°; *methiodide*, m. p. 274—276° (decomp.)] and β-*demethoxysinomenine-hydrates* [*methiodide*, m. p. 280° (decomp.); *semicarbazone*, m. p. 206° (decomp.)], m. p. 129°, $[\alpha]_D^{26} +64·8°$ in chloroform, and m. p. 104°, $[\alpha]_D^{26} +95·2°$ in chloroform, respectively. *Bisdemethylsinomenilidene*, m. p. above 312°, is produced in 40% yield from sinomenine hydrate and aqueous ammonia (*d* 0·9). A. I. VOGEL.

*iso*Quinidine. A. KONOPNICKI and J. SUSZKO (Rocz. Chem., 1929, **9**, 640—660).—See this vol., 97.

Microchemical reactions for hydrastine. M. WAGENAAR (Pharm. Weekblad, 1930, **67**, 57—58).—The alkaloid as precipitated is usually an oil or amorphous solid, which can be caused to crystallise by grinding with sodium hydrogen carbonate; borax gives a crystalline precipitate. The bromine and ferrocyanide reactions are mentioned. S. I. LEVY.

Microchemical reactions for berberine. M. WAGENAAR (Pharm. Weekblad, 1930, **67**, 77—79).—Precipitation by addition of salts is exceedingly sensitive, and will indicate 0·5 mg., at a dilution of 1 : 2000. The reactions with iodine, bromine, and potassium bismuth iodide are also characteristic. S. I. LEVY.

Synthesis of arsenic α-chlorostyryl dichloride. V. IPATIEV, G. RAZUBAIEV, and A. SISOV (Ber., 1929, **63**, [*B*], 174—178; cf. Turner, A., 1925, i, 843).—Arsenic α-chlorostyryl dichloride, m. p. 40·6—41·2°, is obtained crystalline by cooling the product of the action of phenylacetylene on arsenic trichloride at 110°. It cannot be distilled without decomposition. It appears stable to water at the ordinary temperature, but is converted by alkali hydroxide or carbonate or by aqueous ammonia into *arsenic α-chlorostyryl oxide*, m. p. 115—117°, and by hydrogen peroxide into the *arsinic acid*, $C_8H_8O_3ClAs$, m. p. 179—180°.

H. WREN.

Preparation of 4- and 6-hydroxy-3-nitrophenyl-arsinic acids. I. E. BALABAN (J.C.S., 1930, 183).—Reduction of 1-chloro-2 : 4-dinitrobenzene by West's method produces 4- and 6-chloro-3-nitroanilines in 23% and 45% yields, respectively, from which (by the Bart–Schmidt reaction) 4-chloro-3-nitrophenyl-arsinic acid (yield 32·4%) and 6-chloro-3-nitrophenyl-arsinic acid (yield 32·9%) may be obtained. Boiling with 25% aqueous sodium hydroxide converts these acids into the related hydroxynitrophenylarsinic acids.

R. J. W. LE FÈVRE.

Condensation products of aminoarsanilic [3 : 4-diaminophenylarsinic] and arsanilic [*p*-amino-phenylarsinic] acids. P. L. CRAMER [with W. L. LEWIS] (J. Amer. Chem. Soc., 1930, **52**, 229—234).—3 : 4-Diaminophenylarsinic acid condenses with glyoxal sodium hydrogen sulphite, forming 2 : 3-*di-sodium* 2 : 3-*disulpho*-1 : 2 : 3 : 4-*tetrahydroquinoxaline-6-arsinic acid*, hydrolysed by hydrochloric acid to *quinoxaline*-6-*arsinic acid*, not melted at 250°. Condensation of the diamino-acid with maltosone in boiling methyl alcohol gives 3-*glucosidoerythrityl-quinoxaline*-6-*arsinic acid*, purple, not melted at 250°, whilst with lactosone in methyl-alcoholic ethylene glycol the corresponding 3-*galactosidoerythrityl* deriv-ative is obtained; these derivatives are readily hydrolysed by water.

Condensation *products*, all of which char below 100°, of *p*-aminophenylarsinic acid and the following sugars are obtained in presence of methyl alcohol : dextrose, mannose, galactose, arabinose, and xylose. Aqueous solutions of these compounds undergo rapid hydro-lysis which can be followed polarimetrically. *p*-Amino-phenylarsinic acid and ethylene oxide react in presence of sodium hydroxide solution, forming 4-β-*hydroxyethylaminophenylarsinic acid*, m. p. 168°; with phenacyl bromide, 4-*diphenacylamidophenyl-arsinic acid*, m. p. 162·5°, results. The following new compounds are prepared by the usual methods : 3-*amino*-4-*benzenesulphonamido*-, m. p. 205—207° (decomp.); 3-*amino*-4-*p*-*toluenesulphonamido*-, m. p. 160—165° (decomp.); 3-*amino*-4-*p*-*bromobenzene-sulphonamido*-, m. p. 180—185° (decomp.); 3-*amino*-4-*picramido*-, chars at 165°; 4-*picramido*-, not melted at 260°, and 4-*p*-*bromobenzenesulphonamido-phenyl-arsinic acids*, m. p. 210—212° (decomp.).

H. BURTON.

Diarylarsinic acids, halogenodiarylarsines, and the constitution of 10-chloro-5 : 10-dihydro-phenarsazine. C. P. A. KAPPELMEIER (Rec. trav. chim., 1930, **49**, 57—85).—The hydrochloride, m. p.

134°, of diphenylarsinic acid (Grignard and Rivat, A., 1919, i, 460) is formulated as diphenylarsinic acid chloride (dihydroxydiphenylarsonium chloride), $[AsPh_2(OH)_2]Cl$. When this is heated above its m. p. only a small amount of hydrogen chloride is evolved; decomposition occurs mainly thus : $[AsPh_2(OH)_2]Cl \longrightarrow PhCl + PhAsO + H_2O$. When crystallised from acetone the above chloride passes into bisdiphenylarsinic acid chloride, $\{AsPh_2(OH)O·[AsPh_2(OH)_2]\}Cl$, m. p. 114·5° (the second hydrochloride of Grignard and Rivat, *loc. cit.*). The former chloride is undoubtedly the intermediate in the reduction of diphenylarsinic acid to chloro-diphenylarsine by the well-known sulphur dioxide-hydrochloric acid method. The *chloride*, $\{AsPh_2O_2[AsPh_2(OH)_2]_2\}Cl$, m. p. 121°, is obtained when chlorodiphenylarsine dibromide is decomposed by moist air. The diphenylarsinic acid nitrate, $AsPh_2O·NO_3$, of Michaelis (A., 1902, i, 515) is *dihydroxydiphenylarsonium nitrate*, m. p. 122—123° (corresponding *sulphate*, m. p. 119—120°), which on crystallisation from acetone passes into the *nitrate*, $C_{24}H_{23}O_7NAs_2$, m. p. 113° after previous softening. *Dihydroxyphenylbenzylarsonium* and *hydroxytriphenyl-arsonium chlorides* have m. p. 115° and 175—176° after softening at 174°, respectively. The salts of phenarsazinic acid (Wieland and Rheinheimer, A., 1921, i, 371; Burton and Gibson, A., 1925, i, 84) are formulated thus : $[NH(C_6H_4)_2As(OH)_2]X$. Chloro-diphenylarsine dichloride, m. p. about 189° (lit. 174°), on crystallisation from acetone affords dihydroxy-diphenylarsonium chloride, which with thionyl chloride in chloroform regenerates the trichloro-derivative. Whereas chloro- and bromo-diphenyl-arsines form polyhalides, 10-chloro-5 : 10-dihydro-phenarsazine is converted by bromine in chloroform into tetrabromodiphenylamine (cf. Elson, Gibson, and Johnson, A., 1929, 834). Methylation of phenarsazinic acid is not possible, but treatment with thionyl chloride in chloroform suspension affords the *compound* $NH(C_6H_4)_2AsCl_3$. 10-Chloro-5 : 10-dihydrophenarsazine is considered to react like the hydrochloride of a weak base; the formula $\left[N{<}{C_6H_4 \atop C_6H_4}{>}As·H\right]Cl$ is assigned to it (cf. Burton and Gibson, A., 1926, 418; Gibson and Johnson, A., 1929, 945), to explain the colour and the various reactions.

H. BURTON.

Organo-aromatic derivatives of boron. E. PACE (Atti R. Accad. Lincei, 1929, [vi], **10**, 193—196).—Monophenylboron chloride (cf. Michaelis and Becker, A., 1880, 395; 1882, 731), prepared by passing benzene and boron trichloride vapours over platinised asbestos or palladium-black at 500—600°, yields *phenylborine* (or " *boronaniline* "), BH_2Ph, b. p. 193°, when heated with dry, gaseous hydrogen iodide in presence of iodine. *Boronbenzene*, $BPh{:}BPh$, m. p. 155° (decomp.), formed when phenylborine is heated in a current of hydrogen in a reflux apparatus, is unstable in the air, giving rise to a pasty mass of boronoxybenzene (?).

T. H. POPE.

Organic germanium derivatives. II. Tri-phenylgermanium derivatives and their re-actions. C. A. KRAUS and C. B. WOOSTER (J.

Amer. Chem. Soc., 1930, **52**, 372—376; cf. A., 1927, 268).—Treatment of triphenylgermanium bromide with ammonia in presence of a solvent affords ammonium bromide and triphenylgermanium oxide; the oxide arises by hydrolysis of the initially formed triphenylgermaniumamine, $GePh_3 \cdot NH_2$. The product formed from the bromide and liquid ammonia also contained oxide and unchanged material. When the bromide is treated with an excess of potassium amide in liquid ammonia, the salt, $GePh_3 \cdot NHK$, is obtained. This is decomposed by ammonium bromide to the amine. The free amine loses ammonia readily at the ordinary temperature affording a mixture of the corresponding imine and nitride, $(GePh_3)_3N$, m. p. 163—164° (cf. loc. cit.). The nitride is best obtained when the amine is heated at 200°/vac.

Sodium reacts with triphenylgermanium oxide in liquid ammonia forming sodium triphenylgermanide and sodium triphenylgermanoxide (cf. loc. cit.).

H. BURTON.

Synthesis of aromatic mercuro-organic salts. A. N. NESMEJANOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1393—1405).—The preparation of organo-metallic derivatives of mercury by the action of copper powder on the double diazonium and mercuric chloride salts according to Gattermann's method is described. The yields obtained are 60—80% in the case of benzene and naphthalene homologues, 15—45% for halogen-substituted nuclei, and very low for nuclei containing nitro- or carboxyl groups. The double diazonium salts with mercuric chloride were prepared by three methods : (1) diazotisation of the amine, followed by addition of the diazonium salt to an equivalent amount of mercuric chloride, when the double salt was precipitated ; (2) diazotisation of the amine by adding it to a mixture of sodium nitrite and mercuric chloride in hydrochloric acid solution, and (3) diazotisation of the amine by amyl nitrite, and addition to a solution of mercuric chloride under certain conditions. These methods were found to yield different products. Mercury phenyl iodide, m. p. 269°, was obtained by Gattermann's method from the double salt, m. p. 63—64° (decomp.), of mercuric iodide and benzene-diazonium iodide. Mercury phenyl chloride, m. p. 258°, from the double salt (decomp. on heating). Mercury p-tolyl chloride, m. p. 238—239°, from the double salt, m. p. 107°, and the o-tolyl chloride, m. p. 143°, from the double salt (decomp. on heating). Mercury α-naphthyl chloride, m. p. 191°, from the pale yellow double salt, m. p. 120—121°, and the β-naphthyl chloride, m. p. 270°, from the yellow double salt, m. p. 120—125°. Mercury p-hydroxy-phenyl chloride, m. p. 226—227°, from the double salt, m. p. 156°. Mercury o-anisyl chloride, m. p. 180—181°, from the double salt, m. p. 121·5°. Mercury p-phenetyl chloride, m. p. 249—250°, from the double salt, m. p. 109°. Methyl mercury o-chloro-benzoate, m. p. 184·5°, from the double salt, m. p. 121°. Mercury p-chlorophenyl chloride, m. p. 228°, from the double salt, m. p. 124·5°; the p-bromo-compound, m. p. 249·5°, from the double salt, decomp. explosively at 119°, and the p-iodo-compound, m. p. 272·5°, from the double salt, m. p. 120—121·5°. Mercury 2 : 5-dichlorophenyl chloride, m. p. 208°, from the pale yellow double salt, m. p. 147°. The double salt, m. p.

146°, of 2 : 4 : 6-tribromophenyldiazonium chloride and mercuric chloride, and the double salt of p-diazon-iumbenzoic acid and mercuric chloride did not give organo-metallic compounds of mercury by Gatter-mann's method, whilst the yellow double salt of p-nitrophenyldiazonium chloride and mercuric chloride gave only a very small quantity of mercury p-nitrophenyl chloride, m. p. 267—269°.

M. ZVEGINTZOV.

Synthesis of symmetrical aromatic mercuro-organic salts. N. A. NESMEJANOV and E. I. KAN (J. Russ. Phys. Chem. Soc., 1929, **61**, 1407—1410; cf. preceding abstract).—The halide salts of aromatic organo-metallic mercuric derivatives can be transformed into symmetrical di-derivatives of mercury by a number of reducing agents, including copper powder. By using excess in the Gattermann method of decom-posing the double diazonium and mercuric chloride salts, the symmetical di-derivatives are obtained instead of the organo-metallic halides, half the mercury being precipitated as metal. Mercury diphenyl, m. p. 125°; di-α-naphthyl, m. p. 249°; di-p-tolyl, m. p. 243—244°; di-p-bromophenyl, m. p. 243—244°; di-p-iodophenyl, m. p. 270—272°; di-2 : 5-dichlorophenyl, m. p. 237°; di-o-anisyl, m. p. 108°, and di-p-nitrophenyl, decomp. at 320°, were synthesised by this method.

M. ZVEGINTZOV.

Antimony aryl compounds. W. RIDDELL and S. BASTERFIELD (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 45—52).—The following stibinic acids have been prepared from the corresponding amines, generally by the method described by Dunning and Reid (A., 1927, 65 ; 1928, 80) for p-acetamidophenyl-stibinic acid : p-carboxymethylphenyl-, p-carbethoxy-phenyl-, p-carbethoxyaminophenyl-, acetophenone-4-, α-naphthyl-, 4-aminophenyl-4'- (by half-diazotisation of benzidine), 4-carbethoxyaminodiphenyl-4'-, 4-amino-diphenylmethane-4'-, 2-nitro-4-methoxyphenyl-, 2-acet-amido-5-methoxyphenyl-, 2-acetamido-4-methoxyphenyl-, 1 : 4 - phenylenedi-, and 4 : 4' - diphenylmethanedi-stibinic acid. With the exception of acetophenone-4-stibinic acid (deep red) they form buff powders. Anisole-3 : 4-distibinic acid could not be prepared. Benzidine yielded 4-hydroxydiphenylstibinic acid, and not the distibinic acid, by the method of Dunning and Reid (A., 1928, 80).

Azo-dyes have been prepared by coupling diazotised p-aminophenylstibinic acid with phenol, α-naphthol, β-naphthol, and naphthionic acid. 4-Hydroxybenzene-azo-4'-methoxyphenyl-2'-stibinic acid was obtained from the acetamido-compound by hydrolysis, diazotis-ation, and coupling with phenol. A product other than the expected dye was obtained by stibinating, by the action of antimony trichloride, the diazonium chloride from pp'-diphenylbisazo-α-naphthylamine. 1-Naphthaleneazo-α-naphthylamine yielded α-naph-thylstibinic acid under similar treatment, but p-amino-azobenzene yielded azobenzene-p-stibinic acid.

4 : 4'-Diaminostibinobenzene was obtained by re-duction of 4-nitrophenylstibinic acid with sodium hyposulphite, and 1-stibinonaphthalene similarly from α-naphthylstibinic acid. 4 : 4'-Carboxymethylstibino-benzene was only obtained impure. Stibino-com-pounds are readily oxidised, and unstable in acid or

alkaline solutions. No pure azostibino-compound could be obtained by diazotisation of 4 : 4'-diamino-stibinobenzene and coupling with phenol.

R. K. CALLOW.

New type of simple organic derivatives of tin. K. A. KOTSCHESCHKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1385—1391).—The preparation and properties of organic derivatives of tin, of the hitherto unknown type $Ar \cdot SnX_3$, where Ar is an aromatic radical, and X a halogen atom, was investigated. The reactions used to obtain the analogous series of monoalkyl compounds are inapplicable, but by heating 1 mol. of tetraphenylstannane with 3 mols. of stannic chloride in a sealed tube at 210—220°, a good yield of *phenyltrichlorostannane*, b. p. 142—143°/25 mm., was obtained, as a heavy, colourless liquid, which fumed strongly in air. It dissolved in cold water without decomposition, but was partly hydrolysed on boiling. With ammonia solution, a white precipitate of amorphous phenylstannonic acid, $SnPh \cdot O_2H$, was obtained. The action of concentrated hydrobromic or hydriodic acid on a concentrated aqueous solution of the phenyltrichlorostannane gave the corresponding *tribromo-*, b. p. 182—183°/29 mm., and *tri-iodo-*compounds, respectively. Boiling with concentrated hydrochloric acid decomposed it into stannic chloride and benzene. In its preparation, some diphenyldichlorostannane, m. p. 42°, was obtained as a by-product. M. ZVEGINTZOV.

Removal of halogen from some homologous halogenoacyl derivatives of glycylglycine and their fission by *N*-sodium hydroxide at 37°. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1930, 11, 170—182).—The rate of removal of halogen from a number of homologous α-substituted fatty acids in combination with glycylglycine (and in one case leucine) by *N*-sodium hydroxide at 37° was compared. The following have not previously been described; *bromoacetyl-*dl-*leucine*, m. p. 131°, decomp. 156° ; *bromoacetylglycylglycine*, m. p. 174—175° (decomp.) ; dl-α-*bromo-n-butyrylglycylglycine*, m. p. 146—147° (decomp.) ; α-*bromoisobutyrylglycylglycine*, m. p. 145° (decomp.). (All m. p. are uncorr.) Bromine is more readily removed than chlorine from the substituted acetic acid. The character of the amino-acid influences the rate of removal of the halogen, but less strongly than the nature of the fatty acid. The rate of hydrolysis of the ·CO·NH· linkings was also studied. Glycyl chains are very readily hydrolysed.

J. H. BIRKINSHAW.

Influence of constitution of homologous dipeptides of *dl*-phenylalanine and the corresponding halogenoacyl compounds on their power of hydrolysis by alkali hydroxide, erepsin, and trypsin-kinase. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1930, 11, 224—250).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on a series of dipeptides containing *dl*-phenylalanine and the corresponding acyl compounds was examined. These included *potassium trihydrogen benzylmalonate*, m. p. 168—169° (loses carbon dioxide) ; *bromoacetyl-*dl-*phenylalanine*, m. p. 117—118° ; *dl*-alanyl-*dl*-phenylalanine, m. p. 260° (decomp.) ; α-*bromo-n-butyryl-*dl-*phenylalanine*, m. p.

122—123° ; *dl-α-amino-n-butyryl-*dl-*phenylalanine*, m. p. 237° ; α-*bromoisobutyryl-*dl-*phenylalanine*, m. p. 114—115° ; α-*aminoisobutyryl-*dl-*phenylalanine*, m. p. 278° ; dl-α-*bromo-n-valeryl-*dl-*phenylalanine*, m. p. 106·5° ; dl-α-*aminovaleryl-*dl-*phenylalanine*, m. p. 210—211° ; dl-α-*bromoisovaleryl-*dl-*phenylalanine*, m. p. 125° ; dl-*valyl-*dl-*phenylalanine*, m. p. 239—240° ; dl-α-*bromohexoyl-*dl-*phenylalanine*, m. p. 84—85° ; dl-*aminohexoyl-*dl-*phenylalanine*, m. p. 210—211° ; dl-α-*bromopropionyl-*d-*phenylalanine*, $[\alpha]_D^{18}$ —3·85°. (All temperatures uncorr.) The velocity of amination on conversion of the halogenoacyl compounds into the amino-compounds was high when the halogen was in the α-position of a straight chain and greater with the short chains. Bromo-*n*-butyryl-*dl*-phenylalanine is an exception. In hydrolysis of the ·CO·NH· linking with sodium hydroxide, increase in the length of the chain attached to the amino-carbon atom implies increased resistance to alkaline hydrolysis. Branching of the carbon chain and especially a tertiary carbon atom seem to lend stability to the molecule. The halogenoacyl compounds show similar behaviour to the dipeptides. The action of erepsin on the halogenoacyl compounds showed no regularities ; with trypsin-kinase the amount of hydrolysis decreased as the length of the carbon chain increased. The p_H optimum lay between 9 and 8·4.

J. H. BIRKINSHAW.

Mol. wt. of casein. I. T. SVEDBERG, L. M. CARPENTER, and D. C. CARPENTER (J. Amer. Chem. Soc., 1930, 52, 241—252).—Application of the centrifugal sedimentation velocity method to the determination of the mol. wt. of casein (Hammarsten) in phosphate buffer solutions at p_H 6·8 shows that this substance is a mixture of proteins of different mol. wt. Extraction of the casein with 70% alcohol containing 0·1% of *N*-hydrochloric acid affords 33% of soluble material, which has a mol. wt. of about 375,000, as determined by the methods of sedimentation velocity and sedimentation equilibrium (cf. this vol., 233), and appears to be a definite chemical entity. The particle of the soluble casein is not spherical ; the deviation from the spherical shape is of the same order as that found for serum-albumin and -globulin, phycocyan, and hæmoglobin. H. BURTON.

Mol. wt. of amandin and excelsin. T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1930, 52, 279—287).—The specific volumes of amandin at p_H 5·7, and of excelsin at p_H 5·5, are identical with those of the proteins previously studied (A., 1929, 1092 ; this vol., 233). The positions of the absorption maximum (279 μμ) and minimum (253 μμ) for excelsin are the same at p_H 5·5 and 12·2, but the extinction coefficient is higher at the latter p_H. Excelsin has a stronger light absorption than amandin, which shows the same maximum and minimum at p_H 5·7. Determinations of the mol. wt. by the methods of sedimentation equilibrium and sedimentation velocity give values of 208,000±5000 for amandin (stable from p_H 4·3 to about 10), and 212,000±5000 for excelsin (stable from p_H 5·5 to about 10). At p_H 12·2 amandin is disaggregated into molecules of one sixth of the original mol. wt. ; excelsin behaves similarly at p_H 11·9. The mol. wt., molecular radii (3·94—3·96 μμ), sedimentation con-

stants, and molar friction constants of amandin and excelsin are identical, within the limits of experimental error, with the corresponding constants for edestin (*loc. cit.*). H. BURTON.

Acid hydrolysis of proteins. J. ENSELME (Compt. rend., 1930, **190**, 136—138).—The methods of Van Slyke and Sörensen give different results for the amino-nitrogen of the same hydrolysates. The difference is minimal in the early stages, increasing to a maximum, and then decreasing as complete hydrolysis is attained. Various proteins and glycine anhydride have been used with 20 parts of hydrochloric acid (1·46—29·3%). A maximum difference of about 5% is observed in the values obtained by the two methods. The period of increase in the deviation of values obtained by these two methods probably corresponds with the production of polypeptides, and the decrease with the production of amino-acids from the polypeptides.

P. G. MARSHALL.

Determination of oxygen in organic substances by hydrogenation. H. TER MEULEN, H. J. RAVENSWAAY, and J. R. G. DE VEER (Chem. Weekblad, 1930, **27**, 18).—A nickel boat filled with reduced nickel is employed in place of the nickel–asbestos mixture generally used; drying is much facilitated.

S. I. LEVY.

Determination of sulphur in organic material by hydrogenation. H. TER MEULEN, H. F. OPWYRDA, and H. J. RAVENSWAAY (Chem. Weekblad, 1930, **27**, 19—20).—Pure asbestos may be used in place of platinised asbestos if the tube be heated to redness in a furnace. S. I. LEVY.

Interference of nitro-groups in the Zerevitinov method for the determination of active hydrogen. H. GILMAN, R. E. FOTHERGILL, and E. B. TOWNE (J. Amer. Chem. Soc., 1930, **52**, 405—407; cf. A., 1928, 64, 536).—When tetranitromethane and pentabromonitrobenzene are treated with magnesium methyl iodide in *n*-butyl or *iso*amyl ether at 70°, evolution of gas occurs. Pentabromobenzene gives practically no gas under the same conditions, showing that gas formation is due to the nitro-group.

H. BURTON.

Detection of acetic acid. D. KRÜGER and E. TSCHIRCH (Chem.-Ztg., 1930, **54**, 42—44).—A review of tests for the detection of acetic acid indicates that the only trustworthy process which is specific is the microchemical reaction depending on the formation of sodium uranyl acetate. H. F. HARWOOD.

Use of vanadium salts for the differentiation of neutral and acid tartrates and citrates. L. ROSSI (Quim. e Ind., 1929, **6**, 113—114; Chem. Zentr., 1929, ii, 1187).—Acid tartrates or citrates, when added to an ammonium metavanadate solution, give respectively an intense orange-red or yellow coloration. Neutral tartrates and citrates do not give the reaction; addition of small quantities of an acid of moderate strength (*e.g.*, boric or benzoic) causes the coloration to appear. A. A. ELDRIDGE.

