

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

MAY, 1931.

### General, Physical, and Inorganic Chemistry.

New bands in the secondary spectrum of hydrogen. D. S. JOG (Phil. Mag., 1931, [vii], 11, 761—786; cf. Richardson, A., 1930, 387).—The known electronic levels of hydrogen are summarised, and are interpreted on Hund's theory of axial quantisation; the method is applied to the calculation of the electronic terms of the hydrogen molecule.

N. M. BLIGH.

Fine structure in hydrogen band lines. O. W. RICHARDSON and W. E. WILLIAMS (Nature, 1931, 127, 481).—An examination of the spectrum of hydrogen in a large Hilger quartz spectrograph crossed by a reflexion echelon establishes the correlation between the spectrum of molecular hydrogen and atomic helium.

L. S. THEOBALD.

Gaseous discharges. I. Characteristics of the discharges in hydrogen and nitrogen at reduced pressures with an incandescent cathode. II. Influence of the thermal treatment of the electrode on the glow discharge. III. Influence of gas-loading of the cathode on the ignition potential of the glow discharge in hydrogen. E. BADAREU (Bull. Fac. Stiinte Cernăuți, 1929, 3, 221—236, 304—306, 1—8; Chem. Zentr., 1930, ii, 1043).

L. S. THEOBALD.

Cold emission from unconditioned surfaces. W. H. BENNETT (Physical Rev., 1931, [ii], 37, 582—590).—Emission from unconditioned metals in high electric fields and the effect on the emitting surfaces of discharges through hydrogen were investigated. Loose fine particles have a greater influence on the quantity of emission than nature and conditioning of cathode.

N. M. BLIGH.

Clean-up phenomenon in hydrogen. E. HIEDEMANN (Ann. Physik, 1931, 8, [v], 456—474).—The clean-up phenomenon in hydrogen follows a normal (in essentials similar to that described by Johnson) or an abnormal (observed by Mierdel) course depending on the treatment to which the discharge tube has been previously subjected. The normal clean-up is characterised by adsorption of hydrogen, whilst the abnormal appears to be the result of condensation of a mixture of silicon hydrides.

W. GOOD.

Visible spectrum of helium. J. S. TOWNSEND and F. L. JONES (Phil. Mag., 1931, [vii], 11, 679—685; cf. A., 1930, 973).—The relation between the light emitted by a discharge in a gas and the energy of the electrons causing ionisation by collision with the gas molecules was investigated by observations

on the change in intensity of the light due to changes of pressure in helium over the range 20—2 mm., and electron energies 3—4 volts. Bohr's model of the helium atom, requiring a minimum of 20 volts for radiation emission, is not supported.

N. M. BLIGH.

Hyperfine structure of  $\text{Li}^+$ . II. P. GÜTINGER and W. PAULI (Z. Physik, 1931, 67, 743—765).—Theoretical (cf. A., 1930, 1487). Hyperfine separations in the  $\text{Li}^+$  lines,  ${}^3P_{0,1,2}$ — ${}^3S_1$ , are comparable with fine structure separations.

A. B. D. CASSIE.

Vacuum spark spectra to 40 Å.: spectra of Be III, Be IV, B IV, B V, and C V. B. EDLÉN (Nature, 1931, 127, 405—406).—The hydrogen- and helium-like spectra previously traced to Be IV (A., 1930, 263) have been completed with B IV, B V, and C V, and the limit of optical spectra has been brought down to 40.28 Å. Wave-lengths of the series  $1^2S$ — $n^2P$  and  $1^2S$ — $3^2P$ , and  $1^1S$ — $n^1P$  are tabulated. The calculated quantum defect from the series of Be III is  $n-n^* = -0.013 \pm 0.001$ .

L. S. THEOBALD.

Intensity measurements in the atmospheric oxygen band at 7600 Å. W. H. J. CHILDS and R. MECKE (Z. Physik, 1931, 68, 344—361).—The intensity of absorption due to the A-group of oxygen near 7600 Å. was determined by Frerichs' method (*ibid.*, 1925, 31, 305), using a dispersion of 2.6 Å. per mm., and columns of air 14, 33, and 62 metres long. Deviations from Lambert's law were investigated and allowed for, and the statistical weights of the rotational levels were determined.

A. B. D. CASSIE.

Starting potentials of the corona discharge in neon. F. M. PENNING (Phil. Mag., 1931, [vii], 11, 961—980).—Contrary to the results of Huxley (cf. A., 1928, 567), the starting potential of a positive discharge in pure neon was found to be higher than that of a negative discharge. The former could, however, be decreased below the latter by the addition of traces of argon.

N. M. BLIGH.

Photometry of the neon lamp. M. J. DRUYVESTEYN and N. WARMOLTZ (Z. Physik, 1931, 68, 378—394).—Light emitted normally to the cathode of a neon lamp was investigated visually by means of a rotating sector photometer. Fifteen international candles are emitted per amp. passing through the lamp; this intensity is proportional to the current and independent of cathode fall and gas pressure. A study of the influence of helium and argon suggests



that excitation is due to slow electrons of 25 volts energy.  
A. B. D. CASSIE.

**New resonance series of sulphur vapour. III.** J. GENARD (Bull. Acad. roy. Belg., 1931, [v], 17, 184—190).—The extent of the excitation region of the resonance spectrum of  $S_2$  was investigated. Conditions used were other than those giving the optimum fluorescence; excitation was by means of magnesium spark. The lower limit of the excitation spectrum is between 2890 and 2850 Å.  
A. J. MEE.

**Rotational analysis of the  $S_2$  bands.** S. M. NAUDÉ and A. CHRISTY (Physical Rev., 1931, [ii], 37, 490—506; cf. Rosen, A., 1927, 608).—The emission spectrum of  $S_2$  was obtained by means of a Geissler tube, and the bands 9—1 ( $\lambda$  2857·36), 7—0 ( $\lambda$  2860·13), 8—1 ( $\lambda$  2887·84), 9—1 ( $\lambda$  2917·38), and 7—1 ( $\lambda$  2920·28) were investigated. Each band consists of three *R* and three *P* branches; the structure is similar to that of the Schumann-Runge bands of oxygen. Wave numbers and intervals for the lines of each band are tabulated, and the rotational analysis is obtained.  
N. M. BLYGH.

**Spark spectra of chlorine.** K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 105—109; cf. this vol., 276).—The spectrum of Cl III was excited by increasing the spark gap and current in a Geissler tube with tungsten electrodes, one containing a little sodium chloride. Intensities, wave-lengths, and term combinations are tabulated for 29 newly-classified lines. The classification of Cl II lines is extended.  
N. M. BLYGH.

**Band spectra of scandium, yttrium, and lanthanum monoxides.** W. F. MEGGERS and J. A. WHEELER (Bur. Stand. J. Res., 1931, 6, 239—275).—The band spectrum of scandium oxide contains 139 band heads, all degraded towards the red. They are divided into five systems, the 0-0 transitions having heads at 4857·79 and 4858·09, 6017·07, 6036·17, 6064·31, 6079·30 Å. Yttrium oxide gives 120 band heads degraded towards the red, the five 0-0 transitions being 4817·38 and 4818·20, 5939·08, 5972·04, 6096·78, 6132·06 Å. Lanthanum monoxide gives 300 band heads, divided into nine systems, seven of which include all bands shaded towards the red, and the other two of groups of weaker bands shaded away from the red.  
C. W. GIBBY.

**Intensity measurements in the spectrum of manganese.** R. S. SEWARD (Physical Rev., 1931, [ii], 37, 344—361; cf. McLennan, A., 1926, 766; Duffendack, A., 1929, 966).—Relative intensity measurements were made, and full data tabulated for 150 lines of 23 multiplets of Mn I, and 3 of Mn II.  
N. M. BLYGH.

**Fluorescence of zinc vapour.** W. KAPUŚCIŃSKI (Bull. Acad. Polonaise, 1930, A, 453—459).—The fluorescence spectrum of zinc vapour extends from 2130 to 4900 Å., and consists of lines and bands. The triplets originate in levels not directly excited from the ground level.  
A. B. D. CASSIE.

**Optical excitation functions of cadmium and zinc lines.** K. LARCHÉ (Physikal. Z., 1931, 32, 180—181).—A lecture.  
W. GOOD.

**Critical potentials of the spark spectrum of cadmium.** D. COLSON (Proc. Iowa Acad. Sci., 1929, 36, 307).—Excitation by electron impact (8·8—200 volts) was employed.  
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**Second spectrum of xenon.** C. J. HUMPHREYS, T. L. DE BRUIN, and W. F. MEGGERS (Bur. Stand. J. Res., 1931, 6, 287—293).—A partial list of identified terms and their combinations is given.  
C. W. GIBBY.

**Probabilities of recombination into the  $1^2S$  state of caesium.** C. BOECKNER (Bur. Stand. J. Res., 1931, 6, 277—285).—The intensity distribution in the  $1^2S$  series of caesium has been measured between 3184 and 2750 Å. From this and the velocity distribution of the discharge electrons the relative probability of recombination of free electrons into the  $1^2S$  state is shown to fall nearly as the inverse fourth power of the velocity for energies greater than 0·15 volt.  
C. W. GIBBY.

**Measurements in the arc spectrum of rhenium.** W. MEIDINGER (Z. Physik, 1931, 68, 331—343).—A number of lines between 2600 and 3500 Å. and between 4040 and 5300 Å. were measured with an accuracy of  $\pm 0\cdot1$  Å. in the arc spectrum of rhenium.  
A. B. D. CASSIE.

**Absorption spectrum of dissolved mercury.** H. REICHARDT and K. F. BONHOEFFER (Z. Physik, 1931, 67, 780—789).—A furnace containing a quartz absorption vessel which could contain liquids at 200 atm. and 250° is described. A double mercury 2537 Å. line, displaced towards the red, appeared at 120° when the mercury was dissolved in water, at 50° when in methyl alcohol, and at 15° when in hexane. Doubling is a Stark effect due to the electric field within the solution. The doublet separation diminishes with rise of temperature or decreasing density of the solvent. An absorption edge at 2200 Å. is ascribed to ionisation of dissolved mercury atoms.  
A. B. D. CASSIE.

**Fluorescence of mercury vapour under atomic and molecular absorption.** H. NIEWODNICZAŃSKI (Nature, 1931, 127, 406).—The view that the fluorescence of mercury vapour is due mainly to atomic absorption is supported by the author's work on the influence of a magnetic field on fluorescence (A., 1929, 979; cf. Rayleigh, this vol., 137).  
L. S. THEOBALD.

**Spark spectra of mercury.** B. RICARD (Compt. rend., 1931, 192, 618—620).—With the electrodeless discharge new lines have been measured belonging to the Hg II, Hg III, and Hg IV spectra from 4000 to 2700 Å.  
C. A. SILBERRAD.

**Fine structure in the mercury singlet terms.** S. TOLANSKY (Proc. Roy. Soc., 1931, A, 130, 558—578).—By the use of a low-pressure high-frequency electrodeless discharge in pure mercury vapour, which increases the relative and intrinsic intensities of the singlet and inter-combination lines involving upper singlet levels, numerous structure have been examined. An explanation, based on the conception of nuclear spin, is suggested for the origin of the fine structures. This accounts for most of the difficulties and explains the apparent multiplicity of the  $7^1S_0$  level.  
L. L. BIRCUMSHAW.

**Resonance line of mercury on addition of rare gases.** P. KUNZE (Ann. Physik, 1931, 8, [v], 500—520).—The effect of helium, neon, and argon on the emission and absorption of the resonance line of mercury (2537) has been experimentally investigated. A quantitative discussion of the results is given. W. GOOD.

**Hyperfine structure of the mercury resonance line 2537 Å.** I. S. MROZOWSKI (Bull. Acad. Polonaise, 1930, A, 464—503).—The Zeeman effect in absorption was studied for the mercury 2537 Å. line with fields up to 8 kilogauss. Anomalies observed by McNair (A., 1928, 807) between 1 and 3.5 kilogauss in emission appear in absorption. This hyperfine structure and Zeeman effect cannot be explained by ordinary hypotheses.

A. B. D. CASSIE.

**Hyperfine structure of certain mercury lines.** B. VENKATESACHAR and L. SIBAIYA (Mysore Univ. J., 1930, 4, 145—148).—Analyses of the mercury lines 6716, 6123, 6072, and of 4916 Å. are given.

C. W. GIBBY.

**Intensity of mercury lines excited by positive ions.** D. FRISCHE (Proc. Iowa Acad. Sci., 1929, 36, 307—308).—The results were compared with those of investigation of the electron spectrum.

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**Life of the excited state and the fine structure of the mercury arc spectrum.** S. MROZOWSKI (Z. Physik, 1931, 68, 278—283).—It is shown that the times of life of different levels which take part in the production of a multiplet are nearly equal to each other so far as transitions to other levels belonging to the same term system are concerned.

A. J. MEE.

**Thallium-inert gas bands.** H. KREFFT and R. ROMPE (Naturwiss., 1931, 19, 269).—Mixtures of thallium vapour with inert gases give absorption bands in the neighbourhood of the strongest thallium lines (5350 and 3776 Å.). Probably these arise from a thallium-inert gas molecule. The separation of the band heads varies with the inert gas.

W. R. ANGUS.

**Influence of ion density on the arc spectrum of thallium.** H. KREFFT (Naturwiss., 1931, 19, 269—270).—Spectrograms are given showing the influence of different current strengths on the absorption spectrum obtained from a discharge in mixtures of thallium with inert gases. The observed phenomena are discussed.

W. R. ANGUS.

**Determination of energy of dissociation from predissociation spectra.** L. A. TURNER (Z. Physik, 1931, 68, 178—183).—An explanation of the existence of two types of predissociation spectrum is given. In the one the disappearance of fine structure is sharp, in the other gradual.

A. J. MEE.

**Reduction of intensity of spectral lines in strong electric fields.** C. LANCZOS (Z. Physik, 1931, 68, 204—232).—The reduction of the intensity of the emission lines of the hydrogen atom is discussed quantitatively on the basis of wave mechanics, and ascribed to "pre-ionisation." The electric field sets the atom in a state of spontaneous ionisation, so that radioactive disintegration can take place. In

the higher excited states this disintegration takes place in a time which is less than the life of the excited atom, and as radiation transition cannot take place the emission line disappears.

A. J. MEE.

**Zeeman effect of forced radiation transitions produced by inner electric fields.** G. P. ITTMANN and H. C. BRINKMAN (Naturwiss., 1931, 19, 292).—The occurrence of a forbidden line in absorption or emission spectra may be due to two causes, which can be distinguished by a study of the Zeeman effect. The Zeeman effect for transitions which are forced by electric fields by no means agrees with that produced for permitted transitions.

A. J. MEE.

**After-glow and its life in discharge tubes.** D. B. DEODHAR (Nature, 1931, 127, 485).—A strong after-glow persisting for 45 min. has been observed in silica tubes filled with gases at low pressures and excited for 2 min. by induction coils giving an output of 400 volts. The rate of decay is extremely slow. The flash phenomenon recorded by Braddick (this vol., 1) is seen in these after-glows.

L. S. THEOBALD.

**Sensitivity of photographic plates in the region between ultra-soft X-rays and the ultra-violet.** M. SÖDERMAN (Z. Physik, 1931, 67, 790—793).—Schumann plates are best suited to photographing spectra between 50 and 500 Å.

A. B. D. CASSIE.

**Sources of illumination for ultra-violet microscopy.** B. K. JOHNSON (Proc. Physical Soc., 1931, 43, 127—137).—Quantitative measurements have been made of the relative intrinsic brightness of spectrum lines given by various sources of radiation. Spark discharge between cadmium electrodes is the most suitable source of radiation for quartz monochromat microscope objectives computed for a wavelength in the neighbourhood of 0.275  $\mu$ . A special transformer and condenser is described.

W. E. DOWNEY.

**Influence of the crystal-orientation of the cathode on that of an electrodeposited layer.** W. A. WOOD (Proc. Physical Soc., 1931, 43, 138—141).—X-Ray examination shows that the orientation of a copper deposit for small currents is the same as that of the cathode. Nickel at low current densities assumes a distinct orientation. As the current is increased there is a region of no orientation, but at still higher currents the orientation is the same as that of the cathode surface.

W. E. DOWNEY.

**Intensity of X-rays reflected from platinum, silver, and glass.** H. W. EDWARDS (Physical Rev., 1931, [ii], 37, 339—343).—The intensity of a monochromatic beam of X-rays of wave-length 0.69 Å., obtained by reflexion from calcite, was measured on reflexion from platinum, silver, and glass mirrors for angles of incidence varying from 0.75 to 1.25 times the critical angle.

N. M. BUGH.

**Frequencies of characteristic X-radiation for the elements 11 Na to 17 Cl, calculated more accurately than at present with hypotheses extending the classical theory.** S. BJÖRCK (Z. Physik, 1931, 68, 133—144).—Theoretical.

A. B. D. CASSIE.

Mass absorption coefficient of the  $K$  shell according to the Dirac relativistic theory of the electron. L. C. ROESS (Physical Rev., 1931, [ii], 37, 532—555).—Mathematical. With a model atom containing two non-interacting electrons and a fixed nucleus the mass absorption coefficient is calculated with the help of the Dirac relativistic equation. Results for lead, tin, zinc, and aluminium are tabulated and graphed for comparison with experimental data, and with values calculated on a non-relativistic basis (cf. Stobbe, this vol., 138). N. M. BLIGH.

Distribution of electricity in the lithium atom. B. ARAKATZU and P. SCHERRER (Helv. phys. Acta, 1930, 3, 428—435; Chem. Zentr., 1931, i, 13—14).—The scattering of  $X$ -rays by lithium has been examined by the powder method, and the electronic distribution is discussed. A. A. ELDRIDGE.

The ionisation formula and the new statistics. W. ANDERSON (Phil. Mag., 1931, [vii], 11, 685—686).—Remarks on a paper by Chandrasekhar (A., 1930, 833). N. M. BLIGH.

Ionisation of argon, neon, and helium by various alkali ions. R. M. SUTTON and J. C. MOUZON (Physical Rev., 1931, [ii], 37, 379—382; cf. A., 1930, 656).—Caesium, rubidium, potassium, and sodium positive ions from Kunsman catalyst sources and lithium ions from spodumene were used to produce ionisation in helium, neon, and argon. Maximum ionisation was produced in each gas by the alkali ion nearest to it in atomic number (cf. Beeck, A., 1930, 1494). N. M. BLIGH.

Theory of the photo-electric effect in metals. I. TAMM and S. SCHUBIN (Z. Physik, 1931, 68, 97—113).—Theoretical. Photo-emission is related to the potential barrier at the metal surface (surface effect) and to the energy of binding of conduction electrons (volume effect). The influence of surface layers is discussed. A. B. D. CASSIE.

Photo-electric effect and reflexion of electrons at hydrogenised potassium surfaces. W. KLUGE and E. RUPP (Physikal. Z., 1931, 32, 163—172).—An experimental arrangement is described with which parallel investigations of the structure and photo-electric emission of potassium surfaces were carried out. The results support the view that the selective photo-electric effect exhibited by the potassium surface after a glow discharge in hydrogen at low pressure is due to interspersions of potassium in potassium hydride. The investigations of surface structure by electron reflexion lead to the values 7.3 volts for the mean inner potential of potassium and  $5.4 \text{ \AA.} \pm 0.1$  for the lattice constant of potassium hydride (cubic lattice). W. GOOD.

Quantum dynamics of the electron. E. SCHRÖDINGER (Sitzungsber. Preuss. Akad. Wiss., Berlin, 1931, 12 pp.).—Mathematical.

Directions of emission of photo-electrons. P. AUGER and (MLE.) T. MEYER (Compt. rend., 1931, 192, 672—673).

Elastic scattering of slow electrons in argon. E. C. BULLARD and H. S. W. MASSEY (Proc. Roy. Soc., 1931, A, 130, 579—590; cf. Ramsauer and

Kollath, A., 1930, 269, 1495).—With the object of obtaining further insight into the Ramsauer effect, experiments have been carried out in which the angular distribution of slow electrons (velocities from 4 to 40 volts) scattered elastically in argon have been measured over the angular range  $15$ — $125^\circ$ . Scattering curves are obtained showing pronounced maxima and minima. L. L. BIRUMSHAW.