Determination of halogens in cyclic compounds. Bromo-derivatives of *m*-xylenol. L. PALFRAY and (MLLE.) D. SONTAG (Bull. Soc. chim., 1930, [iv], **47**, 118—127).—In the determination of bromine by Baubigny and Chavanne's method (A., 1903, ii, 510; 1904, ii, 203) it is essential to add the silver nitrate before the nitric acid. Replacement of the alkaline sodium sulphite by an alkaline solution of sodium arsenite yields accurate results for bromine in derivatives of *cyclo*hexanediol and of *m*-xylenol, but low results are obtained with chloro-derivatives. Use of butyl alcohol in place of ethyl alcohol in Stepanov's method (A., 1907, ii, 50) gives quicker results than amyl alcohol (cf. Favrel and Bucher, A., 1928, 82), but the results are similar; with the 1:3-and 1:4-dichloro*cyclo*hexanes accurate results are obtained for the *trans*-compounds, but the *cis*-isomerides yield low results. Glycerol cannot be used. R. BRIGHTMAN.

Oxidative degradation of physiologically important substances by Hehner's method. F. LIEBEN and E. MOLNAR (Monatsh., 1929, **53** and **54**, 1—13).—Application of Hehner's method for the determination of glycerol to various substances gives results varying with the type of compound oxidised. Thus, carbohydrates and glucosamine are completely oxidised, but salts of hexosediphosphoric acid are only partly so (56—76; numbers in parentheses indicate the percentage of the theoretical Hehner value) (cf. Fürth and Marian, A., 1926, 428). Compounds of the chitin type are oxidised to the extent of about 66%. The values for phenolic derivatives are much higher than for the corresponding benzene derivatives. Pyrrole and indole are oxidised more readily than quinoline. In these cases oxidation proceeds further with a longer time of heating. With amino-acids generally, a considerable resistance to oxidation is observed; for the aliphatic series the highest value is given by aspartic acid (92·5 after 8 hrs.), whilst for the ring-acids, tyrosine and tryptophan show the highest values (85 and 88·2, respectively, after 2 hrs.). Comparison of the deamination (Kjeldahl) values with the Hehner values shows a close similarity in some cases. Higher Kjeldahl values are given by alanine, glutamic acid, and valine, whilst histidine and proline show higher Hehner values. These differences are ascribed to the relative ease of oxidation of the intermediate nitrogen-free acids. Determinations of the Hehner values of fatty acids show a progressive increase from acetic (<1) to *n*-valeric (67) and then a decrease. Oxalic and malonic acids give almost theoretical values, whilst succinic acid (1·2) is practically unattacked. An analogous series of figures is found for fatty acids using Beckmann's oxidation mixture (cf. Kollmann, A., 1928, 660), but the values are lower. During the oxidation of caseinogen more acetic acid is isolated than is derivable from its alanine content; other amino-acids (*e.g.*, leucine) present are, therefore, oxidised partly to acetic acid. H. BURTON.

Biochemistry.

Carbon monoxide content of the blood of steel-mill operatives. C. J. FARMER and P. J. CRITTENDEN (J. Ind. Hygiene, 1929, **11**, 329—335).—The degree of saturation with carbon monoxide of the blood of steel-mill operatives was found to increase during working hours to an average maximum of 6—7%. In the morning after absence from the mill for 16 hrs. the carbon monoxide content of their bloods had not become zero, but averaged 2% saturation.   W. O. KERMACK.

Crystallographic study of pure carbon monoxide-hæmoglobin. A. K. BOOR (J. Gen. Physiol., 1930, **13**, 307—316).—The recorded crystallographic data of the oxy- and carboxy-hæmoglobins of various animals are derived from impure specimens of the protein. Oxyhæmoglobin was prepared by the method of Marshall and Welker (A., 1913, ii, 568) and carboxy-hæmoglobin by saturation of purified oxyhæmoglobin with pure carbon monoxide. Photomicrographs of the crystals of carboxyhæmoglobin and oxyhæmoglobin of the ox, sheep, pig, dog, rat, horse, and guinea-pig and of the carboxyhæmoglobin of the chicken and turkey are reproduced.
C. C. N. VASS.

Intermediate compounds in the oxygenation of hæmoglobin. J. B. CONANT and R. V. McGREW (J. Biol. Chem., 1930, **85**, 421—434).—Analyses of mixtures of crystalline oxyhæmoglobin with its saturated solution in a phosphate buffer at p_H 6·6, after varying degrees of deoxygenation by exposure to a vacuum, indicated that the solid phase was always exclusively oxyhæmoglobin, whilst the solution contained nothing but completely reduced and completely oxygenated hæmoglobin; the hypothesis of the occurrence of intermediates in the oxygenation of hæmoglobin is therefore rejected.   C. R. HARINGTON.

Decomposition of blood pigment. K. BINGOLD (Klin. Woch., 1929, **8**, 866—873; Chem. Zentr., 1929, ii, 1020).—The decomposition of blood pigment proceeds in two phases; in one it is protected from oxidative decomposition by catalase, and in the other the iron acts as a catalyst in the oxidation. The mechanism of these phases is discussed.
A. A. ELDRIDGE.

Oxidation–reduction potentials and the possible respiratory significance of the pigment of the nudibranch _Chromodoris zebra_. P. W. PREISLER (J. Gen. Physiol., 1930, **13**, 349—359).—A method for purifying the bluish-purple pigment in the blood and tissues of _Chromodoris zebra_, Heilpin, is given; in acid solution its colour is orange-red, in moderately alkaline buffered solutions bluish-purple. Reversible oxidation–reduction changes occur with both the orange-red and the bluish-purple forms, either being reduced to a yellow form by reducing agents. The pigment is soluble in aqueous alcoholic solutions. The oxidation–reduction potential curve agrees well with the standard electrode equation (cf. Conant, A., 1922, ii, 547) with a valency change from oxidant to reductant of 1.   C. C. N. VASS.

Mitogenetic radiation from the blood and tissues of invertebrates. A. POTOZKY, S. SALKIND,
and J. ZOGLINA (Biochem. Z., 1930, **217**, 178—184).—Hæmolymph of crabs and of molluscs acts as a source of mitogenetic radiation with which some oxidative process is associated. The hepatopancreas of the animals is also a source of the radiation.
W. McCARTNEY.

Preservation of ox blood. K. HERING (Arch. Pharm., 1930, **268**, 36—38).—Fresh blood which has been carefully freed from foreign matter and defibrinated may be kept for 12 days if 3% of a caffeine-sodium benzoate mixture is added.   J. W. BAKER.

Fixing action of certain dehydrated chemical reagents. P. B. SEN (J. Roy. Micros. Soc., 1929, **49**, 336—340).—The action of various fixatives on films of dried red blood-corpuscles has been examined, the degree of fixation of the cells after treatment with the reagent being determined by finding to what extent lysis took place when the cells were then treated with distilled water. The reagents tested may be classified into three groups : (1) those, such as acetone and chloroform, which when quite dry cause no fixation, but bring about fixation when they contain small quantities of water ; (2) those, such as pyridine or acetone saturated with formaldehyde, which cause imperfect fixation when quite dry, but bring about good fixation when they contain small quantities of water ; (3) those, such as ethyl or methyl alcohol, which effect good fixation when perfectly dry and are not materially improved by small quantities of water. It is suggested that the degree of fixation is related to the permeability of the cell membrane to the reagent and confirmatory experiments are described.   W. O. KERMACK.

Numbers of molecules and ions in a single cell. A. T. CAMERON (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 151—154).—The number of molecules or ions of any particular kind in a single red blood-corpuscle is calculated by means of the following formula: number of molecules (or ions)$=5·9\times10^{11}\times W/M$, where M is mol. (ionic) wt. and W the amount present in 100 g. of cells. Nearly 99% of the molecules are water and only hydrogen ion (220,000) is present in amount less than one million.   P. G. MARSHALL.

Erythrocyte membrane as a colloid system and its changes. O. LEPESCHINSKAJA [with V. P. SMIRNOVA] (Fol. Hæm., 1928, **36**, 41—93; Chem. Zentr., 1929, ii, 1016).—The (frog's) erythrocyte membrane behaves as a colloidal protein and probably becomes resolved in the plasma into fibrin. Deformation brought about by acids and alkalis suggests that the poikilocytosis of pernicious anæmia may be caused by changes in the p_H of the blood.
A. A. ELDRIDGE.

Distribution of uric acid between plasma and erythrocytes. A. W. KOSSIAKOVA (Biochem. Z., 1930, **217**, 212—215).—In human blood there is always a greater percentage of uric acid in the plasma than in the erythrocytes. When the blood is kept (for 24—48 hrs.) the uric acid content of the plasma does not alter much, but that of the erythrocytes decreases. A stable solution of litmus and methylene-blue is recommended as a standard colour for use in

Benedict's method for the determination of uric acid. W. McCARTNEY.

Distribution of quinine between erythrocytes and blood-plasma. L. BINET and R. FABRE (J. Pharm. Chim., 1930, [viii], **11**, 55—58).—Examination of the blood of a 14-kg. dog at varying intervals of time after the injection of 0·8 g. of quinine hydrochloride showed that the erythrocytes contained more quinine than did the plasma and that it is only slowly eliminated from the former. J. H. BIRKINSHAW.

Origin of plasma-proteins. I. Action of various tissues on serum-proteins. II. Relation of hyperalbuminæmic and hyperglobulinæmic condition to the action of liver and muscle on serum-proteins. III. Nitrogen and sulphur content of liver and muscle in hyperalbuminæmia and hyperglobulinæmia. T. SENSHU (J. Biochem. Japan, 1929, **11**, 47—54, 55—63, 65—68).—I. Cell-free extracts from liver, bone-marrow, spleen, kidney, and muscle have no hydrolytic effect on blood-proteins. The extracted tissue pulp generally acts either on the albumin or globulin of the serum. Extracted liver or kidney pulp hydrolyses only serum-albumin, whilst extracted bone-marrow, spleen, or muscle pulp acts only on serum-globulin. Lung pulp has practically no action on the blood-proteins.

II. The proteolytic activity of liver is increased by hyperalbuminæmia, and that of muscle by hyperglobulinæmia.

III. In hyperalbuminæmia the S : N ratio of the liver-proteins decreased, whilst increase of plasma-globulin is accompanied by an increased S : N ratio of the muscle-proteins. CHEMICAL ABSTRACTS.

Distribution of serum- and plasma-proteins in fish. S. LEPKOVSKY (J. Biol. Chem., 1930, **85**, 667—673).—Figures are given for the nitrogen content and distribution of proteins in the blood-serum and -plasma of various species of fish.
C. R. HARINGTON.

Electro-dialysis of serum. II. Efficacy of blood-protein membranes. III. Efficacy of membranes of other proteins. G. ETTISCH and W. EWIG (Biochem. Z., 1929, **216**, 401—429, 430—448).—II. Electro-dialysis of serum using a blood-protein–collodion membrane as anodic and parchment as cathodic membrane (cf. A., 1928, 785) is further investigated. Gradations of electro-dialysis are obtained according to whether whole blood, serum, hæmoglobin, serum-albumin, or -globulin is brought on to the collodion membrane, and in each case the membrane is prepared in two ways, either by the usual method of impregnation or by shaking the membrane with the protein. The course of electro-dialysis is essentially different using the same membrane but preparing it by the two methods, and is usually longer with the impregnated membrane. The course of electro-dialysis is very similar with a membrane impregnated with whole blood to that with hæmoglobin. It is the same also for a whole-serum as for a serum-albumin membrane. A layer of protein appeared on the cathodic membrane when the p_H of the inner chamber had fallen to 4. An increase of tension (500—1000 volts) often caused an acceleration of electro-dialysis.

B B

III. Further variation of the course of electro-dialysis is obtained by using for the anodic membrane a variety of substances not originating from blood, e.g., egg-albumin, gelatin, gliadin, nucleic acid, etc. The same differences are obtained between membranes obtained by impregnation and by shaking with protein. The course of electro-dialysis using an egg-albumin membrane strongly resembled that with serum-albumin. P. W. CLUTTERBUCK.

Refractometric investigation of serum-protein. I. Determination of total protein content from the refractive index. II. Robertson's method for the determination of protein. D. VON DESEÖ (Biochem. Z., 1930, **217**, 185—196, 197—211).—I. The changes in the refractive index and in the specific gravity of serum which correspond with regular changes in the total protein content have been determined and hence this content can be deduced either from the refractive index (provided allowance is made for the influence of water and of non-protein constituents) or from the specific gravity (if the effect of non-protein matter is taken into account).

II. When protein is coagulated in or salted out from serum the former carries with it bound water and the optical properties of the supernatant liquid are consequently altered. Robertson (A., 1915, ii, 851) did not take this into account and hence the use of his figures frequently gives incorrect results.
W. McCARTNEY.

Determination of protein in blood-serum. F. GRENDEL (Pharm. Weekblad, 1930, **67**, 1—20).—The average increase in refractive index for 1% of pure serum-albumin or -globulin from horse, ox, and man, is 0·00190±5%. In Robertson's determination, the factor 0·00150 must be employed for human or ox globulin, and 0·00130 for horse globulin; the factor for albumin for the three sera is 0·00205. The values obtained by refractometric methods are approximate only. The viscosity method of Naegeli and Rohrer is also unsatisfactory, since the viscosity does not depend only on the total quantity of proteins and the relative proportions of albumin and globulin. The globulin contents of normal horse or ox serum are respectively 5·8 and 5·3%, the albumin contents 3·1 and 3·4%; for normal human serum the figures are globulin 2—2·5 and albumin 5·5—7·0%, being lower for children. S. I. LEVY.

Micro-determination of urea in blood and other body fluids. V. PIOVANO (Rass. Clin. Terap. Sci. Aff., 1928, **27**, 458—466; Chem. Zentr., 1929, ii, 1189).—The method depends on the determination of the carbon dioxide produced by the action of urease.
A. A. ELDRIDGE.

Micro-Kjeldahl method. W. J. YOUNG (Austral. J. Exp. Biol., 1929, **6**, 315—316).—A rapid method especially convenient for the determination of non-protein-nitrogen in blood is described.
T. R. SESHADRI.

Influence of poisons which inhibit oxidation on the formation of ammonia in the blood of mammals and birds. I. ENOCH (Biochem. Z., 1929, **216**, 457—461).—In dog's blood the ammonia content does not increase either in presence of oxygen or after poisoning with carbon monoxide or sodium

cyanide during the first 4 hrs., and after 24 hrs. the same small increase was obtained in all cases. In the blood of geese the ammonia content increases slowly in the unpoisoned animal and more quickly in the poisoned, but in both cases comes to the same final value. The increase in goose blood is much greater than with dog's blood. Addition of small amounts of quinine to goose blood also causes a small increase of the ammonia content. P. W. CLUTTERBUCK.

Physico-chemical state of cholesteryl esters and lecithin in blood-serum and -plasma. M. MÂCHEBŒUF (Rev. gén. Colloid., 1929, **7**, 351—357, 393—405).—See A., 1929, 1326.

Determination of cholesterol in small amounts of blood. D. C. Y. SHEN (Chinese J. Physiol., 1929, **3**, 405—408).—Blood (1 c.c.) is dried on a fat-free filter-paper and extracted with hot chloroform for about 1 hr. The cold extract is made up to 10 c.c. with chloroform, acetic anhydride (2 c.c.) and sulphuric acid (0·2 c.c.) are added, and the mixture, after keeping at a temperature below 25° for 8—24 hrs., when a permanent brown colour develops, is compared colorimetrically with a standard solution of cholesterol in chloroform, treated in the same way. W. O. KERMACK.

Methylglyoxal as the product of glycolysis by blood-corpuscles. E. WIDMANN (Biochem. Z., 1929, **216**, 479—492).—Co-enzyme is necessary for the conversion of hexose into hexosediphosphate and of methylglyoxal into lactic acid, but is unnecessary for the dismutation of hexosediphosphate to methylglyoxal. When, therefore, magnesium hexosediphosphate is treated with the co-enzyme-free blood-corpuscles of horse, sheep, or rabbit (either as macerate or as acetone-dried preparation) the formation of methylglyoxal is readily detected and amounts to 75% of the sugar utilised. P. W. CLUTTERBUCK.

Blood-sugar. So-called protein-sugar in blood. P. RONA and W. FABISCH (Biochem. Z., 1930, **217**, 1—33).—Determinations, by the method of Hagedorn and Jensen and by that employing *B. coli*, of the dextrose content of normal human blood give concordant results, showing that in both cases only dextrose is determined. Dextrose is not formed during the hydrolysis of blood-plasma. W. McCARTNEY.

Reducing substances of pigeons' blood. J. M. GULLAND and R. A. PETERS (Biochem. J., 1930, **24**, 91—103).—Although the total reducing value of pigeons' blood by the Hagedorn and Jensen method is approximately 200 mg. per 100 c.c. only 135 mg. ± 15 mg. of this can be dextrose. The residual reducing values obtained after glycolysis and during insulin convulsions are due to the presence of other reducing substances. Filtrates prepared from the blood by different methods contain different proportions of ergothioneine, uric acid, and glutathione (aliphatic thiol compounds). These substances when determined by a "cold" Hagedorn and Jensen method and referred to dextrose (100) yield the following corresponding values. Uric acid 53, glutathione 17 (hot 45), and ergothioneine 56. Zinc filtrates (Hagedorn and Jensen method) are the most trustworthy for determining reducing substances in avian blood, but

they contain in addition to dextrose, ergothioneine and some other unknown substances reducing the ferricyanide reagent. Approximately 60% of the residual value is not accounted for by ergothioneine. The zinc filtrates do not contain aliphatic ·S·S· and ·SH compounds. There are no significant variations from the normal in birds suffering from vitamin-*B* deficiency. S. S. ZILVA.

Simple calculation of sugar content as determined by the method of Hagedorn and Jensen. S. E. DE JONGH (Biochem. Z., 1929, **216**, 400).—The amount of sugar in mg. as determined by the use of the Hagedorn–Jensen technique may be calculated from the formula $0·358A - B/C$, where A is the mean titration of the blank, B the titration of the unknown solution, and C the mean titration of 2 c.c. of the potassium iodate solution, all in c.c. of thiosulphate solution. P. W. CLUTTERBUCK.

Influence of food on blood-sugar regulation. II. (1) Potato feeding. (2) Influence of calcium chloride solution and Carlsbad water on the sugar tolerance. III. Investigation with Carlsbad water and animals nourished on green food or potatoes. E. GEIGER and H. KROPF (Arch. exp. Path. Pharm., 1930, **147**, 272—280, 281—287).—II. Rabbits fed on a potato diet poor in calcium develop a high fasting blood-sugar level with reduced sugar tolerance. A similar effect results from continued administration of calcium chloride solution if an oat diet is employed, but not with a diet of greens. The high sugar tolerance of rabbits fed on oats is not altered by the administration of Carlsbad water.
III. Administration of Carlsbad water to rabbits on potatoes or greens increases the sugar tolerance and lowers the fasting blood-sugar level. Similar results were obtained with Carlsbad water which had been neutralised with acid, as well as with synthetic solutions containing calcium, sodium, potassium, and magnesium in the same proportions as in the natural water. W. O. KERMACK.

Action of sodium nitrite on blood-sugar. E. HERZFELD and R. KRUGER (Klin. Woch., 1929, **8**, 1174—1175; Chem. Zentr., 1929, ii, 1312).—Injection of sodium nitrite into animals, or normal or diabetic man, leads to a fall, and then a rise, in the blood-sugar. A. A. ELDRIDGE.

Action of physical factors on the catalase of blood. A. I. ALEXEEV (Biochem. Z., 1929, **216**, 301—312).—In man, the intensity of the action of blood-catalase varies considerably during the day, being much greater in the morning. The changes do not run parallel with periods of digestion etc., but are explained in terms of change of physical (*e.g.*, climatic) factors. The catalase activity of the blood decreases on raising and increases on lowering the temperature and is strongly increased under the action of wind. A parallelism is obtained between the catalase activity and the amount of hæmoglobin of the blood. P. W. CLUTTERBUCK.

Blood of cattle and sheep in Australia. J. H. NORRIS and W. E. CHAMBERLIN (Austral. J. Exp. Biol., 1929, **6**, 285—300).—In order to provide standards of

comparison, determinations have been made of sugar, calcium, urea, non-protein-nitrogen, uric acid, creatinine, inorganic phosphate, and in some cases moisture content. The results for uric acid, which are much higher than the maximum found elsewhere, are similar to the high results obtained in the case of human blood in Australia. T. R. SESHADRI.

Determination of diffusible and non-diffusible serum-calcium. D. M. GREENBERG and L. GUNTHER (J. Biol. Chem., 1930, **85**, 491—508).—Of the serum from 12 c.c. of blood, 2 c.c. are used for determination of total calcium, 0·5 c.c. for determination of proteins, and the remainder is subjected to ultrafiltration in a special apparatus, the diffusible calcium being determined in the filtrate. After formation of the clot no further change takes place in the calcium of the serum in contact with the clot within 24 hrs. Changes of p_H from 7 to 8, brought about by varying the tension of carbon dioxide, had no effect on the partition between diffusible and non-diffusible calcium. The ratio of chloride in the ultrafiltrate to chloride in the serum is the same as that obtained by membrane distribution (cf. Loeb and Nichols, A., 1927, 584). Since the distribution of non-diffusible and diffusible calcium at constant p_H and protein concentration conforms to the Langmuir adsorption isotherm (J. Amer. Chem. Soc., 1918, **40**, 384) the limiting amount of calcium which can be bound by the serum-proteins, whatever the concentration of ionic calcium, is not much greater than that normally present. C. R. HARINGTON.

Distribution of chlorine in blood. Relation to the acid–base equilibrium. A. LANDAU, G. GLASS, and S. KAMINER (Compt. rend. Soc. Biol., 1929, **101**, 594—596; Chem. Zentr., 1929, ii, 1703).—The normal chlorine contents of blood, plasma, and corpuscles, respectively, are : 2·70—3·02, 3·41—3·62, and 1·70—1·95 g. per litre. The relation corpuscle-chlorine/plasma-chlorine normally varies only between 0·47 and 0·55, but is affected by pathological conditions. A. A. ELDRIDGE.

Vanadium in the blood of the *Ascidia*. M. AZÉMA and H. PIED (Compt. rend., 1930, **190**, 220—222).—The precipitates from the blood of three species of the *Ascidiidæ* and two *Botryllidæ* obtained after treatment with boiling alcohol were examined in the arc spectrum. Vanadium occurred in all species, but only in traces in the second group ; in addition silicon, aluminium, sodium, magnesium, and calcium were observed in the precipitates or in the filtrates, whilst titanium and traces of silver were found in the precipitates from both species of the *Botryllidæ*. Phosphorus was observed in all the precipitates with the exception of that derived from *Phallusia mamillata*. C. C. N. VASS.

Distribution of zinc in the blood of man and the higher animals. A. I. BURSTEIN (Biochem. Z., 1929, **216**, 449—456).—The concentration of zinc in the corpuscles is greater than that in the plasma of the blood of man, ox, sheep, dog, rabbit, and guineapig, the ratio of the concentrations varying from 1·88 to 2·68. Tables show the concentration of zinc in mg. per 100 c.c. and also the above ratios. P. W. CLUTTERBUCK.

Action of chloroform on mammalian plasma and serum. P. BORDET (Compt. rend. Soc. Biol., 1929, **100**, 751—753 ; Chem. Zentr., 1929, ii, 1554—1555).—Reactivation to coagulability of inactive rabbit's serum by treatment with chloroform takes place only with sera of high serozyme content. Chloroform in serum both causes (in presence of lime) the formation of thrombin and arrests its decomposition. A. A. ELDRIDGE.

Normal antithrombin and its relation to the production of thrombin by cytozyme or chloroform. P. BORDET (Compt. rend. Soc. Biol., 1929, **100**, 753—755 ; Chem. Zentr., 1929, ii, 1554).—Serum activated by chloroform can be inactivated by addition of aged inactive serum, and it cannot then be activated by chloroform. Antithrombin is decomposed at 65° and is precipitated from solution with chloroform. Thrombin originating from the action of cytozyme on serum is also decomposed by antithrombin. A. A. ELDRIDGE.

Antigenic properties of colloidal metals. L. A. SILBER and W. FRIESE (Zhur. exp. Biol. Med., 1929, **11**, 128—135).—Long-continued intravenous injection of colloidal iron or gold into rabbits induces in the serum the ability to react with the colloidal metals at great dilution. CHEMICAL ABSTRACTS.

Antigenic properties of arsenic. V. TSCHERNOKHVOSTOV and L. KATZ (Zhur. exp. Biol. Med., 1929, **11**, 136—141).—Colloidal arsenious sulphide can act as a real antigen. CHEMICAL ABSTRACTS.

Hæmolytic action of saponin. K. HARA (J. Biochem. Japan, 1929, **11**, 69—78).—The action is least at p_H 7·0. CHEMICAL ABSTRACTS.

Hæmolytic component of phenylhydrazine hydrochloride. E. V. ALLEN and I. H. PAGE (Arch. exp. Path. Pharm., 1930, **147**, 211—218).—Administration of hydrazine sulphate or of semicarbazide to a dog does not cause a reduction in the number of its red blood-cells. Diphenylhydrazine and azobenzene produce marked hæmolysis, whilst nitrobenzene, aniline, and acetanilide exhibit a similar effect. It is concluded that the phenyl group plays the essential rôle in hæmolysis by phenylhydrazine. W. O. KERMACK.

Dextrose and normohæmolysins. I. DJURICIC (Compt. rend. Soc. Biol., 1929, **100**, 1224—1225 ; Chem. Zentr., 1929, ii, 1704).—Dextrose has no influence on hæmolysis by hæmolysin ; hence the mechanism is not that in hypertonia and is not accompanied by colloidal changes of the proteins of the surface layer. A. A. ELDRIDGE.

Hæmolysis. I. Pancreas-lipase. II. Purification of an amboceptor of hæmolysis. III. Combination of a purified amboceptor with erythrocytes. H. VON EULER and E. BRUNIUS (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 4, 6 pp., No. 8, 6 pp. ; A, No. 5, 6 pp.).—A series of researches designed to throw light on the analogy between the action of complement on erythrocytes in the presence of amboceptor, and the action of lipase on substrate in the presence of albumin. I. The hæmolytic action of lipase prepared from pig's pancreas by the method of Willstätter and Waldschmidt-Leitz

(A., 1923, i, 403) was unchanged by previously heating the enzyme at 70° for 10 min. The hæmolysis was, however, inhibited by the addition of serum from the dog or guinea-pig, whilst the hæmolysis produced by the unheated enzyme was not affected. The factor producing the hæmolysis which is inhibited by serum is therefore thermolabile. Comparable results were obtained using erythrocytes which had been sensitised by digestion with amboceptor for an hour at 37°.

II. Dogs were immunised by the injection of goat's red blood-corpuscles and from the serum a concentrated preparation of amboceptor was obtained by first precipitating the globulin with 30% saturated ammonium sulphate and then increasing the saturation to 46%, when the amboceptor was completely precipitated. The precipitate was dissolved in water, dialysed free from salt, and the amboceptor precipitated with colloidal ferric hydroxide and taken up with $0.3M$-disodium hydrogen phosphate. The phosphate was precipitated with magnesium acetate and ammonia, and the amboceptor adsorbed from acid solution by clay suspension and again set free by sodium phosphate. A concentration of 25 times the original was obtained.

III. Purified amboceptor was prepared from the immune serum of the dog as above, but finally precipitated repeatedly with one third saturated ammonium sulphate instead of the adsorption by clay, giving a concentration 30—33 times the original. The degree of absorption of this preparation by erythrocytes was identical with that of an immune serum of the same amboceptor concentration. It is calculated that 0.02 sq. m. of erythrocyte-surface combines with 500 amboceptor-units.   K. V. THIMANN.

Human brain. M. VERESS (Magyar orvosi Arch., 1929, [ii], **29**, 74—83; Chem. Zentr., 1929, ii, 1019).—Iron detected in normal human brain does not originate from hæmoglobin of red blood-corpuscles.
                                    A. A. ELDRIDGE.

Glutathione content of the stomach. H. C. CHANG and S. M. LING (Chinese J. Physiol., 1929, **3**, 341—352).—At rest the sulphydryl contents of the mucous membrane from the pylorus and fundus regions of the dog's stomach, determined by Tunnicliffe's method, are not significantly different. No change occurs as the result of activity either after a meal or after injection of histamine.
                                    W. O. KERMACK.

Preparation of glutathione from yeast and liver. N. W. PIRIE (Biochem. J., 1930, **24**, 51—54; cf. Hopkins, A., 1929, 1491).—The tissue is treated with a mixture of sulphuric acid, alcohol, and ether, and to the filtrate, after being made $0.5N$ with sulphuric acid, cuprous oxide is added. The cuprous compound is then decomposed with hydrogen sulphide and glutathione is crystallised from the concentrated solution.   S. S. ZILVA.

Glutathione content of denervated skeletal muscle. M. OKUDA (J. Biochem. Japan, 1929, **11**, 183—190).—Diminution in weight of denervated muscle follows an increase in its glutathione content; increased metabolism may be indicated.
                                    CHEMICAL ABSTRACTS.

Enzyme activity of mummified muscle. E. SEHRT (Klin. Woch., 1929, **8**, 1177—1178; Chem. Zentr., 1929, ii, 1419).—Muscle of a 3000-year-old mummy showed strong precipitin, glycolytic enzyme, and respiratory enzyme reactions.
                                    A. A. ELDRIDGE.

Creatine and phosphoric acid content of various portions of the heart. H. VOLLMER (Z. ges. exp. Med., 1929, **65**, 522—534; Chem. Zentr., 1929, ii, 1020).—The ventricle of the calf's or lamb's heart often contains twice as much inorganic phosphoric acid as the auricle or aorta; in young animals the quantities are equal or in the ratio 1 : 0.8. The ratio of the creatine contents is about the same, 75% being combined with phosphoric acid. In man the ratio of creatine values is 1 : 0.28.
                                    A. A. ELDRIDGE.

Solubility of glycogen. M. KERLY (Biochem. J., 1930, **24**, 67—76).—Glycogen from mussels prepared without boiling with alkali takes from 3 to 4 days to reach saturation in water. A similar sample boiled for $2\frac{1}{2}$ hrs. with 60% potassium hydroxide gives a slightly higher value within a few hours. The solubility in water of mussel-glycogen not boiled with potassium hydroxide at 0° is 16%, at 20° 17.7%, and at 37° at least 40%; that from skeletal muscle of frogs 14.9% at 20°, and from rabbit liver 21% at 20°. Curves are given showing the decreasing solubility of glycogen with increasing concentration of alcohol in the presence of potassium acetate, potassium trichloroacetate, potassium chloride, potassium hydroxide, and trichloroacetic acid. When glycogen prepared from mussels is precipitated with alcohol after two precipitations the nitrogen content of the preparation increases, the phosphorus content remaining nearly constant. A micro-modification of Pflüger's method of determining glycogen based on its solubility in aqueous alcohol is described.   S. S. ZILVA.

Fats of Japanese birds. VIII, IX. R. KOYAMA (J. Soc. Chem. Ind. Japan, 1929, **32**, 210—212B).—The properties of the fats obtained from various Japanese birds are described.   A. A. GOLDBERG.

Fats of Japanese birds. X. R. KOYAMA (J. Soc. Chem. Ind. Japan, 1929, **32**, 255—256B).—The characteristics of the fats of *Merula eumomus*, Temminck, *M. pallida*, Gmelin, *M. chrysolaus*, Temminck, and *M. celænops celænops*, Stejneger, are recorded.
                                    C. C. N. VASS.

Unsaturated fatty acids of human liver. I—III. P. MÜLLER (Arch. exp. Path. Pharm., 1930, **147**, 219—234, 235—239, 240—244).—I. Samples of crude oil from human livers had iodine values varying from 77.5 to 148.5. The higher the percentage of fat in liver the lower was the average iodine value. Attempts to separate the saturated and unsaturated fatty acids through their lead salts were unsuccessful because of the oxidation of the unsaturated acids during the process. When the methyl esters of the crude fatty acids were distilled at 0.2—0.5 mm. considerable losses occurred in the unsaturated acids and separation was incomplete, but by brominating certain of the fractions oleic acid and arachidonic acid were detected.

II. By a modification of the method a second un-

saturated acid, $C_{16}H_{26}O_2$, containing three double linkings was also detected and isolated as the *hexabromide*, $C_{16}H_{26}O_2Br_6$, m. p. 122°.

III. The percentage of highly unsaturated fatty acids in the liver-fat was determined by converting them into their bromine additive products and weighing the solid bromo-derivatives. When the percentage of fat in the liver increased the percentage of highly saturated fatty acids decreased, but to such a degree that the percentage of these acids calculated on the original liver is approximately constant.

W. O. KERMACK.

Skin. III. Sugar content of the skin under physiological and pathological conditions. E. URBACH and G. SICHER (Arch. Derm. Syph., 1929, **157**, 160—182; Chem. Zentr., 1929, ii, 907).—Values of the sugar content of the skin and blood, respectively, are : man 47, 98; rabbit 117, 109; guinea-pig 119, 117; rat 80, 83; dog 60, 92; mouse 53, 108 mg. per 100 g. (c.c.). After administration of sugar the skin-sugar increases like the blood-sugar and returns to normal values. The skin-sugar is diminished by insulin. The effect of pathological conditions of the skin is described. A. A. ELDRIDGE.

Spectrographic analysis of the ash of organs. P. DUTOIT and C. ZBINDEN (Compt. rend., 1930, **190**, 172—173).—Though the range of the spectra studied does not include all the mineral elements, *e.g.*, boron, the same metals have been observed as were found in the blood (A., 1929, 952). Silver accumulates in the uterus, ovaries, and thyroid, in small quantities in the other organs, with traces in the heart, spleen, and kidney. Aluminium is found in all the organs, especially in the lungs, kidney, heart, and suprarenal glands. Cobalt and nickel are found in all organs except the liver, but to a greater concentration in the pancreas. Chromium occurs in traces in all the organs, somewhat more concentrated in the thyroid and spleen. Copper is abundant in the lungs, liver, and heart, and least in the kidney and spleen. Lead is relatively abundant in all organs, especially in the pancreas, liver, and thyroid, and least in the spleen, uterus, and ovaries. Tin occurs in all organs, chiefly in the brain, spleen, and thyroid. Zinc predominates in the genital organs and the thyroid, but is absent from the heart. Titanium accumulates in the lungs; only traces occur in the other organs.

C. C. N. VASS.

Determination of total chlorides in tissue. W. R. MANKIN (Med. J. Austral., 1929, **2**, 358—366).—The material (0·2—1·0 g.) is digested with 0·01N-silver nitrate solution (5—10 c.c.) and concentrated nitric acid (5 c.c.) in a boiling water-bath until the volume is 3 c.c., the cooled solution being diluted and titrated with 0·01N-ammonium thiocyanate. Egg-white and -yolk contained, respectively, 1·39—2·02 and 1·23—1·74 mg. of chlorine per g. There is considerable variation, but for the same egg the white usually contains more chlorine than the yolk.

CHEMICAL ABSTRACTS.

Iodine as a biogenic element. XIX. Iodine content of the normal animal organism. XX. Influence of oral administration of small amounts of inorganic iodine on the iodine content of the animal organism. E. MAURER and H. DUCRUE (Biochem. Z., 1930, **217**, 227—230, 231—235).—XIX. The iodine content of various organs of female rabbits has been determined. Great variations were found in the proportion of iodine in the thyroid glands and differences were also found in the iodine contents of the two halves of the glands. Of the other parts investigated the ovaries had the highest iodine content. The iodine content of the various parts of the organism does not depend on that of the thyroid gland.

XX. Small doses of potassium iodide were administered to female rabbits and after 24 hrs. the iodine content of various organs was determined. In all parts various increases were found and only in those concerned with iodine excretion was the increase great. After 96 hrs. the iodine content in almost all parts had fallen to the normal level.

W. McCARTNEY.

Microscopical examination of wool fibres. R. BURGESS and C. RIMINGTON (J. Roy. Micros. Soc., 1929, **49**, 341—348).—When wool fibres are treated with Pauly's reagent staining takes place only where the epithelial scales of the fibres have sustained damage. The test has been found of great practical value in the technical examination of wool fibres. By the application of the Totani reaction evidence has been obtained that both tyrosine and histidine in the fibre unite with the Pauly reagent to produce the brownish-red colour. W. O. KERMACK.

The sulphur linking in wool. C. RIMINGTON (Biochem. J., 1930, **24**, 205—207).—Free ·S·S· or ·SH groups are not present in undamaged wool and can be induced only by the action of alkalis or of ultra-violet radiation. S. S. ZILVA.

Secretion and composition of milk in non-physiological activity of the male mamma. A. TRAUTMANN and P. LUY (Deut. tierärztl. Woch., 1929, **37**, 305—307; Chem. Zentr., 1929, ii, 1176).—The milk of a he-goat had d 1·028—1·035, and contained : dry substance 14·9, ash 0·85, fat 4·5%. The effect of hormonal preparations was investigated.

A. A. ELDRIDGE.

Factors affecting yield and quality of milk. II. Variations in successive lactations. J. GLEN and A. C. M'CANDLISH (J. Agric. Sci., 1930, **20**, 45—52; cf. Kay and M'Candlish, A., 1929, 487).—Milk and butter-fat production of cows rises to a maximum at the fifth lactation period corresponding with 7 years of age, after which yields fluctuate but show a downward tendency. The milk-fat percentage is highest in the first lactation, drops markedly in the second, remains steady with a downward tendency for several lactations, and then decreases. E. HOLMES.

Fate of caseinogen in milk retention. C. PORCHER and E. MUFFET (Compt. rend. Soc. Biol., 1929, **100**, 1049; Chem. Zentr., 1929, ii, 1025).—The leucocytary enzymes appear to decompose caseinogen readily, removing phosphorus and leaving a heat-coagulable protein. A. A. ELDRIDGE.

Mode of combination of calcium in milk and its significance in clotting by rennin. M. RÜDIGER and K. WURSTER (Biochem. Z., 1929, **216**, 367—

399).—The clotting power of rennin is favourably influenced by addition of calcium chloride to milk up to a concentration of 1·42%, but above this is inhibited. By addition of calcium chloride to milk and whey the acid content is increased to a maximum and then remains constant. The shift of p_H is not sufficient to account for the acceleration of clotting by calcium chloride, which is due chiefly to change in the phosphate relationships. From comparison between an inorganic phosphate system and milk it is shown that calcium and phosphate ions in the normal concentrations of milk cannot exist as stable ions, but are retained in solution colloidally by caseinogen. The buffering properties of milk are chiefly due to the system calcium phosphate–caseinogen–citric acid.

P. W. CLUTTERBUCK.

Effect of the pancreas secretion on the alkali reserve of the blood and on the hydrogen-ion concentration of the gland. E. HAMMARSTEN and E. JORPES (Acta med. Scand., 1928, 68, 10 pp.; Chem. Zentr., 1929, ii, 1022).—After injection of secretin into cats the p_H of the pancreas was increased, whilst the alkali reserve of the blood remained unchanged. A. A. ELDRIDGE.

Rôle of ions and electrolytes in the process of physiological stimulation. O. V. NICOLAIEV (Zhur. exp. Biol. Med., 1929, 11, 114—126).—By increasing the calcium chloride or sodium hydrogen carbonate content of the perfusing solution, salivary secretion by an isolated salivary gland (dog) is increased; increase of the amount of sodium or potassium chloride, or addition of hydrogen or magnesium chloride, diminishes the salivary flow. Hence ions play an essential rôle in the physiological responsiveness of tissue. CHEMICAL ABSTRACTS.

Fractionation of Australian snake venoms. I. Venom of death adder (Acanthophis antarcticus). C. H. KELLAWAY, M. FREEMAN, and F. E. WILLIAMS (Austral. J. Exp. Biol., 1929, 6, 245—260).—Heating the proteose fraction of the venom caused a diminution of activity. Quantitative fractionation of the venom by extraction with 45% ethyl alcohol is unattended by any loss of total activity of the venom. When injected subcutaneously in mice or guinea-pigs the insoluble fraction has but little of the toxicity of the whole venom, whereas it possesses all the coagulant activity. The soluble fraction contains the "neurotoxic" principle, which has a curare-like action. The hæmolytic activity is evenly distributed in both fractions, whereas more of the substance which stimulates plain muscle is present in the soluble fraction. Both fractions are equally toxic by intravenous injection in mice and guinea-pigs. T. R. SESHADRI.

Production of bile pigments in vitro. A. VON CZIKE (Deut. Arch. klin. Med., 1929, 164, 236—242; Chem. Zentr., 1929, ii, 1318).—Bilirubin was produced in citrate or hirudin plasma kept at 37° for 24 hrs. Its appearance is not due to liberation of adsorbed bilirubin, but is apparently due to enzyme action.

A. A. ELDRIDGE.

Detection of bile pigments in urine. J. GLASS (Med. Welt, 1929, 3, 824—825; Chem. Zentr., 1929, ii, 1189).—Sodium nitrite and concentrated hydrochloric acid are employed separately. A. A. ELDRIDGE.

Determination of gaseous tension in urine and other liquids containing carbonate. F. MAINZER and C. T. SHEN (Pflüger's Archiv, 1929, 222, 1—11; Chem. Zentr., 1929, ii, 919).—A method for the determination of the gaseous tension of small quantities of urine is described. The oxygen pressure in human urine is 23—101 (average 54) mm., and the carbon dioxide pressure 43—102 (average 81) mm.

A. A. ELDRIDGE.

Colorimetric detection of acetone in urine. C. STICH (Pharm. Zentr., 1929, 70, 681).—A modification of the standard nitroprusside test for the detection of acetone in urine is described. E. A. LUNT.

Detection of acetone and acetoacetic acid in urine. P. HORKHEIMER (Münch. med. Woch., 1929, 76, 1128—1129; Chem. Zentr., 1929, ii, 1052).—Lange's nitroprusside reaction indicates the presence of acetoacetic acid in diabetic urine; with 0·007% a violet ring is obtained in 2 min. A. A. ELDRIDGE.

Detection of ketonic substances in urine. J. BAZOWSKI and H. SZANCER (Pharm. Zentr., 1930, 71, 4—5).—The methods of detection are discussed. It is sufficient to employ first Lange's ring test; if this gives a negative result, Lieben's iodoform test should be applied. It is not necessary to distinguish between acetone and acetoacetic acid. S. I. LEVY.

Determination of sugar in urine. K. BODENDORF and A. KOWNATZKI (Apoth.-Ztg., 1929, 44, 636—637; Chem. Zentr., 1929, ii, 920).—The urine is treated with Fehling's solution in excess, and the excess is determined colorimetrically.

A. A. ELDRIDGE.

Lipin excretion. VII. Partition of fæcal lipins in bile fistula dogs. W. M. SPERRY (J. Biol. Chem., 1930, 85, 455—463).—As in normal dogs, the fæcal lipins of dogs with a bile fistula on a fat-free diet are confined almost entirely to the solid fractions of the fæces. The lipins of both bacterial and non-bacterial fractions were of similar composition, and therefore presumably of similar origin; the distribution of total lipins as between bacterial and non-bacterial portions was variable. When fat was administered to such dogs the unabsorbed portion appeared in the non-bacterial solid fraction of the fæces. C. R. HARINGTON.

Viscosity of pathological blood-sera. E. H. FISHBERG (J. Biol. Chem., 1930, 85, 465—475).—The viscosity of blood-serum varies relatively little with dilution, or with changes in p_H; it is increased by saturation with carbon dioxide in presence of the red blood-corpuscles, and is diminished by addition of cholesterol or of carbamide; bile acids cause an increase in viscosity. That these phenomena are due to a special state of the serum-proteins is indicated by the fact that the viscosity of exudates runs parallel to their tendency to form gels. The results afford an explanation of the diminished viscosity of the blood-serum in uræmia and the increased viscosity in cyanosis and in obstructive jaundice.

C. R. HARINGTON.

Reciprocal action of chloride and alkali on the body in acute diseases. C. ACHARD and M. ENACHESCO (Compt. rend., 1930, 190, 91—93).—In

a normal subject administration of chloride (10—15 g.) produces a large chloride excretion and an alkaline urine with excretion of carbonate. In cases of pneumonia a similar administration produces only a slight rise in urinary p_H and carbonate excretion along with slight hastening of the usual chloride crisis. In angina and acute rheumatism it produces only a slight chloride excretion without alkaline urine. In catarrhal jaundice half the salt is excreted, showing a less stubborn chloride retention, whilst the acid–base equilibrium is temporarily modified and the alkali reserve is scarcely affected. Administration of sodium hydrogen carbonate in cases of pneumonia, angina, or pleurisy is followed by a rapid increase in the alkalinity of the blood and urine without any effect on chloride excretion. In acute disease with chloride retention the body appears to have an affinity for chloride which must be satisfied before excretion can occur. P. G. MARSHALL.

Allergens. III. Pollen of *Alopecurus* (foxtail grass). L. F. LOEB (Klin. Woch., 1929, 8, 926—927; Chem. Zentr., 1929, ii, 1023).—The substance giving a skin reaction in hay-fever is contained in the precipitate obtained on addition of alcohol to the aqueous extract. Either it is a protein or is combined with protein, or it is active only in presence of a protein. A. A. ELDRIDGE.

Influence of inorganic elements on blood regeneration in nutritional anæmia. V. C. MYERS and H. H. BEARD (J. Amer. Med. Assoc., 1929, 93, 1210—1212).—When iron (0·5 mg. daily) is administered to rats rendered anæmic by an exclusive milk diet, traces (0·01—0·5 g. (?)) of manganese, nickel, copper, germanium, and arsenic all promote hæmoglobin regeneration. CHEMICAL ABSTRACTS.

Iron and blood regeneration. Effect of ultraviolet rays on blood regeneration and iron metabolism. S. OSATO and S. TANAKA (Z. ges. exp. Med., 1929, 65, 692—704; Chem. Zentr., 1929, ii, 1022).— Animals with experimental anæmia experienced rapid blood regeneration when irradiated with ultra-violet rays. Reserve iron was mobilised from the liver and (when present) spleen and used in the production of blood pigment. There was a simultaneous retention of iron. A. A. ELDRIDGE.

Calcium metabolism in arthritis. E. F. F. COPP (Arch. Int. Med., 1930, 45, 136—146).—A patient suffering from hypertrophic osteo-arthritis on a normal diet was found to have a positive calcium balance (retention). This was converted into a negative balance by use of a diet low in calcium. Phosphoric acid greatly retarded loss of calcium from the system, much more than hydrochloric acid or sodium salicylate. The latter salt and acids increased, and sodium hydrogen carbonate lowered, the calcium excreted in the urine. A case of atrophic osteo-arthritis showed a negative calcium balance. This was converted into a positive balance by a high-calcium diet. The greatest positive balance was shown during administration of phosphoric acid. J. H. BIRKINSHAW.

Inhibition of lactic acid formation in cancer and muscle. S. T. HARRISON and E. MELLANBY (Biochem. J., 1930, 24, 141—157).—The aërobic and anaërobic glycolysis of cancer tissue is inhibited by pancreatic extract; amylase-containing extracts from malt diastase, takadiastase, and salivary gland also inhibit glycolysis. Cancer tissue does not form lactic acid from hexosediphosphate or hexosemonophosphate. In the soluble muscle-enzyme system the production of lactic acid from hexosediphosphate but not from hexosemonophosphate is inhibited by pancreatic extract. S. S. ZILVA.

Effect of transplanted tumours on basal metabolism. Y. YOSHIDA (Japan. J. Gastroenterol., 1929, 1, 93—116).—The growth of a fowl sarcoma is accompanied by an increase in blood-lactic acid and a decrease in -sugar and (with fluctuation) -lipoids; the ratio of albumin to globulin decreases, whilst the amino-nitrogen and fibrinogen increase. CHEMICAL ABSTRACTS.

Lactic acid production in tumours. A. I. VIRTANEN (Suomen Kem., 1929, 2, 19—22).—The optimum reaction for lactic acid production by tumour tissue is about p_H 7·0, the activity falling to about 50% of the maximum at p_H 6·0. The reaction optimum in the case of lactic acid-producing bacteria is p_H 6·2, and in blood p_H 7·5—8·0. W. O. KERMACK.

Composition of melanotic pigment. F. SCHAAF (Klin. Woch., 1929, 8, 1066—1068; Chem. Zentr., 1929, ii, 1551).—It is improbable that sulphur is an integral constituent of melanin. A. A. ELDRIDGE.

Physico-chemical theory of caries. D. ENTIN (Z. Stomatol., 1929, 27, 239—274; Chem. Zentr., 1929, ii, 1706).—Caries is regarded as latent avitaminosis-D. The salivary phosphorus, calcium, potassium, reducing substances, d, f. p., conductivity, and viscosity were determined. Dental enamel and dentin behave as semi-permeable membranes towards solutions of salts and dyes. A. A. ELDRIDGE.

Bile-protein in diabetes. I. GAVRILA and A. MOGA (Compt. rend. Soc. Biol., 1929, 101, 404—406; Chem. Zentr., 1929, ii, 1024).—In diabetes the bile-protein is increased. A. A. ELDRIDGE.

Presence of pancreatic enzymes in the bile. H. L. POPPER (Wien. klin. Woch., 1929, 42, 800—803; Chem. Zentr., 1929, ii, 1168).—In certain pathological conditions the bile, which usually contains no diastatic enzyme, showed high diastatic values. A. A. ELDRIDGE.