Diffraction of electrons in mercury vapour. F. L. ARNOT (Proc. Roy. Soc., 1931, A, 130, 655—667; cf. preceding abstract).—By means of the apparatus previously described (A., 1930, 6), the angular distributions of electrons of 15 different velocities (8.6—800 volts) scattered in mercury vapour have been measured over an angular range of  $18$ — $126^\circ$ . L. L. BIRUMSHAW.

Scattering of high-velocity electrons in hydrogen as a test of the interaction energy of two electrons. H. C. WOLFE (Physical Rev., 1931, [ii], 37, 591—601).—Mathematical. N. M. BLIGH.

Absorption coefficient for slow electrons in thallium vapour. R. B. BRODE (Physical Rev., 1931, [ii], 37, 570—573; cf. A., 1930, 657).—The absorption coefficient was obtained by sending a beam of electrons through thallium vapour and measuring the decrease in intensity of the beam as a function of the vapour pressure; plotted against the velocity of the electrons there is a minimum at 1.4 and a maximum at 4.5 volts. N. M. BLIGH.

Liberation of electrons by collision with positive ions at low gas pressures. II. Silver, aluminium, potassium, sodium, and mercury in hydrogen, nitrogen, mercury vapour, and rare gases. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1931, 68, 162—173).—The yield of electrons due to collision in hydrogen and nitrogen increases with the amount of gas, but in the rare gases is independent of this factor. It increases with the energy of collision, but above 1000 volts the increase is small. In general the number of electrons set free is greater the smaller is the mass of the ion colliding. A. J. MEE.

Pyrometry and the radiation properties of heated metals. R. HASE (Proc. Physical Soc., 1931, 43, 212—216).—It is experimentally shown that the maximum of the energy emitted by a radiating metal is proportional to the square root of the specific resistance at zero and to the sixth power of the absolute temperature, instead of to the fifth power as in the case of a black body. The results are in good agreement with theoretical predictions, based on Maxwell's theory. W. E. DOWNEY.

Direct measurement of molecular velocities. I. F. ZARTMAN (Physical Rev., 1931, [ii], 37, 333—391; cf. Eldridge, A., 1928, 108; Lammert, A., 1929, 970).—A method is described in which molecules condense on a glass plate fastened to a rapidly revolving cylinder. A stream of bismuth molecules having velocities of 168—673 m. per sec. was spread over a band 3 cm. wide; the vapour was found to consist of 40% Bi and 60% Bi<sub>2</sub> at  $851^\circ$ . N. M. BLIGH.

Positive ion emission from thin platinum films on glass. R. A. NELSON (Rev. Sci. Instr.,

1931, [ii], 2, 173—179; cf. this vol., 26).—An apparatus for the production of  $\text{Na}^+$  or  $\text{K}^+$  ions from an equipotential surface of controlled thermionic activity is described. The positive ion current from platinised glass was greater than that from un-platinised glass at the same temperature. A new effect, the existence of a maximum and minimum in the positive thermionic current—electrolysis potential curves, was more pronounced with the equipotential emitter.  
N. M. BLYGH.

Interchange of translational, rotational, and vibrational energy in molecular collisions. C. ZENER (Physical Rev., 1931, [ii], 37, 556—569).—Mathematical. The change in internal energy of molecules on collisions is investigated. The interchange of vibrational and translational energy for a collision in line of an atom and diatomic molecule, and the interchange of rotational and translational energy for the collision in a plane of an atom and a rigid symmetrical molecule are examined.  
N. M. BLYGH.

At. wt. of oxygen. Relative amounts of the three isotopes. R. MECKE and W. H. J. CHILDS (Z. Physik, 1931, 68, 362—377).—The intensities of absorption of the  $\text{AO}^{16}\text{O}^{16}$  band due to a few metres of air and of the  $\text{A}'\text{O}^{16}\text{O}^{18}$  band due to the earth's atmosphere were compared, and the isotope ratio  $\text{O}^{16}:\text{O}^{17}:\text{O}^{18}$  was found to be  $630 \pm 20:0.2:1$ . The at. wt. of oxygen is accordingly  $16.0035 \pm 0.0003$ , and the mass spectrographic wt. of an element is 1.00022 times its chemical at. wt.  
A. B. D. CASSIE.

At. wt. of iodine. Analysis of iodine pentoxide. G. P. BAXTER and A. Q. BUTLER (J. Amer. Chem. Soc., 1931, 53, 968—977).—Thermal decomposition of iodine pentoxide produced by dehydration of iodic acid affords the iodine: oxygen ratio 3.17262, compared with 3.17330 deduced from accepted at. wt. The discrepancy is attributed to abnormal composition of the pentoxide.  
J. G. A. GRIFFITHS.

Chlorine isotope of nuclear mass 39. G. HETTNER and J. BÖHME (Naturwiss., 1931, 19, 252).—An examination of the rotation-vibration lines of hydrogen chloride in the vicinity of  $1.7 \mu$  has demonstrated the existence of a chlorine isotope with the nuclear mass 39 (cf. Becker, A., 1930, 393).  
R. CUTHILL.

Connexion between relative proportions of isotopes and core moments of certain elements. H. SCHÜLER and J. E. KEYSTON (Z. Physik, 1931, 68, 174—177).—A quantitative relation between the relative proportions of the isotopes of certain elements can be found if the isotopes are considered as even and odd. This classification is related to the nuclear moment for a given atom, and in consequence the relative proportions of isotopes are also related to this quantity.  
A. J. MEE.

Radioactive decomposition appearances in fluorite. L. GOEBEL (Z. Krist., 1931, 76, 457—458; cf. Leitmeier, A., 1926, 367).—The coloration of fluorite is due to radioactive action liberating fluorine which escapes, leaving free calcium in colloidal form. When the particles of calcium are smallest, a green

colour results; blue, violet, or colourless material arises from progressively larger particles. Changes in size of the particles, and consequently in colour, can be effected by heat, pressure, or radiation, and the changes can be followed by the ultramicroscope. This change may, however, be due to the liberated calcium atoms forming a definite lattice, a view supported by the detection in an X-ray photograph of faint indications of a line corresponding with the calcium lattice.  
C. A. SILBERRAD.

Absorption of  $\beta$ -rays by matter. G. FOURNIER and M. GUILLOT (Compt. rend., 1931, 192, 555—557).—By a slight modification of the method previously described (cf. A., 1926, 880) the following mass absorption coefficients ( $\mu/\rho$ ) for  $\beta$ -rays from radium- $D+E$  have been determined: boron 16.4; phosphorus, white (solid or liquid) 20.9, red 20.2; vanadium 19.7; arsenic 20.9; bromine 23.0; sodium 16.8.  
C. A. SILBERRAD.

Number and internal absorption of  $\gamma$ -rays from radium- $D$ . E. STAHEL (Z. Physik, 1931, 68, 1—11; cf. this vol., 281).—The number of  $\beta$ -rays emitted by internal conversion of the 263 X units  $\gamma$ -radiation from disintegration of 100 radium- $D$  nuclei was determined by means of a Geiger counter. Assuming an internal conversion coefficient corresponding with 97% absorption, this gives an emission of one  $\gamma$ -quantum by each disintegrating nucleus.  
A. B. D. CASSIE.

Initial charge of the recoil atoms produced during the disintegration of radon. W. MUND, P. CAPRON, and J. JODOGNE (Bull. Soc. chim. Belg., 1931, 40, 35—74).—The initial charge on the recoil atoms of radon is positive and approximates to  $2e$ , corresponding with the loss of two electrons. The charge originates in the primary disintegration, and is not a result of subsequent collisions with other particles.  
H. F. GILLBE.

Electronic energy levels of the elements: sizes and electronic states of atoms in metallic crystals. W. HUME-ROTHERY (Phil. Mag., 1931, [vii], 11, 649—678; cf. A., 1930, 1233).—Theoretical. If  $Z$  is the atomic number the interatomic distances in the crystals vary as  $1/Z$ ,  $1/Z^2$ ,  $1/Z^3$ , and  $1/Z^5$  for elements at the beginning of the first, second, third, and fourth periods, respectively, whilst the electronic energy levels vary linearly as  $Z^2$ ,  $Z^4$ ,  $Z^6$ , and  $Z^{10}$  for the  $N_1$  electrons of the outermost group of electrons of the atomic core or ion. This correspondence is examined in detail and plotted for the groups concerned, and is applied to a discussion of the interatomic distances in the crystals of the transitional elements of the long periods, and a method is suggested for determining the electronic states of the atoms in the solid crystals. It is concluded that the transition process begins in the solid crystals at group VI, and in the free atoms at group III. For the valency electrons it is shown that in groups 0, IA, and IIA a linear relation exists between  $n^2V$  and  $Z^{2.3}$  for the members of any one group, where  $V$  is the ionisation potential and  $n$  the electron quantum number. In group 0 the interatomic distances agree with the law of the sub-groups  $d/n=(1/aZ)^2$ , previously deduced.  
N. M. BLYGH.

**Statistics of nuclei.** P. EHRENFEST and J. R. OPPENHEIMER (*Physical Rev.*, 1931, [ii], 37, 333—338).—Mathematical. N. M. BLIGH.

**Statistics of complex systems according to the new quantum mechanics.** J. WIGNER (*Math. Naturwiss. Anz. Ungar. Akad. Wiss.*, 1929, 46, 576—582; *Chem. Zentr.*, 1930, ii, 3502—3503).

**Arrangement of protons and electrons in the atomic nucleus.** W. M. LATIMER (*J. Amer. Chem. Soc.*, 1931, 53, 981—990).—Theoretical. From a consideration of the relative abundance of elements and of the number of protons and electrons in atomic species the at. wts. of which are approximately integral multiples of 4, an arrangement of electrons and protons in a geometrical space lattice in the atomic nuclei consistent with the numbers of "extra" electrons in the heavier elements is suggested. Each  $\alpha$ -particle is situated at the corner of a tetrahedron, and combination of such tetrahedra leads to a face-centred cubic lattice of  $\alpha$ -particles. Since an  $\alpha$ -particle is represented as a tetrahedral arrangement of 4 protons about an electron pair, the insertion of an electron pair at each point about which four spin vectors converge, as in the  $\alpha$ -particle, leads to a diamond-type lattice of electron pairs.

J. G. A. GRIFFITHS.

**Band spectrum of tin oxide. I. Analysis of the vibration systems of the bluish-violet bands.** P. C. MAHANTI (*Z. Physik*, 1931, 68, 114—125).—The wave-lengths of the heads of bands due to tin oxide between 3200 and 4600 Å. were determined by a concave grating, 6—18 Å. per mm. Most of the bands were fitted to three systems. The heat of dissociation for the ground state is  $3.66 \pm 0.1$  volts.

A. B. D. CASSIE.

**Simple relations between molecular spectra and structure.** H. DESLANDRES (*Compt. rend.*, 1931, 192, 521—525; cf. this vol., 283).—Further examples of relations between the frequencies of certain lines or bands, the "fundamental frequency" (1062.5), and atomic number are given in conformity with the formula previously deduced.

C. A. SILBERRAD.

**Absorption spectra of aqueous solutions of the coloured ions Cu, Cr, and Co.** M. KAHANOWICZ and P. ORECCHIONI (*Z. Physik*, 1931, 68, 126—132).—The extinction coefficients for infinitely dilute electrolytic solutions containing nickel, copper, chromium, and cobalt were determined throughout the visible spectrum. The photometric curves show three phases of absorption which can be ascribed to molecules, free ions, and complex ions, respectively.

A. B. D. CASSIE.

**Absorption of light and constitution. II. Heteropolar organic compounds.** A. BURAWOY (*Ber.*, 1931, 64, [B], 462—492; cf. this vol., 144).—The absorption of light by onium salts depends on conjugated systems. These, like those of homopolar compounds (*loc. cit.*), have polar construction and their absorption of light increases with their length and degree of polarity. Positively-charged atoms function as negative terminal atoms of the conjugated systems in cations. In harmony, the bathochromic action increases in the sequence  $NR_2 < O \cdot R <$

$S \cdot R$ , hence not with the positive, but with the negative character. In homopolar compounds and in cations, and in contrast to the positively-charged groups, further uncharged groups have increased bathochromic action in the sequence  $O \cdot R < S \cdot R < NR_2$ , when they are in conjunction with the conjugated system causing absorption, that is, when they are terminal members of the chromophore group and consequently increase the polarity. If they are not terminal members of the chromophore group, their hypsochromic effect is strong in case of direct substitution but weak in union to aromatic substituents. The complete spectrum of a compound is regarded as the resultant of the absorption bands of different chromophoric groups and isolated bands as a consequence of particularly favoured chromophors. These different chromophors are not formed in the same molecule, but in different "electron-isomeric" molecules. Small persistence is not a specific property of  $R$  bands, but is to be attributed to the presence of only a very small amount of radical-like molecules in a compound.

Addition of acid causes principally a change in the degree of polarity of the conjugated system in so far as it alters only the negative terminal group.

The groups  $C^+ \cdot NH_2$ ,  $C^+ \cdot OH$ ,  $C^+ \cdot SH$  arise from the groups  $C \cdot NH$ ,  $C \cdot O$ ,  $C \cdot S$ . Positively-charged atoms have a more strongly bathochromic action and are therefore more negative than the corresponding uncharged atoms. In the conjugated system of a cation, the most positive atom invariably gives the electron to the anion, and is therefore the negative terminal atom. Addition of an acid molecule to an  $R$  chromophor annihilates the corresponding bands; consequently  $R$  bands do not occur in the spectra of cations.

The absorption of light of *aci*-salts or their anions is attributed to conjugated systems and subsidiarily to  $R$  chromophors. In this connexion, negatively-charged atoms behave as positive groups (atoms); in particular, the negatively-charged oxygen atom comports itself as the nitrogen of an amino-group. It is bathochromic only when it is the terminal atom of a chromophor. In anions in branchings of a conjugated system, the positive groups  $O \cdot R$ ,  $S \cdot R$ ,  $NR_2$  have a hypsochromic effect.

A chromophor is an atom or a group which is necessary for the occurrence of an absorption band, independently of possible substituents which merely cause displacement of the bands. The absorption of light by organic compounds is attributable (1) to unsaturated individual atoms characteristic for the free radicals ( $R$  chromophors) and (2) to conjugated systems, therefore groups of atoms ( $K$  chromophors).

It is proposed to replace the conception of "auxochromic groups" by "auxochromic atoms." The latter are the terminal atoms of the chromophoric groups. The atoms O, S, N of the groups  $O \cdot R$ ,  $S \cdot R$ ,  $NR_2$  and all negatively-charged atoms in anions are positive auxochromic atoms; the atoms N, O, S of the groups  $C \cdot N$ ,  $C \cdot O$ ,  $C \cdot S$ ,  $N \cdot N$ ,  $N \cdot O$ , together with all positively-charged atoms in cations, are negatively auxochromic atoms, whereas the uncharged carbon atom is amphoteric.

H. WREN.

**Absorption of synthetic spinels coloured by manganese and chromium.** K. SCHLOSSMACHER (Z. Krist., 1930, 75, 399—409; Chem. Zentr., 1931, i, 438).

**Colours of inorganic salts.** M. N. SAHA and S. C. DEB (Nature, 1931, 127, 485; cf. A., 1930, 272).—Absorption spectra of chromic and ferrous chlorides obtained in a vacuum furnace at 1000—1400° show bands at 4100 and 4350 Å., respectively. These bands are ascribed to Cr<sup>+++</sup> and Fe<sup>++</sup> and are due to magnetic transitions in the *d*<sup>3</sup> and *d*<sup>6</sup> shells. Continuous absorption from 3000 to 2200 Å., the limit of the apparatus used, is also observed and is ascribed to the Cl<sup>-</sup> ion. L. S. THEOBALD.

**Optical connexion between the phosphorescence of alkali halides and solutions of complex halides of lead and thallium.** H. FROMHERZ (Z. Physik, 1931, 68, 233—243).—An extension to the heavy metals of earlier work on the complex halides of copper and silver (cf. A., 1929, 626).

A. J. MEE.

**Colouring and luminescence by Becquerel radiation. III.** K. PRZIBRAM (Z. Physik, 1931, 68, 403—422; cf. A., 1924, ii, 85; 1927, 393).—Work on the colouring of rock salt is summarised. Colouring is due to two large classes of centres: neutralised cations, and neutral atoms in irregular surroundings. Many different centres are distinguished, and come under one of these two classes. Pressure favours disturbance of the crystal lattice, and so increases the rate of colouring of a crystal. Radioluminescence and the action of Becquerel radiation were studied; many natural minerals owe their colour to Becquerel radiation.

A. B. D. CASSIE.

**Exact solution of the Harries-Hertz collision problem, and its application to experimental arrangement in Raman effect experiments.** H. BARTELS and C. H. NORDSTROM (Z. Physik, 1931, 68, 42—63).—Theoretical. The number of collisions suffered by an electron in traversing a given thickness of gas is redetermined by Bartels' method (A., 1930, 1336) instead of the original diffusion method. The earlier method fails at low densities of scattering material, when the number of collisions depends on the direction of incidence of the electrons. The results are applied to scattering of light by turbid media, and it is concluded that turbid media give no greater intensity of Raman radiation than do clear media.

A. B. D. CASSIE.

**Transition probability in the Raman effect.** L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1931, 68, 257—259).—A formula is developed for the relation between the intensities of Stokes and anti-Stokes lines. There is some ground for a general formula for the probability of a transition.

A. J. MEE.

**Raman spectrum of hydrogen peroxide.** S. VENKATESWARAN (Nature, 1931, 127, 406).—A Raman frequency of 875 accompanied by a weak component at 903 cm.<sup>-1</sup> has been observed in the Raman spectrum of an aqueous solution of Merck's perhydrol. Other diffuse bands have been obtained.

L. S. THEOBALD.

**Modified scattering by hydrogen halides.** E. O. SALANT and A. SANDOW (Physical Rev., 1931, [ii], 37, 373—378; cf. Wood, A., 1930, 978).—Raman lines of gaseous hydrogen chloride, bromide, and iodide, and liquid hydrogen chloride and bromide were measured. The shifts of the first two gases agree with the infra-red bands; that of hydrogen iodide does not agree, and is considered the more accurate determination of the (0,1) HI vibrational transition. Intensities of scattering are in the reverse order of those of absorption, in agreement with the Hill-Kemble theory of scattering by diatomic gas molecules (cf. A., 1929, 865). The lines scattered by the liquids differ in appearance from, and show smaller shifts than, those of the gases; the differences in the shifts are too large to be attributed to a Lorentz-Lorenz force, and are evidence of quantum-mechanical molecular interactions (cf. Breit and Salant, A., 1930, 1496). N. M. BLIGH.

**Raman effect in water and in some solutions.** R. BRUNETTI and Z. OLLANS (Atti R. Accad. Lincei, 1930, [vi], 12, 522—529).—The effect was studied with water, with solutions of nitric acid, of nitrates of sodium, ammonium, potassium, barium, aluminium, lanthanum, cerium, and thorium, of hydrochloric acid, and cerium chloride. The effect of the nitrate ion is to cause depolymerisation of the water, which, however, does not become homogeneous.

F. G. TRYHORN.

**Raman effect and problems of constitution. II. Cyano-compounds.** A. DADIEU (Ber., 1931, 64, [B], 358—361; cf. A., 1930, 1162).—Measurements of the Raman spectra of the following compounds are recorded: acetonitrile, *o*-toluonitrile, hydrogen and potassium cyanide, methyl- and ethyl-carbylamine, phenyl- and  $\alpha$ -naphthyl-carbimide, ethyl thiocyanate, ethyl-, isobutyl-, phenyl-, and *p*-tolyl-thiocarbimide. The presence of a treble linking is established in the thiocarbimides, to which the constitution  $R \cdot N \llcorner C$  is therefore ascribed, thus indicating a structural difference from the carbimides,  $R \cdot N : C : O$ . The data for the carbylamines do not accord with either of the classical structures, but are interpreted by the formula  $R \cdot N \equiv C$ ; an analogous constitution appears appropriate to carbon monoxide, fulminic acid, and all other compounds containing "bivalent" carbon. In hydrocyanic acid the *iso*-form is calculated to be present to the extent of about 0.5%. H. WREN.