Behaviour of the animal organism in pancreatic diabetes towards various carbohydrates. II. Sodium hexosediphosphate. W. ILJIN (Z. ges. exp. Med., 1929, 65, 399—410; Chem. Zentr., 1929, ii, 1025).—In cats after extirpation of the pancreas sodium hexosediphosphate which was injected subcutaneously suffered fission; the carbohydrate was utilised and the phosphoric acid excreted in the urine. Diminution of urinary and blood-sugar resulted. A. A. ELDRIDGE.

Blood-amylase in bacterial infections. M. E. MAGARAM (Zhur. exp. Biol. Med., 1929, 11, 142—146).—Fasting does not affect the blood-amylase of the rabbit. Amylase activity increases immediately prior to parturition. Injection of diphtheria (and

sometimes dysentery) toxin, and diphtheria cultures considerably increases the blood-amylase.

<div style="text-align:right">CHEMICAL ABSTRACTS.</div>

Gaseous exchange in fever caused by naphthyl-amine-yellow or by β-tetrahydronaphthylamine. J. DUDLEY and V. KOSKOVSKI (Compt. rend. Soc. Biol., 1929, **100**, 1234—1236, 1238—1240; Chem. Zentr., 1929, ii, 1710).

Physiological characteristics of fever. I. Water balance. II. Distribution of chlorides. M. SUPONITZKA (Zhur. exp. Biol. Med., 1929, **11**, 41—53, 54—62).—During the first hours of fever water migrates from the blood to the tissues, the swelling capacity of which is increased. The blood-chlorine at first rises considerably, then migration into the tissues occurs. Chlorine becomes concentrated in the affected organs.

<div style="text-align:right">CHEMICAL ABSTRACTS.</div>

Exophthalmic goitre. Protein content of the cerebrospinal fluid. W. O. THOMPSON and B. ALEXANDER (Arch. Int. Med., 1930, **45**, 122—124).— In 15 cases of exophthalmic goitre the concentration of protein in the fluid was within the lower limits of normal. After subtotal thyroidectomy there was a definite increase in protein concentration accompanying a gain in body-weight and a reduction in basal metabolism. J. H. BIRKINSHAW.

Hæmochromatosis: copper content of the liver. E. H. FUNK and H. ST. CLAIR (Arch. Int. Med., 1930, **45**, 37—45).—Analysis of the organs of a man, 44 years of age, who died of hæmochromatosis showed that the liver contained 140 mg. of copper per kg., or 331·8 mg. for the entire organ. The spleen contained less than 1 mg. The iron of the liver was at least 6·2 g. per kg. or 14·7 g. for the entire organ. J. H. BIRKINSHAW.

Blood-sugar in diseases of the heart. M. CHASANOV (Klin. Woch., 1929, **8**, 934—936; Chem. Zentr., 1929, ii, 903).

Electrolyte content of blood-serum in heart and vascular diseases. J. TEPLOW and A. KOSCHEVNIKOVA (Klin. Woch., 1929, **8**, 1222—1223; Chem. Zentr., 1929, ii, 1023).—In circulatory diseases the ratio of potassium to sodium in the blood-serum is nearly always normal. In decompensation of cardiac activity the calcium, chlorine, and inorganic phosphorus fall, whilst the potassium content remains unchanged. In sclerosis of the arteries of the heart the potassium : sodium ratio is generally increased.

<div style="text-align:right">A. A. ELDRIDGE.</div>

Sugar metabolism and water economy. I. H. TATERKA and F. OESTREICHER (Klin. Woch., 1929, **8**, 1401—1402; Chem. Zentr., 1929, ii, 1421).—In cardiac œdema there is a low fasting blood-sugar value, postponed but more marked effect of insulin, and slower rise and fall of blood-sugar (with lower maximal values) after administration of dextrose than in normal cases. A. A. ELDRIDGE.

Behaviour of cholesteryl ester in the blood-serum in hepatic disease. H. WENDT (Klin. Woch., 1929, **8**, 1215—1218; Chem. Zentr., 1929, ii, 1023).—Human bile contains an enzyme which hydrolyses cholesteryl ester; dog's bile does not contain the enzyme, and therefore both cholesterol and its ester are present. A. A. ELDRIDGE.

Relation between changes in the alkali reserve and relative chlorine and sodium content of the blood in experimental immobilisation of intestine and in histamine shock. F. D. ALSINA (Compt. rend. Soc. Biol., 1929, **100**, 1098—1101; Chem. Zentr., 1929, ii, 1022).—The changes in the alkali reserve are accompanied by a relative increase in blood-sodium and decrease in blood-chlorine.

<div style="text-align:right">A. A. ELDRIDGE.</div>

Nature of the toxic product arising from closure of the intestine. A. BLANCHETIÈRE and L. BINET (Compt. rend. Soc. Biol., 1929, **101**, 14—17; Chem. Zentr., 1929, ii, 1023).—On occlusion of the intestine there is present a single-chain substance of proteose character, probably arising from the decarboxylation of leucine; it is possibly *iso*amylamine.

<div style="text-align:right">A. A. ELDRIDGE.</div>

Urea content of blood and cerebrospinal fluid. L. RICHON, M. VIGNEUL, and J. GIRARD (Compt. rend. Soc. Biol., 1929, **100**, 747—748; Chem. Zentr., 1929, ii, 1023).—The blood and cerebrospinal fluid of a child with acute nephritis contained per litre, respectively, 3·59 and 1·229 g. of urea.

<div style="text-align:right">A. A. ELDRIDGE.</div>

Metabolism in pneumonia. I. Excretion and determination of organic acid. I. GREENWALD (J. Biol. Chem., 1930, **85**, 447—454).—The method of Van Slyke and Palmer (A., 1920, i, 459; ii, 131) for the determination of organic acids is improved by preliminary treatment of the urine with Lloyd's reagent, which eliminates the necessity for a correction for creatine and creatinine. The modified method gives much lower results than the original one, but added organic acids can be quantitatively recovered. The fact that the excretion of organic acid is increased in pneumonia is confirmed.

<div style="text-align:right">C. R. HARINGTON.</div>

Spleen. IV. Formation of colourless form of hæmoglobin after splenectomy. G. B. RAY and L. A. ISAAC (J. Biol. Chem., 1930, **85**, 549—558).— In the blood after splenectomy a discrepancy exists between the total pigment as determined by the method of Stadie and the hæmoglobin determined either spectrophotometrically or by oxygen capacity. Since the discrepancy cannot be explained by the presence of any known derivative of hæmoglobin, it is suggested that the blood contains a non-functional colourless form of hæmoglobin designated "leucohæmoglobin." C. R. HARINGTON.

Variations in mineral composition of bone in normal and rachitic rats and in rats cured of rickets. J. ALQUIER, (MLLE.) L. ASSELIN, (MLLE.) M. KOGANE, and (MLLE.) G. S. DE SACY (Compt. rend., 1930, **190**, 334—336).—The total ash, calcium, and phosphorus content of bones of 100 rats, 85 of which had been rendered rachitic, has been determined at different periods of growth. In the normal rat, although the phosphorus content remains constant, the total ash and calcium present increase with increase in body-weight, that is, with increasing age. In rachitic rats, if growth has not become active (total body-weight not above 90 g.), the total ash, calcium,

and phosphorus remain normal, but in rats where the body-weight has increased to 100—110 g. the deficiency of calcium and phosphorus becomes marked. Rats which have been cured of rickets by addition of irradiated dried milk, irradiated ergosterol, or cod-liver oil to the diet exhibit a marked increase in mineral matter, the calcium content exceeding the normal value, but if the cure is effected by irradiation of the original diet growth is slow, the calcium content remains normal, but there is a marked deficiency in total ash and phosphorus. J. W. BAKER.

Experimental scurvy. V. Calcium and phosphorus metabolism of guinea-pigs fed on a diet free from vitamin-C. T. NAGAYAMA and T. MUNEHISA (J. Biochem. Japan, 1929, 11, 191—201).—The urinary elimination of calcium and phosphorus by scorbutic guinea-pigs, although depending on the amount of food ingested, generally increases at first, and subsequently tends to decrease. As the urinary calcium decreases much fæcal calcium is present. Serum-calcium and -phosphorus are normal. CHEMICAL ABSTRACTS.

Glutathione, cytochrome, and hydrogen-ion concentration in developing hen embryos. H. YAOI (Japan. J. Exp. Med., 1928, 7, 135—143).—The glutathione content of hen embryos is maximal at the 12—14th day; the cytochrome content is negligible from the 4th to the 11th day, but then increases, approaching the adult level at hatching. The p_H is at first low, but becomes constant (7·4) at the 14—15th day. CHEMICAL ABSTRACTS.

Iodine content of pigs, and passage of iodine from the mother to the fœtus and new-born pigling. H. COURTH (Landw. Jahrb., 1929, 69, 565—598; Chem. Abstr., 1929, ii, 1550).—The pig's thyroid gland contains 4—7 mg. of iodine. Iodine was not detected in the ovaries. The small quantity of iodine present in the fœtal thyroid gland towards the end of gestation is not attributed to embryonic activity of the gland. The sow delivers the greater part of her iodine reserve particularly in the colostrum. A. A. ELDRIDGE.

Nomogram deriving basal metabolism from height-weight co-ordinates. C. BRUEN (J. Biol. Chem., 1930, 85, 607—609).—A simplified chart for the graphic solution of the equation of Du Bois and Du Bois (Arch. Int. Med., 1916, 17, 863) is given. C. R. HARINGTON.

Effect of humidity of the air on metabolism. Hypotony in warm and moist atmosphere. J. LEFÈVRE and A. AUGUET (Compt. rend., 1930, 190, 326—328).—By means of a specially constructed chamber (ibid., 1929, 188, 515), the effect of varying conditions of humidity on metabolic processes has been investigated with sheep at 19—20°. When the humidity does not exceed 80—85% the subject can readily give off its latent heat (up to 26—38 g.-cal.) by evaporation, but when the humidity exceeds 90%, evaporation becomes very small and the latent heat accordingly reduced. This effect is produced, not by a rise in the body temperature, but by a decrease of approximately 20% in the metabolic processes. J. W. BAKER.

Influence of nutritive condition on the dextrose tolerance test. V. J. HARDING and F. H. VAN NOSTRAND (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 293—301).—Du Vigneaud and Karr's results on the effect of a single meal of fat after starvation on the dextrose tolerance of rabbits is not confirmed, the tolerance being increased. This divergence is explained by the fact that emaciated rabbits have a much lower tolerance than well-nourished animals, and it is therefore necessary to use only standardised animals in good condition for such experiments. P. G. MARSHALL.

Influence of proteins and their normal decomposition products on sugar content of blood. E. LUNDSGAARD (Biochem. Z., 1930, 217, 125—146).—Subcutaneous administration of glycine or of glutamic acid to rabbits causes hyperglycæmia only if the dose reaches 3 g. per kg. Oral administration of 5 g. per kg. does not cause hyperglycæmia. In dogs, oral administration of glycine, alanine, or meat does not affect the blood-sugar level and in men who have consumed large quantities of meat there is no change in the blood-sugar content. Only when excessive doses are given can proteins or amino-acids cause hyperglycæmia when orally administered. W. MCCARTNEY.

Hyperglycæmia resulting from administration of amino-acids. E. LUNDSGAARD (Biochem. Z., 1930, 217, 147—161).—Determinations of the sugar, ammonia, and amino-acid contents of the blood of rabbits to which glycine, ammonium lactate, or glutamic acid was subcutaneously or orally administered show that the hyperglycæmia produced by amino-acids has no connexion with that produced by ammonia, but is due to the action of the acids as such. Hyperglycæmia due to administration of ammonium salts first appears when the ammonia content of the blood reaches 0·65—0·80 mg. per 100 c.c. In rabbits hyperglycæmia due to amino-acid administration first appears when the amino-nitrogen content of the blood exceeds 50 mg. per 100 c.c. in the case of glycine and in the case of glutamic acid when it exceeds 25 mg. per 100 c.c. Hyperglycæmia due to amino-acids is a toxic phenomenon without general physiological importance. W. MCCARTNEY.

Metabolism of amino-acids. III. Glycogen formation after oral administration of amino-acids to white rats. R. H. WILSON and H. B. LEWIS (J. Biol. Chem., 1930, 85, 559—569).—Definite gluconeogenesis was observed in white rats as the result of feeding with caseinogen, gelatin, or glycine, in each case supplemented with butter. Marked gluconeogenesis resulted from the administration of d- or dl-alanine to fasting rats by stomach tube; less effect was observed with glutamic acid, and little or no effect with glycine and leucine. These differences may be partly due to differences in the rates of absorption and in the specific dynamic effects of the amino-acids concerned. C. R. HARINGTON.

Animal calorimetry. XXXIX. Specific dynamic action in the normal and phloridzinised dog. W. H. CHAMBERS and G. LUSK (J. Biol. Chem., 1930, 85, 611—626).—Glutamic acid has no specific dynamic effect in normal or phloridzinised dogs (cf.

Rapport and Beard, A., 1929, 213). The specific dynamic effect of glycine is dependent on the amount administered and independent of the weight of the animal; moreover, its effect, as also that of meat, is exercised equally in the normal and phloridzinised dog. The oxidation of dextrose can therefore play no part in the development of the effect. The energy required for the transformation of amino-acids into dextrose in diabetes is probably derived from fat, which itself exercises a small specific dynamic effect in normal, but not in phloridzinised dogs.

C. R. HARINGTON.

Muscle contraction without production of lactic acid. E. LUNDSGAARD (Biochem. Z., 1930, **217**, 162—177).—In rabbits and frogs poisoned with sodium iodoacetate the post-mortal production of lactic acid in striped muscle is totally inhibited and this inhibition may take place without damage to the contractive power of the muscle. When muscles in this condition are caused to contract the phosphagen present is rapidly and totally converted into hexose-phosphate. It is concluded that phosphagen may be the energy-producing substance in muscle contraction and that the production of lactic acid causes progressive re-synthesis of the decomposed phosphagen.

W. MCCARTNEY.

Formation of lactic acid in desiccated amphibian muscles. E. C. SMITH and T. MORAN (Proc. Roy. Soc., 1930, B, **106**, 122—131).—The effects produced by drying and by freezing the sartorius muscles of the frog are the same. The amount of lactic acid formation reaches a maximum somewhat below −2°, or when 79% of the water is removed, and coincides approximately with the point of instantaneous death. It is improbable that any separation of sodium hydrogen carbonate or sodium phosphate occurs at this temperature and concentration, and the changes cannot therefore be connected with salt-precipitation. K. V. THIMANN.

Carbohydrate metabolism. I. A dextrose-lactic acid cycle involving muscle and liver. H. E. HIMWICH, Y. D. KOSKOFF, and L. H. NAHUM (J. Biol. Chem., 1930, **85**, 571—584).—In anæsthetised or decerebrate dogs the lactic acid content of the blood of the femoral vein was distinctly greater than that of the femoral arterial blood during exercise of the lower limbs; at the same time the hepatic arterial blood contained much more lactic acid than the hepatic venous blood. During exercise of the upper extremities an absorption of lactic acid occurred in the leg muscles, causing a reversal of its distribution as between the femoral arterial and venous blood. Evisceration caused a gradual increase in the lactic acid content of the arterial blood. The distribution of dextrose between the arterial and venous blood of the limbs and liver was in the reverse direction from that of the lactic acid. It appears therefore that a cycle exists in which lactic acid formed by the muscles is converted into carbohydrate by the liver and again distributed by this organ to the muscles in the form of dextrose. C. R. HARINGTON.

Duration of life of particular parts of frog's heart in liquids of various ionic compositions. N. A. POPOW and A. A. KUDRJAWZEW (Arch. exp. Path. Pharm., 1930, **147**, 331—338).—The life of separate parts of a frog's heart beating in salt solution is reduced by the removal of calcium. In normal Ringer solution, the bulbus usually continues to beat for the longest time, whilst in calcium-free Ringer solution the venous sinus usually survives longest.

W. O. KERMACK.

Relation between carbohydrate and fat metabolism. I. S. G. GENES and Z. DINERSTEIN (Zhur. exp. Biol. Med., 1929, **11**, 5—11).—In dogs on a diet loaded with sugar or neutral fat a definite relationship between the intermediate metabolic products of fat and carbohydrate exists, and is well marked in the peripheral blood. Loading with fat or sugar respectively causes an increase or a decrease in ketonic substances and a decrease or an increase in lactic acid.

CHEMICAL ABSTRACTS.

Nature and biological availability of almond carbohydrates. A. F. MORGAN, C. M. STRAUCH, and F. BLUME (J. Biol. Chem., 1930, **85**, 385—404).—Almonds of different crops varied in composition particularly in respect of their carbohydrate content. Defatted almond meal contained about 30% of carbohydrates, 47·8% of which is characterised as " available " (i.e., hydrolysable by acid); this fraction was composed for the most part of sucrose, pentoses, and pentosans, together with small amounts of starch and other polysaccharides, and reducing sugars. Rats fed on a diet composed of 70% of almond meal and 30% of almond oil excreted two to three times the weight of fæces excreted by normal animals; the almond diet had a pronounced laxative effect. When rats were fasted for 24 hrs. and fed with the almond diet for 24 hrs. their total glycogen content and blood-sugar were lower than those of rats after a 24 hrs. fast followed by 24 hrs. on a normal diet. The latter result indicates the possible dietetic use of the almond meal in diabetes and other diseases.

C. R. HARINGTON.

Relative nutritive values of carbohydrate and related substances. H. ARIYAMA and K. TAKAHASI (Biochem. Z., 1929, **216**, 269—277).—The determination of the relative nutritive values of 28 different carbohydrates and related substances (e.g., pentoses, hexoses, di- and poly-saccharides, dextrin, di-hydroxyacetone, glycerol, mannitol, glyceric, gluconic, and mucic acids was investigated, the substances being fed to white rats along with a basic diet of flesh powder, butter, and salts, and the resulting increases in weight being regarded as a measure of the relative nutritive values. The assimilation limits for these substances per 100 g. body-weight are tabulated and compared with those obtained by Mendel and Jones (J. Biol. Chem., 1920, **43**, 491).

P. W. CLUTTERBUCK.

Comparison of the nutritive properties of soya-bean "milk" and cow's milk. E. TSO (Chinese J. Physiol., 1929, **3**, 353—362).—Feeding experiments on albino rats show that soya-bean " milk " has a vitamin-A content approximately equal to that of cow's milk and that it is richer in vitamin-B. The deficiency of soya-bean " milk " in minerals can readily be supplied by the addition of suitable salts, whilst the protein is adequate if sufficient quantities are given. W. O. KERMACK.

Nitrogen metabolism in sheep on high-protein diets. J. STEWART (J. Agric. Sci., 1930, 20, 1—17).—Bi-weekly nitrogen balances, determined for five sheep fed with high-protein diets (containing linseed cake), showed in three cases nitrogen equilibrium during the first part of the tests and a negative balance towards the end of the 3- or 4-month period. This suggests some important but undetermined factor in the metabolism of excessive protein diet.
E. HOLMES.

Influence of age of animal on nucleic acid and coagulable nitrogen content of tissues of sheep. T. B. ROBERTSON and M. C. DAWBARN (Austral. J. Exp. Biol., 1929, 6, 261—275).—Improvements in the original method of determining nucleic acid and coagulable nitrogen in tissues of animals are described (cf. A., 1929, 715). In every organ the nucleo-cytoplasmic ratio falls considerably with age and the fall is not the same in different organs. The total amount of nucleic acid in the adult cerebrum is 50% less than in that of the new born; the total amount in the skin is also diminished with growth, whereas in the other organs it is greater in the adult. The curve relating the percentage increases of total nucleic acid and protein content with growth is sigmoid and indicates that the synthesis of nucleic acid is catalysed relatively to that of the protein. The anomalous nature of skeletal muscle is attributed to the presence of an extranuclear nucleic acid (inosic acid).
T. R. SESHADRI.

Influence of cereals on retention of calcium and phosphorus in children and adults. H. B. BURTON (J. Biol. Chem., 1930, 85, 405—419).—The calcium and phosphorus retention of children and adults on diets of which wheat or oats formed the cereal constituent was determined. Better retention was obtained with the wheat than with the oats; in the second case a larger amount of mineral matter was lost with the relatively bulky fæces. A minor difference observed was the lower retention of calcium and phosphorus by girls than by boys under similar conditions.
C. R. HARINGTON.

Influence of a low- and high-calcium diet on development and chemical composition of the skeleton in swine. R. E. EVANS (J. Agric. Sci., 1930, 20, 117—125; cf. this vol., 107).—Skeletons of young pigs fed on a ration composed mainly of cereal grain with the addition of cod-liver oil showed distinct lack of calcification, the percentage of ash being 12% lower than in bones of normal animals. Calcification of bones proceeds up to maturity, but a difference of 360 g. of tricalcium phosphate was found between the mature bones of normal and calcium-deficient sows. The ratio of lime to phosphate is almost the same in the different bones of the same individual, as well as in the normal and rachitic bones of swine. The main characteristic of the bones in low-calcium rickets is a low ash content, but the composition of the ash is normal.
E. HOLMES.

Stimulation of the respiratory centre by salts of lower fatty acids. TIEMANN (Arch. exp. Path. Pharm., 1930, 148, 102—110).—Intravenous injection of the sodium salts of n-butyric, β-hydroxybutyric, or valeric acid stimulates the breathing of dogs,

whether in light narcosis or under morphine or chloral hydrate. The effect is therefore not dependent on the acidity of the injected substance. Salts of propionic, isobutyric, and acetoacetic acid are without effect.
K. V. THIMANN.

Behaviour of glucose ureide in the animal body with special reference to blood-sugar. K. WATANABE (J. Biochem. Japan, 1929, 11, 79—102).—Intraperitoneal injection of glucose ureide into rabbits causes the greater increase of bound blood-sugar, whilst that of dextrose and urea together influences chiefly the free sugar. Injection of the mixture increases the blood-urea to a greater extent than does that of the compound. In fasting or hypoglycæmic (insulin) animals injection of glucose ureide raises to normal values the bound, but not the free, blood-sugar.
CHEMICAL ABSTRACTS.

Toxic action of methyl alcohol. G. MARINESCO, S. Z. DRAGANESCO, and D. GRIGORESCO (Semana Méd., 1929, 36, 745—748).—The action is described and compared with that of ethyl alcohol. After fatal acute intoxication the following quantities of ethyl and methyl alcohol, respectively, were found : brain, 0·84, 1·25; 0·405, 0·47, 0·524; heart, 0·84, 0·924, 1·136; 0·39, 0·413; liver, 0·195, 0·24, 0·44; 0·24, 0·33, 0·36, 0·53; eye-ball, 0·18, 0·276, 0·242; 0·42, 0·64, 0·90; testicle, —; 0·868%.
CHEMICAL ABSTRACTS.

Presence of thiocyanates in the human organism. Post-mortem transformation of veronal, dial, and gardenal into cyanogen compounds. Significance in toxicology. E. KOHN-ABREST, (MLLE.) H. VILLARD, and L. CAPUS (Compt. rend., 1930, 190, 281—284).—The unexpected presence of thiocyanates in the viscera in certain cases in which there was no reason to suspect cyanide poisoning is ascribed to the administration of hypnotics of the barbituric series; the partial conversion of these into thiocyanates under the influence of putrefaction is experimentally demonstrated.
R. CHILD.

Effect of acetylcholine on the blood-sugar. M. LABBÉ, F. NEPVEUX, and L. JUSTIN-BESANÇON (Compt. rend. Soc. Biol., 1929, 100, 795—796; Chem. Zentr., 1929, ii, 1023).—Subcutaneous administration of acetylcholine causes a fall in blood-sugar.
A. A. ELDRIDGE.

Effect of acetylcholine on the pancreatic secretion. M. VILLARET, L. JUSTIN-BESANÇON, and R. EVEN (Compt. rend. Soc. Biol., 1929, 101, 7—8; Chem. Zentr., 1929, ii, 1023).—The pancreatic secretion following the administration of acetylcholine contains lipase, amylase, and trypsin.
A. A. ELDRIDGE.

Effect of synthalin on gaseous exchange. F. KLEIN and R. WEISS (Endokrinol., 1928, 1, 321—322; Chem. Zentr., 1929, ii, 1174).—Small doses of synthalin do not affect the respiratory quotient of rabbits. Larger doses reduce the oxygen requirement and the quotient rises.
A. A. ELDRIDGE.

Arrest of the internal secretion of the pancreas during decamethylenediguanidine hypoglycæmia. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1929, 101, 141—143; Chem. Zentr., 1929,

i, 1022).—Synthalin hypoglycæmia is accompanied by a diminution of the secretion of insulin.

A. A. ELDRIDGE.

[Pharmacology of] *Allium sativum.* F. A. LEHMANN (Arch. exp. Path. Pharm., 1930, **147**, 245—264).—Certain of the pharmacological actions of the pressed juice from the tubers of *A. sativum, e.g.,* toxic action on *Paramecium caudatum* and formation of methæmoglobin, are dependent on the presence of a sulphur-containing oil which can be separated by extraction with ether or by steam-distillation. The fractions of the oil of high b. p. are especially active. The activity of the oil decreases when mixed with blood *in vitro.* W. O. KERMACK.

Effect of yohimbine on blood-sugar. S. HANSON (Compt. rend. Soc. Biol., 1929, **101**, 601—603, 603—605, 605—607; Chem. Zentr., 1929, ii, 1704).—Yohimbine causes a slight rise in blood-sugar; in small doses it suppresses adrenaline hyperglycæmia, although with larger doses the rise is observed. The increase by yohimbine of the hypoglycæmic action of insulin is discussed. A. A. ELDRIDGE.

Effect of ergotamine on the threshold of sugar excretion. G. EDA (J. Biochem. Japan, 1929, **11**, 13—29).—Ergotamine (0·3—0·5 mg.) does not affect, or only slightly lowers, the dextrose threshold in mild diabetes. Protein with fat exclusively diminishes the assimilative capacity and raises the threshold value in dogs, when ergotamine lowers the threshold. Ergotamine represses alimentary hyperglycæmia without affecting the threshold of excretion.

CHEMICAL ABSTRACTS.

Pilocarpine hyperglycæmia. I. A. ORRÙ (Boll. Soc. Ital. Biol. sper., 1928, **3**, 135—137; Chem. Zentr., 1929, ii, 1422).—The hyperglycæmia caused by subcutaneous injection of pilocarpine (5—25 mg. per kg.) into rabbits is, up to a certain limit, proportional to the dose and to the duration of action, and is followed by hyperglycæmia. A. A. ELDRIDGE.

Effect of atropine on respiratory metabolism. F. KERTI (Klin. Woch., 1929, **8**, 1408; Chem. Zentr., 1929, ii, 1424).—Of 20 cases of disturbance of the endocrine system, 14 showed an increased fasting oxygen requirement after subcutaneous injection of atropine; in 4 cases the value was diminished, and in 2 cases unaltered. A. A. ELDRIDGE.

Physiological rôle of the tertiary amino-group in the pyrrolidine–piperidine nucleus. Importance of isomerism. R. HAZARD and M. POLONOVSKI (Compt. rend., 1930, **190**, 214—216).—Compared with their corresponding tertiary bases, the *N*-oxides of tropine and ψ-tropine produce a reduced cardiovascular effect. Whilst nortropine behaves as a weakened tropine, nor-ψ-tropine exerts an effect equally as strong as that of ψ-tropine and appears to possess a true cardiovascular reaction.

C. C. N. VASS.

Pharmacological testing of brucine derivatives. W. THOMS (Arch. Pharm., 1930, **268**, 57—58).—Comparative physiological tests have been made with brucine and its various quaternary derivatives (see this vol., 229). With white mice brucine has a quicker and more violent action than the derivatives, whilst with frogs, symptoms of tetanus and paralysis occur more quickly with the derivatives, but the effect of brucine is of longer duration.

J. W. BAKER.

Action of caffeine on the protein fraction of blood. J. SZELÓCZEY and I. SÁRKÁNY (Biochem. Z., 1930, **217**, 218—226).—Caffeine-sodium benzoate alone or with water was intramuscularly administered to rabbits and after various intervals the protein fraction of their blood was examined. It was found that while the effect of the drug lasted the albumin-globulin quotient of the fraction first decreased and then increased and that in the case of caffeine alone the first phase was shorter than the second, whilst in that of caffeine and water this phase was the longer.

W. McCARTNEY.

Determination of salvarsan, its fate in blood, and passage into cerebrospinal fluid. T. HIRAMATSU (Sei-i-kwai Med. J., 1929, **48**, 133—154).—The blackening of osmic acid by arsenic is proportional to the amount present. To 0·1 c.c. of blood are added 0·1 c.c. of distilled water and 3 drops of 20% thiosalicylic acid solution; the mixture is filtered and 3 drops of 1% osmic acid solution are added to the filtrate, the colour being compared with those of standards. The sensitivity is 0·0025 mg. Osmic acid may be added directly to serum or cerebrospinal fluid, the sensitivity being 0·001 mg. After large doses, salvarsan remained in the blood of rabbits for more than 24 hrs.; when more than 0·06 g. per kg. was used, cerebrospinal fluid gave a slight reaction after 5 hrs. CHEMICAL ABSTRACTS.

Toxicity of arsenobenzene compounds. S. KIEŁBASINSKI (Przemysł Chem., 1929, **13**, 553—557).—1% "Neosalutan" is quantitatively precipitated from solution by sulphuric acid at 50—60°, leaving in solution toxic oxidation products, which reduce iodine. A "toxicity number" is proposed, being the number of c.c. of *N*-iodine solution necessary to oxidise the toxic soluble constituents of 1 g. of the preparation in question; the toxicity number usually found is 0·06—0·10, but one of 0·20, representing 0·8% of toxic arsenic, has no noticeable toxic action on animals, whilst at a value of 0·30 half the animals injected die. The same method can be applied without modification to "neosalvarsan," whilst derivatives of salts of aminohydroxyarsenobenzene with formaldehyde-sulphuric acid possess normally a higher toxicity number.

R. TRUSZKOWSKI.

Metabolism during lead poisoning. A. CARNI (Trud. Mat. Ukrain. gosud. Inst. pat., 1928, **6**, 227—234).—In chronic poisoning of dogs and cats by oral administration of lead–protein the nitrogen elimination was greater than the nitrogen absorption, but the nitrogen metabolism was qualitatively unchanged. Azotæmia gradually develops. After 1 month the alkali reserve decreased; the blood-inorganic phosphorus increased, and the acid-soluble decreased.

CHEMICAL ABSTRACTS.

Distribution of colloidal lead in the tissues after intravenous injection. W. J. DILLING and E. F. HAWORTH (J. Path. Bact., 1929, **32**, 753—763).—The lead is concentrated first in the large

phagocytic cells of the spleen and occasionally in the endothelial cells; much is collected in the Kupfer cells of the liver. Some is found in the alveolar wall cell of the lungs and the leucocyte-like cells of the inter-alveolar spaces. There is much lead in the kidneys. Excretion in the urine, bile, and alimentary tract is variable. CHEMICAL ABSTRACTS.

Determination of small quantities of lead with special reference to urine and biological materials. A. G. FRANCIS, C. O. HARVEY, and J. L. BUCHAN (Analyst, 1929, 54, 725—735).—To an aliquot portion of the urine (100 c.c.) nitrosyl-sulphuric acid is gradually added with amyl alcohol to prevent frothing. After boiling to one third the volume, concentrated nitric acid is added and final traces of organic matter are removed by boiling. The solution is diluted, the silica filtered off, volatilised, and the residual liquid added to the original solution. Citric acid, a copper solution (2 mg. of copper per c.c.), and a few drops of " masked " methyl-orange solution are added, and concentrated ammonia is run in until the colour changes from grey to green, after which hydrogen sulphide is passed for 1 hr. The sulphides are collected and the filter-paper is destroyed by wet combustion, when the lead and copper are present as sulphates. Lead peroxide is then deposited on a platinum anode and separated as sulphate, which is washed with alcohol and concentrated sulphuric acid and dissolved in ammonium acetate. A suitable proportion of this solution is transferred to a Nessler cylinder and to it and to a control solution are added potassium cyanide solution, ammonia, water, and 2 drops of sodium sulphide solution. A solution containing 0·01 mg. of lead per c.c. is run into the control solution until a match is obtained, the exact match being made with a fresh control, to which 1 c.c. less of the lead solution is added, and the sulphide added last. With biological materials the nitrosylsulphuric acid is omitted. Large quantities of iron salts in the electrolyte must be avoided. Lead ranging from 0 to 0·133 mg. per litre was found in 55 samples of normal urines. D. G. HEWER.

Absorption by animals of mercury from contaminated air. A. STOCK and W. ZIMMERMANN (Biochem. Z., 1929, 216, 243—248).—The amounts of mercury absorbed by guinea-pigs which were caused to breathe air charged with small amounts of mercury are determined. The amounts of mercury retained after breathing the air for one day in one case amounted to 53 γ, but did not increase with further exposure. The amount of mercury stored in the body decreased very slowly when the animal was placed in mercury-free air, after 3—4 weeks one half and after 5 weeks one quarter of the mercury remaining. The mercury accumulated in the liver and particularly in the lungs. The amount of mercury retained by the stomach, intestine, muscle, blood, and bones was strikingly low and was quickly and completely lost when the animal was placed in mercury-free air.
P. W. CLUTTERBUCK.

Fatty degeneration of the liver in phosphorus poisoning. E. MISLOWITZER and E. L. LOEWE (Biochem. Z., 1929, 216, 362—366).—The increase of ether-soluble phosphorus of the liver in phosphorus

poisoning is due to an increased infiltration of this material (cf. Gubser, A., 1928, 1156; Loewy, A., 1927, 792; 1928, 325). P. W. CLUTTERBUCK.

Influence of irradiation on the iodine and bromine fractions of the animal body, especially after administration of iodine. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1929, 216, 336—361).—An electrodialyser is described and used to separate thyroxine and salts. Bromine is a normal physiological constituent of the white mouse. The mean iodine, bromine, and chlorine contents of the white mouse are 3·42, 10·11, and 514·9 mg. per 100 g. of dry material, respectively. The water content of the animal is 67·3%. The ratio of organic to inorganic iodine is 1·85, of non-dialysable to dialysable bromine 0·624, and of chlorine 0·297. When 8·5 mg. of iodine as sodium iodide is injected into the mouse, the bromine content is decreased and the chlorine content remains unchanged. By injection of inorganic iodine, the organic iodine is at first increased. Irradiation by the mercury lamp decreases the ratio of organic to inorganic iodine in both normal and injected animals, increases the organic bromine at the expense of the inorganic, and has no effect on the distribution of chlorine. P. W. CLUTTERBUCK.

Kinetics of enzyme reactions : Schütz's law. E. A. MOELWYN-HUGHES, J. PACE, and W. C. M. LEWIS (J. Gen. Physiol., 1930, 13, 323—334).—Theoretical deductions of Schütz's law on the basis of the law of mass action (cf. Northrop, A., 1924, i, 1267) and on the basis of Langmuir's adsorption theory (cf. A., 1917, ii, 19) are given. Attention is directed to the possible error which may arise if Schütz's constant is used to calculate the critical increment. The true critical increment for an enzymic reaction is equal to twice the critical increment calculated from Schütz's constant if the heat of decomposition of the hydrolysis products–enzyme complex is neglected. The true critical increment of the tryptic hydrolysis of caseinogen at 30° and 40° at p_H 8·9 is 14,400 g.-cal.
C. C. N. VASS.

Structure and enzyme reactions. VIII. Physical state of the sorbent. S. J. PRZYŁECKI and M. GURFINKEL (Biochem. J., 1930, 24, 179—189).—In the system oil–starch–amylase, starch undergoes adsorption at the water–oil interface to an extent of 26·3% from 1% and 34·2% from 0·5% solutions in the presence of 5 g. of oil. The presence of 1·4% of propyl alcohol or of 0·71% of butyl alcohol reduces adsorption to about one half. About 68% of the adsorbed starch is deposited as a precipitate from emulsions of oil in starch solution on the resolution of the emulsion. The adsorption of amylase on oil is very small, not exceeding 5%. The precipitated starch at the surface does not react with amylase. In the ovalbumin–starch–amylase system starch undergoes adsorption to about 63% on the protein membranes present in the foam formed when ovalbumin solutions are shaken. The addition of alcohol leads to elution of starch. A portion of the adsorbed starch is deposited as a precipitate on the resolution of the foam. Amylase is adsorbed to the extent of about 30%. If the protein is absent the velocity of hydrolysis is only 3·5% more if the system is shaken;

without shaking retardation amounts to 12·7%, whilst when amylase is added 24 hrs. after shaking it amounts to 52%. The degree of inhibition due to ovalbumin is proportional to the extent to which it is coagulated. In the system caseinogen–glycogen–amylase, when the caseinogen is coagulated in the presence of glycogen the latter is occluded within the precipitate and is thereby protected from the action of amylase in the medium, only 24% of the adsorbed glycogen being hydrolysed. The occluded glycogen is not eluted by alcohols. In the system gelatin–starch–amylase the inhibitive effect on the hydrolysis of starch due to the presence of gelatin increases with concentration of the latter and is greater at 25° than at 37°. S. S. ZILVA.

Combined effect of salivary, pancreatic, and malt amylases on starch. P. RONA and J. HEFTER (Biochem. Z., 1930, **217**, 113—124).— Starch could not be converted into dextrose by the combined action of any two of the three amylases : salivary, pancreatic, malt, and hence the results of Pringsheim and Leibowitz (A., 1926, 715) have not been confirmed. W. McCARTNEY.

β-Glucosidase. I. Fission of amygdalin. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1929, **79**, 591—602).—Amygdalin is now known to be a β-d-mandelonitrile glucoside in which the sugar complex is gentiobiose, and the three enzymes formerly supposed to be necessary for its complete hydrolysis, viz., amygdalase, prunase, and oxynitrilase, may be reduced to two, for β-glucosidase can split off both dextrose residues in turn, yielding first prunasin and finally mandelonitrile. This conclusion is based on a study of the relative rates of liberation of dextrose and hydrogen cyanide in the action of emulsin and autolysed yeast juice on amygdalin. J. H. LANE.

β-Glucosidase. II. Hydrolysis of cellobiose. R. WEIDENHAGEN.—See this vol., 301.

Application of the mass action law to the enzymic decomposition of sucrose. R. WEIDENHAGEN and E. LANDT.—See this vol., 301.

Lactic acid formation in muscle extracts. V. Comparison between soluble starch and glycogen in respect of lactic acid formation and phosphoric ester accumulation. VI. Influence of irradiation on lactic acid formation and phosphoric ester accumulation from glycogen. D. STIVEN (Biochem. J., 1930, **24**, 169—171, 172—178).— V. During the first 40—50 min. of incubation the rate of lactic acid formation and the rate of phosphoric ester accumulation in the presence of extracts from the perfused skeletal muscle are greater with glycogen than with soluble starch. At the end of 2 hrs., however, the lactic acid formation from soluble starch is practically the same as that from glycogen.

VI. In twelve of thirteen experiments it has been possible to increase the rate of lactic acid formation from glycogen if the muscle extract be irradiated before incubation. In one case the rate of lactic acid formation in the irradiated sample was three times that in the control. Irradiation leads also to alteration of the phosphoric ester accumulation. The shorter irradiations resulted in an increase of the extent of the ester accumulation, the longer irradiations produced a decrease. The highest rates of lactic acid formation coincide with a decrease of the ester accumulation. In only one case was the lactic acid formation decreased after long irradiation and in this case the ester accumulation was almost completely inhibited. S. S. ZILVA.

Enzymic hydrolysis of diphosphoglyceric acid. H. KOBAYASHI (J. Biochem. Japan, 1929, **11**, 173—181).—With taka-phosphatase, but not with kidney phosphatase, the optimal p_H differs for α- and β-glycerophosphate. Kidney phosphatase hydrolyses αβ-diphosphoglyceric acid to the extent of 70% at p_H 8·0 in 24 hrs. at 37°. With taka-phosphatase this ester is hydrolysed optimally at p_H 5·6, as are α- and β-glycerophosphates, but with the purified enzyme the hydrolysis takes place equally well at p_H 2·9 or 5·5, with minimal activity at p_H 4·0. The second peak in the curve at about p_H 3·0 is attributed to the hydrolysis of the β-glycerophosphate, so that the specific hydrolysis is different for the α- and β-esters. CHEMICAL ABSTRACTS.

Enzymic hydrolysis of different phosphoric esters. K. ASAKAWA (J. Biochem. Japan, 1929, **11**, 143—172).—The optimal p_H differs for taka-phosphatase and kidney-phosphatase and for the different esters. CHEMICAL ABSTRACTS.

Malt pectinase. J. J. WILLAMAN (Arkiv Kemi, Min., Geol., 1929, **10**, A, No. 3, 4 pp.).—Pectinase preparations from two different samples of malt were identical in activity, as measured by their rate of hydrolysis of commercial citrus pectin. After heating at 100° for 10 min. the enzyme still possesses some activity. By precipitation first with 50% and then with 87% alcohol, a more active material is obtained. K. V. THIMANN.

Mechanism of oxidative processes. XXII. Mode of action of oxidases and peroxidases. H. WIELAND and H. SUTTER (Ber., 1930, **63**, [B], 66—75; cf. A., 1928, 921).—The oxidase action is determined by volumetric measurement of the oxygen absorbed during the dehydrogenation of quinol or pyrocatechol. The absolute activity of the potato-enzyme varies within very wide limits according to the variety. The activity of the enzyme in the skin is about four times as great as in the skin-free tuber. In spite of a large excess of quinol and oxygen the rate of absorption of the gas diminishes with the time. This effect is not due to the benzoquinone produced, but is attributable to the direct action of oxygen on the enzyme. Hydrocyanic acid has a restricting influence. The sensitiveness of the phenol-oxidase of apple towards oxygen is greater than that of the potato-enzyme, whereas hydrocyanic acid has a less marked influence. The phenolases of cherry, radish, and green pea also appear to be sensitive towards oxygen. Comparison of the behaviour of the skin and substance extracts of potato towards quinol and nitrate indicates the probability that two different enzymes are involved.

The behaviour of horse-radish peroxidase towards pyrogallol has been examined in the presence of ethyl hydrogen peroxide, ethyl peroxide, dihydroxymethyl peroxide, peracetic acid, and disuccinyl peroxide.

The activation of peroxides appears to require the presence of at least one hydroxyl group. Disubstituted peroxides are completely inactive. Since the monosubstituted compounds lag far behind hydrogen peroxide it is probable that they have scarcely any biological significance and that the behaviour of peroxides in this respect must be discussed solely with reference to the parent compound. H. WREN.

Mechanism of action of the oxidoreductases. K. SHIBATA (Acta Phytochim., 1929, 4, 373—379).— The theory of oxidases, peroxidases, and catalases is discussed and the view is expressed that the essential action is the activation of water or of hydrogen peroxide. Certain complex metal salts exhibit, not only oxidase, but also peroxidase and catalase activity, and the view that they are analogous to the natural enzymes is supported by the fact that mutual interference may occur when both are present simultaneously. W. O. KERMACK.

Oxidase-like actions of certain complex metal salts. Y. SHIBATA and K. SHIBATA (Acta Phytochim., 1929, 4, 363—371).—The oxidation of myricetin in aqueous alcoholic solution is much accelerated by the presence of many complex cobalt-ammine salts as well as by certain complex salts of nickel, zinc, cadmium, chromium, and silver. The catalytic actions of these salts resemble those of the natural enzymes as they are inhibited by acidity of the medium, by boiling, and by certain chemical substances, e.g., cyanides, hydroxylamine, and mercuric chloride. The catalytic action is also inhibited by the presence of certain cobaltammine salts which themselves are inactive. W. O. KERMACK.

Catalase action of organically-combined iron. H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 5, 6 pp.).—Pyratin, prepared from hæmin by Schumm (A., 1928, 1263), decomposes hydrogen peroxide about 20 times as rapidly as hæmin. Its activity decreases with time, and also in high concentrations of hydrogen peroxide. The activity is rapidly reduced by treatment with hydrogen sulphide. The catalase action of hæmin, hæmo-chromogen, and derivatives is closely connected with their iron content (cf. this vol., 302). K. V. THIMANN.

Lipase. H. VON EULER and S. GARD (Arkiv Kemi, Min., Geol., 1929, 10, A, No. 2, 7 pp.).—The liver of the rat and pig was freed from fat, extracted first with acetone, then with equal parts of acetone and ether, and finally with ether, dried, and powdered. The lipase was then extracted with glycerol, and the extract centrifuged. The action of this lipase solution at p_H 8 on monobutyrin, ethyl acetate, and glycine ethyl ester in the presence of albumin and calcium chloride was examined. The results were compared with the lipolysis produced by hydrochloric acid. The hæmolyses produced by this extract, by blood-serum, and by intestinal mucosa were also compared. K. V. THIMANN.

Stereochemical specificity of esterases. I. Affinity of liver-esterases for optically active alcohols. D. R. P. MURRAY and C. G. KING (Biochem. J., 1930, 24, 190—198).—The l-forms of methyl-

n-hexylcarbinol, phenylmethylcarbinol, and methyl-β-phenylethylcarbinol inhibit sheep-liver esterase about four to five times as strongly as the d-forms. On the other hand, with rabbit-liver esterase there is no difference in the inhibiting action of the d- and l-alcohols. S. S. ZILVA.

Asymmetric esterification caused by the esterase of pig pancreas. P. RONA and R. AMMON (Biochem. Z., 1930, 217, 34—41).—When powdered pig pancreas acts on mixtures of water, isoamyl alcohol, and d-, l-, or dl-lactic acid the amyl ester of the d-acid is formed more rapidly than are the esters of the l- and dl-acids. W. McCARTNEY.

Stereochemical specificity of taka-esterases. P. RONA, R. AMMON, and M. WERNER (Biochem. Z., 1930, 217, 42—49).—Measurements of dissociation and hydrolysis constants show that the compound of taka-diastase with the methyl ester of l-mandelic acid is hydrolysed twice as rapidly as is the corresponding d-compound and that the affinity of the taka-diastase for the d-ester is five times as great as it is for the l-ester. The quantitative investigation of the optical specificity of the taka-esterases is now complete. W. McCARTNEY.

Arginase method for arginine determinations; analysis of proteins. A. HUNTER and J. A. DAUPHINEE (J. Biol. Chem., 1930, 85, 627—665).— Fresh liver, finely minced, is extracted by shaking for 10 min. with an equal volume of 75% glycerol, the mixture is heated in a water-bath to 58° for 5 min., cooled, and filtered; the filtrate contains 80—100 units of arginase per c.c., the unit being the amount of enzyme required to liberate 0·5 mg. of carbamide-nitrogen from 10 mg. of arginine in 30 min. at 37°. A stable solid preparation of the enzyme may be obtained by making the extraction with water, and evaporating the filtered extract in thin layers in an air-current. Conditions are described for the recovery of 99·4 ±0·1% of the theoretical amount of ammonia from carbamide by means of urease; application of this technique to the solution resulting from the action of arginase on arginine enables the latter to be determined with an error of 0·5%. The method has been applied to the determination of arginine in protein hydrolysates either directly or after precipitation with phosphotungstic acid. A correction is made if necessary for the deaminising effect of the liver extract on other amino-acids. The arginine contents of the following proteins have been thus determined : gelatin 15·48, caseinogen 7·99, edestin 26·7, gliadin 4·78, globin 7·72, fibrin 14·31, ovalbumin 10·36%. C. R. HARINGTON.

Substrate in peptic synthesis of protein. H. BORSOOK, D. A. MACFADYEN, and H. WASTENEYS (J. Gen. Physiol., 1930, 13, 295—306).—Peptic digests of egg-white show a marked decrease in the amount of synthesis which can be effected by pepsin in the concentrated digests, with the lengthening of the period of digestion. The amount of protein synthesised is independent of the p_H to which the digest is exposed in the absence of pepsin. Synthesis can also be effected by pepsin in concentrated solutions of proteose or peptone, but the protein differs from the plastein synthesised from the whole digest. The cessation

of synthesis by pepsin in a digest is due to the attainment of a true equilibrium, since after removal of the synthesised protein the residual digest on concentration affords more protein, providing it still contains the specific complex which results from primary hydrolysis of the protein molecule by pepsin.

C. C. N. VASS.

Enzymic proteolysis. V. P. RONA and H. A. OELKERS (Biochem. Z., 1930, **217**, 50—112).—When solutions of egg-albumin were treated with pepsin there was a slight increase in the osmotic pressure during the period before chemical action began, and when it did begin the osmotic pressure fell. In the case of caseinogen and trypsin, during the same period, the increase in osmotic pressure was great and only when decomposition of the protein had proceeded to a considerable extent did the pressure begin to fall. The osmotic pressure of egg-albumin solutions did not increase as a result of the action of trypsin. These results confirm the views previously advanced concerning the changes which occur in the period before decomposition of proteins by enzymes begins.

W. McCARTNEY.

Caseinogen-splitting action of papain, and mechanism of the acceleration by hydrogen cyanide. S. SATO (J. Fac. Agric. Hokkaido Imp. Univ., 1929, **24**, No. 4, 101—151).—The quantity of caseinogen digested in unit time is proportional to the concentration of papain. The velocity coefficient of the unimolecular reaction gradually becomes maximal and then decreases, the maximum value being attained earlier for larger amounts of papain. The temperature coefficient varies from 4·0 at 40—50° to 0·6 at 80—90°; the optimal p_H is 6·5. Appreciable amounts of amino-acids are not formed. The activating action of potassium cyanide is attributed to that of hydrogen cyanide molecules; removal of hydrogen cyanide with air decreases the velocity to the original value.

CHEMICAL ABSTRACTS.

Origin of inosinic acid. M. V. BUELL (J. Biol. Chem., 1930, **85**, 435—445).—Aqueous extracts of the muscles of the ox, pig, rabbit, and of man (but not of the rat) have the power of deaminising adenine nucleotide to give inosinic acid. The deamination proceeds most rapidly at p_H 6·0 and more readily with adenine nucleotide from muscle than with that from yeast. The results explain the occurrence of inosinic acid and also that of hypoxanthine in muscles which lack adenase.