**Raman spectra of some organic halides.** C. E. CLEETON and R. T. DUFFORD (Physical Rev., 1931, [ii], 37, 362—372).—Raman spectra obtained by helium excitation (cf. Wood, A., 1929, 741) were photographed, and results tabulated and discussed for 19 simple organic halides not previously reported, including magnesium methyl bromide and iodide and ethylidene chloride and iodide. It is shown that in many cases the observed frequencies can be expressed in terms of four assumed fundamentals (five in the cyclic compounds), two of which are not observed. The application of available theory is discussed.

N. M. BLIGH.

**Raman lines of cyclopropane and valency properties of some organic compounds.** R. C. YATES

(Physical Rev., 1931, [ii], 37, 616—618; cf. A., 1930, 1349).—Mathematical. Three fundamental wave-numbers for cyclopropane are calculated from the equations of motion of a system of three particles vibrating in a plane. The character of a single linking acting adjacent to a double linking in acet-aldehyde and to a triple linking in acetonitrile is studied.  
N. M. BLYTH.

Mass spectra of glasses, salts, and metals and construction of a circular mass-spectrograph. H. MURAWEIN (Ann. Physik, 1931, 8, [v], 353—432; cf. this vol., 407).—The method of investigating mass spectra is described. A strong emission of sodium, potassium, magnesium, calcium, a considerable emission of silicon and oxygen, and an irregular weak emission of heavy metals from Lindemann, Jena, Thüringen, lead, uranium, and silver glass, alundum cement, and combustion glass have been investigated mass-spectrographically in the temperature range 900—1600° Abs. The mechanism of the emission appears to be due both to electrolysis and to ionisation by impact. Mass spectrograms of aluminium phosphate, Kunsman's mixture, tungsten, platinum, and copper were also studied.  
W. GOOD.

Transparency of glasses to ultra-violet rays. P. GILARD, P. SWINGS, and A. HAUTOT (Bull. Acad. roy. Belg., 1931, [v], 17, 235—248).—The effect of differing concentrations of constituents of glasses on their ultra-violet transmission is examined. Transparency increases with silica content, but there is an optimum concentration, depending on the other substances present. The concentration of lime has little effect on the transparency. Increase in barium oxide or alumina is favourable; increase in potassium is more favourable than a corresponding increase in sodium concentration. The addition of boron trioxide extends the transparency.  
A. J. MEE.

Electrolytic valve action. I. Tantalum oxide layer. A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1931, 68, 145—161).—Experiment shows that the layer responsible for valve action in the case of tantalum consists of a compact non-porous layer of Ta<sub>2</sub>O<sub>5</sub>. The active layer has the same dielectric constant when in the electrolyte as when in the dry state, and this value is known. This fact may be utilised to determine the thickness of the layer, and it is found that this amounts to 82 m $\mu$  when the layer is produced by a voltage of 100.  
A. J. MEE.

Electric conductivity of liquid hydrocarbons in thin layers. L. BRÜNINGHAUS (J. Phys. Radium, 1931, [vii], 2, 69—85).—A more detailed account of work already noted (this vol., 285).

Mechanism of the "electric" discharge in solid insulators. I. II. A. VON HIPPEL (Z. Physik, 1931, 67, 707—724; 68, 309—324).—The paths of electrons in crystals during electrical discharges were studied. Results suggest that the potential variations giving mechanical strength to a crystal also determine its electrical resistance.  
A. B. D. CASSIE.

Reciprocal relations in irreversible processes. I. L. ONSAGER (Physical Rev., 1931, [ii], 37, 405—

426).—Mathematical. Thermoelectric phenomena, transference phenomena in electrolytes, and heat conduction in an anisotropic medium are considered as examples of coupled irreversible processes, and a general class of reciprocal relations is deduced by a new theoretical treatment from the principle of microscopic reversibility.  
N. M. BLYTH.

E.M.F. of dielectrics. K. LARK-HOROVITZ (Nature, 1931, 127, 440).—Previous work by the author is discussed.  
L. S. THEOBALD.

Dielectric constant and electric moment of some amines. P. N. GHOSH and T. P. CHATTERJEE (Physical Rev., 1931, [ii], 37, 427—429).—Using a heterodyne null-beat method (cf. Mahanti, A., 1930, 841) the dipole moment  $\times 10^{18}$  for methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, and triethyl-amines gave the values 0.99, 0.90, 0.82, 0.99, 0.90, and 0.82 e.s.u., respectively. Values of the dielectric constant are also given, and, except in the case of methylamine, increase with the b. p. of the compound. The polar groups NH<sub>2</sub>, NH, and N in the respective amines are mainly responsible for the development of the dipole moment of the molecule.  
N. M. BLYTH.

Dielectric constant of water as determined by a resonance method. E. P. LINTON and O. MAASS (J. Amer. Chem. Soc., 1931, 53, 957—964).—Sources of error in the method of Cuthbertson and Maass (A., 1930, 523) have been investigated. With liquids of high dielectric constant, results are best obtained with a high-power oscillating circuit permitting the determination of the resonance point by means of the harmonic instead of the fundamental. Provided the conductivity of the medium is less than a certain value ( $4 \times 10^{-6}$  ohm<sup>-1</sup> in the case of water), the resonance point is independent of the conductivity. The dielectric constants at 25° are: ether 4.255, ethylene dichloride 10.38, water 79.2, and hydrogen peroxide at 0° 93.5 (cf. *loc. cit.*).  
J. G. A. GRIFFITHS.

Dependence of the molecular polarisation of gaseous  $\alpha\beta$ -dichloroethane on temperature. R. SÄNGER (Helv. phys. Acta, 1930, 3, 461—463; Chem. Zentr., 1931, i, 229).—A lecture (cf. this vol., 147).  
A. A. ELDRIDGE.

Variations with temperature and frequency of dielectric loss in a viscous mineral insulating oil. H. H. RACE (Physical Rev., 1931, [ii], 37, 430—446).—From measurements of dielectric loss using an open quartz insulated cell over a wide range of frequency and temperature, Debye's theory of polar molecules has been extended to give simple expressions for conditions of maximum loss per cycle.  
N. M. BLYTH.

Theory of dielectrics. J. H. J. POOLE (Phil. Mag., 1931, [vii], 11, 995—996).

Mol. volume and density at the absolute zero. G. L. CHABORSKI (Bul. Chim. pura appl., Bukarest, 1929, 31, 53—66; Chem. Zentr., 1930, ii, 1046).—By the use of Longinescu and Chaborski's "molar concentration"  $C_m = 1000d/M$  equations are derived for evaluating the mol. volume and density at 0° Abs.:  $V_0 = 1000/C_m$ ;  $d_0 = MC_m/1000$ ;  $C_m = C_m + 1000(v-b)/b^2$ , where  $v-b$  is the covolume and  $b$  is



van der Waals' correction. Values for 47 organic compounds have been computed. Traube's (A., 1902, ii, 551) values for  $b$  at  $0^\circ$  for isopentane, water, and methyl alcohol are criticised, and new values computed. A. A. ELDRIDGE.

Refractive indices of mixed crystals of magnesium and zinc sulphates. M. W. PORTER (Z. Krist., 1930, 75, 288—300; Chem. Zentr., 1930, ii, 3500).—The pure salts,  $XSO_4 \cdot 7H_2O$ , have  $n_a$  1.4321, 1.4567;  $n_\beta$  1.4551, 1.4800;  $n_\gamma$  1.4605, 1.4840;  $d$  1.679, 1.968, respectively. Values for nine mixed crystals are recorded. A. A. ELDRIDGE.

Production of residual double refraction by pressure in certain glasses at atmospheric temperature. F. C. HARRIS (Phil. Mag., 1931, [vii], 11, 745—748).—The residual double refraction produced in specimens of glass by cooling under pressure having been found to decrease after keeping for 4 years, specimens of different composition were subjected to high pressures for long periods at atmospheric temperature, and observations were made in sodium light by a Babinet compensator. N. M. BLYGH.

Magnetic rotatory power of some higher fatty acids. C. SALCEANU (Compt. rend., 1931, 192, 675—677).—The specific magnetic rotatory powers,  $\rho/d$  ( $d$  density), for  $\lambda=578$   $\mu$ , of decoic, lauric, myristic, palmitic, and stearic acids are respectively 1.509, 1.545, 1.577, 1.596, and  $1.612 \times 10^{-2}$ . Perkin's law regarding the molecular magnetic rotatory power of members of a homologous series is only approximately followed. C. A. SILBERRAD.

Molecular association. G. G. LONGINESCU (Bul. Chim. Soc. Române Stiin., 1930, 31, 21—76).—A review.

Application of space-energy to the calculation of chemical, electrical, and gas-kinetic transformations of energy, matter, and form. R. VON DALLWITZ-WEGENER (Z. Elektrochem., 1931, 37, 25—33).—A summary and an extension of previous publications (cf. A., 1929, 885). The calculation of the energy changes involved in chemical reactions and galvanic cells from cohesion pressures is described. The modifications necessitated in the second law of thermodynamics by the introduction of the concept of space-energy are discussed; it is asserted that the possibility of a perpetual motion of the second kind must be conceded. R. CUTHILL.

Variable valency, especially in compounds of sulphur and tellurium. T. M. LOWRY (Bull. Soc. chim. Belg., 1931, 40, 91—104).—A survey. H. F. GILLBE.

Co-ordination. III. Energy of co-ordination. F. J. GARRICK (Phil. Mag., 1931, [vii], 11, 741—744; cf. A., 1930, 1096).—The consistency of the electrostatic theory of co-ordination and values of the energy of co-ordination with general theories and established energy quantities is examined. From the lattice energy and heat of formation of some of the group of hexamine chlorides isomorphous with  $[Ni(NH_3)_6]Cl_2$ , the cycle lattice energy of the chloride of the central cation (zinc, iron, and manganese)—lattice energy of the ammine+heat of formation of

amine, gives the energy of co-ordination in good agreement with the theoretical value. A possible extension of the method to the energies of co-ordination of hydrates is considered. N. M. BLYGH.

Quantum theory of chemical binding in polyatomic molecules. W. HEITLER and G. RUMER (Z. Physik, 1931, 68, 12—41).—Heitler and London's theory of chemical binding in diatomic molecules (Physikal. Z., 1930, 31, 185) is extended to polyatomic molecules. A formula is deduced for the exchange energy due to interaction of pairs of atoms in the molecule, assuming only one atom not in an  $S$  state. In general, molecular states of least multiplicity give binding and greatest multiplicity repulsion of the component atoms. Examples discussed are hydrogen cyanide, which theory predicts as  $H \cdot C \cdot N$ , cyanic acid,  $O \cdot C \cdot N \cdot H$ , molecules of the type  $(H \cdot A)_2$ , which are stable provided  $A$  has a valency greater than two, hydrazine, and dicyanogen.  $NH_2 \cdot NH_2$  and  $CN \cdot CN$  are unstable for large separations of the components  $NH_2$  and  $CN$ , respectively, but activation may overcome this potential barrier, and binding result for smaller separations. A. B. D. CASSIE.

Magnetism and molecular structure. II. Influence of position isomerism on diamagnetic susceptibilities. S. S. BHATNAGAR and R. N. MATHUR (Phil. Mag., 1931, [vii], 11, 914—926).—Using the apparatus previously described (cf. A., 1930, 1096), magnetic susceptibility determinations were extended to  $n$ - and  $iso$ -propyl and  $n$ - and  $tert$ -butyl alcohols at temperatures up to  $50^\circ$ ;  $o$ -,  $m$ -, and  $p$ -tolyl methyl ether,  $o$ - and  $m$ -toluidine,  $o$ - and  $p$ -phenetidine, and  $n$ - and  $iso$ -butyric acid at  $40^\circ$ , and  $n$ - and  $iso$ -butyl bromide at  $20^\circ$ . For the benzene derivatives the influence of the size of the substituent groups on the difference between the susceptibilities was studied. Results for the alcohols cannot be explained by differences in the degrees of molecular association. An explanation on the basis of the electronic significance of valency linkings is given. N. M. BLYGH.

Significance of magnetic measurements for chemical problems. W. KLEMM (Z. angew. Chem., 1931, 44, 250—259).—A survey of the theory of magnetism in its chemical aspects, with details of some particular cases and an account of methods of measurement. H. F. GILLBE.

Change in the relative concentration of paramagnetic  ${}^2\Pi_{3/2}$  and diamagnetic  ${}^2\Pi_{1/2}$  molecules in nitric oxide. E. BRODY, T. MILLNER, and R. SCHMID (Z. Physik, 1931, 68, 395—402).—The ground state of nitric oxide is a  ${}^2\Pi$  term, the levels being separated by 343 g.-cal. per mol. At the ordinary temperature the two forms are present in almost equal numbers, but at lower temperatures the diamagnetic  ${}^2\Pi_{1/2}$  predominates. This was shown by diminution in the intensity of absorption bands arising in the  ${}^2\Pi_{3/2}$  level relative to those arising in the  ${}^2\Pi_{1/2}$  level. At the temperature of liquid air the paramagnetic form almost disappeared. A. B. D. CASSIE.

Suggestions for rational symbolisation of organic and inorganic compounds and their

applicability to the discussion of the properties of compounds. W. MADELUNG (Z. Elektrochem., 1931, 37, 197—218).—Old and new methods of representing molecular structure are described and discussed in the light of modern electronic conceptions. It is suggested that electronic formulæ could be simplified by indicating whether an atom has its complete octet or is 1 or 2 electrons short by the use of symbols in different type or by the use of an index number.  
E. S. HEDGES.

**Directed valency in polyatomic molecules.** J. C. SLATER (Physical Rev., 1931, [ii], 37, 481—489; cf. A., 1930, 675).—Theoretical. The interactions of atoms in polyatomic molecules and the directional effects of valencies are described and discussed qualitatively; illustrations from the structure of metals and of organic and inorganic compounds are given.  
N. M. BLYTH.

**Orbital valency.** J. H. BARTLETT, jun. (Physical Rev., 1931, [ii], 37, 507—531).—Mathematical. The interaction of two atoms, each with one  $2p$  electron, is studied with the help of an atomic wave function (cf. Kemble and Zener, A., 1929, 623). The views of Heitler on orbital valency and of Slater on directed valency are supported.  
N. M. BLYTH.

**X-Ray spectrograph for wave-length determinations in air.** S. ZEIDENFELD (Rev. Sci. Instr., 1931, [ii], 2, 153—163).—A Bragg type spectrograph with a rotating crystal was designed for the accurate recording and measurement of wave-lengths which could be investigated in air. The approximate range is 0.5—2.0 Å. A special type of double crystal holder is described.  
N. M. BLYTH.

**New methods of interpreting photographs with convergent X-rays.** C. KRATKY (Z. Krist., 1931, 76, 517—524; cf. this vol., 413).  
C. A. SILBERRAD.

**X-Ray determination of the form and boundary surfaces of submicroscopic crystals.** R. BRILL (Z. Krist., 1930, 75, 217—227; Chem. Zentr., 1930, ii, 3699).—A discussion. The method has been applied to the examination of highly disperse electrolytic nickel.  
A. A. ELDRIDGE.

**Hydrochloric acid as an etching agent for galena.** E. STOICOVIC (Z. Krist., 1931, 76, 310—314).—Aqueous hydrochloric acid containing about 17% HCl is satisfactory.  
C. A. SILBERRAD.

**Lattice energy of wurtzite.** B. GROSS (Z. Krist., 1931, 76, 562—568).—The molecular lattice energy is  $-10.71e^2/d$ , where  $e$  is the electronic charge and  $d$ , the shorter side of the unit cell, is 3.84 Å. This gives as the molar lattice energy  $-919$  kg.-cal.  
C. A. SILBERRAD.

**Dependence of lattice dimensions on crystal size.** J. E. LENNARD-JONES (Z. Krist., 1930, 75, 215—216; Chem. Zentr., 1930, ii, 3505).—Mathematical.  
A. A. ELDRIDGE.

**Structure of films. I. Transformations of the lattice of cellulose nitrate film. II. Structure of nitrated and acetylated cotton.** J. J. TRILLAT (J. Phys. Radium, 1931, [vii], 2, 65—68).—I. A dried film of cellulose trinitrate from acetone

was compared by X-ray examination with that of the original product. New lines were observed in the spectrogram of the film and it seems that whilst some of the trinitrate in the film is in its original form a portion of it is in a new crystalline form. The dried film retains tenaciously about 1% of acetone. Nitrated cotton containing less than 12% N gives rise to films which are almost entirely amorphous.

II. The "amorphous" films of cellulose nitrate and acetate consist partly of truly amorphous material and partly of crystallites having no definite orientation. The greater is the degree of nitration of cotton, the more complete is the orientation of the crystallites.  
E. S. HEDGES.

**Crystal structure of sputtered deposits.** (MISS) Z. DĘBIŃSKA (Bull. Acad. Polonaise, 1930, A, 460—463).—Deposits several  $\mu\mu$  thick show no crystal structure until heated beyond a critical temperature: platinum 250—300°, gold 150—200°.  
A. B. D. CASSIE.

**Nomenclature of space-groups.** C. MAUGUIN (Z. Krist., 1931, 76, 542—558).—A complete system of nomenclature for space-groups is given based on that used by the author and that of Hermann (cf. A., 1930, 21).  
C. A. SILBERRAD.

**Mauguin's nomenclature.** C. HERMANN (Z. Krist., 1931, 76, 559—561; cf. preceding abstract).—A criticism.  
C. A. SILBERRAD.

**Tabular synopsis of the distribution of crystal types of the elements arranged according to long periods.** H. PERLITZ (Z. Krist., 1931, 76, 473—474).—The elements are arranged in long periods with graphs of types of crystal structure exhibited by each. Various relations between such structures and the position in the table are brought out.  
C. A. SILBERRAD.

**Structure of plastic sulphur.** J. J. TRILLAT and J. FORESTIER (Compt. rend., 1931, 192, 559—561).—A thread of plastic sulphur, drawn out rapidly immediately after formation, can be extended to eight or ten times its initial length. Such a thread is flexible at first, but after a few days becomes brittle. X-Ray examination shows that the sulphur is not amorphous, but possesses a structure analogous to that of metal wire or cellulose thread with  $a$  9.35 Å. The change of ordinary plastic sulphur to rhombic is greatly accelerated by exposure to X-rays.  
C. A. SILBERRAD.

**Structure of solid  $N_2O_4$  at the temperature of liquid air.** L. VEGARD (Z. Physik, 1931, 68, 184—203).—A new apparatus for determining the structure of a solidified gas is described. In the case of nitrogen peroxide the elementary cube contains twelve  $NO_2$  molecules. Each of these is symmetrical, and they form three mutually perpendicular chains.  
A. J. MEE.

**Dimensions of the  $ClO_4$  group in perchlorates.** C. A. SCHUSTERIUS (Z. Krist., 1931, 76, 455).—The irregularity of the tetrahedra defined by the oxygen atoms in the  $ClO_4$  group is confirmed by ionisation measurements on ammonium and potassium perchlorates (cf. Zachariasen, A., 1930, 1351).  
C. A. SILBERRAD.

Cubic high-temperature structure of perchlorates. H. BRAEKKEN and L. HARANG (Z. Krist., 1930, 75, 538—549; Chem. Zentr., 1931, i, 214).—The temperature, lattice constant (Å.), and  $d_{\text{calc.}}$  (assuming 4 mols. per unit cell) are, respectively: sodium perchlorate 314°, 7.08±0.02, 2.26; potassium perchlorate 310°, 7.50±0.02, 2.15; rubidium perchlorate 300°, 7.70±0.01, 2.66; caesium perchlorate 230°, 7.98±0.02, 3.00; ammonium perchlorate 243°, 7.67±0.02, 1.71; silver perchlorate 160°, 7.00±0.01, 3.96; thallium perchlorate 280°, 7.70±0.01, 4.37. The lattice is face-centred; space-group  $T^2$  or  $T^3$ .

A. A. ELDRIDGE.

Structure of salts of the type  $R'PF_6$ . H. SEIFERT (Z. Krist., 1931, 76, 455—456).—Potassium, ammonium, and caesium hexafluorophosphates crystallise in the cubic system with face-centred lattice. The unit cells contain 4 mols., and have respectively  $a$  7.76, 7.92, and 8.19 Å. The great similarity in chemical behaviour exhibited by hexafluorophosphoric and similar acids with perchloric acid indicates tetrahedra of fluorine around each phosphorus atom, with the remaining fluorine atoms elsewhere, and not a  $PF_6'$  complex.

C. A. SILBERRAD.

Symmetry of crystals of potassium dichromate. A. SCHUBNIKOW (Z. Krist., 1931, 76, 469—472).—Photographs support the conclusion (cf. A., 1912, ii, 155) that potassium dichromate crystallises in the asymmetric class of the triclinic system (cf. Terpstra, etc., A., 1929, 18; this vol., 27).

C. A. SILBERRAD.

Crystal structure of some fluorides of the eighth group. F. EBERT (Z. anorg. Chem., 1931, 196, 395—402; cf. A., 1929, 1254).—The crystal structure of iron, cobalt, rhodium, and palladium trifluorides is of trigonal rhombohedral symmetry, with 1 mol. in the unit cell;  $d_{\text{calc.}}$  3.56, 3.89, 5.64, and 5.15 Å., respectively, and distances between the anions and cations 2.05, 2.02, 1.98, and 2.06 Å., respectively. Palladium difluoride possesses a tetragonal structure, with 2 mols. in the unit cell;  $a$  4.93,  $c$  3.38 Å.,  $d_{\text{calc.}}$  5.8, and distance between cations and anions 2.15 Å.

H. F. GILBE.

Precision measurements of the lattice constant of cuprous oxide. M. C. NEUBURGER (Z. Physik, 1931, 67, 845—850).—This constant redetermined by the powder crystal method is  $4.252 \pm 0.002$  Å.

A. B. D. CASSIE.

Crystal form of nickel oxides. O. G. BENNETT, R. W. CAIRNS, and E. OTT (J. Amer. Chem. Soc., 1931, 53, 1179—1180).—Nickelous oxide, subjected to temperatures not greater than 110°, compared with the oxide outgassed at 285°, is a better adsorbent of carbon dioxide at 56°. X-Ray data show that the low-temperature oxide is a new cubic modification of which the edge of unit cube is 4.64 Å.,  $d$  is 4.8, and unit cell contains 4 mols. The crystal is not of the face-centred cubic type.

J. G. A. GRIFFITHS.

Crystal structure of dihydrodecaborane,  $B_{10}H_{14}$ . H. MÖLLER (Z. Krist., 1931, 76, 500—516).—The substance has a unit cell with  $a$  14.46,  $b$  20.85,  $c$  5.69 Å. containing  $8B_{10}H_{14}$ ; space-group  $V_h^1$ , with rhombic lattice  $\Gamma_0'$ . The 8 mols. are arranged in four

pairs. If the boron atoms are in a chain this must be much folded or bent, but a double-ring, naphthalene-like structure is equally probable.

C. A. SILBERRAD.

Space-group of arsenic tri-iodide. D. HEYWORTH (Z. Krist., 1930, 75, 574; Chem. Zentr., 1931, i, 214). H. BRAEKKEN (Z. Krist., 1930, 75, 574; Chem. Zentr., 1931, i, 214).

Crystal structure of the tri-iodides of arsenic, antimony, and bismuth. H. BRAEKKEN (Z. Krist., 1930, 74, 67—72; Chem. Zentr., 1930, ii, 1033).—Bismuth iodide shows di-trigonal symmetry, but arsenic and antimony iodides are only trigonal. For arsenic tri-iodide, antimony tri-iodide, and bismuth tri-iodide the values for  $a$  and  $c$  are 7.187 and 21.39, 7.466 and 20.892, and 7.498 and 20.676 Å., respectively; 6 mols. per unit cell.

L. S. THEOBALD.

Gradual transition of crystalline sodium nitrate. F. C. KRACEK and E. POSNJAK (J. Amer. Chem. Soc., 1931, 53, 1183—1184).—The properties change over a range of temperatures rather than suddenly at a definite transition point. The coefficient of expansion above 150° increases to a maximum at 275° and then decreases rapidly to a normal value beyond 280°; the absorption of heat during rise of temperature is maximal at 275.5°, and with fall of temperature evolution of heat commences at 278°. The crystals are uniaxial to the m. p.; small changes occur in X-ray patterns and in the solubility curve in the transition region.

J. G. A. GRIFFITHS.

Crystal structure of cubic carborundum. H. BRAEKKEN (Z. Krist., 1930, 75, 572—573; Chem. Zentr., 1931, i, 213—214).—The face-centred cube has  $a$   $4.348 \pm 0.005$  Å.

A. A. ELDRIDGE.

Crystal structure of iron silicide,  $FeSi$ . F. WEVER and H. MÖLLER (Z. Krist., 1930, 75, 362—365; Chem. Zentr., 1930, ii, 3505).—The substance has  $a$   $4.467 \pm 0.001$  Å., with 4 mols. in the unit cell; space-group  $T^4$ .

A. A. ELDRIDGE.

Crystal structure of magnesium nitride. G. HÄGG (Z. Krist., 1930, 74, 95—99; Chem. Zentr., 1930, ii, 1033).—Powder photographs indicate a cubic structure with  $a$  9.93 Å. The translation group is space-centred with 12 mols. in the unit cell. All 36 magnesium atoms cannot be equivalent.

L. S. THEOBALD.

Crystal structure of hambergite,  $Be_2BO_3(OH)$ . W. H. ZACHARIASEN (Z. Krist., 1931, 76, 289—302).—The unit cell contains 8 mols., and has  $a$  9.73,  $b$  121.8,  $c$  4.42 Å.; space-group  $V_h^1$ . Each beryllium atom is at the centre of a nearly regular tetrahedron of three oxygens and one hydroxyl, average distances Be-O (or OH) 1.74 Å., O-O (or OH) 2.80 Å. Each boron is at the centre of a nearly equilateral triangle of oxygens, B-O (average) 1.35 Å., O-O 2.35 Å. The tetrahedra and triangles share corners only. Each oxygen is linked to two berylliums and one boron, each hydroxyl to two berylliums only.

C. A. SILBERRAD.

Crystal structure of koppite. E. BRANDENBERGER (Z. Krist., 1931, 76, 322—334).—Analysis of koppite gave: CaO 15.88, MnO 0.01, MgO 0.27,

$\text{Fe}_2\text{O}_3$  9.73,  $\text{Ca}_2\text{O}_3$  8.15,  $\text{La}_2\text{O}_3$  1.68,  $\text{TiO}_2$  0.75,  $\text{ZrO}_2$  0.61,  $\text{Nb}_2\text{O}_5$  56.43,  $\text{Ta}_2\text{O}_5$  0.15,  $\text{Na}_2\text{O}$  2.89,  $\text{K}_2\text{O}$  1.64,  $\text{H}_2\text{O}$  1.09,  $\text{H}_2\text{O}$  0.00,  $\text{F}_2$  1.53; total 100.81%, less O for F 0.65;  $d$  4.56. It crystallises in the cubic system; the unit cell contains 32 metallic and 56 anionic atoms, and has  $a$  10.37 Å. C. A. SILBERRAD.

**Crystal structure of eulytite.** G. MENZER (Z. Krist., 1931, 76, 454).—Eulytite,  $\text{Bi}_4(\text{SiO})_3$ , space-group  $T_h^6$ , has a body-centred lattice; the unit cell contains 4 mols.,  $a$  10.272 Å. The silicon is situated at the centres of tetrahedra of oxygen atoms, O—O 2.65 Å., each oxygen belonging to two tetrahedra. Each silicon is equidistant from 8 bismuths, Si—Bi 3.55 Å., Bi—Bi 3.80 Å.; each bismuth is equidistant from 6 silicons. C. A. SILBERRAD.

**Formula of tourmaline.** F. MACHATSKI (Z. Krist., 1931, 76, 475—476).—Niggli's formula for tourmaline (cf. *ibid.*, 1930, 75, 502) is criticised and  $\text{Mg}_3\text{Al}_5[\text{Si}_6\text{O}_{27}\text{B}_3]_2\text{CaMg}(\text{OH},\text{F})_4$ , or more generally  $\text{Y}_8[\text{Si}_6\text{O}_{27}\text{B}_3]_2\text{XY}(\text{OH},\text{F})_4$ , suggested. C. A. SILBERRAD.

**Molecular unit of pyrosmalite.** B. GOSSNER and F. MUSSGUG (Z. Krist., 1931, 76, 525—528).—The formula  $(\text{MnFe})\text{Si}_3\text{O}_7 \cdot 3(\text{MnFe})(\text{OH},\text{Cl})_2$  is deduced for pyrosmalite. It has a unit cell with  $a$  13.44,  $c$  7.20 Å., containing 4 such mols. Space-group  $D_{3h}^6$ ,  $a : c = 1 : 0.536$ . C. A. SILBERRAD.

**Structure of hardystonite,  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ .** B. E. WARREN and O. R. TRAUTZ (Z. Krist., 1930, 75, 525—528; Chem. Zentr., 1931, i, 248).—Hardystonite has  $a$  7.83,  $c$  4.99 Å.; space-group  $D_{3h}^6$ . The arrangement of the atoms is similar to that in melilite. A. A. ELDRIDGE.

**Structure of apatite,  $(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$ .** S. NÁRAY-SZABÓ (Z. Krist., 1930, 75, 387—398; Chem. Zentr., 1931, i, 247).—Apatite has  $a$   $9.37 \pm 0.01$ ,  $c$   $6.88 \pm 0.01$  Å., space-group  $C_{6v}^{2h}$ , with 2 mols. in the unit cell. A. A. ELDRIDGE.

**Structure of apatite.** I. M. MEHREL (Z. Krist., 1930, 75, 323—331; Chem. Zentr., 1930, ii, 3530).—Jumilla apatite has  $a$  9.36,  $b$  6.85,  $c$  6.85 ( $\pm 0.02$ ) Å., with 2 mols. of  $\text{CaF}\text{Ca}_4(\text{PO}_4)_3$  in the unit cell; space-group  $C_{6v}^{2h}$ . A. A. ELDRIDGE.

**Structure of anthophyllite,  $\text{H}_2\text{Mg}_7(\text{SiO}_3)_8$ .** B. E. WARREN and D. I. MODELL (Z. Krist., 1930, 75, 161—178; Chem. Zentr., 1930, ii, 3730—3731).—X-Ray investigation supports the formula  $\text{H}_2\text{Mg}_7(\text{SiO}_3)_8$  instead of  $\text{MgSiO}_3$ . Anthophyllite has  $a$  18.5,  $b$  17.9,  $c$  5.27 Å., with 4 mols. in the unit cell; space-group  $V_h^1$ . A. A. ELDRIDGE.

**Structure of analcime,  $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ .** W. H. TAYLOR (Z. Krist., 1930, 74, 1—19; Chem. Zentr., 1930, ii, 1054—1055).—No indications of a symmetry lower than pseudo-cubic have been obtained; space-group  $O_h^2$ . It is hence assumed that the basis of structure is a linking of oxygen tetrahedra; the atoms of silicon and aluminium, which are here assumed to be equivalent, are in the centre of the tetrahedron, the water mols. occupy the  $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$  positions, whilst the 16 sodium atoms are distributed over  $[0, \frac{1}{2}, \frac{1}{2}]$ . In agreement with optical properties, this arrangement permits a tetragonal symmetry for the unit cell. L. S. THEOBALD.

**Space lattice of natrolite.** F. HALLA and E. MEHL (Z. Krist., 1930, 75, 421—429; Chem. Zentr., 1931, i, 438).—Natrolite has  $a$   $18.384 \pm 0.004$ ,  $b$   $18.715 \pm 0.027$ ,  $c$   $6.632 \pm 0.008$  Å. The face-centred unit cell contains 8 mols. of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ; space-group  $V_h^{23}$  (holohedral),  $C_{6h}^{18}$  or  $V_7^7$  (hemihedral). A. A. ELDRIDGE.

**Crystallographic relationships of crocoite, lautarite, and dietzite.** B. GOSSNER and F. MUSSGUG (Z. Krist., 1930, 75, 410—420; Chem. Zentr., 1931, i, 437—438).—Crocoite has  $a$  6.28,  $b$  7.48,  $c$  7.16 Å.;  $\beta$   $102^\circ 33'$ . The unit cell contains 4 mols. of  $\text{PbCrO}_4$ ;  $d_{\text{calc.}}$  6.0, space-group  $C_{6v}^{2h}$ . Lautarite has  $a$  7.18,  $b$  11.38,  $c$  7.34 Å.,  $\beta$   $106^\circ 22'$ . The unit cell contains 4 mols. of  $\text{CaI}_2\text{O}_6$ ;  $d_{\text{calc.}}$  4.59, space-group  $C_{6v}^{2h}$ . Dietzite has  $a$  10.16,  $b$  7.30,  $c$  14.03 Å.,  $\beta$   $106^\circ 32'$ ; since it has  $d$  3.617 the formula  $7\text{CaI}_2\text{O}_6 \cdot \text{CaCrO}_4$  cannot be correct. The formula is  $\text{CaI}_2\text{O}_6 \cdot \text{CaCrO}_4$  with a limited possibility of mutual replacement. A. A. ELDRIDGE.

**Scattering of X-rays and the structure of vitreous solids.** J. T. RANDALL, H. P. ROOKSBY, and B. S. COOPER (Z. Krist., 1930, 75, 196—214; Chem. Zentr., 1930, ii, 3506).—X-Ray investigation of quartz, wollastonite, borax, potassium and sodium feldspars, a borosilicate glass, sodium silicate, boron trioxide, potassium borate, and dextrose indicates that glasses are composed of small crystallites ( $10^{-6}$  to  $10^{-7}$  cm.). The connexion between crystal size and lattice dimensions is discussed. A. A. ELDRIDGE.

**[Crystal] structure of carbamide.** R. W. G. WYCKOFF (Z. Krist., 1930, 75, 529—537; Chem. Zentr., 1931, i, 214—215).—Carbamide has  $a$  5.670,  $c$  4.726 Å. (powder method). A. A. ELDRIDGE.

**Crystal structure of guanidonium chloride.** W. THEILACKER (Z. Krist., 1931, 76, 303—309).—Contrary to previous statements (cf. Delitsch, A., 1874, 576) guanidonium chloride is very hygroscopic and crystallises in the rhombic system,  $a : b : c = 0.842 : 1 : 1.416$ . The unit cell contains 8 mols.,  $a$  7.76,  $b$  9.22,  $c$  13.06 Å.; space-group  $V_h^{18}$ . The lattice is ionic  $[\text{C}(\text{NH}_2)_3]^+\text{Cl}^-$ , and the guanidonium ion exhibits no symmetry. C. A. SILBERRAD.

**Crystal structure of *p*-nitrostilbene.** E. HERTEL and G. H. ROEMER (Z. Krist., 1931, 76, 467—469).—*p*-Nitrostilbene,  $d$  1.293, crystallises in the rhombic system. The unit cell contains 8 mols.,  $a$  7.94,  $b$  28.3,  $c$  10.22 Å. Space-group  $C_{2v}^{2h}$  or  $V_h^{11}$ . The length of 2 mols. is 28.3 Å. (for stilbene 24.84 Å.). C. A. SILBERRAD.

**Translations in some artificial crystals.** O. MÜGGE (Z. Krist., 1931, 76, 359—369).—Pinol glycol,  $\text{C}_{10}\text{H}_{16}\text{O}(\text{OH})_2$ , monoclinic,  $a : b : c = 0.8400 : 1 : 0.7692$ ,  $\beta$   $89^\circ 03'$ ,  $2E = 40^\circ 40'$ ; pinocamphoroxime,  $\text{C}_{10}\text{H}_{16} \cdot \text{NOH}$ , monoclinic,  $a : b : c = 1.5042 : 1 : 1.2326$ ,  $\beta$   $87^\circ 54'$ ; pinonic acid oxime,  $\text{C}_{10}\text{H}_{16}\text{O}_2 \cdot \text{NOH}$ , rhombic holohedral,  $a : b : c = 0.900 : 1 : 1.063$ ; *r*-propionylmethylamine, monoclinic holohedral,  $a : b : c = 1.0492 : 1 : 0.5766$ ,  $\beta$   $89^\circ 24'$ . Other data on optical and cohesion properties, cleavage, translations, etc. are given for the foregoing and for hexagonal silver iodide, borneol, acet-2 : 4-dichloro-

anilide, *p*-xylylene dichloride, 2:4:6-tribromotoluene, isobenzil, *z*-sobrerol, and methylarsonic acid.

C. A. SILBERRAD.

**Polymerisation in the crystal lattice.** Crystal structure of trinitroresorcinol and trinitrophenol-glucinol. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1931, B, 12, 139—150).—The principal periods of identity of the crystals of 2:4:6-trinitro-resorcinol and -phenol-glucinol are practically identical, and the space-groups are almost certainly the same, probably  $C_{2v}^2$ . In each case the lattice is built up of groups of molecules in threes, with the symmetry  $C_3$ . Nevertheless, the equilibrium diagram for the binary system shows the absence of complete miscibility in the solid state. R. CUTHILL.

**Amino-acids. IV.** G. TAKAHASHI, T. TAGINUMA, and K. HAYAKAWA (Proc. Imp. Acad. Tokyo, 1931, 7, 57—60).—Optical and crystallographic measurements have given the following results: *l*-leucine,  $[\alpha]_D^{25} +15.51^\circ$ , *d*-leucine,  $[\alpha]_D^{25} -11.16^\circ$ , rhombic,  $a:b:c=1.5139:1:1.0025$ , negative double refraction,  $n_a 1.5331$ ,  $n_\beta 1.5361$ ,  $n_\gamma 1.5514$ ; *l*-norleucine,  $[\alpha]_D^{25} -21.5^\circ$ , *d*-norleucine,  $[\alpha]_D^{25} +18.3^\circ$ , rhombic,  $a:b:c=1.3929:1:2.8662$ , positive double refraction,  $n_a 1.5074$ ,  $n_\beta 1.5104$ ,  $n_\gamma 1.5400$ ; histamine picrate, m. p. 232—233°, monoclinic,  $a:b:c=1.2216:1:1.2266$ , positive double refraction,  $n_a 1.6922$ ,  $n_\beta 1.7135$ ,  $n_\gamma 1.7535$ . E. S. HEDGES.

***d*- and *l*-Rhamnitol trihydrates.** R. NOVÁČEK (Z. Krist., 1931, 76, 569—571; cf. Valentin, this vol., 62).—*d*- and *l*-Rhamnitol trihydrates are rhombic bisphenoidal,  $a:b:c=0.9947:1:1.1759$ ;  $2V_N 52^\circ 30'$ ,  $n_a^\beta 1.442$ ,  $n_b^\beta 1.492$ ,  $\gamma-\alpha 0.06$ . C. A. SILBERRAD.

**Crystallography of some  $\alpha$ -hydroxyamino-sulphonates and  $\alpha$ -hydroxyamides.** J. THOREAU and J. VERHULST (Bull. Soc. chim. Belg., 1931, 40, 18—34).—The crystallographic constants of a number of the compounds have been determined.

H. F. GILLBE.

**Crystal structure of diphenylpolyenes.** J. HENGSTENBERG and R. KUHN (Z. Krist., 1930, 75, 301—310; Chem. Zentr., 1930, ii, 3505—3506).—CHPh·CH·CH·CHPh,  $a 7.71$ ,  $b 11.70 \text{ \AA}$ ,  $\beta 97^\circ$ ; number of mols. in unit cell ( $z$ ) 4; space-group  $C_{2h}^2$ . Ph·[CH·CH·]<sub>3</sub>Ph,  $a 6.33$ ,  $b 7.43$ ,  $c 14.43 \text{ \AA}$ ;  $z 2$ ;  $C_{2h}^2$ . Ph·[CH·CH·]<sub>4</sub>Ph,  $a 6.25$ ,  $b 7.44$ ,  $c 16.03 \text{ \AA}$ ;  $z 2$ ;  $C_{2h}^2$ . The molecules of hexatriene and octatetraene are thus constructed very similarly. Ph·[CH·CH·]<sub>5</sub>Ph,  $a 10.25$ ,  $b 7.66$ ,  $c 21.2 \text{ \AA}$ ;  $z 4$ ; probably  $V_h^5$ . Ph·[CH·CH·]<sub>6</sub>Ph,  $a 10.20$ ,  $b 7.60$ ,  $c 23.58 \text{ \AA}$ ;  $z 4$ . Ph·[CH·CH·]<sub>7</sub>Ph,  $a 10.2$ ,  $b 7.57$ ,  $c 25.95 \text{ \AA}$ ;  $z 4$ . A. A. ELDRIDGE.