C. R. HARINGTON.

Uricase and its action. S. J. PRZYLECKI (Biochem. J., 1930, **24**, 81).—The uricolytic activity of the author's uricase preparation purified by dialysis in the presence of antiseptics such as thymol is due to bacterial action (cf. A., 1928, 1055).

S. S. ZILVA.

Mechanism of alcoholic fermentation. A. N. LEBEDEV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1199—1201).—Polemical.

Selective fermentation of dextrose and lævulose by brewer's yeast. H. IVEKOVICH (Biochem. J., 1930, **24**, 4—5; cf. A., 1927, 592; Hopkins, A., 1928, 1158).—Dextrose is fermented 1·78 times as rapidly as lævulose.

S. S. ZILVA.

Decreasing rate of fermentation. O. RAHN (J. Bact., 1929, **18**, 207—226).—The assumption that the decrease in the rate of fermentation caused by products of fermentation is proportional to their concentration divided by the limiting concentration leads to a formula giving a fermentation constant which represents the rate corrected for retardation by the products. For alcoholic fermentation, $Kt = \log_e 2L/(2L-x)$, where t is the time, L the limiting concentration of alcohol, and x the amount of sugar decomposed; for lactic fermentation $Kt = Y \log_e L(L-x)$, the factor Y representing the number of acting yeast-cells. In both alcoholic and lactic fermentations the relationship between the rate of fermentation and the amount of product added is linear.

CHEMICAL ABSTRACTS.

Formation of pyruvic acid as an intermediate phase in the alcoholic degradation of sugars. Isolation of pyruvic acid as the chief product of fermentation. C. NEUBERG and M. KOBEL (Biochem. Z., 1929, **216**, 493—496).—By the action of an acetone-dried preparation of a bottom yeast on magnesium hexosediphosphate, a yield of 90% of pyruvic acid may be obtained providing that the correct proportion exists between the substrate and enzyme concentration, the latter being greater than is necessary for the production of methylglyoxal, but less than is necessary to bring about complete fermentation in the experimental time.

P. W. CLUTTERBUCK.

Phosphoric esters of alcoholic fermentation. R. ROBISON and W. T. J. MORGAN (Biochem. J., 1930, **24**, 119—132).—Methods are described for the separation and investigation of the phosphoric esters produced during fermentation of sugars by yeast preparations. Sources of error in the conclusions reached from the results obtained with the aid of these and other methods are discussed. The distribution of total esterified phosphorus among the four known esters, estimated by the application of these methods, is given for a number of fermentation experiments with yeast-juice, zymin, and dried yeast. Some indication has been obtained of the presence of a fifth ester, but this can at most form only a very small proportion of the fermentation products. The effect of varying the rate of addition of phosphate on the relative proportions of the different esters has been studied. Hexosemonophosphate was obtained in maximum yield when the fermentation was rapid and inorganic phosphate was in considerable excess. Trehalosemonophosphate, on the other hand, increased in amount when the fermentation was continued for some time after the addition of phosphate, but again decreased if the fermentation was prolonged. A sparingly soluble crystalline form of barium trehalosemonophosphate is described.

S. S. ZILVA.

Enzymic carbohydrate degradation. R. NILSSON (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 1, 6 pp.).—Fermentation of dextrose in presence of phosphates, by a mixture of co-zymase, zymophosphate, and yeast which has been washed free of co-zymase, produces carbon dioxide and a hexosemonophosphate, the barium salt, α_D +14·9°,

of which corresponds with the formula $C_6H_{11}O_5PO_4Ba$ (see Euler, Myrbäck, and Runehjelm, A., 1928, 1158). Sodium fluoride suppresses the reaction.

K. V. THIMANN.

Problems of affinity. H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1929, **10**, A, No. 4, 7 pp.).—The insoluble residue left when yeast is washed with water contains an invertase. The effect of phenol on the rate of inversion of sucrose by this invertase and by the water-soluble invertase was determined, the percentage inhibition being the same in each case. Phenol also exercises considerable inhibition on the action of mutase on acetaldehyde. The conception is developed that the inhibition or poisoning produced by phenol and by protoplasm-poisons of the toluene type is due to the poison affecting the affinity between enzyme and substrate.

K. V. THIMANN.

Peroxidase reaction during alcoholic fermentation. G. WOKER and E. BLUM-SAPAS (Biochem. Z., 1930, **217**, 236—252).—The colours produced and the times required for them to reach their maxima when mixtures of yeast and dextrose solution and of yeast and water were tested, immediately after preparation or after intervals of from 1 hr. to 3 weeks, for the presence of acetaldehyde with p-phenylenediamine and hydrogen peroxide, have been observed. The results showed that acetaldehyde was always produced, although it appeared much earlier in the case of the yeast–dextrose mixture than in that of the yeast–water mixture.

W. McCARTNEY.

Effects of certain chemical compounds on the course of gas production by baker's yeast. S. E. BRANHAM (J. Bact., 1929, **18**, 247—264).—A simple gas meter is described. With mercuric chloride, mercurochrome, metaphen, and hexylresorcinol the greatest amount of gas was formed at dilutions causing relatively slight initial inhibition; with chloramine-T, tincture of iodine, and sodium hypochlorite there was sudden activity at dilutions causing complete inhibition for 1—2 hrs. Mercuric or sodium chloride at high (non-inhibitory) dilution caused a transient initial stimulation, whilst silver nitrate caused no increase of fermentation. CHEMICAL ABSTRACTS.

Chemical investigation of "bios." I. B. T. NARAYANAN (Biochem. J., 1930, **24**, 6—18).—A method of fractionation of "bios" from hydrolysed yeast based on the removal of impurities at various stages with baryta, lead acetate, alcohol, silver, and platinic chloride, and on the precipitation of the active principle with phosphotungstic acid is described. Doses of this concentrate of the order of 0·01 mg./c.c. stimulate the growth of yeast. This preparation is more active than those obtained by Eddy (A., 1925, i, 342) and Miller (Science, 1924, **59**, 1927). Inositol is not an essential unit of "bios" (cf. Eastcott, A., 1928, 1056). The latter is not identical with vitamin-B_p from which it can be separated. S. S. ZILVA.

Acid production, respiration, oxidase reaction, and reducing power of various species of Aspergillus. H. TAMIYA and T. HIDA (Acta Phytochim., 1929, **4**, 343—361).—A large number of species of Aspergillus, cultivated under definite conditions, have been examined in respect of the quantity and nature of the acids produced, the extent of the respiration, the indophenol-oxidase reaction, and the power of reducing methylene-blue with and without the addition of succinic acid. Amongst the acids observed were gluconic acid, citric acid, and oxalic acid, as well as kojic acid. W. O. KERMACK.

Utilisation of micro-organisms for human food materials. VIII. Proteins. IX. Nucleic acid. X. Carbohydrates of the mycelium of Aspergillus oryzæ. R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, **32**, 243—244B, 245B, 245—247B).—VIII. The protein is obtained in 0·35% yield from the mycelium by extraction with 1% sodium hydroxide solution and precipitation with dilute acetic acid. It contains N 14·78, P 1·77, ash, 2·66%, S trace. Acid hydrolysis of the protein yields about 4% of reducing sugars, chiefly glucosamine. Repeated digestion of the residual mycelium with pepsin in 1% hydrochloric acid solution yields a peptone containing 17% N (of which 10·1% is free amino-nitrogen), 0·59% of ash, but no phosphorus. It is soluble in water or dilute alcohol and is precipitated by phosphotungstic acid, copper hydroxide, and lead acetate. The nitrogen distribution determined by Van Slyke's method and the amounts of several amino-acids of the protein, peptone, and mycelium are tabulated.

IX. The nucleic acid contains N 13·16, P 7·01%, and yields on hydrolysis guanine, adenine, hypoxanthine, and probably uracil. Of the total nitrogen content in the mycelium 15·8% is nucleic acid-nitrogen.

X. From the alcoholic extract of the dried mycelium mannitol and trehalose were isolated, whilst mannose, lævulose, trehalose, an unidentified polysaccharide, and considerable quantities of dextrose and glucosamine were identified in the residual syrup. The ratio of the fermentable reducing sugars to the unfermentable was 1 : 2·7. Amylose (cf. Schmidt, A., 1925, i, 868) and glycogen were isolated as water-soluble polysaccharides. Treatment of the protein-free residues (VIII) with 10% sodium hydroxide solution and precipitation of the filtrate with hydrochloric acid, gave a substance which yielded, on hydrolysis with 2·5% hydrochloric acid, 35·5% of reducing sugars, chiefly glucosamine, whilst hydrolysis with 75% hydrochloric acid yielded 80·6% of reducing sugars. C. C. N. VASS.

Utilisation of micro-organisms for human food materials. XIV—XVI. Culture of Aspergillus oryzæ. III. Relation between the hydrogen-ion concentration of the medium and the yield of mycelium. IV. Influence of sodium chloride, sodium sulphate, and sugar concentration on the growth of the mycelium. V. Relation between the duration of culture, yield and nitrogen content of mycelium, and sugar concentration. R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, **32**, 306B, 307B, 308B).—III. Two optimum p_H values for the growth of the mycelium in a given synthetic medium in which the carbohydrate is supplied as sucrose, dextrose, dextrin, or soluble starch, and nitrogen as ammonium chloride or nitrate, potassium nitrate, or urea, are obtained; the values

found are 4·5 and 5·6, which lie on either side of the isoelectric point of the mycelium (cf. Robbins, A., 1924, i, 475), which appears to be at about p_H 5·0. *A. oryzæ* is capable of growth over the range p_H 1·8—9·0.

IV. The maximal yield of mycelium is obtained, using the foregoing synthetic medium in the presence of sodium chloride or sulphate, when the concentration of the latter is 0·5%; the yield decreases with increasing salt concentration and growth is inhibited by concentrations greater than 10%. The yields of mycelium produced by 40—60 hrs.' culture in media containing 1—5% of sugar are nearly constant, but decrease with higher sugar concentrations; for a period of 10 days' culture in the presence of 1% of sugar the economical coefficient is 39·8%, whilst in the presence of 3—10% of sugar the coefficient is nearly constant, ranging from 27·0 to 29·9%.

V. The yield of mycelium, produced by *A. oryzæ* growing in a synthetic medium in which sucrose was the sole source of carbon and urea a source of nitrogen, increases rapidly from the 2nd to the 6th day, remains nearly constant for 2 days, and gradually decreases to about one half the maximum at the 17th day. The economical coefficient is highest at the 3rd day (30·2%), and decreases gradually to 9·2% at the 17th day. The nitrogen content of the mycelium decreases gradually, from 5·89% at the 2nd to 3·02% at the 17th day.   C. W. SHOPPEE.

Action of micro-organisms on the odorous principle of rhizoma iridis. A. VON LINGELSHEIM (Arch. Pharm., 1930, **268**, 1—7).—When a culture of *Trichoderma* and related fungi, obtained originally from *Iris pallida*, is grown on a medium containing powdered iris the original characteristic violet odour is destroyed and a strong terpene odour develops. Similar observations have been made during the decay of various species of violet plants, the growth of the fungus being observed simultaneously, and it is suggested that the irone present in the plant is converted into a terpene derivative (? α-pinene) by the action of the micro-organism. In support of this view it is found that when traces of oil of violets, an aqueous extract of the oil, or even of artificial ionone are added to cultures of the fungi, the characteristic violet odour disappears and is replaced by a terpene odour. The significance of this change and of the reverse change of a terpene into a violet odour, which has been observed in human urine, is discussed.   J. W. BAKER.

Soluble enzymes secreted by the *Hymenomycetes*. Antioxygenic function of hydrocarbons and terpenes. L. LUTZ (Compt. rend., 1930, **190**, 218—220).—Pinene, limonene, caryophyllene, cymene, and styrene exert in sunlight a considerable antioxygenic effect as shown by the decolorisation of methylene-blue contained in the media on which six species of the fungi were grown. Cineole had no effect on the oxidising powers of the fungi (cf. A., 1926, 869).   C. C. N. VASS.

Metabolism of anaërobes. IV. Nature of the volatile acids produced by *Cl. histolyticum* from proteins. W. S. STURGES, L. B. PARSONS, and E. T. DRAKE (J. Bact., 1929, **18**, 157—167).—Cultures

grown in buffered pork in glass bombs thrice evacuated to the vapour pressure of water and sealed in a vacuum were acidified and the gases removed; carbon dioxide, ammonia, and acetic acid were present in the molar ratio 1 : 2 : 2. This ratio cannot be accounted for by the decarboxylation of dicarboxylic amino-acids preceded or followed by reductive deamination, or of monocarboxylic acids, or the degradation of chains by oxidative processes.   CHEMICAL ABSTRACTS.

Reduction phenomena in the lactic acid fermentation. W. N. SCHAPOSCHNIKOV and J. P. ZACHAROV (Biochem. Z., 1929, **216**, 325—329).—Methylene-blue, potassium nitrate, and sulphur introduced into fermentation mixtures sown with pure cultures of *B. Delbrücki* were reduced to leuco-base, nitrite, and hydrogen sulphide, respectively.
P. W. CLUTTERBUCK.

Influence on bacterial viability of various anions in combination with sodium. F. W. FABIAN and C. E. A. WINSLOW (J. Bact., 1929, **18**, 265—291).—Experiments on the viability of *Escherichia coli* showed that the stimulating effect of various sodium salts at low concentration was a direct function of the sodium content, and that inhibition at higher concentration depends on the sodium and hydrogen-ion concentrations. If the latter are favourable, the phosphate ion stimulates growth. Assumption of antagonism or specific salt effect in such cases is frequently unnecessary.
CHEMICAL ABSTRACTS.

Degradation of carbohydrate by *B. coli*. Isolation of methylglyoxal. C. FROMAGEOT (Biochem. Z., 1929, **216**, 467—474).—Magnesium hexosediphosphate on digestion at 37° with an alcohol–ether dry glycolase preparation of a culture of *B. coli* gave methylglyoxal in 89·72% yield.
P. W. CLUTTERBUCK.

Quantitative conversion of methylglyoxal into pure *d*(−)-lactic acid by *B. fluorescens*. E. WIDMANN (Biochem. Z., 1929, **216**, 475—478).—*B. fluorescens* converts methylglyoxal rapidly and quantitatively into optically pure *d*(−)-lactic acid.
P. W. CLUTTERBUCK.

Nitrifying bacteria. D. W. CUTLER (Nature, 1930, **125**, 168).—A new group of organisms has been discovered which produces nitrite when grown in a culture containing 0·06% NaCl, 0·002% $CaCl_2$, 0·005% $MgSO_4$, 0·03% of potassium hydrogen phosphate, 0·1% of sucrose, and an ammonium salt. The organisms isolated from a sugar-beet effluent filter-bed produce nitrite more freely from ammonium lactate, whilst those isolated from soil prefer the phosphate. Nitrite formation occurs over a wide p_H range from 4·5 to 7·9. The new organisms have characteristics distinct from those of *Nitrosomonas* and *Nitrosococcus*.   L. S. THEOBALD.

Chemotherapy of tuberculosis. II. G. MEISSNER and E. HESSE (Arch. exp. Path. Pharm., 1930, **147**, 339—359; cf. A., 1928, 1286).—Tubercle bacilli are stained in the peritoneal cavity of the mouse or in guinea-pig serum only by certain dyes which are basic in nature and therefore positively charged. This fact has been correlated with the

negative charge which tubercle bacilli bear, when suspended in serum under the same conditions. In addition to the dyes previously employed, about 2000 compounds have been tested by Wright's method as to their bacteriostatic action with reference to tubercle bacilli growing in blood. The compounds include salts of 48 elements and certain other metallic compounds and 145 alkaloids and alkaloidal derivatives. The inorganic salts are inactive, but of the alkaloids conessine and harmine are active as well as certain derivatives of quinine, viz., α-*iso*quinine, ethyl*apo*-quinine, and aminohydroquinine. Eucupin, opto-chin, and vuzin are inactive. The activity of indamine-blue in promoting the cure of guinea-pigs lightly infected with tuberculosis has been confirmed. W. O. KERMACK.

Lipins of tubercle bacilli. X. Lipin fractions from avian tubercle bacilli. XI. Phosphatide fraction from avian tubercle bacilli. XII. Lipin fractions from bovine tubercle bacilli. R. J. ANDERSON and E. G. ROBERTS (J. Biol. Chem., 1930, **85**, 509—517, 519—528, 529—538).—X. Moist avian tubercle bacilli (3515 g. of dry material) were extracted successively with a mixture of alcohol and ether and with chloroform. The alcohol–ether solution was evaporated under diminished pressure and the final aqueous suspension was extracted with ether; some wax which separated was added to the chloroform extract. The material extracted by ether was separated into acetone-soluble fat (77·3 g.) and phosphatide (79·7 g.); the chloroform extract yielded 379·5 g. of wax, and the aqueous solution 3·61 g. of polysaccharide.

XI. Figures are given for the constituents yielded by the above-mentioned phosphatide on hydrolysis. This phosphatide resembles in composition that obtained from human tubercle bacilli (A., 1927, 1114), except that it contains less ether-soluble and more water-soluble constituents than the latter.

XII. Bovine tubercle bacilli (3941 g. of dry material) were extracted by the method described above for the avian bacilli, and yielded acetone-soluble fats (131·7 g.), phosphatide (60·5 g.), wax (336 g.), and polysaccharide (40·3 g.). C. R. HARINGTON.

Chemical changes accompanying the growth of avian tubercle bacilli on Long's synthetic medium. A. G. RENFREW, S. L. BASS, and T. B. JOHNSON (Amer. Rev. Tuberculosis, 1929, **20**, 114—121).—The copper reduction curve suggests that the organism does not produce the same carbohydrate combination as does the human tubercle bacillus.
CHEMICAL ABSTRACTS.

Chemical changes accompanying the growth of timothy bacilli on Long's synthetic medium. S. L. BASS and T. B. JOHNSON (Amer. Rev. Tuberculosis, 1929, **20**, 122—127).—Timothy and avian tubercle bacilli form sugar of low reducing power, whilst the reducing power of the sugar formed in human tubercle bacilli is variable and increases to a maximum. The same sugar combination does not function in the three organisms.
CHEMICAL ABSTRACTS.

Action of formaldehyde, hydrogen peroxide, and white phosphorus on tuberculin. J. F. HEYMANS and C. HEYMANS (Compt. rend. Soc. Biol., 1929, **101**, 153—155; Chem. Zentr., 1929, ii, 1018).—Tuberculin, which is not decomposed by the above reagents, is exceptional among proteins.
A. A. ELDRIDGE.

The water-soluble substance of Friedländer's bacillus in relation to the identity of antibodies. C. E. LIM and T. J. KUROTCHKIN (Chinese J. Physiol., 1929, **3**, 409—418).—Guinea-pigs could not be sensitised to a solution of the soluble specific substance of Friedländer's bacillus by injecting them with the precipitate obtained when a solution of soluble specific substance is mixed with homologous anti-serum. Guinea-pigs could not be passively sensitised by the administration of immune serum from which the antibody had been removed by precipitation with a solution of the soluble specific substance. A similar result was obtained with serum from which the agglutinins had been removed by adsorption. The complement-fixing properties of the serum decreased with increased removal of precipitin, but complete absence of complement-fixing power was never attained. It is concluded that the agglutinating, precipitating, and complement-fixing substances in immune serum are probably identical.
W. O. KERMACK.

Composition of diphtheria toxin-antitoxin floccules. J. R. MARRACK and F. C. SMITH (Proc. Roy. Soc., 1930, **B, 106**, 1—19).—Spectrophotometric observations on the ultra-violet absorption curves of solutions of the floccules produced by the interaction of preparations of diphtheria toxin and of antitoxin (in such a proportion as to give most rapid flocculation) are consistent with the view that the floccules consist essentially of pseudoglobulin. Experiments on the flocculation by various salts of dispersions of these floccules in distilled water indicate that the pseudoglobulin is in the denatured condition. The presence of unspecific protein in the mixtures of toxin and antitoxin does not increase the precipitate obtained, which further is largely independent of the conditions employed. It appears therefore that the precipitate consists essentially of the active substances and not of unspecific material. The percentage of lipin in the floccules was likewise small.
W. O. KERMACK.

Penetrative power of the bactericidal rays in the ultra-violet as emitted by carbon. DE W. VORSTER (J. Dental Res., 1929, **9**, 641—651).—Gentian-violet, methylene-blue, eosin (1 in 100), or mercurochrome (1 in 4000) used as sensitiser decreases the germicidal action of the rays of carbon on *Staphylococcus aureus*. Saliva is opaque to the rays.
CHEMICAL ABSTRACTS.

Negative staining of bacteria. W. C. DORNER (Stain Tech., 1930, **5**, 25—27).—Attention is directed to the usefulness of Burri's Indian ink technique and of nigrosine. When these substances are applied to a liquid on a slide which is subsequently dried, a uniform dark film, in which the bacteria remain unstained, is produced. H. W. DUDLEY.

Hæmatein, its advantages as a stain. S. I. KORNHAUSER (Stain Tech., 1930, **5**, 13—15).—Mayer's

"hæmalum" stain is preferred to the usual hæmatoxylin mixtures. H. W. DUDLEY.

Mechanism of staining. II. A. E. STEARN and E. W. STEARN (Stain Tech., 1930, **5**, 17—24).—A discussion of the rôle of adsorption and chemical combination in connexion with the processes of staining. H. W. DUDLEY.

Equilibria and "automatins." H. ZWAARDEMAKER (Arch. Néerland. Physiol., 1929, **14**, 565—591).—An equi-radioactive equilibrium demonstrated by the cessation of heart beat has been obtained in an isolated frog's heart when perfused (a) alternately with two Ringer solutions, the one containing an α-, the other a β-ray source, (b) with a Ringer solution containing a radioactive element supplying one kind of rays and irradiated externally with the opposite kind of rays, (c) with an admixture of the perfusion fluids obtained by perfusing the heart with two Ringer solutions which contain sources of α- and β-rays or have been irradiated by such rays, and (d) when the heart has been simultaneously irradiated by two opposed sources of α- and β-rays. When the heart is at rest "automatinogen" is given off to the perfused liquid. Irradiation externally or by dissolved radioactive sources converts "automatinogen" into two radioactive antagonistic substances termed α- and β-"automatins." The free energy furnished to the heart by irradiation is 1 microerg per sec. per g., but since the greater part of this energy reaches water molecules and protoplasm, it is considered that the "automatins" are produced by an autocatalytic chain reaction as evidenced by the latent period following irradiation. The heart frequency is a function of the concentration of the potassium, the intensity of the irradiation, and the quantity of "automatin" produced. Curves, resembling adsorption curves, are given showing the concentration of potassium as opposed to thorium, uranium, ionium, and radon for equi-radioactive equilibrium. Choline, eosin, nicotine, and d-adrenaline in the presence of calcium stimulate the formation of β-automatin from potassium, whilst histamine, ephedrine, fluorescein, trypaflavin, and l-adrenaline activate uranium; these substances do not modify the duration of the latent period.
C. C. N. VASS.

Heart hormone. Action of active substances. R. RIGLER and F. TIEMANN (Pflüger's Archiv, 1929, **222**, 450—459; Chem. Zentr., 1929, ii, 1551).—The chief agent in the "substances actives" is unspecific, and apparently belongs to the histamine class of substances. A. A. ELDRIDGE.

Adrenaline therapy. A. J. ANTHONY (Arch. exp. Path. Pharm., 1930, **148**, 93—101).—Subcutaneous administration of adrenaline or ephetonine, or oral administration of ephetonine, increases the respiratory quotient immediately, and usually also the blood-pressure and blood-sugar. K. V. THIMANN.

Effect of extracts of suprarenal cortex on the blood-calcium. L. MIRVISH and L. P. BOSMAN (Brit. J. Exp. Biol., 1929, **6**, 350—354).—An extract of suprarenal cortex lowered the blood-calcium by 30% in 24 hrs. It is similar in action to the hormone of the ovary. E. BOYLAND.

Effect of testicular extracts on blood-calcium. L. MIRVISH and L. P. BOSMAN (Brit. J. Exp. Biol., 1929, **6**, 355—359).—The injection of the alcoholic extract of testis into rabbits produces a fall in blood-calcium. E. BOYLAND.

Pressor substance from bull's prostate gland. J. B. COLLIP (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 165—168).—Extracts of bull's prostate gland exert a pressor effect similar to that of adrenaline, although the return to normal blood-pressure is more gradual in the former. Subcutaneous injection of prostatic extracts produces hyperglycæmia in rabbits, and its effect on the isolated uterus of the rat is similar to that of adrenaline. P. G. MARSHALL.

Preparation of œstrin. G. F. MARRIAN (Nature, 1930, **125**, 90—91).—The yields of œstrin can be greatly increased by acidification of urine before ether extraction. Losses during initial saponification can be minimised by saturating the saponified mixture with carbon dioxide before extraction with ether. The most potent preparation of œstrin obtained by introducing these modifications of method had an activity of 8×10^6 mouse units per g.
L. S. THEOBALD.