**Crystalline form of a new modification of 2:4-dinitroanisole.** M. H. WERTHER and J. A. BAAK (Z. Krist., 1930, 73, 572; Chem. Zentr., 1930, ii, 1070—1071).—The monoclinic, prismatic crystals, m. p. 94.55°, of the modification described by Alphen (A., 1930, 337) have  $a:b:c=0.6920:1:1.3158$ ,  $\beta 113^\circ 14'$ ,  $d^{15} 1.546$ . L. S. THEOBALD.

**Crystal structure of pentaerythrityl tetraformate.** M. A. BREDIG (Z. Krist., 1930, 74, 49—55; Chem. Zentr., 1930, ii, 1034).—The compound crystallises differently from the tetra-acetate and nitrate; it has  $a 19.80$ ,  $b 9.90$ , and  $c 11.70 \text{ \AA}$ ; space-

group  $V_h^5$ . The crystal structure shows racemate bimolecules of  $C_5H_{12}O_8$  as micro-units in agreement with Weissenberg's hypothesis. L. S. THEOBALD.

**Crystal structure of *n*-amylammonium chloride.** S. B. HENDRICKS (Z. Krist., 1930, 74, 29—40; Chem. Zentr., 1930, ii, 1033).—The carbon atoms in the hydrocarbon chain are arranged rectilinearly.

L. S. THEOBALD.

**Röntgen data of monoalkylammonium iodides.** R. W. G. WYCKOFF (Z. Krist., 1930, 74, 25—28; Chem. Zentr., 1930, ii, 1033—1034; cf. preceding abstract).—Photographs of crystals of members with  $C_4$  to  $C_{12}$  give for the tetragonal unit cell the constant value  $a 5.18 \text{ \AA}$ . The height of the cell is about 2.10  $\text{ \AA}$  larger for each carbon atom. The determination of atomic positions is not yet possible, since the arrangement of adjacent carbon atoms about a vortical axis is not in agreement with that of other compounds. L. S. THEOBALD.

**X-Ray diagram of collagen (fibre-period).** R. O. HERZOG and W. JANCKE (Z. physikal. Chem., 1931, B, 12, 228—229; cf. A., 1927, 69).—The reasons for believing in the existence of a period of identity of about 20  $\text{ \AA}$  along the fibre-axis of collagen are detailed (cf. Herrmann, Gerngross, and Abitz, this vol., 27). R. CUTHILL.

**Theory of the magnetisation curve of sugar crystals.** N. S. AKULOV (Z. Physik, 1931, 67, 794—807).—Mainly theoretical. The measurements of the magnetisation curves for the symmetrical axes of single iron crystals are in formal agreement with those of Honda, Masumoto, and Kaya (A., 1928, 823).

J. FARQUHARSON.

**Ferromagnetism.** N. TUNAZIMA (Z. Physik, 1931, 67, 817—825).—Theoretical. The connexion of the theories of Weiss and Heisenberg and of Ewing, Honda, and Okubo is demonstrated. The formula of Steinhaus and Gumlich is derived as a special case.

J. FARQUHARSON.

**Diamagnetism, field strength, and crystal structure.** W. J. DE HAAS (Nature, 1931, 127, 335—336).—The diamagnetic susceptibility of pure crystals of bismuth has been measured as a function of field strength at 14° and 20° Abs.

L. S. THEOBALD.

**Charge distribution and diamagnetic susceptibility of atoms and ions.** G. W. BRINDLEY (Phil. Mag., 1931, [vii], 11, 786—792).—Slater's method of calculating charge distributions (cf. A., 1930, 1234) leads to susceptibility values in closer agreement with experiment than those calculated by Pauling (cf. A., 1927, 394). N. M. BLIGH.

**Magnetic properties of thin, electrolytically deposited cobalt films.** E. P. T. TYNDALL and W. W. WERTZBAUGHER (Proc. Iowa Acad. Sci., 1929, 36, 297).—In general the films behave like iron films, but the specific properties depend largely on the acidity of the electrolyte. CHEMICAL ABSTRACTS.

**Strain and diamagnetic susceptibility.** H. E. BANTA (Physical Rev., 1931, [iii], 37, 634—637).—The magnetic susceptibility of copper and silver, measured by the Gouy method, was found to be increased up to 20% and 3%, respectively, by anneal-

ing at red heat for 15 min. in carbon dioxide; the increase is probably due to release of occluded gases or to oxidation or recombination of impurities. The effect reported by Bitter (cf. A., 1930, 1505) due to straining beyond the elastic limit was not found.

N. M. BLIGH.

Alteration in the electrical resistance of purest electrolytic iron in transverse magnetic fields. O. STIERSTADT (Z. Physik, 1931, 67, 725—742).—The change in resistance of electrolyte iron is considerably less than that of other samples of iron containing impurity.

J. FARQUHARSON.

Dependence of the resistance of ferromagnetic metals on temperature. G. BORELIUS (Ann. Physik, 1931, [v], 8, 261—266).—It is shown that the electrical resistance of ferromagnetic metals can be regarded as the sum of a resistance which is dependent on temperature in the normal way, and a resistance the magnitude of which depends on the demagnetisation.

W. GOOD.

Change of resistance in magnetic fields. H. BETHE (Nature, 1931, 127, 336—337).—Theoretical.

L. S. THEOBALD.

Change of resistance in a magnetic field of single crystals of bismuth. R. A. NELSON and G. R. WATSON (Proc. Iowa Acad. Sci., 1929, 36, 304).

CHEMICAL ABSTRACTS.

Resistance of bismuth in alternating magnetic fields. W. W. MACALPINE (Physical Rev., 1931, [ii], 37, 624—633).—The production with a 50-watt tube of a field of 100 gauss at  $10^6$  cycles, and a potentiometer method of measuring the behaviour in it of a bismuth wire at liquid air temperature are described. The resistance of the bismuth was found to follow the instantaneous values of the field.

N. M. BLIGH.

Strength of wetted salt crystals. A. SMEKAL (Physikal. Z., 1931, 32, 187—192).—Experiments are described which show that by dissolving away the surface of loaded salt crystals it is impossible in the statical sense to realise ideal lattice tenacity.

W. GOOD.

Crystallographic investigation of some mechanical properties of metals. III. Damping of lateral vibration of aluminium crystal plates. IV. Internal slip of metals. Y. KIDANI (J. Fac. Eng. Tokyo, 1931, 19, 107—113, 115—129; cf. A., 1930, 1101).—The logarithmic decrement of lateral vibration of aluminium crystals depends on the crystallographic orientation.

IV. Mechanical properties of metals are discussed from the point of view that as the individual grains are variously oriented, they will slip by different amounts under the influence of an external load.

C. W. GIBBY.

Nature of solidity. M. PÓLÁNYI (Metallwirt., 1930, 9, 553—558; Chem. Zentr., 1930, ii, 1031).—Starting from the different distribution of atoms in liquids and solids, the different plastic behaviour of amorphous and crystalline substances is discussed.

L. S. THEOBALD.

Peculiarity of sylvite. X. JOHNSEN (Z. Krist., 1931, 76, 456—457).—When sodium chlorate crystallises on a cleavage face of sylvite a preponder-

ance of lævorotatory crystals is obtained, supporting the view that sylvite displays enantiomorphous hemihedry (O).

C. A. SILBERRAD.

Physico-chemical studies of organo-metallic compounds. H. GILMAN, L. L. HECK, and J. A. LEERMAKERS (Proc. Iowa Acad. Sci., 1929, 36, 270).—A study of mol. wt., conductivity, absorption spectra, and reaction towards oxygen, nitrous oxide, and hydrogen (in presence of platinum).

CHEMICAL ABSTRACTS.

Peltier effect in single crystals of bismuth. H. E. FAGAN (Proc. Iowa Acad. Sci., 1929, 36, 300—301).

CHEMICAL ABSTRACTS.

Thermo-electric properties of Monel metal. E. MESCHTER (Science, 1931, 73, 132—133).—The curves  $dE/dt$  against  $t$  show maxima at  $100^\circ$  and  $87^\circ$  for two rods of Monel metal.

L. S. THEOBALD.

Electrical resistance of titanium, zirconium, and their mixed crystals. J. H. DE BOER and P. CLAUSING (Physica, 1930, 10, 267—269; Chem. Zentr., 1931, i, 28).—The specific resistance of titanium at  $0^\circ$  is about 0.475; the temperature coefficient is approx. 0.00425.

A. A. ELDRIDGE.

Extension of Ramsay and Young's b.-p. rule. T. S. WHEELER (Phil. Mag., 1931, [vii], 11, 441—449).—For any system in equilibrium there is a linear relation between the reciprocals of the temperatures (Abs.) at which two given powers of a variable or pair of variables are in a constant ratio corresponding with the equation  $\log(\text{variable}) = a + b/T$ , where  $T$  is the temperature and  $a$  and  $b$  are constants. It is found empirically that the following rule, of which Dühring's rule is a special case, holds fairly accurately over temperature ranges of about  $100^\circ$ : the temperatures (Abs.) for which the vapour pressures of a liquid or of a pair of liquids are in a constant ratio satisfy a linear equation.

R. CUTHILL.

Heat capacities at low temperatures of manganese sulphide, ferrous sulphide, and calcium sulphide. C. T. ANDERSON (J. Amer. Chem. Soc., 1931, 53, 476—483).—The heat capacities have been determined between  $58^\circ$  and  $297^\circ$  Abs. The heat capacity curve of manganese sulphide exhibits a double cusped maximum between  $135^\circ$  and  $150^\circ$  Abs. Extrapolation of the heat capacity curves to  $0^\circ$  Abs. is effected by means of Debye and Einstein functions and the entropy,  $S_{298}$ , of manganese, ferrous, and calcium sulphides is computed to be 18.7, 16.1, and 13.5 entropy units, respectively. These values, in conjunction with existing data, yield the corresponding free energies,  $\Delta F_{298}$ , —64,000, —23,600, and —109,800 g.-cal., respectively.

J. G. A. GRIFFITHS.

Additive calculation of molecular heats of gases. M. TRAUTZ (Ann. Physik, 1931, [v], 8, 267—285).—It is shown how for a compound of which the mol. wt., approximate critical temperature, and approximate constitution are known,  $C_v$  may be calculated empirically.

W. GOOD.

M.-p. curves of monobasic fatty acids. A. M. KING and W. E. GARNER (J.C.S., 1931, 578—580).—Theoretical. The minimum in the m.-p. curves of the monobasic fatty acids can be accounted for on the

basis of the probability of attachment of the molecule to the crystal surface. This factor also enters into the relationship between heat of crystallisation and temperature. The entropy change on crystallisation can be represented by the relationship  $Q/T = 0.002698n - 0.0061 + 0.00475 \sum_{i=1}^n \log_{10} [n/(n-2)]$ .

A. J. MEE.

**Entropy, elastic strain, and the second law of thermodynamics: the principles of least work and of maximum probability.** W. S. KIMBALL (J. Physical Chem., 1931, 35, 611—623).—Theoretical. A new mechanical aspect of entropy is presented.

L. S. THEOBALD.

**Specific heat of electricity in ferromagnetics.** E. C. STONER (Proc. Leeds Phil. Soc., 1931, 2, 149—158; cf. A., 1930, 1101).—In calculating the specific heat of electricity from thermoelectric data for metals it is not in general possible to obtain agreement with the experimental data if the free electrons alone are considered; it is necessary to treat a metal as an equilibrium distribution of neutral atoms, positive ions, and free electrons. The assumption that in a ferromagnetic metal the carriers are ions or atoms with fewer electrons than are required for a completed configuration leads to the relationship  $f\Delta\sigma_e = -\Delta S_e$ , where  $\Delta\sigma_e$  is the change in the specific heat of electricity per electron at the Curie point,  $\Delta S_e$  the change in the atomic heat, and  $f$  the number of electrons missing per atom. This equation is in agreement with existing experimental data.

R. CUTHILL.

**Physical properties of compressed gases. I. Nitrogen.** W. E. DEMING and (Miss) L. E. SHUPE (Physical Rev., 1931, [ii], 37, 638—654).—Theoretical. A graphical process is applied to the compressibility data obtained by Bartlett and others (cf. A., 1930, 678, 679) and from the accurate  $p-v-T$  data obtained values of the specific volume, density, fugacity,  $C_p$ ,  $C_v$ ,  $C_p - C_v$ ,  $\mu$ , and the coefficients  $(-p/v)(dv/dp)_T$  and  $(T/v)(dv/dT)_p$  are calculated, tabulated, and illustrated graphically for 14 pressures and 12 temperatures in the ranges 20—1200 atm., and  $-70^\circ$  to  $600^\circ$ .

N. M. BLYTH.

**Physical constants of silicon tetrafluoride and tungsten and molybdenum hexafluorides.** O. RUFF and E. ASCHER (Z. anorg. Chem., 1931, 196, 413—420).—The m. p., b. p., heat of sublimation in kg.-cal., latent heat of evaporation in kg.-cal., Trouton constant,  $d_{m.p.}$ , and mol. vol. at m. p. of tungsten hexafluoride are  $2.3^\circ$  (420 mm.),  $17.5^\circ$ , 8.72, 6.25, 21.5, 3.515, and 84.9, respectively, and of molybdenum hexafluoride  $17.5^\circ$  (406.5 mm.),  $35^\circ$ , 8.30, 6.36, 20.6, 2.551, 82.4. Silicon tetrafluoride has b. p.  $-95.0^\circ$ , and heat of sublimation 6.19 kg.-cal. Equations for the sublimation pressure and vapour-pressure curves of silicon tetrachloride, tungsten hexafluoride, and molybdenum hexafluoride are given. (See also Patnode and Papish, A., 1930, 1104.)

H. F. GILLBE.

**Heat of formation of nitrogen trifluoride.** O. RUFF and H. WALLAUER (Z. anorg. Chem., 1931, 196, 421—428).—The heat of formation of nitrogen trifluoride, determined from the reaction with hydrogen at 6 atm., is  $26 \pm 2$  kg.-cal.

H. F. GILLBE.

**Optical determination of the heat of dissociation of salt vapours.** A. TEREININ (Physica, 1929,

9, 283—286; Chem. Zentr., 1931, i, 238).—Polemical. G. H. VISSER (*ibid.*).—A reply. A. A. ELDRIDGE.

**Absolute temperature scale.** D. D. JACOBUS (Abs. Theses Mass. Inst. Tech., 1931, 7, 54—56).—An apparatus is described for the direct comparison of the platinum resistance and gas scales of temperature between  $0^\circ$  and  $500^\circ$  with an error of  $0.001\%$ , and for the determination of the thermodynamic temperature of the m. p. of ice by measurements with helium and hydrogen. The helium data yield  $273.15_8^\circ$  Abs., and the hydrogen data  $273.19_7^\circ$  Abs., and the true value is regarded as  $273.16^\circ \pm 0.02^\circ$  Abs.

H. F. GILLBE.

**Determination of heat of vaporisation of aliphatic alcohols using an adiabatic microcalorimeter.** E. BARTOSZEWICZÓWNA (Rocz. Chem., 1931, 11, 90—94).—The recorded heats of vaporisation at  $20^\circ$  are: methyl 287.0, ethyl 224.3, propyl 180.1, isopropyl 175.8, butyl 149.5, and isobutyl alcohol 147.2 g.-cal.

R. TRUSZKOWSKI.

**Calculation of the volume correction in van der Waals' equation.** G. L. CHABORSKI (Bul. Chim. pura appl., Bukarest, 1929, 31, 119—132; Chem. Zentr., 1930, ii, 1047).—The value of  $b$  for any temperature may be calculated from  $d_i$  and  $V_0$ . Values of  $b_{b.p.}$  are computed for 92 substances. To a first approximation  $b$  is a linear function of temperature.

A. A. ELDRIDGE.

**Velocity of sound in carbon dioxide.** H. O. KUESER (Physikal. Z., 1931, 32, 179).—The velocity of sound in gaseous carbon dioxide increases with increasing frequency between  $0.5$  and  $3 \times 10^5$  sec. $^{-1}$ , thereafter attaining the constant value  $268.2 \pm 0.3$  metres per sec. Assuming the increase in velocity is due to a change in  $\gamma$ , a value for the latter equal to 1.40 is obtained.

W. GOOD.

**Calculations of velocity of sound in nitrogen tetroxide.** F. VERHOEK and F. DANIELS (J. Amer. Chem. Soc., 1931, 53, 1186—1187).—Unpublished data for the dissociation of nitrogen tetroxide afford values for the velocity of sound, calculated by means of Einstein's equation,  $1.5$ — $3.0$  metre sec. $^{-1}$  less than those observed by Kistiakowsky and Richards (this vol., 314), suggesting a constant error in theory or experiment. The heat of dissociation of the oxide is 13,960 g.-cal. per mol. at constant volume.

J. G. A. GRIFFITHS.

**Classical thermodynamics and the chemical constant.** A. AKOPIAN (Z. Physik, 1931, 67, 851—859).—From classical thermodynamics, general expressions are derived for the constant  $J_{a_i} = J_i$  in the formula for  $\log p^{a_i}$ , and for the constant  $J$  found in the formula for  $\log K_p$ , and the relationship between  $J$ ,  $n_i$ , and  $J_{a_i}$  is deduced. This does not lead to the Nernst relation  $J = \sum n_i J_i$ , but the latter follows on introduction of the Nernst heat theorem.

J. W. SMITH.

**Vapour-pressure diagram.** G. CALINGAERT (Chim. et Ind., 1931, 25, 307—308).—If the logarithm of the vapour pressure of a liquid is plotted against a modification of  $1/T$  a straight line is obtained. The lines for similarly constituted organic liquids, e.g., alkyl bromides, converge to a point.

D. K. MOORE.

**Equation of state of propellant gases.** A. D. CROW and W. E. GRIMSHAW (Phil. Trans., 1931, A, 230, 39—73).—A method has been developed for measuring the pressure of the gases resulting from the explosion of a propellant, and an expression has been established for the energy losses due to cooling of the gases by the walls of the explosion vessel. From the experimental results the equation of state of the gaseous mixture is found to be  $p_0 = 84.80 \{ (\Sigma g \cdot \text{mols.}) / g \} T_0 / (1/\Delta - \eta)$ , where  $\Delta$  is the density and  $\eta$  the co-volume;  $\eta$  may be evaluated from the hard-kernel values of the mol. radii, increased by 2.5%, of the constituent gases, according to the equation  $\eta = 1.092 \times 10^{25} \times \Sigma [(0.5\sigma_g)^3 \cdot g]$ , where  $0.5\sigma_g$  is the hard-kernel molecular radius and  $g$  the number of g.-mol. per g. for each component gas. Under the conditions of the experiment  $\Delta$  is of the order of 0.25—0.025, and the pressure and temperature attain values of 3800 kg. per cm.<sup>2</sup> and 4000° Abs., respectively. The mean mol. heats of carbon dioxide, hydrogen, water, and carbon monoxide plus nitrogen at temperatures between 2000° and 4000° have been calculated from the equation  $\bar{c}_r = 6 + (7/15)(T/1000) + (16/45)(T/1000)^2 + \dots$ , where  $\bar{c}_r$  is the mean mol. heat between 0 and  $T^\circ$  Abs.; this equation is more satisfactory than that of Bjerrum at temperatures above 3000° Abs. The equilibrium constant of the reaction  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  has been calculated at temperatures between 1000° and 4200° Abs. by various formulæ.

H. F. GILLBE.

**Molecular heats and critical data.** M. TRAUTZ (Ann. Physik, 1931, 8, [v], 433—455; cf. this vol., 417).—By examination of the variation of  $(C_p - 3R/2) - M^2$  with temperature simple whole-number relationships connecting the values of  $C_p$  for different gases are found. The values of  $M^2/T_c^2$  are also found to bear simple ratios to each other,  $a$  being a simple whole number or a fraction composed of small integers.

W. GOOD.

**Pressure-volume-temperature values for ammonia to 1000 atm. from 30° to 200°.** F. G. KEYES (J. Amer. Chem. Soc., 1931, 53, 965—967).—Data are tabulated.

J. G. A. GRIFFITHS.

**Constants of the Beattie-Bridgeman equation of state with Bartlett's  $P$ - $V$ - $T$  data on hydrogen.** W. E. DEMING and (Miss) L. E. SHUPE (J. Amer. Chem. Soc., 1931, 53, 843—849; cf. A., 1930, 679; Bartlett and others, *ibid.*, 678; A., 1928, 698).—Pressures as high as 1000 atm., within the range  $-70^\circ$  to  $300^\circ$ , are reproduced with a maximum root mean square deviation of 0.4% at densities less than 0.024 mol. per c.c., and with a maximum deviation of 2.1% at  $d=0.027$  and  $-70^\circ$ , by inserting the values  $R=82.0489$ ,  $a=56.18$ ,  $A_0=124,040$ ,  $c=20 \times 10^6$  (units: atm., c.c., g.-mol.) in the Beattie-Bridgeman equation of state (A., 1927, 819): below the critical density,  $0.0154$ ,  $b=-7.22$  and  $B_0=20.22$ , whilst above the critical density,  $b=-19.68$  and  $B_0=17.50$ . The calculated pressures become markedly too low at very high densities. Evidence for the predominance of repulsive forces between the molecules at  $d > 0.018$  is adduced. J. G. A. GRIFFITHS.

**Equations for vapour pressure and latent heat, including approximate equations for solid com-**

**pounds containing a gaseous component.** L. J. GILLESPIE (Proc. Amer. Acad. Arts Sci., 1930, 66, 153—165).—Mathematical. Methods for applying the equations to experimental data are described.

CHEMICAL ABSTRACTS.

**Anomalous velocity distribution in thin layers of lubricant.** H. UMSTÄTTER (Kolloid-Z., 1931, 54, 220—226).—A mathematical discussion of the validity of the Hagen-Poiseuille law and relations between viscosity, mol. wt., temperature, and the form of the molecules.

E. S. HEDGES.

**Characteristic equation for mixtures of ethylene and argon.** P. GLANSDORFF (Bull. Acad. roy. Belg., 1931, [v], 17, 203—216).—The equation  $V = N_1 V_1 + N_2 V_2 + N_1 N_2 \phi_{12}$ , where  $V_1$  and  $V_2$  are the molecular volumes of the constituents and  $\phi_{12}$  is a function of temperature and pressure only, is suggested as a characteristic equation for binary mixtures. It is applied to mixtures of ethylene and argon.

A. J. MEE.

**Beattie-Bridgeman equation of state and Bartlett's  $P$ - $V$ - $T$  data for a 3:1 hydrogen-nitrogen mixture.** W. E. DEMING and (Miss) L. E. SHUPE (J. Amer. Chem. Soc., 1931, 53, 860—869; cf. Bartlett and others, A., 1930, 678; 1928, 698).—Between  $-70^\circ$  and  $300^\circ$ , pressures are reproduced with deviations of less than 0.3% at densities less than 0.0245 mol. per c.c., whilst at  $d=0.027$  the calculated pressure is 2.5% too low at  $-70^\circ$ . At high densities, repulsive forces between the molecules predominate. Constants for the mixture derived by combination of the constants of the constituents afford calculated pressures with a root mean square error of less than 1.17% at densities smaller than 0.007.

J. G. A. GRIFFITHS.

**Influence of low temperatures on the thermal diffusion effect.** T. L. IBBS and K. E. GREW (Proc. Physical Soc., 1931, 43, 142—156).—Measurements of thermal diffusion at temperatures between  $15^\circ$  and  $-190^\circ$  have been made on mixtures of neon with helium, hydrogen, and argon and of helium with argon and nitrogen. The ratio  $k_t$  of the coefficient of thermal diffusion to the coefficient of ordinary diffusion generally decreases at low temperatures. For helium-neon and hydrogen-neon mixtures with low liquefying points, the change in  $k_t$  between  $15^\circ$  and  $-190^\circ$  is small. The bearing on theory is discussed.

W. E. DOWNEY.

**Refractivity of a binary mixture and its relation to the molecular size of the components.** T. ISHIKAWA (Chikashige Anniv. Vol., 1930, 275—294).—Formulæ relating the refractive index to the composition are critically reviewed and a theoretical equation is derived. The refractive indices of binary mixtures of alcohols and of alcohols with benzene have been determined, and by application of the equation consistent values for the molecular diameters  $\sigma$  of the alcohols are obtained. When applied to known optical data the equation yields for non-polar substances values of  $\sigma$  which are concordant with the values derived from viscosity measurements and from the relation between van der Waals'  $b$  and the volume of the molecule; for polar molecules the agreement is less satisfactory. Contrary to the



Lorentz-Lorenz formula, the new equation indicates that the molecular dimensions of *n*-propyl and butyl alcohols are greater than those of the *iso*-compounds, and that the dimensions of a single molecule in a liquid, whether associated or not, are the same as in the gaseous state and may be calculated from optical data for a mixture of the liquid with another, chemically indifferent, liquid of known molecular diameter.

H. F. GILLBE.

**Molar refraction of methyl alcohol. I. Influence of the concentration in a non-polar solvent. II. Influence of temperature on solutions in a non-polar solvent.** M. VELASCO (Anal. Fis. Quím., 1931, 29, 15—20, 171—176).—I. The molecular refractivity of solutions of methyl alcohol in benzene is a linear function of  $z$ , where  $z$  is the molar fraction of the alcohol. The concentration is therefore without influence on the polarisation of the polar component, and the linking involved in the association of the dipoles of the alcohol does not influence the forces acting on the peripheral electrons.

II. The influence of temperature on the molar refraction of benzene solutions of methyl alcohol has been investigated. The refractive indices of the components and of the solutions are given by  $n = a + bT$ , where  $a$  and  $b$  are 1.5142 and  $-0.00068$  for benzene and 1.3386 and  $-0.00043$  for methyl alcohol. The molar refraction of the solutions increases slightly with rise of temperature, and the increase is greatest in the more concentrated solutions. The effect is due to an increase of electronic polarisation of the alcohol, caused probably by an increase in the number of the molecules for which the velocity is sufficiently large to disturb the peripheral electrons of other molecules with which they collide. H. F. GILLBE.

**Electrochemical examination of the system aluminium chloride-sodium chloride.** V. A. PLOTNIKOV and P. T. KALITA (J. Russ. Phys. Chem. Soc., 1930, 62, 2195—2202).—Maximal conductivity of fused mixtures containing 19.2—49 mol.-% NaCl is found at the eutectic, whilst for solid mixtures the conductivity rises with sodium chloride content. The conductivity of solidified melts is increased 200-fold by the addition of 1.7% of sodium sulphate. Aluminium is deposited on the cathode and the current is conveyed chiefly by sodium ions.

R. TRUSZKOWSKI.

**Physical properties of the ternary system phenol-benzene-water.** S. H. WEIDMAN and L. E. SWEARINGEN (J. Physical Chem., 1931, 35, 836—843).—The densities, viscosities, surface tensions, and refractive indices have been measured at 25° for homogeneous mixtures over a wide range.

L. S. THEOBALD.

**Influence of temperature on the dielectric constants of some glasses in the softening interval.** G. TAMMANN and W. BOEHME (Z. anorg. Chem., 1931, 197, 1—17).—The dielectric constants of salicin, brucine, selenium, phenolphthalein, and colophony increase linearly with rise of temperature until the sp. vol. and refractive index curves exhibit breaks; this temperature corresponds with that at which the brittleness characteristic of the vitreous state appears. At higher temperatures the increase of the dielectric

constant is linear, but is more rapid since the fraction of the dielectric constant due to molecular polarisation is zero for a material in the vitreous form, but becomes evident when the material passes into the condition of a highly viscous liquid. The magnitude of the change of the principal physical properties as the glass passes through the softening interval is proportional to the appropriate temperature coefficient for the vitreous condition. Neither the Maxwell nor the Clausius-Mosotti relation applies to salicin and brucine. The temperature-log conductivity curves for selenium, salicin, and phenolphthalein are linear, but a break occurs at the temperature at which threads may be drawn from the glass. The dielectric constants of some boron, lead, and barium glasses have been measured up to 700°; the increase with rise of temperature is at first small and linear, but at 200—300° the dielectric constant commences to increase rapidly and more than doubles by 600°. The form of the various curves bears no simple relation to the composition of the glass, but the asymptotic temperature approximates closely to the cohesion temperature in several cases; when plotted logarithmically, breaks occur in the neighbourhood of the temperature at which brittleness appears.

H. F. GILLBE.

**Segregation in continuous series of mixed crystals.** G. TAMMANN and A. RUPPELT (Z. anorg. Chem., 1931, 197, 65—89).—The mean temperature of segregation in mixed crystals of potassium and sodium bromides and potassium and sodium iodides has been determined by observation of the temperatures at which opalescence appears and disappears. Moisture accelerates the process of segregation. In mixed crystals of lithium and sodium bromides segregation occurs between 20 and 60 mol.-% of sodium bromide, the maximum effect being at 200°. The temperatures obtained for the system potassium chloride-sodium chloride lie rather below those derived from the cooling curves. Measurements have been made also with mixed crystals of potassium chloride and iodide, bromide and iodide, and chloride and bromide; segregation does not appear to take place in the last-named system. Microscopical investigation of sodium nitrate-potassium nitrate melts indicates that a continuous series of mixed crystals is formed, since no eutectic is visible and the crystallites increase in size on heating to 200°. On cooling, the large crystallites break down into numerous small crystals, as a result of segregation; this process is reversible, and is catalysed by water at the ordinary temperature, although not at 100°. The system sodium metaphosphate-potassium metaphosphate has been examined; the salts have only limited mutual solubility, and segregation of the mixed crystals has been observed with mixtures containing 90 mol.-% of the potassium salt, at about 370°. The opalescence shown by mixed crystals is discussed; at high temperatures it may result from the aggregation of molecules of the same kind, whereas at low temperatures, when caused by the action of water, it is due to the appearance of a new, finely-dispersed phase. The formation and breakdown of mixed crystals has been correlated with the differences

$\Delta a$  of the lattice parameters of the component salts; for values of  $\Delta a$  less than 0.115 Å. continuous series of mixed crystals are formed; for  $\Delta a$  0.135—0.144 Å. a break occurs in the series, and at higher values the miscibility in the solid state is very limited. Segregation occurs only when  $\Delta a$  exceeds about 0.05 Å.

H. F. GILLBE.

The  $\delta$  and  $\beta$  transformations of brasses. D. IITSUKA (Chikashige Anniv. Vol., 1930, 305—309).—Observations on zinc-copper alloys containing 45—60% Cu confirm the view that double transformations take place in the  $\beta$  and  $\gamma + \beta$  alloys, and also, contrary to the report of Ruer and Kremers (A., 1930, 161), in the  $\alpha + \beta$  alloys.

H. F. GILLBE.

Solid solutions of the copper-silver system. D. STOCKDALE (Inst. Metals, Mar., 1931, Advance copy, 14 pp.).—The mutual solubilities of copper and silver have been determined by means of microscopic examination of quenched specimens and at low temperatures by measurement of the electrical resistance of quenched wires. For the latter purpose a differential method, which shows up small abrupt changes in the resistance of alloys, is described. The copper-rich solidus near the triple point is lowered very suddenly by the addition of a few tenths of 1% Ag. The solubility of silver in copper at the eutectic temperature is 8.2% by weight, 4.7% at 700°, 0.7% at 400°, and at the ordinary temperature silver is almost insoluble in copper. The silver-rich solidus is nearly a straight line joining the m. p. of silver with the point 8.8% Cu and 778.5°. The solubility of copper in silver at the eutectic is 8.8%, 5.8% at 700°, 1.1% at 400°, and about 1% at the ordinary temperature. "Standard silver" containing 7.5% Cu is a uniform solid solution only between 750° and 810°.

O. J. WALKER.

X-Ray study of the copper end of the copper-silver system. R. W. DRIER (Ind. Eng. Chem., 1931, 23, 404—405).—X-Ray spectrographic examination of samples of copper containing 0.003—1.0% Ag shows that at the ordinary temperature silver is not soluble in copper. There is evidence, however, that copper is soluble in silver.

E. S. HEDGES.

Constitution of the cadmium-rich alloys of the system cadmium-silver. P. J. DURRANT (Inst. Metals, Mar., 1931, Advance copy, 15 pp.).—The constitution of the alloys containing from 0 to 40 wt.-% Ag has been reinvestigated by thermal and micrographic methods. The liquidus consists of four smooth curves intersecting with three peritectic horizontals at 343°, 592°, and 640°. The following solid solutions exist: I 0—6%, II 18—33.5%, and III 36.2—39% Ag. In phase II, which includes the solid solutions  $\epsilon$  and  $\delta$  described by Petrenko and Federov (A., 1911, ii, 281, 800), the solidus and liquidus are roughly parallel and do not intersect, as was previously thought, at 25 at.-% Ag. No transformations below the solidus have been detected in any of the solid solutions, but III has not been examined below 400°.

O. J. WALKER.

The silver-rich aluminium-silver alloys above 600°. T. P. HOAR and R. K. ROWNTREE (Inst. Metals, Mar., 1931, Advance copy, 6 pp.).—Using aluminium of high purity the system aluminium-

silver has been investigated above 600° up to 15 wt.-% Al, and Petrenko's diagram (A., 1905, ii, 635) has been modified. The  $\alpha/\beta$  and  $\beta/\gamma$  peritectics are found to be at 779° and 729°, respectively, instead of at 770° and 723°, and the  $\alpha/\alpha + \beta$  and  $\alpha + \beta/\beta$  boundaries slope towards the axis with rise of temperature and are not vertical. The  $\beta$ -phase possibly consists of  $\text{Ag}_4\text{Al}$  and not  $\text{Ag}_3\text{Al}$ . The resemblance between this system and the aluminium-copper system is pointed out.

O. J. WALKER.

Eutectic point in the system silicon-aluminium. H. KOTO (Chikashige Anniv. Vol., 1930, 303—304).—The eutectic corresponds with 11.7% Si and 578°.

H. F. GILLBE.

Electrical conductivity of alloys at low temperatures. J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 25—32).—The resistances of lead-bismuth, lead-antimony, and bismuth-thallium alloys have been measured down to temperatures of about 4.2° Abs. Bismuth tends to increase the superconductivity transition temperature, whilst the presence of antimony in some cases causes a lowering and in others a raising of the superconducting point. The lead-bismuth alloy shows a superconducting point 1.6° higher than any previously obtained.

W. GOOD.

Superconductivity of alloys. J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 53—64; cf. preceding abstract).—Alloys of members of the bismuth group with lead, tin, thallium, and gold show, with the exception of lead-antimony, a pronounced elevation of the superconducting point, whilst silver-thallium alone shows a transition temperature higher than that of the pure conductor alone.

W. GOOD.

Ternary silver alloys. III. System Ag-Cu-Al. IV. Mechanical properties of some ternary silver alloys. S. UENO (Chikashige Anniv. Vol., 1930, 57—75, 77—83).—III. The system has been studied by thermal analysis and photomicrography. The  $\alpha$  solid solution of the system Ag-Al dissolves copper to form a ternary solid solution, and the  $\beta$  solid solution, composed of  $\text{AlAg}_3$  and  $\text{AlAg}_2$ , dissolves copper and  $\text{CuAl}_2$ . The temperature of the Cu-Ag eutectic is first raised from 776° to 796° and then lowered to 525° as a result of the incidence of a reaction involving the production of  $\text{CuAl}_2$ . The complex reactions in copper-rich Al-Cu systems disappear on addition of 5% Ag, a series of homogeneous solid solutions being formed. The temperature of the  $\text{CuAl}_2 + \epsilon$  eutectic in the Al-Cu system is lowered from 545° to 502° on addition of silver, and that of the  $\text{AlAg}_2 + \epsilon$  eutectic from 565° to 502° on addition of copper, on account of the occurrence of an invariant reaction at the latter temperature.

IV. The Brinell hardness, malleability, and corrosion-resistance of the ternary alloys Ag-Cu-Zn, Ag-Al-Zn, and Ag-Cu-Al have been investigated. The maximum hardness of the 10% Zn alloys in the Ag-Al-Zn system occurs at 10% Al, i.e., in the ternary  $\beta$  alloy, and of the 20% Zn alloys at 3% Al +  $\beta$ . The hardness of the 30% Zn alloys in the Ag-Cu-Zn system increases to a maximum on increase

of the silver content up to 50%, whilst in presence of 10% Zn the maximum is at 30% Ag, *i.e.*, in the binary silver-copper eutectic. Two maxima occur in the 5% Al alloys in the system Ag-Cu-Al, *viz.*, at 10% and 70% Ag. The corrosion-resistance towards hydrochloric acid of Ag-Cu-Zn alloys containing 30% Zn diminishes on addition of silver to a minimum at the composition corresponding with the binary silver-copper eutectic; increase of the silver content greatly reduces the rate of corrosion of the alloys by 0.5*N*-ammonia solution. Increase of the aluminium content beyond 10% very greatly increases the rate of corrosion of Ag-Al-Zn alloys by acid or ammoniacal solutions. The malleability of Ag-Cu-Zn alloys containing 10% Zn is a minimum at 20–30% Ag, whilst that of Ag-Al-Zn alloys containing 20% Zn falls rapidly as the aluminium content increases up to 3%.

H. F. GILLBE.

**Metallographic investigation of the iron-silicon-carbon alloys. I. Transformations of silicon steels.** T. SATÔ (Tech. Rep. Tôhoku, 1931, 9, 53–103).—The equilibria in the system iron-carbon-silicon have been determined by micrographical examination and by magnetic and dilatometric analysis and the results are shown by sectional diagrams for alloys containing 0.5–8% Si and 0–0.8% C. With increasing silicon content the magnitude of the A1 and A3 transformations decreases and the temperature of the magnetic change point decreases almost linearly, reaching 660° with 8% Si; the carbon content has no influence on the magnetic transformation. The austenite field in the stable system, iron-silicon-graphite, extends to about 7% Si, but in the metastable system iron-silicon-Fe<sub>3</sub>C it extends to more than 8% Si. The solubility of carbon in the  $\alpha$  and  $\delta$  phases increases at temperatures above the A1 point with increasing silicon content and the separation of carbide from these solid solutions on cooling becomes more difficult to suppress so that, even on quenching, carbide readily separates along the crystal boundaries. The peritecto-eutectic reaction,  $\delta + \text{liquid} \rightleftharpoons \gamma + \text{graphite}$ , in the stable system takes place at 1195° in the alloy with 0.37% C and 6.5% Si.

A. R. POWELL.

**Metallographic investigation of the ternary alloys of the iron-tungsten-carbon system. I. Carbides in tungsten steels. II. Transformation and constitution of tungsten steels.** S. TAKEDA (Tech. Rep. Tôhoku, 1931, 9, 21–52, 165–202).—I. The system tungsten-carbon-iron contains three carbide phases, namely, WC, a ternary solid solution ( $\eta$ ) with a composition approximating to Fe<sub>3</sub>W<sub>3</sub>C, and a solid solution ( $\theta$ ) of tungsten and iron in Fe<sub>3</sub>C. The  $\theta$ -phase is ferromagnetic and the other two are non-magnetic. The  $\eta$ -phase is coloured by etching with an alkaline solution of potassium ferrocyanide and is unstable in alloys with a high carbon content, decomposing into iron and WC when the alloy is cooled slowly or annealed. The compound WC is a hard grey constituent formed in high-carbon steels by decomposition of the  $\eta$ -phase or by reaction between liquid and austenite. The magnetic changes in alloys containing  $\theta$  usually take place in two steps at temperatures between 0° and 400°, depending on the composition and previous heat treatment of the alloy;

an excess of tungsten lowers the critical point below 200° and an excess of iron raises it towards 400°.

II. The constitution of steels with up to 15% W and 1.5% C has been determined by dilatometric, magnetic, and microscopic analyses; the system contains a metastable equilibrium between iron,  $\theta$ , and  $\eta$ , and a stable equilibrium between iron, carbon, and WC. Immediately after solidification the alloys consist entirely of metastable phases, but after annealing the metastable state persists only in steels with a low carbon content. The field of existence of the  $\gamma$ -phase decreases with increasing tungsten content and finally disappears with 12% W; addition of carbon enlarges the  $\gamma$ -field up to 0.33% C, then diminishes it again. The ( $\gamma + \delta$ ) field disappears with 0.33% and reaches its maximum at 0.2% C; with increasing tungsten content it gradually becomes smaller and finally ceases to exist in the alloy with 14.5% W; the homogeneous  $\delta$ -field exists only in alloys with less than 0.2% C. At 735° the peritecto-eutectoid reaction  $\gamma + \eta \rightleftharpoons \alpha + \theta$  takes place; the univariant point of this reaction corresponds with the composition 1% W, 0.9% C, 98.1% Fe. The binary eutectoid temperature for the reaction  $\gamma \rightleftharpoons \alpha + \eta$  rises with increasing tungsten content to 1335°, at which point the peritecto-eutectic reaction,  $\text{liquid} + \delta \rightleftharpoons \gamma + \eta$ , occurs; similarly, the temperature of the binary eutectoid reaction  $\gamma \rightleftharpoons \theta + \eta$  rises to 1085°, at which point a ternary eutectic reaction,  $\text{melt} \rightleftharpoons \gamma + \theta + \eta$ , takes place. In low-carbon alloys a binary eutectoid reaction  $\alpha \rightleftharpoons \eta + \varepsilon$  (Fe<sub>3</sub>W<sub>2</sub>) occurs.