Crystalline "menformon." E. LAQUEUR, E. DINGEMANSE, and S. KOBER (Nature, 1930, **125**, 90; cf. A., 1929, 850).—Colourless platelets, recrystallisable from 70% alcohol, subliming at 130—150° and 0·01 mm., have been obtained. The crystals (C 78·61%, H 8·25%) are similar to those described by Doisy and by Butenandt (this vol., 118), and yield the same X-ray spectrum as that given by earlier preparations. The degree of spreading on water indicates a carbon chain of not more than 25 atoms. Other crystals containing a hydroxyl group (cf. Marrian, A., 1929, 1495) were encountered during the purification of the original material. Since a substance of greater activity (14×10^6 units per g.) has been produced in certain cases it is still not certain that the crystalline menformon now obtained is the pure hormone. L. S. THEOBALD.

Ovarian hormone and blood-cholesterol. S. MORI and M. REISS (Endokrinol., 1928, **1**, 418—421; Chem. Zentr., 1929, ii, 1551—1552).—Injection of "hormovar" into rats caused an increase in blood-cholesterol which depended on the dose.
A. A. ELDRIDGE.

Cow's ovaries during pregnancy. G. F. CARTLAND, F. W. HEYL, and E. F. NEUPERT (J. Biol. Chem., 1930, **85**, 539—547).—During pregnancy the concentration of œstrin increases in the corpus luteum and decreases in the remaining ovarian tissue; simultaneously the neutral fat of the corpus luteum increases, whilst the phospho- and sulpho-lipins decrease; no change was observed in the cholesterol of the corpus luteum or in any lipin constituents of the rest of the ovary. C. R. HARINGTON.

Insulin. I. Standardisation with white mice. H. HORSTERS and H. BRUGSCH (Z. ges. exp. Med., 1929, **65**, 569—573; Chem. Zentr., 1929, ii, 1021).—The conditions which must be observed in the test are described, and the limiting values obtained for commercial preparations are recorded.
A. A. ELDRIDGE.

Insulin in human organs. H. Brugsch (Z. ges. exp. Med., 1929, **65**, 574—593; Chem. Zentr., 1929, ii, 1021).—The pancreas contains 10—100 Toronto units; in only one (case of death from starvation) practically none was found. Other values (for average weight of organ) are : heart 70—900, kidneys 110—300, muscle 1600—3150, liver 68—605 Toronto units. A. A. Eldridge.

Decomposition of aqueous solutions of insulin by heat. E. Trocello (Rass. Clin. Terap. Sci. Aff., 1928, **27**, 504—505; Chem. Zentr., 1929, ii, 1311).— Solid insulin was kept without change at 37—40° for 1 yr., whilst an aqueous solution kept at 42° became completely inactive in 3 months. A. A. Eldridge.

Increase of insulin content of blood after reflex stimulation of vagus. H. van Goor (Arch. Néerland. Physiol., 1929, **14**, 535—548).—In rabbits stimulation of the vagus causes a decrease in the sugar content of the blood, shown by Ahlgren's technique to be due to the secretion of insulin. An analogous condition occurs in man on prolonged respiration in a closed system. C. C. N. Vass.

Insulin and glycæmin. III. O. Loewi (Klin. Woch., 1929, **8**, 391—393; Chem. Zentr., 1929, ii, 441).—It is no longer considered that glycæmin, as well as lack of insulin, is always of causal significance of the appearance of hyperglycæmia. A. A. Eldridge.

Influence of insulin on narcotised animals. H. Horsters and H. Brugsch (Arch. exp. Path. Pharm., 1930, **147**, 193—210).—Administration of narcotics to rabbits inhibits the convulsions accompanying insulin hypoglycæmia, independently of any effect of the narcotic on the blood-sugar level. W. O. Kermack.

Effect of insulin on the amylolytic activity of saliva and blood. T. Gayda (Arch. Sci. biol., 1928, **12**, 197—202; Chem. Zentr., 1929, ii, 1421).— The action of insulin is accompanied by a marked increase in the amylolytic activity of saliva, but not of the blood-serum. A. A. Eldridge.

Appearance of sugar in urine after injection of insulin. E. Wiechmann (Deut. Arch. klin. Med., 1929, **164**, 172—174; Chem. Zentr., 1929, ii, 1312).— In jaundice without diabetes 18 g. of dextrose were excreted per day after treatment with insulin. A. A. Eldridge.

Effect of thyroid gland and pancreas on the carbohydrate exchange of the liver. R. Siegel (Klin. Woch., 1929, **8**, 1069—1071; Chem. Zentr., 1929, ii, 1702).—The sugar content of the liver of white mice 1 min. after death was 347 mg. per 100 g., rising in 10 min. to 851 mg. Injection of thyroxine a few hours before death accelerated the hydrolysis of the glycogen, the sugar content of the liver rising in 10 min. to 1020 mg. per 100 g., whilst injection of insulin maintained subnormal values. Metabolic disturbance in diabetes and the effect of lack of insulin on the action of the thyroid gland are discussed. A. A. Eldridge.

Preparation of two active and specific thymus substances, and their effect on the lime and phosphate content of rabbit's serum. A.

Nitschke (Z. ges. exp. Med., 1929, **65**, 637—650; Chem. Zentr., 1929, ii, 1172).—Fresh calf's thymus, finely divided, was stirred with an equal quantity of 10% acetic acid and the mixture heated at 70°. The p_H of the cooled liquid was adjusted to 8—9 with sodium hydroxide, and then with hydrochloric acid to the isoelectric point of the protein. An equal volume of alcohol was added, the mixture was filtered after 3 hrs., and 80% of the filtrate was evaporated. Injection of the extract causes a fall in the serum-calcium and -phosphorus of the rabbit. A. A. Eldridge.

Vitamin-A in animals. B. von Euler and H. von Euler (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 3, 6 pp.).—The serum of the ox, rat, pig, and a young healthy man gave the antimony trichloride reaction for carotenoid or vitamin-A, whilst the serum of the guinea-pig and an old man gave negative results. Extracts of ox liver give a strong positive reaction, corresponding with 168 Lovibond units per g. of fresh liver. In rats, the pale red liver gives a stronger reaction than the normal reddish-brown liver. K. V. Thimann.

Relative vitamin-A value of the body and liver oils of certain fish. B. Ahmad and J. C. Drummond (Biochem. J., 1930, **24**, 27—36).—The colorimetric and biological values for vitamin-A obtained with a number of fish-body and -liver oils agreed within reasonable limits. This is contrary to Schmidt-Nielsen's findings (Kon. Norsk. Videnskab., **1**, Nos. 15, 29, 63; **2**, No. 13), possibly on account of differences in technique and of his attempt to express results of the biological test, which is liable to wide variations, in terms of the units proposed by the U.S. Pharmacopœia. S. S. Zilva.

Antimony trichloride reaction for vitamin-A. P. Karrer, B. von Euler, and H. von Euler (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 2, 6 pp.).—The antimony trichloride reaction of Carr and Price (A., 1926, 870) is specific for the group of carotenoid substances, for which it is a group reaction. The comparative intensity of blue coloration produced is as follows, carotene being taken as 100; bixin 160, xanthophyll 41, γ-crocetin 350, dihydro-α-crocetin 240. Measurements of the principal spectroscopic bands are given. The reaction is ascribed to the presence of a system of conjugated double linkings. K. V. Thimann.

Antimony trichloride reaction for vitamin-A. E. R. Norris and A. E. Church (J. Biol. Chem., 1930, **85**, 477—489).—The colour reaction described by Carr and Price (A., 1926, 870) has been studied in detail. The colour produced by a chloroform solution of the unsaponifiable matter of cod-liver oil is composed of blue and green in the ratio of 1 : 0·4 Lovibond unit; on keeping, it fades completely without the development of a red colour. The colour is not affected by saturated fatty acids and oils, or by traces of light petroleum or ethylene dichloride; in presence of oleic acid or of unsaturated oils, however, the rate of fading is increased and the linearity of the relationship between concentration of extract and intensity of colour is destroyed. With purified preparations of vitamin-A it is important to work at sufficiently

low concentrations in order to obtain quantitative results.   C. R. HARINGTON.

Vitamins-*A* and *-D*. I—VII. W. KERPPOLA (Skand. Arch. Physiol., 1929, **56**, 173—180, 181—187, 188—195, 196—200, 201—206, 207—209, 210—215; Chem. Zentr., 1929, ii, 1050—1051).—I. The colour re-actions given by cod-liver oil and various condensation substances, and variations produced by ultra-violet irradiation, oxidation, or removal of saponifiable constituents, are described.

II. The antimony trichloride reaction is not given by extracts of the lungs and liver of rats maintained on a diet free from vitamin-*A*.

III. Under certain conditions the reactions of cod-liver oil parallel those of ergosterol.

IV. The antimony trichloride colour reactions of portions of a number of food-plants have been studied.

V. The unsaponifiable fraction of cod-liver oil affords a chromogen, m. p. $145.5°$ (acetate, m. p. $111°$), forming triclinic crystals similar to those of cholesterol.

VI. Chloroform extracts of human and animal organs have been tested by the antimony trichloride reaction.

VII. The same reaction has been applied to a chloroform extract of human blood-serum.
                                         A. A. ELDRIDGE.

Absorption spectra in relation to vitamin-*A*, R. A. MORTON, I. M. HEILBRON, and F. S. SPRING (Biochem. J., 1930, **24**, 136—140; cf. Rosenheim and Webster, A., 1929, 1202).—Whilst the absorption curve attributed to vitamin-*A* has not so far been resolved, that of dehydroergosterol shows three distinct bands at 342, 326, and 311 $\mu\mu$, and an inflexion at about 297 $\mu\mu$. Further, the intensity of absorption of dehydroergosterol is not greater than one sixth of that shown by the absorbing constituent of liver oils. Rosenheim and Webster's criticism of the selective absorption of liver oils being used as a criterion for vitamin-*A* is contested also on general grounds.
                                          S. S. ZILVA.

Hypervitaminosis-*A*. I. Effects of an over-dose of biosterol on the salt metabolism of rabbits. T. MUNEHISA (Sei-i-kwai Med. J., 1929, **48**, No. 5, 57—81).—Elimination of calcium, phos-phorus, magnesium, and nitrogen was increased by hypodermic administration of biosterol to rabbits. Injection of olive oil into controls produced smaller increases in salt metabolism, but pathological symp-toms were absent.   CHEMICAL ABSTRACTS.

Vitamin-*B* content of grass seeds in relation-ship to manures. M. J. ROWLANDS and B. WILKIN-SON (Biochem. J., 1930, **24**, 199—204).—Grass seed from a soil manured with dung is richer in vitamin-*B* than seeds from a similar soil manured with artificial manure. An alcoholic extract of pig's dung contains vitamin-*B*.   S. S. ZILVA.

Concentration of vitamin-*B₂*. B. T. NARA-YANAN and J. C. DRUMMOND (Biochem. J., 1930, **24**, 19—26).—The active principle obtained by precipit-ation of the hydrolysate or the alcoholic extract of yeast by lead acetate is adsorbed by fuller's earth over a range of p_H extending from 6·8 to 0·1, the adsorption increasing as the acidity is raised. The vitamin cannot, however, be removed from the adsorbent by extraction with baryta, acid 50% alcohol, alkaline 50% alcohol, or hot dilute hydrogen chloride at p_H 6·8. Unsatisfactory results were obtained with "norit" as an adsorbent. The vitamin is almost completely precipitated from the lead acetate fraction by 70% alcohol after previously clearing the solution with 50% alcohol. The stability of vitamin-*B₂* to heat, acids, and alkali is confirmed. It is not destroyed by hydrogen peroxide or nitrous acid (cf. Levene, A., 1928, 1405; Chick, A., 1929, 853), nor is it appreciably soluble in butyl alcohol.   S. S. ZILVA.

Heat-stability of the (anti-dermatitis, " anti-pellagra ") water-soluble vitamin-*B₂*. H. CHICK and M. H. ROSCOE (Biochem. J., 1930, **24**, 105—112). —Vitamin-*B₂* from yeast or yeast extract is much more stable at high temperatures in acid (p_H 5·0—7·0) solutions than when the reaction is alkaline. The extract obtained by boiling the yeast with 0·01% acetic acid is more suitable than yeast itself, owing to the formation of toxic substances in the latter during heating, especially when the reaction is alkaline. No loss in the vitamin potency takes place on heating yeast at p_H 5·0 for 2 hrs. at 90—100°. A loss of 50% was recorded on heating the yeast for 4—5 hrs. at 123°. At p_H 3·0 the loss was the same both with yeast and yeast extract. At p_H 9·5—10 about 30% of the vitamin originally contained in the yeast extract is lost in 10 days at the ordinary temperature; on heating for 2 hrs. at 98—100° (p_H 8·3) the loss is about 50%, and on autoclaving for 4—5 hrs. at 122—125° (p_H 8·3—10) between 75 and 100%.
                                          S. S. ZILVA.

Further evidence for a third accessory "*B*" factor. V. READER (Biochem. J., 1930, **24**, 77—80; cf. A., 1929, 1203).—Further evidence is produced for the existence of this factor. It is present in the mercuric sulphate precipitate of the Kinnersley and Peters process for the concentration of vitamin-*B₁*.
                                          S. S. ZILVA.

Lactic acid and lactacidogen in the organism during avitaminosis-*B* in the dog. K. TANAKA (Fol. endocrin. Japon., 1928, **4**, 39—40).—Lactic acid in the dog's jugular vein and carotid artery is in-creased during avitaminosis-*B*; it is increased in muscle and decreased in the liver. The weight and the actual and percentage iodine contents of the thyroid gland are increased.   CHEMICAL ABSTRACTS.

Antiscorbutic potency of apples. M. F. BRACE-WELL, E. HOYLE, and S. S. ZILVA (Biochem. J., 1930, **24**, 82—90).—Bramley's Seedling was markedly more active than a number of other varieties of apples which differ among themselves comparatively very much less in their vitamin-*C* content. There was no indication that the character of the soil, the age of the tree, or the season has any bearing on the anti-scorbutic activity of the apple. Bramley's Seedlings picked from the same tree 14 days before the normal crop are approximately of the same antiscorbutic activity. There was little loss in the vitamin-*C* con-tent of apples stored at 1° in the air or at 10° in a mixture of carbon dioxide, nitrogen, and oxygen for about 3 months. The activity of the gas-stored apples deteriorated, however, to a greater extent than

that of the cold-stored apples. Imported dessert apples showed a higher activity when the time elapsing between the picking of the fruit and the testing was shorter. There was no indication of any very marked difference in activity which could be correlated with the difference in variety amongst the imported varieties. Heating of Bramley's Seedlings in their skins scarcely affected their antiscorbutic activity. S. S. ZILVA.

Vitamin-C content of fresh sauerkraut and sauerkraut juice. B. CLOW, A. L. MARLATT, W. H. PETERSON, and E. A. MARTIN (J. Agric. Res., 1929, **39**, 963—971).—Experiments in which 10, 5, and 2·5 g. daily of fresh raw sauerkraut were fed per animal to guinea-pigs for 60 days, and 10 g. of sauerkraut juice for 75 days, indicate that the 5 g. level of fresh sauerkraut prevented the development of scurvy, whilst a similar quantity of the juice cured animals with definite symptoms of the disease. One half the vitamin-C content of cabbage is lost in making sauerkraut. E. HOLMES.

Preparation and properties of vitamin-C fractions from lemon juice. H. L. SIPPLE and C. G. KING (J. Amer. Chem. Soc., 1930, **52**, 420—423).—Decitration of lemon juice by treatment with lead acetate, subsequent removal of lead with phosphoric acid, concentration of the residual solution below 50°, and precipitation of solid material with alcohol, causes no loss in vitamin-C activity of the alcohol-free solution. When decitrated lemon juice containing lead acetate is brought to p_H 7·4—7·6 with ammonia, a lead complex which contains practically all the vitamin is precipitated. Dissolution of this complex in acetic acid and reprecipitation causes a diminution in the total solids of the lead-free preparation. The extraction of such a lead-free preparation with n-butyl alcohol removes colouring matter only, and evaporation of the residual aqueous solution gives a solid preparation, purified further by dissolution in 98% alcohol and treatment with ether, whereby inactive material (mainly ammonium salts) is precipitated. Evaporation of the alcoholic ethereal solution gives solid material (0·56 mg.≡1 c.c. of original juice), which on extraction with ether is deprived of inactive, amorphous material. The final preparation (0·28 mg. ≡1 c.c. of original juice) is chiefly carbohydrate in nature. All experiments are carried out in an atmosphere of nitrogen at relatively low temperature. Lead acetate cannot be replaced by barium acetate, nor can sodium hydroxide be used in place of ammonia, in the above purification. H. BURTON.

Preservation of the antiscorbutic vitamin in lemon juice. J. WILLIAMS and J. W. CORRAN (Biochem. J., 1930, **24**, 37—50).—Potassium metabisulphite inactivates the antiscorbutic vitamin in lemon-juice at 15—18° at measurable velocity. Lemon-rind oil, although not such a good preservative against fermentation, has a less destructive action on the antiscorbutic potency, 0·07% of rind oil having a less injurious effect in this respect than 0·275%. Lemon-juice adjusted with hydrochloric acid to p_H 1·6 preserves its antiscorbutic activity for 14 months at the ordinary temperature, the zone of optimum stability lying between 1·6 and 2·2. At p_H 1·4 and

below, the vitamin is very much less stable. Sodium benzoate, formic acid, and oil of cloves exert a destructive action on vitamin-C. Sucrose does not preserve the vitamin, whilst there are indications that dextrose may. S. S. ZILVA.

Possible preparation of highly active ergosterol (vitamin-D) from raw coffee. L. VON NOEL and F. DANNMEYER (Strahlenther., 1929, **32**, 769—771; Chem. Zentr., 1929, ii, 1707).—The unsaponifiable fraction of coffee oil, having [α] —150°, contained an unstable crystalline substance, [α] —200°, which with digitonin gives no compound insoluble in alcohol; on absorption of oxygen and diminution of rotatory power, however, it tends to form such a compound. The spectrum is that of irradiated ergosterol, but on exposure to air becomes that of unirradiated ergosterol. A. A. ELDRIDGE.

Cereals and rickets. III. Rachitic properties of maize, wheat, and oats ; effect of irradiation and of mineral supplements. H. STEENBOCK, A. BLACK, and B. H. THOMAS (J. Biol. Chem., 1930, **85**, 585—606).—On diets composed for the most part of wheat, oats, or yellow maize, rats showed deficient calcification, the deficiency increasing in the order mentioned ; satisfactory calcification was obtained in all cases when the cereals were irradiated. Supplementation of the non-irradiated cereals with calcium carbonate (the optimum amount being 1%) improved the calcification markedly ; simultaneous supplementation with phosphoric acid had little or no effect. Of the three cereals the oats were consumed least satisfactorily, probably owing to deficiency of vitamin-B_1 and -B_2, particularly of the latter.
C. R. HARINGTON.

Origin of chlorophyll and its relationship to the blood pigments. F. M. SCHERTZ (Science, 1929, **70**, 258—259).—A discussion of Noack and Kiessling's work (A., 1929, 727). L. S. THEOBALD.

Electrical effects accompanying the decomposition of organic compounds ; relation to photo-synthesis and plant nutrition. M. C. POTTER (Zentr. Bakt. Par., 1929, II, **78**, 56—65; Chem. Zentr., 1929, ii, 759).—Catalysis and synthesis in living plants are always accompanied by $E.M.F.$, which is a sign of vitality. Gases liberated by organic compounds are activated ; the quantity of ionised carbon dioxide is important in photo-synthesis. The difference between catalytic and synthetic enzymes is discussed. A. A. ELDRIDGE.

Physiology of fruit. I. Changes in respiratory activity of apples during senescence at different temperatures. F. KIDD and C. WEST (Proc. Roy. Soc., 1930, **B**, **106**, 93—109).—The amount of respiration of ripe apples after picking rises to a peak of about 1·5 times the original value and then falls. The time of reaching the peak varies inversely with the temperature, the temperature coefficient of the carbon dioxide production being about 5·4 for a rise of 20°, whilst that for the rate of protoplasmic change involved is considerably higher. Death from fungal disease supervenes after about the same amount of carbon dioxide has been evolved at all temperatures. K. V. THIMANN.

Limiting factors in carbon dioxide assimil-ation. T. H. VAN DEN HONERT (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1008—1020).—The carbon dioxide assimilation by a filamentous alga belonging to the genus *Hormidium* has been investig-ated to determine the relation between assimilation velocity and the factors temperature, light intensity, and carbon dioxide concentration. The assimilation velocity is directly proportional to the light intensity up to an arbitrary intensity 1·99. Above this value the effect of increasing illumination becomes increasingly small, a doubling of the intensity at the value 6·18 causing only a 5% increase in assimilation velocity. The influence of rise of temperature is greater the greater is the illumination intensity. At low carbon dioxide concentrations the assimilation velocity is proportional to the concentration. The assimilation process may be reduced to a catenary process on the assumptions that it consists of (*a*) a diffusion process by which the carbon dioxide is transferred from the external medium to the chloro-plast, (*b*) a photochemical process, and (*c*) a dark chemical process.   F. G. TRYHORN.

Importance of oxygen in the formation of urea in mushrooms. N. N. IVANOV and M. I. SMIRNOVA (Zhur. exp. Biol. Med., 1929, **11**, 79—89).—Urea is produced in mushrooms only in presence of oxygen, although in hydrogen the urea content remains unaltered. In the absence of oxygen ammonia is not absorbed from its salts.   CHEMICAL ABSTRACTS.

Effect of summer and winter temperatures on the catalase of pine-needles ; reply to criticism. F. C. GREEN, M. E. M'ENDARFER, O. S. ORTH, and W. E. BURGE (Proc. Roy. Irish Acad., 1929, **39**, B, 156—159).—The catalase content of pine needles (*Pinus strobus*), gathered when the temperature was below 0°, was 5—6 units and remained constant when the needles were stored at −5°. When kept at 22° the catalase content rose to 10—11 units, and at 35° to 42 units (cf. Doyle and Clinch, A., 1928, 1408).   J. H. BIRKINSHAW.

Enzyme chemistry of heredity. H. VON EULER and H. NILSSON (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 6, 6 pp.).—Young buds of barley have a considerable catalase content, which is restricted to the coleophyll. Of two Mendelian varieties, one con-taining chlorophyll (dominant) the other white (recessive), the former has the higher catalase content, $K \times 10^{-3}$ at 0° in 10-day seedlings being about 45 for the green and from 7 to 23 in the white. This is the first instance of enzyme activity occurring as a Mendelian factor.   K. V. THIMANN.

Reducing power of the roots of *Graminæ* : reduction of calcium nitrate. III. G. SANI (Atti R. Accad. Lincei, 1929, [vi], **10**, 197—201 ; cf. A., 1920, i, 209).—The reduction of calcium nitrate by pulped maize roots is inhibited by small proportions of potassium hydroxide, chloroform, or formaldehyde, and also by heating or drying. In small quantity, citric acid enhances the action, but sulphurous acid is without effect. The reaction of the medium changes from acid to alkaline during the reduction, the ultimate arrest of the change being probably due to the alkalinity.   T. H. POPE.

Evolution of nitrogen during germination. R. BONNET (Bull. Soc. Chim. biol., 1929, **11**, 1025—1061).—A more detailed account of work already published (A., 1929, 1204).

Histochemical investigation of the tanning material in the leaves of *Carpinus betulus* at different times. A. NIETHAMMER (Biochem. Z., 1929, **216**, 462—466).—Considerable amounts of tannins are present in the leaves of *C. betulus* during the whole growth period and are detectable in both the epidermis and the parenchyma.
                                  P. W. CLUTTERBUCK.

Variation of the cellular permeability of a ligneous plant during growth. B. SOYER (Compt. rend., 1930, **190**, 205—207).—The permeability of the wood and the leaf of the oak to a solution of potassium nitrate has been measured from May to October. The cell permeability was found to be complementary to the large spring and autumn metabolic activities.
                                  C. C. N. VASS.

Microchemical reactions for the study of per-meability in plants. A. NIETHAMMER (Mikrochem., 1929, **7**, 314—317).—The microscopical examination of wheat grains which had been soaked in various solutions for different periods of time showed that whilst copper sulphate, mercury chlorophenoxide, and mercury toluenesulphonamide did not penetrate to the interior of the grain, and mercuric sulphate and chloride did so only after a prolonged period of treat-ment, nickel sulphate and nitrate readily penetrated completely. Potassium thiocyanate resembled the nickel salts in this respect, whilst potassium sulphate could be detected in the embryo only after treatment for 20 hrs.   H. F. HARWOOD.

Anatomy and microchemistry of the fruit of *Gardenia florida*, L., and other species of *Gar-denia* and comparison with the fruit of *Randia dumetorum*, Lam. (*Gardenia dumetorum*, Roxb.). T. MUNESADA (Arch. Pharm., 1930, **268**, 13—22).—Mainly morphological. A detailed account of the action of various chemical reagents on the different tissues of the fruits of six species of *Gardenia*.
                                  J. W. BAKER.