A. R. POWELL.

**Solubility of calcium carbonate in water containing an alkali chloride.** R. DUBRISAY and R. FRANÇOIS (Compt. rend., 1931, 192, 741–743).—That the reaction  $\text{CaCO}_3 + 2\text{KCl} \rightleftharpoons \text{K}_2\text{CO}_3 + \text{CaCl}_2$  is responsible for the fixation of potassium in agricultural soils is made probable by the fact that solutions which are saturated with calcium carbonate show increasing alkalinity and increasing content of calcium with increasing concentration of potassium chloride.

C. A. SILBERRAD.

**Solubility of nitrogen in water at high pressures and temperatures.** J. B. GOODMAN and N. W. KRASE (Ind. Eng. Chem., 1931, 23, 401–404).—A method for determining the solubility of gases in liquids at ordinary and higher temperatures and at pressures from 100 to 1000 atm. is described. The solubility of nitrogen in water has been measured between 0° and 170° and at pressures of 100, 125, 200, and 300 atm. and curves are given showing the deviations from Henry's law. The departures are attributed to the solvent rather than to a peculiarity of nitrogen. These results and the existence of a minimum solubility at constant pressure are discussed in relation to solvent density, viscosity, internal pressure, surface tension, association, compressibility, and thermal expansion, but no definite conclusion is reached.

E. S. HEDGES.

**Solubility of U.S.P. chemicals.** W. SCHNELLBACH and J. ROSIN (J. Amer. Pharm. Assoc., 1931, 20, 227–233).—The following solubilities (g. in 100 g. of solvent) at 25° are recorded: (a) in water: sodium dihydrogen phosphate (anhydrous), 48.69 g.; methylene-

bluc, 2.3 g.; emetine hydrochloride, 16.53 g.; (b) in ethyl alcohol: ferric chloride, 51.45 g.; methylene-blue, 1.47 g.; sodium diethylbarbiturate, 0.313 g.; sulphonal, 13.9 g.; vanillin, 48.42 g.; (c) in glycerol: potassium chlorate, 1.055 g.; potassium citrate, 28.20 g.  
H. E. F. NOTTON.

**Solubilities of salts in ethylene glycol and its mixtures with water.** H. M. TRIMBLE (Ind. Eng. Chem., 1931, 23, 165—167).—Metallic salts in general are less soluble in ethylene glycol than in water, but the sequence of the salts is the same. Halides with a marked tendency to form hydrates are very soluble, and hydrated salts are more soluble than the corresponding anhydrous salts. The effect of temperature is not marked except in the case of magnesium ammonium chloride, but unstable solutions are temporarily formed in the boiling solvent, from which the salt is soon precipitated in an amorphous form. The ternary systems formed by glycol and water in combination with potassium iodide, bromide, chloride, and sulphate, sodium chloride, and copper sulphate pentahydrate have been examined at 30°.

H. A. PIGGOTT.

**Theory of solubility.** P. A. BOND (Proc. Iowa Acad. Sci., 1929, 36, 262—263).—The theory postulates two forces, (a) tending to arrange substances in the lattice forms of the solid state, and (b), thermal, tending to break up such forms.

CHEMICAL ABSTRACTS.

**Langmuir's adsorption isotherm.** R. S. BRADLEY (Phil. Mag., 1931, [vii], 11, 690—696).—Mathematical. The temperature variation of the constants in Langmuir's equation is derived theoretically for the adsorption of gases on charcoal, and the results are found to be in accord with those of Zeise (cf. A., 1928, 1182).

N. M. BLIGH.

**Adsorption of di-substituted benzene derivatives.** B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1931, 6, 74—79).—The adsorption by charcoal of *o*-, *m*-, and *p*-nitrophenols, -nitroanilines, and -dinitrobenzenes in benzene solution has been measured. The nitrophenols and nitroanilines are adsorbed in the order  $p > m > o$ , which is the inverse order of their solubilities in benzene. Similarly, *m*-dinitrobenzene is less adsorbed and more soluble than the *o*- and *p*-compounds, but *o*-dinitrobenzene is both more soluble and more adsorbed than *p*-dinitrobenzene. It is suggested that the dipole moment, which is much greater for *o*- than for *p*-dinitrobenzene, may affect the adsorption through electrostatic forces. The order of the *m*. *p*. and of the molecular association appears to support this view.

A. A. LEVI.

**Discontinuous nature of the process of sorption of gases and vapours by porous solids.** A. J. ALLMAND and L. J. BURRAGE (Proc. Roy. Soc., 1931, A, 130, 610—632).—Adsorption isothermals for carbon dioxide, carbon tetrachloride, benzene, water, and amyl alcohol have been determined at 25° by a static method (Allmand and Puttick, this vol., 160), using four different de-gassed charcoals, the pressure range being 0.13—19.2 mm. Measurements were also made with silica gel and benzene, water, and carbon tetrachloride, respectively. All these isothermals afford evidence of discontinuity, in some

cases very marked and in others barely exceeding the limits of experimental error. These and previous results are discussed. The authors' views agree largely with those of Goldmann and Póányi (A., 1928, 579) and of Semenov (A., 1930, 851).

L. L. BIRCUMSHAW.

**Heat of adsorption of certain organic vapours by charcoal at 25° and 50°.** J. N. PEARCE and G. H. REED (J. Physical Chem., 1931, 35, 905—914).—The heats of adsorption of methyl and methylene chlorides, chloroform, and carbon tetrachloride by a steam-activated, acid-washed coconut charcoal of 0.28% ash content have been determined at 25° and 50° by the method previously described (A., 1928, 481). The heats of adsorption can be represented by the equation  $h = aX^b$ , where  $a$  and  $b$  are specific constants, and  $X$  is the number of c.c. adsorbed per g. of charcoal. The mol. heat of adsorption increases with the number of chlorine atoms in the molecule. The temperature coefficient is very small.

L. S. THEOBALD.

**Adsorption of gases by glass walls. VIII. Hydrogen chloride.** M. CRESPI and E. MOLES (Anal. Fis. Quím., 1931, 29, 146—157).—With hydrogen chloride, as with other gases, there is a slow absorption and a rapid adsorption which occur simultaneously. The former predominates, and the result of the whole process accords with the Freundlich equation. The results of previous workers are reviewed and Scheuer's values (A., 1909, ii, 991) shown to involve a considerable error.

H. F. GILLBE.

**Desorption of gases from molecularly plane glass surfaces.** J. R. CURRY (J. Physical Chem., 1931, 35, 859—873).—The desorption of air, carbon monoxide and dioxide, hydrogen, ammonia, ethylene, and toluene from molecularly plane surfaces at -78° and 25° has been determined. Except in the case of carbon dioxide, desorption is complete at fairly low temperatures (150—250°). Contact with water vapour causes a change in the surface of the glass and subsequent adsorption of toluene and hydrogen is increased and desorption is retarded, but the glass surface tends to become molecularly plane after repeated desorption experiments. Water vapour itself is strongly adsorbed and is expelled continuously as the temperature is raised. The surface of a fresh, unwashed tube of soft glass is rendered molecularly plane by continued heating at a temperature slightly below the *m*. *p*.

L. S. THEOBALD.

**Direct measurement of the adsorption of soluble substances by the bubble method.** D. M. GANS and W. D. HARKINS (J. Physical Chem., 1931, 35, 722—739).—The adsorption of *p*-toluidine and of isoamyl alcohol in the air-solution interface has been directly measured by the bubble method. The results agree with those of McBain and Davies (A., 1927, 1022) in that adsorption increases with concentration until it reaches a constant value greater than that which corresponds with a unimolecular film. In general, however, the adsorption now measured is less than that obtained by McBain and Davies (*loc. cit.*). The adsorption appears to decrease as the adsorbing bubbles decrease in size and may approach the value for each solute which is given by

the usual adsorption equation and by experiments with insoluble films. L. S. THEOBALD.

**Adsorption of ions and sols by freshly-prepared precipitates and its influence on the formation of Liesegang rings. II.** A. C. CHATTERJI and S. C. VARMA (*Z. anorg. Chem.*, 1931, **196**, 247—256).—During the formation of lead chromate by the interaction of lead acetate and potassium chromate no chromate ions are adsorbed by the precipitate, but a part of the lead chromate goes into the aqueous phase as a result of the peptising action of the chromate ions. Freshly-precipitated and washed lead chromate does not adsorb more than 5% of chromate ions, and the amount adsorbed decreases with increase in the concentration of the potassium chromate. The freshly-prepared precipitate adsorbs a considerably greater amount of lead chromate sol. The adsorption of a sol of lead chromate stabilised by gelatin decreases as the concentration of gelatin increases and at sufficiently high concentrations of gelatin the adsorption is reduced to zero. This fact is believed to explain the difficulty of obtaining periodic structures of lead chromate in concentrated gelatin gels. The cause of the spaces between the bands of precipitate is traced to adsorption of the peptised sol by each band of precipitate and not to adsorption of the reacting electrolyte as assumed by Bradford. E. S. HEDGES.

**Adsorption compounds.** E. NEGRI (*Arch. Farm. sperim.*, 1931, **51**, 193—215).—The precipitation of tricalcium phosphate in an aqueous cod-liver oil emulsion by successive addition of phosphoric acid, calcium chloride, and ammonia results in the formation of a stable compound which liberates fat when treated with hydrochloric acid. The proportion of fat thus adsorbed gradually increases if the quantity of fat is kept constant while the adsorbing surface is increased. If, however, this surface remains unchanged while the amount of oil is increased, the adsorbed fat increases in absolute amount but diminishes relatively to the total amount of oil present. These results are considered to indicate the formation of adsorption compounds. T. H. POPE.

**Heats of wetting and of adsorption on zinc oxide.** W. W. EWING (*Ind. Eng. Chem.*, 1931, **23**, 427—429).—The heats of adsorption of gaseous carbon dioxide, sulphur dioxide, ammonia, water, benzene, xylene, and pyridine, and the heats of wetting of liquid water, benzene, xylene, pyridine, "nujol," linseed oil, and solutions of zinc oleate in benzene and in pyridine by zinc oxide have been measured. The effect of particle size of the pigment has also been studied, using water vapour as the adsorbed vapour. The heats of wetting or of adsorption vary with the nature of the liquid or gas, and the tenacity with which the adsorbed material is held, as measured by the speed of outgassing, also varies with the nature of the gas, but there seems to be no direct relation between the two. Carbon dioxide and pyridine have about the same heats of adsorption, but the former is readily released and the latter is not. The heat of adsorption of water is greater than its heat of wetting, perhaps indicating that the heat of adsorption is made up of the heat of wetting and the heat of condensation.

The heat of adsorption is directly proportional to the surface of the adsorbent and is independent of the size of the particles. E. S. HEDGES.

**Surface tensions of aqueous solutions of *p*-toluidine.** R. C. BROWN (*Phil. Mag.*, 1931, [vii], **11**, 686—690).—Values obtained by different methods are in fair agreement with those of Gans and Harkins (*cf. A.*, 1930, 991). N. M. BLIGH.

**Thermodynamic study of surface tension, affinity, and rate of adsorption. IX. Change of variables.** R. DEFAY (*Bull. Acad. roy. Belg.*, 1931, [v], **16**, 1425—1441).—Mathematical (*cf. A.*, 1930, 686). C. W. GIBBY.

**Thermodynamic study of surface tension, affinity, and rate of adsorption. X.** R. DEFAY (*Bull. Acad. roy. Belg.*, 1931, **17**, 73—89; *cf. A.*, 1930, 1109).—Mathematical. Equations similar to that of Duhem and Margules are derived for processes of adsorption. J. R. I. HEPBURN.

**Thermodynamic study of surface tension, affinity, and rate of adsorption. XI.** R. DEFAY (*Bull. Acad. roy. Belg.*, 1931, [v], **17**, 217—234).—Theoretical. A. J. MEE.

**Molecular theory of surface energy: the surface energy of the liquefied inert gases.** R. S. BRADLEY (*Phil. Mag.*, 1931, [vii], **11**, 846—849).—Mathematical. The calculated surface energy for argon and helium is in satisfactory agreement with observed values. N. M. BLIGH.

**Problems of the boundary state. (SIR) W. HARDY** (*Phil. Trans.*, 1931, **A. 230**, 1—37).—Films are considered as a fourth state of matter characterised by the sharing of the energy with the adjacent phases. The most promising view of the boundary state in liquids is that it is due to the formation of chains of highly-polarised molecules stretching through the lubricant from one enclosing solid to the other. Each chain has little strength in shear, great strength in tension, and in both the strength decreases as the chain lengthens. The intensity of polarisation at any level in a chain is the sum of two terms of the same sign contributed independently by the fields of attraction at the ends. The influence of each field diminishes as the distance from the solid face increases, and the least value of the sum of the two terms is at a mean value surface or surfaces. In the only instance in which the position is known with certainty the mean value surfaces for slip and for break coincide, but this is after the joint has been frozen. The Leslie pressure is considered as the osmotic pressure of the lubricant. If the molecular chains help to support the loading by their resistance in compression, in which case the expression for the Leslie pressure would include two terms, one representing the rigidity of the structure, the other representing the defect in mobility, the Leslie pressure becomes strictly analogous to the swelling pressure of a gel. Difficulties in the acceptance of a Leslie pressure in air and the presence of a complete air-gap are discussed. The total strength of all the chains of molecules in tension increases as the length of the molecules of which they are built increases, whilst the total strength of all the chains in shear decreases and, when allowance is made for perturbation due to

the end groups of atoms, the relation in both instances is always linear. When the length of the molecules is great enough strength in shear vanishes. The strength in tension must be due to the lateral fields of attraction of the molecules, at least as much as to the fields at the ends. The decrease in the strength in shear may be due merely to the increase in the moment of the applied force.

E. S. HEDGES.

**Optical investigation of thin metallic films, especially of silver.** W. REINDERS and L. HAMBURGER (Rec. trav. chim., 1931, 50, 351—376).—The light absorption and ultramicroscopic structure of thin silver films formed in a vacuum have been investigated. Their structure depends on their thickness, the temperature of their formation, and on the nature of the under-surface. Silver films formed in a high vacuum at the ordinary temperature and of average thickness of less than two atoms are invisible in the ultramicroscope, but slightly thicker films show a mosaic pattern of ultramicros. The invisible films of subatomic thickness were developed in various ways, but no method of carrying out this process gave a trustworthy record of the structure of the primary deposit. Using a solution of a silver salt as developer films as thin as  $10^{-10}$  to  $10^{-11}$  cm. or 0.001 atom average thickness could be developed, but development with metal vapours required considerably thicker films. The developed structure of these thin primary films shows no linked mosaic form, but only individual nuclei. This indicates that only a few of the larger aggregates formed are capable of development. Aggregates of three atoms can be developed, but single atoms or two-atom aggregates cannot. The particle size of these thin sublimates shows a frequency distribution according to a probability law. The mean nuclear size decreases with decreasing mobility of the atoms in the under-surface.

J. W. SMITH.

**Anomalous flow of a strong solution of lithium chloride through narrow glass tubes.** G. W. S. BLAIR and R. K. SCHOFFIELD (Phil. Mag., 1931, [vii], 11, 890—896).—Flow-pressure curves for nearly saturated solutions of lithium chloride were obtained and compared with those for glycerol-water mixtures of the same viscosity. The Poiseuille law is not obeyed. The curves are linear, but give a small intercept on the pressure axis, indicating that small strains are not dissipated immediately during flow, probably due to the tendency of the ions to maintain a non-random distribution. Using tubes of different radius and length, it was found that the simple  $r^4$  law (where  $r$  is the radius) is not exactly obeyed, indicating anomalous flow close to the wall of the tube.

N. M. BLIGH.

**Equilibria in osmotic systems in which forces act. II. Osmotic systems in which there is an active membrane permeable for more than one substance.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1133—1139; cf. this vol., 163).—The previous theoretical treatment is extended to the case of an active membrane permeable for more than one substance.

O. J. WALKER.

**Highly-polymerised compounds. L. Molecular complexity of compounds of high mol. wt.**

H. STAUDINGER (Z. physikal. Chem., 1931, 153, 391—424; cf. this vol., 465).—A summary of previous work on the determination of the mol. wts. of highly-polymerised compounds. Viscosity data, in particular, show that in dilute solutions of such compounds the dispersed particles are not micelles but single molecules of very high mol. wt., and there is good reason for believing that these large molecules persist in the solid state. It is considered that X-ray analysis in itself is of little value for the determination of molecular complexity.

R. CUTHILL.

**Temperature of maximum density of aqueous solutions. Deviations from the law of Despretz.** N. GREGG-WILSON and R. WRIGHT (J. Physical Chem., 1931, 35, 624—628).—The lowering of the temperature of maximum density of amine solutions shows that the law of Despretz does not hold for the more concentrated solutions. The relative densities at 5° and the coefficients of expansion between 12.5° and 15° are tabulated.

L. S. THEOBALD.

**Fictive volumes of sodium sulphate in aqueous solutions of sulphuric acid and of iodine in an aqueous solution of potassium iodide.** R. E. GIBSON (J. Physical Chem., 1931, 35, 690—699; cf. A., 1927, 508).—The specific volumes of solutions of sodium sulphate in approximately 5% and in 10% sulphuric acid at 25° are used to calculate the fictive volume of sodium sulphate in these solutions. The curves connecting this with concentration show peculiarities which are correlated with the formation of sodium hydrogen sulphate in solution. The specific volumes of iodine in a 49% solution of potassium iodide at 25° show that the fictive volume of the iodine for solutions containing 10—50% I is 0.2396 c.c. per g. A large amount of interaction between iodine and potassium iodide is thus precluded.

L. S. THEOBALD.

**Volume of electrolyte solutions.** O. REDLICH (Naturwiss., 1931, 19, 251).—From the Debye-Hückel theory it is deduced that the partial molar volume of an electrolyte in dilute solution is a linear function of the square root of the concentration. This relation agrees with the experimental data and is of value for the determination of the partial molar volume at infinite dilution.

R. CUTHILL.

**Viscosity of electrolytes.** H. FALKENHAGEN (Nature, 1931, 127, 439—440).—A discussion.

L. S. THEOBALD.

**Dielectric constants of solutions of electrolytes.** R. FÜRTH (Physikal. Z., 1931, 32, 184—187).—The dielectric constant decreases rapidly with increasing concentration, passes through a minimum, and then increases continuously. The significance of this general observation is discussed.

W. GOOD.

**Colloids prepared by molecular stream condensation methods. I. Organosols of alkali metals.** A. J. RABINOVITSCH, V. A. KARGIN, and E. B. FODIMAN (Kolloid-Z., 1931, 54, 288—295).—An improvement on the method of Roginsky and Schalnikov (A., 1927, 1137) for preparing organosols of the alkali metals by the simultaneous condensation of the vapours of the metal and the organic liquid is described and a method developed for measuring the

electrical conductivity and cataphoretic migration velocity of these sols in a vacuum. All the organosols obtained were negatively charged. Sols of sodium in ethyl ether and ethylamine, and sols of potassium in ethyl ether, ethylamine, and propylamine prepared by this means are fairly stable; they coagulate slowly in the dark and rapidly in the light. Attempts to prepare pure potassium sols in benzene, toluene, and tripropylamine were unsuccessful, the solvent undergoing decomposition. The sols may be purified by a second condensation and they are then more stable and have a higher cataphoretic migration velocity. After repeated purification sols of sodium and potassium in ethyl ether and sols of potassium in propylamine and ethylamine precipitate to form the compact metal. The electrical evidence leads to the view that the surface of the particles is the seat of ionogenic groups, the alkali metal cation being directed towards the dispersion medium. Both potassium and sodium sols in ethylamine contain the metal partly in a molecularly dispersed form. The molecular solutions are left when the colloidal dispersed particles coagulate.