Preparation of large microtome sections of hard woods. H. NIESEMANN (Arch. Pharm., 1930, **268**, 23—24).—The technique of the preparation of large microtome sections of hard woods is described in detail, together with staining processes.
                                  J. W. BAKER.

Cell walls in wood. I. Structure of the cell wall and distribution of chemical constituents. G. W. SCARTH, R. D. GIBBS, and J. D. SPIER (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 269—279).—By the use of differential solvents the distribution of cellulose, lignin, and pectin has been studied, although the presence of pectin cannot be precluded in the middle lamella from the evidence obtained. In general, those parts which stain more readily with phloroglucinol–hydrochloric acid have a greater resistance to sulphuric acid (*e.g.*, the middle lamella, ray cells, etc.). The presence of hydrochloric acid does not accelerate the rate of removal of lignin by glycerol α-monochlorohydrin, although it does when ethylene glycol or glycerol is used as solvent. At

p_H 5·59 and 4·63 the middle lamella and secondary wall can be distinguished by differential staining. Lignin extraction reduces the tendency to differential staining.　　　　　　　　　　　　P. G. MARSHALL.

Cell walls in wood. II. Effect of solvents on permeability of red spruce heartwood. G. W. SCARTH and J. D. SPIER (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 281—288).—Untreated air-dried "sapwood" was found to be freely permeable to water, whilst "heartwood" was not permeable to any extent even at a pressure of 100 lb. per sq. in. A very slight increase in the permeability of heartwood was observed after previous boiling in water for 12 hrs. Prolonged extraction with alcohol–benzene mixture, xylene, acetone, etc., to remove resins, followed by boiling water, produced no increased permeability beyond that effected by boiling water alone. Extraction with lignin solvents was equally ineffective.
　　　　　　　　　　　　P. G. MARSHALL.

Hemicelluloses. I. Hemicelluloses of wheat bran. F. W. NORRIS and I. A. PREECE (Biochem. J., 1930, **24**, 59—66).—Hemicellulose of wheat bran yields four fractions chemically and physically distinct, two of them containing small amounts of uronic acid residues. It was found from hydrolysis experiments that hemicellulose B_2 appears to be a glucosan, whilst the other fractions are largely composed of pentose residue. A method of preparation and purification of hemicellulose is described and is based on the following principle. After removing pectin and lignin from the bran, the hemicelluloses are extracted with sodium hydroxide. Hemicellulose A is precipitated by acetic acid from the extract, hemicellulose B by a half volume of acetone from the mother-liquor, and hemicellulose C by further treatment with acetone. Hemicellulose B is resolved into hemicelluloses B_1 and B_2.　　　　S. S. ZILVA.

Variations in the composition of the fresh branches of *Amelanchier vulgaris*, Mœnch. M. BRIDEL and J. RABATÉ (J. Pharm. Chim., 1930, [viii], **11**, 49—55).—See this vol., 121.

Variation of the colour of plants during drying. Oroberol, a chromogen obtained from *Oberus tuberosus*, L. M. BRIDEL and C. CHARAUX (Compt. rend., 1930, **190**, 202—204).—When the leaves are air-dried or exposed to ether vapour they assume a bluish-black colour due to the action of a soluble enzyme on the principal chromogen following plasmolysis. *O. tuberosus* contains two glucosides, *oroboside*, which is hydrolysed by emulsin, and a *glucoside* hydrolysed by rhamnodiastase. The chromogen *oroberol*, $C_{18}H_{14}O_8$, m. p. 290°, is isolated from green dried leaves by extraction with boiling 60% alcohol, removal of the alcohol, filtration, and precipitation with sulphuric acid; the precipitate is dissolved in ether, the solution dried and evaporated to dryness, and the residue dissolved in boiling water, from which oroberol crystallises. It is optically inactive, and a reducing agent. The colours of its solutions in acid and alkali and with ferric chloride are recorded.
　　　　　　　　　　　　C. C. N. VASS.

Corylopsin, a crystalline constituent of the bark of *Corylopsis spicata*. S. HATTORI (Acta Phytochim., 1929, **4**, 327—341).—Corylopsin is ob-

tained in about 5% yield from the bark of *C. spicata* by extraction with 40% alcohol, filtration from tannin-like material which separates after partial concentration, and further evaporation of the alcohol until a thin syrup remains, from which corylopsin, $C_{13}H_7O_2(OMe)(OH)_6,H_2O$, needles from dilute alcohol, is obtained. When recrystallised, it has m. p. 239° after melting with frothing at 145—150° followed by resolidification, $[\alpha]_D$ −41·6° in methyl alcohol; it reduces Fehling's solution and ammoniacal silver nitrate, decolorises potassium permanganate solution and bromine water, and exhibits the properties of a phenol. It contains a lactone ring and forms a *penta-acetyl* derivative, $C_{13}H_8O_3(OMe)(OAc)_5$, m. p. 208—209°, $[\alpha]_D$ −33·85° in chloroform. Methylation by diazomethane yields dimethylcorylopsin, $C_{13}H_7O_2(OMe)_3(OH)_4,2H_2O$, m. p. 198—199°, which when oxidised by potassium permanganate in alkaline solution yields an acid, $C_{10}H_3O_4(OMe)_3$, m. p. 260—262°, and a lactone, $C_9H_3O_2(OMe)_3$, m. p. 76—77°. On treatment with bromine, corylopsin yields a *compound*, $C_{14}H_{16}O_9Br_2$, m. p. 84—85°, and with hydrobromic acid forms an additive *compound*, $C_{14}H_{17}O_9Br$, m. p. 156—157°. Mixed m. p. determinations show that corylopsin and dimethylcorylopsin are respectively identical with bergenin and methylbergenin (cf. Tschitschibabin *et al.*, A., 1929, 574).　　　　　　　　　W. O. KERMACK.

Fluorescent glucosides of *Diervilla diervilla* and *Symphoricarpos occidentalis*. D. R. McCULLAGH, C. H. A. WALTON, and F. D. WHITE (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 159—163).—Stems of *S. occidentalis* (wolfberry) are extracted with 85% alcohol and the alcohol is removed, the residue being taken up in water and treated successively with neutral and basic lead acetates. The basic lead precipitate is then decomposed, but all attempts to crystallise the product (a glucoside contaminated with some dextrose) failed. From the products of hydrolysis with hydrochloric acid æsculetin (4 : 5-dihydroxy-coumarin) was isolated, and showed the typical blue fluorescence in aqueous solution. The glucoside in *Diervilla* (bush honeysuckle) extract can be obtained crystalline (long needles losing water of crystallisation at 201—205°). It gives a more green fluorescence in alcoholic ammonia than æsculin. From the hydrolysis products acetylfraxetin (m. p. 193—195°) was obtained. The glucoside is therefore fraxin (glucoside of the monoethyl ether of trihydroxy-coumarin).　　　　　　　　P. G. MARSHALL.

Constituents of the white dittany (*Dictamnus albus*). H. THOMS and C. DAMBERGIS (Arch. Pharm., 1930, **268**, 39—48; cf. A., 1923, i, 639).—From the light petroleum extract of the residue obtained by evaporation of an 85% alcoholic extract of dittany root is isolated a crystalline lactone *fraxinellone*, $C_{14}H_{16}O_3$, m. p. 117°, $[\alpha]_D^{15}$ −38·39°. A further quantity is obtained from the accompanying oil after hydrolysis with alcoholic potassium hydroxide, evaporation, precipitation of acidic and lactonic substances with dilute sulphuric acid, and removal of acids with sodium carbonate, and from the balsam fraction in which a small quantity of dictamnolactone is also found, the amount of the atter substance present

being much less than that in the samples of dittany previously examined (*loc. cit.*). Bromination of fraxinellone gives a monosubstituted *bromo*-derivative, $C_{14}H_{15}O_3Br$, m. p. 130°. Although no methoxyl or carbonyl groups can be detected in fraxinellone itself, it is converted by heating with acetic anhydride saturated with hydrogen chloride in a sealed tube at 160—170° into *fraxinellone methyl ketone*, $C_{16}H_{18}O_4$, m. p. 169—170°, $[\alpha]_D^{15} -47.50°$ (p-*nitrophenylhydrazone*, m. p. 198°), probably by the replacement of a hydrogen of the ·CH group adjacent to the hetero-atom by an acetyl group in a manner similar to that which occurs with coumarin (UNGER, private communication). A further similarity to coumarin is found in the reduction of fraxinellone with sodium and alcohol (the reaction being completed in a sealed tube at 160—180°), when phenolic and non-acidic products are obtained, similar treatment of coumarin yielding coumarin and o-ethylphenol. Oxidation of fraxinellone with various reagents gave no identifiable products, whilst ozonolysis gives an acid and a substance which reduces silver nitrate and forms a p-nitrophenylhydrazone and a semicarbazone. From a comparison of the reactions of fraxinellone and other substances isolated from the *Rutaceæ*, xanthotoxin and bergaptan, it is considered probable that the new lactone possesses the carbon skeleton I or II.
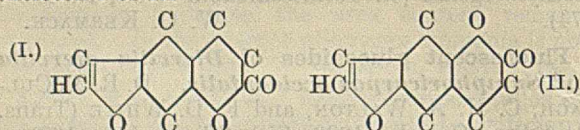
The composition previously assigned to dictamnolactone is confirmed and, like fraxinellone, it is converted similarly into *dictamnolactone methyl ketone*, $C_{18}H_{20}O_6$, m. p. 168° (sinters 155°). From the aqueous solution obtained after evaporation of the alcohol from the original dittany root extract, chloroform extracts dictamnine [*hydrochloride*, m. p. 195°; chloroplatinate, sinters 210°, not melting at 250° (cf. *loc. cit.*, m. p. 152°); *picrolonate*, m. p. 178°; chloroaurate, m. p. 152°, decomp. 171°], whilst from the residual aqueous solution potassium bismuth iodide precipitates trigonelline and choline. J. W. BAKER.

Demonstration of formation of formaldehyde in living plants during chlorophyllic photosynthesis, by means of dimethyldihydroresorcinol. G. POLLACCI and M. BERGAMASCHI (Atti R. Accad. Lincei, 1929, [vi], **10**, 687—689).—Experiments with the aquatic plant, *Elodea canadensis*, in presence of " dimedon " (cf. Klein and Werner, A., 1926, 439), show that formaldimedon is formed when the conditions for photosynthesis under the influence of chlorophyll are fulfilled. Although the dimedon exerts a narcotic influence on the plants, these are not killed but retain their power of assimilation. T. H. POPE.

New amino-compound in the jack bean and a corresponding new enzyme. I. M. KITAGAWA and T. TOMIYAMA (J. Biochem. Japan, 1929, **11**, 265—271).—See this vol., 121.

Enzymic substance contained in koji made of rice in different degrees of its polishing. M. ITO (J. Biochem. Japan, 1929, **11**, 111—141).—The koji-enzyme is produced by the reciprocal action of the *Aspergillus oryzæ* and the rice material itself in presence of water. The composition of the ash, carbohydrate, and nitrogenous substances, respectively, is important in determining the starch-liquefying, carbohydrate-hydrolytic, and protein-splitting activity of the enzyme. Koji made from rice in different phases of polishing has different qualities and enzymic activities.

CHEMICAL ABSTRACTS.

Purification of soya-bean protein. II. Influence of water on purification by lower alcohols. M. MASHINO (J. Soc. Chem. Ind. Japan, 1929, **32**, 312B; cf. A., 1928, 436).—The amount of carbohydrate extracted from crude soya-bean protein by aqueous methyl or ethyl alcohol increases with increasing dilution until it reaches a maximum at 70% or at 40% alcohol, respectively. The crude protein extracted also increases with increasing dilution, about threefold and tenfold with the respective solvents. C. W. SHOPPEE.

Protein content of grass, chiefly meadow foxtail (*Alopecurus pratensis*), as influenced by frequency of cutting. F. T. SHUTT, S. N. HAMILTON, and H. H. SELWYN (J. Agric. Sci., 1930, **20**, 126—134).—Work during two seasons shows that the protein content of herbage and its digestibility increase with shortening of the period between cuttings, due in the first season to the fact that protein decreases with age, but in the second to incursion of white Dutch clover. Total yields of protein and dry matter per acre tend to decrease with frequency of cutting. E. HOLMES.

Protein content of grass as related to stage of growth. F. T. SHUTT (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 133—140).—The results are given of a comparison, for two seasons, of protein and fibre content, and total dry matter and protein in the crops from four plots of pasture cut (*a*) weekly, (*b*) fortnightly, (*c*) every three weeks, and (*d*) for hay with aftermath. The young grass in (*a*), (*b*), and (*c*) contained 21, 19, and 17% of protein and 19, 21, and 22% of fibre, respectively, in the first season, and in the second season 29, 23, and 21% and 17, 19, and 20%. The increase in protein was associated with an increase of white Dutch clover. Plot (*d*) gave 10 and 13% of protein, and 29 and 27% of fibre. The total yield of protein per acre was highest from (*c*) in the first season, and in the second season it was about equal from (*a*), (*b*), and (*d*) and least from (*c*). Plot (*d*) gave the highest yield of dry matter, and this yield appears to be inversely proportional to the frequency of cutting. The essential value of the close grazing system lies in furnishing throughout the season pasturage rich in protein of a particularly digestible and nutritious character. R. K. CALLOW.

Extracts from the woolly-pod milkweed, *Asclepias eriocarpa*. J. F. COUCH (Amer. J. Pharm., 1929, **101**, 815—821).—The poisonous constituent is a complex organic acid, insoluble in water, acids, chloroform, and ether, soluble in aqueous alkalis and in alcohol, non-glucosidal, and non-hæmolytic; it contains no amino-group. It is present as a salt which is extracted by hot water; addition of barium hydroxide precipitates the barium

salt from the extract, the precipitate is treated with sulphuric acid to liberate the organic acid, which is extracted by sodium carbonate solution and then reprecipitated by addition of hydrochloric acid.

S. I. LEVY.

Unsaponifiable matter of ego oil. M. TSUJI-MOTO (J. Soc. Chem. Ind. Japan, 1929, **32**, 324B).—Ego oil (from the seeds of *Styrax japonica*), d_4^{15} 0·9387, n_D^{15} 1·4814, affords 7·1% of unsaponifiable matter, containing 1·7% of sterols and a *substance* ("*egonol*"), $C_{19}H_{18}O_5$, m. p. 116° (*monoacetyl* derivative, m. p. 107°), which contains one methoxyl group. Egonol adds rather less than 2 atoms of bromine in ethereal solution, giving a *compound*, m. p. 164°; catalytic hydrogenation experiments were inconclusive, and a semicarbazone could not be obtained.

C. W. SHOPPEE.

Detection of oil in twigs. R. HAYNES (Stain Tech., 1930, **5**, 29).—The penetration of oil applied to dormant twigs was demonstrated by cutting sections about 20 μ thick which were stained with Sudan IV and then with methylene-blue. The oil is distinguished as brilliant red droplets, very much larger than those of the naturally occurring fat. H. W. DUDLEY.

Chemical and physical variations of waters of the strait of Georgia in relation to phytoplankton. A. H. HUTCHINSON, C. C. LUCAS, and M. McPHAIL (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 177—187).—The period of greatest diatom quantity normally follows the period of lowest salinity, and the most favourable conditions for phytoplankton growth occur in the 10-yard region, where mixing of the sea-water and Fraser river water takes place. Abundance of phytoplankton lowers the soluble silica and phosphates. P. G. MARSHALL.

Influence of oxygen on the volatilisation of iodine. P. DANGEARD (Compt. rend., **190**, 131—133).—The emission of iodine by fresh sea-weeds has been examined both in air and in an atmosphere of nitrogen, and is found to be diminished and finally inhibited in the latter. External oxygen is therefore necessary for the volatilisation of iodine. This explains why the most active types of *Laminaria* are found in the most highly aerated waters and why the activity is greater in air than in water.

P. G. MARSHALL.

Mineral content of the jujube. M. P. BENOY (J. Agric. Res., 1929, **39**, 949—951).—Comparative data are given for the mineral constituents on a moisture-free basis, and of the ash, of dates, seeded raisins, and the jujube or Chinese date, *Zizyphus jujuba*, Mill. E. HOLMES.

Titanium in cryptogams. G. BERTRAND and C. VORONCA-SPIRT (Bull. Soc. chim., 1930, [iv], **47**, 102—104).—See A., 1929, 1113.

Copper as an element necessary to plants. A. QUARTAROLI (Annali Chim. Appl., 1929, **19**, 467—519).—The importance of so-called catalytic elements such as iron, manganese, copper, zinc, and arsenic in animal nutrition is discussed, these elements apparently exerting a function analogous to that of the vitamins. Determinations of the proportions of copper and manganese in about 300 Italian soils of different origins and types show that, in general, the proportion of manganese is ten times that of copper. In the more vital organs of plants, however, the proportion of copper is of the same order as, and often in excess of, that of manganese. In any one plant organ, the amount of copper is comparatively high in the early stages of growth, but it diminishes gradually as the organ ages; the manganese, on the other hand, continuously accumulates. Such organs as seeds, leaves, buds, filiform roots, etc. contain appreciably more copper than secondary organs such as trunks, branches, and shells. T. H. POPE.

Phosphorus-containing constituents of plants. V. Solubility of the phosphorus-containing constituents of rye embryos. Z. KOEHLER (Bull. Acad. Polonaise, 1929, B, 237—254).—Air-dried rye embryos have a mean total phosphorus content of 3·11% (calculated as phosphorus pentoxide), whilst that of defatted embryos is 3·548%. Of this latter quantity about 11% corresponds with mineral phosphorus pentoxide, whilst 44% is accounted for as phytic phosphorus pentoxide (cf. A., 1927, 1227). When the defatted embryos are extracted with distilled water about 69% of the total phosphorus passes into the extract. When the extracting liquid is hydrochloric acid the quantity of phosphate in the extract decreases to a minimum of 19% with 0·05% acid and then increases again with increasing concentrations of acid, being 71·42% with 5·0% acid. Dilute sodium hydroxide solution extracts rather less phosphorus than does distilled water. With very dilute acid, distilled water, or alkaline solution, the extracts contain a considerable quantity of plant-proteins, which partly account for the increase in the phosphorus extracted with acid more dilute than 0·05%. W. O. KERMACK.

Starch-liquefying action of sandal leaf extracts. B. N. SASTRI (J. Indian Inst. Sci., 1929, **12**, A, 251—252).—Healthy leaf extract contains more of the starch-liquefying principle than diseased leaf extract. P. G. MARSHALL.

Aucuba or yellow mosaic of the tomato plant : reaction of infected juice. W. F. BEWLEY and B. J. BOLAS (Nature, 1930, **125**, 130).—A marked action occurs when the expressed juice from a tomato plant is mixed with an aqueous colloidal solution of tomato chlorophyll; a brown colour develops with apparent destruction of the chlorophyll. The reaction is sensitive to light and is accelerated by an intensity of 800 ft.-candles at 30°. L. S. THEOBALD.

Spike disease of sandal (*Santalum album*, Linn.). VI. Nitrogen metabolism in healthy and spiked sandal leaves. N. NARASIMHAMURTHY and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, **12**, A, 153—163).—Increases in total water-soluble nitrogen, in basic nitrogen, and in total amino-nitrogen are characteristics of the diseased leaves when compared with normal leaves. E. A. LUNT.

Spike disease of sandal (*Santalum album*, Linn.). VII. Factors influencing diastatic activity. VIII. Composition of leaf-tissue fluids. IX. Composition of stem-tissue fluids. B. N. SASTRI and M. SREENIVASAYA. **X. Seasonal variations in healthy and diseased trees.**

A. V. V. IYENGAR (J. Indian Inst. Sci., 1929, **12**, **A**, 233—238, 239—244, 245—250, 295—305).—VII. Dialysis of enzyme extracts produces a greater loss of activity in spiked than in healthy leaves. The greater enzymic activity of diseased extracts is due mainly to a decrease in calcium (121·5 mg. per 100 c.c.), increase in phosphate and amino-nitrogen, and increased buffering power with a lower p_H. Activators are present in spiked leaf extracts, but no inhibitors are found in healthy leaf extracts.

VIII. Healthy leaves give a greater percentage of tissue fluid than diseased leaves, and the fluid has a higher content of ash and calcium, together with a lower content of maltose and reducing sugars.

IX. Spike disease causes variations in composition of the stem-tissue fluid similar to those occurring in leaf-tissue fluid. The high gradient of calcium concentration from stem to leaf tends to disappear after onset of the disease, showing that the mechanism of transport is impaired.

X. The highest ash values are recorded towards the end of the hot spring for the fluid from both diseased and healthy trees, the increase in silica content being particularly marked in disease. The electrical conductivity of diseased tissue fluid is greater than that of fluid from healthy trees.   P. G. MARSHALL.

Chemotherapy of organic dyes in plant diseases. G. TRUFFAUT and I. PASTAC (Compt. rend., 1929, **189**, 1013—1015).—Dyes kill parasitic fungi by a process of staining following penetration of the protoplasm. In laboratory experiments Raulin's culture medium is used (with varying additions of dye) and inoculated with *Rhizopus nigricans* or *Penicillium glaucum*. Malachite-green alone is ineffective in preventing growth, as the high surface tension prevents penetration. Soaps and sulphoricinates cannot be used to reduce the surface tension on account of their susceptibility to chemical reagents, but some adhesives recently introduced (eucarnite, iporite, etc.) are effective. Crystal-violet is harmful to the healthy leaves of plants, but auramine kills the parasite without damage to the plants, two or three treatments with the dye solution at intervals of three days being usually sufficient. Wheat blighted by *Tilletia fœtens* and *Triciti* is rendered healthy by 2 hrs.' immersion in the dye solution followed by drying; the germinating power is not impaired.   P. G. MARSHALL.

Double electrode for micro-determination of hydrogen-ion concentration. L. SMOLÍK (Biochem. Z., 1930, **217**, 216—217; cf. A., 1926, 927).—The apparatus has been modified so that determinations can be made using two or three drops of liquid.
                               W. McCARTNEY.

Silver chloride electrode in contact with Ringer's solution. J. W. LANGELAAN (Arch. Néerland. Physiol., 1929, **14**, 592—597).—The Ag| AgCl electrode, in contact with Ringer's solution, behaves as a reversible chlorine electrode which is insensitive to the sodium hydrogen carbonate of the solution, to dissolved carbon dioxide, and to small amounts of lactic and nitric acids. The value

calculated for the potential of the half-cell with reference to the normal hydrogen electrode as zero is 0·287 volt.   C. C. N. VASS.

Micro-determination of iodides in the presence of other salts. J. F. REITH (Biochem. Z., 1929, **216**, 249—268).—A number of methods for the micro-determination of iodine are comparatively investigated. The sensitivity of the iodine–starch reaction, the possibility of the oxidation of hydrogen iodide by air, and the influence of p_H and concentration of potassium iodide on the thiosulphate titration of very dilute iodide solutions are investigated. Curves summarise the disturbances caused by the presence of nitrites and bromides with the different methods.
                               P. W. CLUTTERBUCK.

Determination of volatile substances. G. GAZENKO (Biochem. J., 1930, **24**, 55—56).—A description of a closed system in which the air is continuously circulated, by means of a pump, until the volatile substance in the solution to be analysed has been completely transferred to, and absorbed in, an appropriate standard solution.   H. W. DUDLEY.

Importance of sublimation for pharmacological investigation. E. KEESER and J. KEESER (Arch. exp. Path. Pharm., 1930, **147**, 360—365).—Compounds such as barbituric acid derivatives and other hypnotics and certain alkaloids when injected into a rabbit may be recovered from the brain by careful sublimation, the crystals so obtained being identified by their shape and by micro-chemical reactions.   W. O. KERMACK.

Modifications in Mendel and Goldscheider's colorimetric determination of lactic acid. H. J. FUCHS (Biochem. Z., 1930, **217**, 405—408; cf. A., 1926, 212; 1929, 110).—The special sulphuric acid specified by the above authors may be replaced by the ordinary pure acid if the concentration of the veratrol solution is raised from $\frac{1}{8}\%$ to 20%. Under these conditions the determination is twice as sensitive without losing its specificity.   K. V. THIMANN.

Micro-detection of fats. A. NIETHAMMER (Biochem. Z., 1930, **217**, 436—439).—In a modification of the author's method (A., 1929, 1114) the fat is sublimed off directly from the tissue, and the fatty acids of which it consists are identified by their characteristic microcrystalline appearance, of which examples are given. The method can be used for following the changes during ripening of seeds.   K. V. THIMANN.

Determination of sucrose by Hanes' modification of the Hagedorn–Jensen method. E. H. CALLOW (Biochem. J., 1930, **24**, 57—58).—The sucrose is inverted and is determined by Hanes' modification (A., 1929, 478). The quantity of invert-sugar present is obtained from a curve giving the relationship of this sugar to the thiosulphate equivalent of the ferricyanide reduced.   S. S. ZILVA.

Determination of uric acid. L. T. MARGOLIN and S. F. BUCHTEYEV (Zhur. exp. Biol. Med., 1929, **11**, 110—113).—The stability of the sodium cyanide solution used in Benedict's method was examined.
                               CHEMICAL ABSTRACTS.