E. S. HEDGES.

**Colloidal synthesis of readily crystallisable organic substances.** N. VON WEIMARN (Kolloid-Z., 1931, 54, 296—306).—Colloidal solutions of naphthalene, papaverine, camphor, salol, and benzophenone are not stable for more than a few seconds at the ordinary temperature, but may be kept stable indefinitely at  $-80^{\circ}$  in the form of a glass, the dispersion medium being 68% sucrose solution. A very stable sol of anthracene may be prepared by pouring a 0.025% alcoholic solution of anthracene into a large volume of water, with vigorous stirring. Phenanthrene sols can be prepared similarly, but are less stable in virtue of the greater solubility; they are fairly stable at  $0^{\circ}$  when the dispersion medium contains sucrose. Anthraquinone sols prepared in this way are more stable. Anthracene and phenanthrene sols are described as unidimensional colloids, the crystalline particles being of microscopic size in two directions and of colloidal thickness. Anthraquinone forms a two-dimensional colloid, the length of the particles exceeding colloidal size.

E. S. HEDGES.

[Relations of] gum arabic to colloidal silver and gold. J. VOIGT (Kolloid-Z., 1931, 54, 307—310).—Pure gum arabic has no reducing action on silver oxide or chloroauric acid solutions either with or without the aid of ultra-violet radiation. The protective effect of gum arabic, however, is reduced by irradiation with ultra-violet light and simultaneously the viscosity of the sol decreases. Arabic acid has a different absorption spectrum after the irradiation. The use of gum arabic sols as a vehicle for the injection of colloidal silver is discussed.

E. S. HEDGES.

**Physico-chemical properties of gum arabic-water systems and their interpretation.** R. TAFT and L. E. MALM (J. Physical Chem., 1931, 35, 874—892).—The viscosities, densities,  $f. p.$ ,  $p_H$  values, and conductivities of gum arabic-water systems have been determined. In agreement with Thomas and Murray (A., 1928, 706), most of the properties are best explained by the assumption that purified gum arabic

is a strong organic electrolyte of high equivalent weight and not a distinct colloidal phase.

L. S. THEOBALD.

**Diffusion of colloid particles. I. Abnormally high diffusion velocities in hydrophilic sols. II. New ion effect in hydrophilic sols.** H. R. BRUNS (Kolloid-Z., 1931, 54, 265—272, 272—278.—I. An apparatus previously described (this vol., 302) has been used to determine the diffusion velocities of the particles of two kinds of soluble starch and of gum arabic. In each case exceptionally high values were obtained and the diffusion constants were higher the more readily soluble were the colloids and the more stable the sols. From the diffusion constants the values 1.9 and 1.4  $m\mu$  were calculated for the radii of the particles of two different soluble starch sols, and 0.85  $m\mu$  for gum arabic particles. The values are thus not far removed from those obtained for true molecular solutions and are scarcely consistent with viscosimetric and dialysis data. The anomalies cannot be explained by the presence of an equilibrium portion of the colloid in the molecular state of solution, nor by the presence of electrolytes.

II. The diffusion constants of sols of soluble starch and of gum arabic are lowered very considerably by adding small quantities of electrolytes. The effect is relatively greatest at low concentrations (1 milliequiv. per litre), and further additions produce little more change. The magnitude of the decrease in diffusion velocity increases with the valency of the ion with an opposite charge to that of the colloid; on the other hand, the effect produced by the ion of similar charge to the colloid decreases with increasing valency of the ion and is in general less marked.

E. S. HEDGES.

**Dispersoidological study of silver salts in aqueous alcohol, acetone, and diethyl ketone solutions. I.** S. ISHII (Bull. Chem. Soc. Japan, 1931, 6, 53—60).—The solubility of highly purified silver iodide in solutions of potassium iodide in aqueous ethyl alcohol and aqueous acetone of varying composition has been measured and the results are expressed graphically. The decrease in solubility when acetone is diluted with water corresponds with the increase of dielectric constant of the mixture.

E. S. HEDGES.

**Polyatomic hydroxy-compounds in the synthesis of electronegative sols. VII. Formation of ferric hydroxide sols in the presence of polymeric carbohydrates.** A. DUMANSKI and V. S. PUTSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 2249—2259).—The systems ferric chloride-sodium hydroxide or ammonia-polysaccharide are represented graphically, using triangular co-ordinates. The diagrams obtained with inulin and dextrin are the most similar to those previously obtained for monoses. The peptising action of the various carbohydrates studied increases in the order: inulin > dextrin > soluble starch > gum arabic. The protective action of gum arabic is, however, greater than that of starch. The peptising action diminishes after a certain point with increasing alkalinity, and is greater at the same alkalinity using sodium hydroxide than ammonia. The peptising action of polysaccharides is on the whole feebler than that of monoses.

R. TRUSZKOWSKI.

**Specific inductive capacity and mol. wt. of colloids.** N. MARINESCO (Compt. rend., 1931, 192, 625—628).—The mol. wt. of a colloid can be determined from the equation  $M = \lambda RT / 3c\eta v$ , where  $\lambda$  is the wave-length of anomalous dispersion of the dissolved colloid,  $R$  the gas constant,  $T$  the absolute temperature,  $c$  the velocity of light,  $\eta$  the viscosity, and  $v$  the specific volume of the colloid in solution. Calculated in this way the mol. wt. of gelatin is 11,300.

C. A. STLBERRAD.

**Dielectric constant of protein solutions. I. Zein.** J. WYMAN, jun. (J. Biol. Chem., 1931, 90, 443—476).—Two methods, based on resonance, are described for measuring the dielectric constant of solutions of zein in 70% *n*-propyl alcohol. Anomalous dispersion is present, and the zein molecule is highly polar; a value of  $60 \times 10^{-18}$  e.s.u. is deduced for the permanent electric moment. Gelation of zein solutions on keeping is not accompanied by a change in dielectric constant.

A. COHEN.

**Graphical method for calculation of partial specific volumes of proteins.** T. KATSURAI (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 7—8).—In the determination of the mol. wt. of proteins by the ultracentrifugal method the partial specific volume of the protein is calculated from pycnometric measurements. A graphic method which enables the specific volume to be read directly from the density of the solution is described.

E. S. HEDGES.

**Dielectric constant and structure of thixotropic sols.** S. S. KISTLER (J. Physical Chem., 1931, 35, 815—829).—The degree of hydration derived from the dielectric constants increases with the oscillation frequency. With a wave-length of 32.7 cm. dialysed sols of aluminium and ferric oxides show little hydration until an electrolyte is added. The first small addition of electrolyte produces the largest depression of the dielectric constant, which is very near to that of water. No change of the dielectric constant of the thixotropic sols before and after gelation could be detected. The viscosity of the intermicellar solution is practically the same in the gel and in the sol before gelation. Thixotropy is best explained by the assumption that some form of oriented anisotropy of the water, probably chains of water molecules, extends from the surface of each colloidal particle and tends to link it with those surrounding it.

L. S. THEOBALD.

**Colloidal ferric oxide and various factors which influence its ability to catalyse the decomposition of hydrogen peroxide.** R. J. KEPFER and J. H. WALTON (J. Physical Chem., 1931, 35, 557—577).—The decomposition of aqueous solutions of hydrogen peroxide by colloidal ferric oxide, prepared by the method of Sorum (A., 1928, 703), has been investigated in the dark at 30—60°. The reaction is approximately unimolecular, but the values of  $k$  increase as the reaction progresses. Between 30° and 60°,  $k_{t+10}/k_t$  is approximately 2.33, indicating that the decomposition is a true chemical reaction independent of a process of diffusion. Doubling the concentration of catalyst between the limits 0.286 and 2.281 g. per litre increases the rate of decomposition

2.2 times. The effect of additions of sodium or barium chloride, potassium sulphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, hydrochloric acid, sodium hydroxide, and copper sulphate has also been determined. For the first three electrolytes, the curves show (i) a marked decrease in catalytic activity followed by a gradual decrease, both of which are due to adsorption of chloride ions by the sol, (ii) a second marked decrease due to coagulation of the sol, and (iii) a region of little change corresponding with further adsorption of electrolyte by the coagulated sol. For the other electrolytes modified curves are obtained and these are explained by changes in the stability of the solutions of hydrogen peroxide. A mechanism involving the formation of ferric acid or a higher oxide of iron as an intermediate compound is suggested.

L. S. THEOBALD.

**Liquid ammonia as a lyophilic dispersion medium. II. Ammono-gels of cellulose acetate.** R. TAFT and J. E. STARECK (J. Physical Chem., 1931, 35, 578—587; cf. this vol., 164).—Cellulose acetate is readily dispersible in liquid ammonia, and sols containing 60 g. or more of the acetate in 100 c.c. of the medium have been obtained. Two types of gels, one heat-reversible and the other heat-irreversible, have been obtained; the former results when a sol of 10 g. of acetate in 100 c.c. of liquid ammonia is kept in a bath of boiling ammonia for several days, and the latter when a sol is allowed to warm to the ordinary temperature. The setting points of the reversible gels are lower than their m. p. The time required for gelation of the irreversible gels depends on concentration, temperature, and water content of the dispersion medium. The effect of water on dispersion in liquid ammonia has also been determined. Small quantities of cellulose acetate can be dispersed in the presence of large amounts of water, and as little as 0.05 g. of acetate in 100 c.c. of liquid ammonia may give rise to a gel. The gels form more rapidly and are firmer in structure at an optimum concentration of water, but in the absence of water precipitation takes place.

L. S. THEOBALD.

**Determination of the hydrogen-ion concentration in gold sols.** T. R. BOLAM and J. CROWE (J. Physical Chem., 1931, 35, 602—610).—The conditions affecting the determination of hydrogen-ion concentration in gold sols by means of the hydrogen electrode have been investigated. This electrode gives satisfactory results with Nordenson sols or with sols prepared by Zsigmondy's method and buffered with alkaline phosphate, or with Zsigmondy's sols in which potassium carbonate is replaced by sodium citrate. In the unbuffered Zsigmondy sols the displaced *E.M.F.* is attributed to the removal of carbon dioxide by the hydrogen used. Curves showing the change in  $p_H$  of the gold sol with increasing concentration of sodium (as hydroxide, phosphate, or citrate) are given. The unsatisfactory behaviour of the electrode reported by previous investigators is discussed.

L. S. THEOBALD.

**Optimum conditions for the formation of silica gel from alkali silicate solutions. II.** R. C. RAY and P. B. GANGULY (J. Physical Chem.,



1931, 35, 596—601; cf. A., 1930, 413).—Previous work has been extended to solutions of sodium silicate in which the ratio  $\text{Na}_2\text{O} : \text{SiO}_2$  is 1 : 3.3 and 1 : 4.0. The curves enclosing the area of gel formation are similar to that obtained (*loc. cit.*) for the ratio 1 : 2.25. The presence of silica in the higher ratio solutions either as colloidal aggregates or as definite complex silicate ions does not affect the conditions of gel formation to any extent. Provided that dilution is sufficient to prevent gel formation, solutions of sodium silicate can be titrated against ferric chloride with potassium ferrocyanide as indicator. The heats of reaction for ferric chloride and sodium silicate decrease as the ratio  $\text{SiO}_2 : \text{Na}_2\text{O}$  increases; this is taken to indicate that different ferric silicates are formed in solution. L. S. THEOBALD.

**Influence of heating on formation of ultramicroscopic particles in salt crystals.** R. MATTHÄI (*Z. Physik*, 1931, 68, 85—96).—Determinations of the number of ultramicroscopic particles in transparent crystals show the influence of impurities in quantities too small for detection chemically. The number of ultramicroscopic particles in natural and artificial rock salt reaches a definite value when the crystal is raised to a definite temperature; it reaches a maximum at  $400^\circ$ , and vanishes just below the m. p. The increase may be attributed to coagulation, and the diminution to dissolution in the crystal. The impurity, therefore, is least dispersed at  $400^\circ$ . This agrees with the minimum light absorption at this temperature, assuming the impurity to be the absorbing medium. A. B. D. CASSIE.

**Temperature and stability of colloidal solutions.** S. I. DJATSCHKOVSKI (*Kolloid-Z.*, 1931, 54, 278—284).—The effect of low temperatures on the stability of a large number of colloidal solutions has been studied in some cases by observation of the coagulation process and in others by measuring the electrical conductivity of the sol before and after freezing. The general results show that typical hydrophilic colloids, such as albumin, hæmoglobin, tungstic acid, etc., do not coagulate at low temperatures; semi-colloids of the type of soaps and starch coagulate incompletely and reversibly, the coagulum going into solution again on warming. Protected sols do not coagulate. Non-dialysed silicic acid coagulates and hydrophobic sols in general coagulate. Well-dialysed sols of ferric hydroxide give a "schlieren" effect after freezing due to the production of an ultramicrocrystalline suspension. Non-dialysed sols of ferric hydroxide are not coagulated by freezing, indicating that the presence of electrolytes has a protective effect. The addition of alcohol also protects most colloids from coagulation by freezing. Whether the colloid is coagulated or not, a certain amount of it always remains in the form of a sol. By a step-wise lowering of temperature or by freezing sols for different intervals of time fractional coagulation of the sol may be effected, the coarser particles suffering coagulation first. E. S. HEDGES.

**Effect of stirring on the rate of coagulation of gold sol.** E. JONES (*Trans. Faraday Soc.*, 1931, 27, 51—58).—The coagulation of a gold sol by electrolytes under controllable conditions of stirring has been

investigated. Stirring produces a marked acceleration in coagulation when the concentration of electrolyte is sufficiently great to cause rapid coagulation. The formation of air bubbles in the sol is partly effective in causing this acceleration. Coagulation is retarded or inhibited by stirring when the electrolyte concentration is such as to give rise to slow coagulation. This may be accounted for by a disruption of the incomplete outer layer of the double layer on the particles, causing a temporary increase of charge, and, in consequence, a decrease in coagulation velocity. F. G. TRYHORN.

**Mechanism of the mutual coagulation process.** H. B. WEISER and T. S. CHAPMAN (*J. Physical Chem.*, 1931, 35, 543—556).—The mutual coagulation of standard sols of varied types has been studied. Complete mutual coagulation of two sols of opposite sign may take place over a range of concentrations which may be either narrow or wide. Further, for a given series of positive sols, the order of optimum concentration for mutual coagulation may vary widely with the nature of the negative sols. These facts are explained on the view that the precipitating power of positive for negative sols is not determined solely by the charge on the particles. Mutual adsorption of colloidal particles independent of charge, the presence of precipitating ions as impurities in the sols, and interaction between stabilising ions are all factors which affect the mutual coagulation process. Complete mutual coagulation is not, in general, due to interaction and removal of the stabilising electrolytes of the oppositely charged sols, although this factor may play an important part in some cases. L. S. THEOBALD.

**Action of electrolytes on substantive dyes.** L. MEUNIER and M. LESBRE (*Compt. rend.*, 1931, 192, 840—842).—The colour of a solution of Congo-red in pure water changes to blue on the gradual addition of an electrolyte, and coagulates with precipitation of blue particles consisting of larger blue and smaller red particles. In small concentration an electrolyte (*e.g.*, 0.005*N*-sodium chloride) has a protective effect on a 0.005% solution of the dye, although the subsequent addition of a large amount of electrolyte (*e.g.*, 0.2*N* in sodium chloride) produces coagulation. A solution which exhibits protective action shows a maximum transmission for light of 6100 Å., and consequently maximum dispersion, which explains the protective effect (*cf.* Boutaric, A., 1925, ii, 863). The concentrations at which different electrolytes cause the colour change in a 0.001% solution of the dye are in agreement with the Schulze-Hardy law. C. A. SILBERRAD.

**Kinetic study of Liesegang rings.** L. BULL and (MLLE.) S. VEIL (*Compt. rend.*, 1931, 192, 682—683; *cf.* this vol., 301).—A further graphic study of the formation of Liesegang rings, an image of the drop of silver nitrate on the dichromated gelatin being passed through a slit on to a moving photographic film. The velocity of diffusion varies inversely as the square root of the time, and the production of a principal ring causes a temporary retardation of the diffusion. C. A. SILBERRAD.

**Periodicity and its basis.** M. COPISAROV (*Kolloid-Z.*, 1931, 54, 257—265).—A review is made of

the conditions for the formation of different types of periodic structures involving the operation of mechanical, physical, and chemical factors. An attempt is made to embrace the most diverse forms of periodic structures and chemical reactions from the point of view that they are forms of expression of a periodic principle. Some experiments on the formation of periodic structures by the condensation of vapours are also described. When carbon dioxide is released rapidly from a cylinder and led through a long glass tube cooled in ether, solid carbon dioxide appears in the form of bands along the sides of the tube. A similar periodic structure appears in the sublimate produced when ammonium carbonate is heated in a long glass tube closed at one end; carb-amido gives a less marked effect. When magnesium is ignited near the closed end of the tube, bands of magnesium oxide are formed along the tube. In some cases a spiral structure is obtained instead of discontinuous bands, and an analogy with the helical course of the explosion wave in gaseous mixtures described by Campbell and Finch (A., 1928, 1099) is suggested. Bands of ammonium carbamate have been obtained in the diffusion of dry ammonia and carbon dioxide towards each other in a glass tube (cf. Hedges, A., 1929, 1154). E. S. HEDGES.

**Influence of light on the osmotic pressure of certain colloidal solutions.** I. S. HORIBA and H. BABA (Chikashige Anniv. Vol., 1930, 245—260).—The osmotic pressure of colloidal solutions of carbon, silver, gold, ferric hydroxide, arsenious sulphide, Prussian-blue, Congo-red, and haemoglobin is increased by exposure to visible radiation; no effect is observed with a gelatin sol. In many cases the conductivity undergoes a parallel change. Possible causes of the phenomena are discussed. H. F. GILLBE.

**Pectography. Study of solutions by progressive desiccation.** P. BARY (J. Chim. phys., 1931, 28, 1—13).—A microscopical study has been made of the washed dry deposit formed on a slide placed in an inclined position in a small beaker containing the solution to be investigated, which is then allowed to evaporate slowly (e.g., at 60° for aqueous solutions). The nature of the deposit is dependent on the temperature, the vapour pressure of the solvent, the rate of removal of the vapour, and on the nature of the solvent and solute, and always falls into one of three classes, viz., crystalline, amorphous (points or small filaments), or continuous without visible structure. The addition of hydrophilic colloids to aqueous solutions of crystallisable substances modifies or suppresses the crystalline form, whilst such colloids alone give scaly films. With simple suspensions a striped pattern results owing to progressive coagulation on concentration. Pectographs of typical crystalloid and colloidal solutions, including those of metallic oxides and sulphides, gums, tannins, colouring matters, etc., are illustrated and discussed. Pectographs of colouring matters are dependent on the rate of evaporation and on the chemical constitution, and in their stablest forms the deposits are usually composed of gels or lyophobic granules. The bearing of the results on the production of periodic formations is discussed and it is shown that simple colloidal

solutions may be differentiated from suspensions in that (1) they tend to form gels, (2) the Tyndall effect is absent, (3) they show the Schwedov rigidity effect, (4) they obey an exponential viscosity-concentration law instead of Einstein's linear law.

J. GRANT.

**Hydroxide systems in ferric oxide colours.** H. WAGNER (Kolloid-Z., 1931, 54, 310—314).—A microscopical and X-ray spectrographic examination of technically important ferric oxide products has been carried out. The accepted views of the course of ageing of ferric hydroxide and aluminium silicate systems are applicable to these substances. Mars-yellow has an amorphous structure, whilst ferric oxide-yellow and ferrite-yellow have a goethite space lattice. Mars-yellow usually gives a calcium carbonate X-ray diagram and sienna generally gives lines due to hydrated silica in addition to those of goethite. A method for the characterisation of ochre by selective adsorption of dyes has been worked out and affords a distinction between the German material rich in amorphous hydrates and the French product which is aged and contains kaolin. E. S. HEDGES.

**Electrophoretic velocities of gelatin and ovalbumin in different concentrations of their mixtures and the effect of ultra-violet irradiation.** E. B. R. PRIDEAUX and F. O. HOWITT (Biochem. J., 1931, 25, 391—402).—The mean velocities of albumin are higher than those of gelatin both in acid and in alkaline solutions. Neither the curve of gelatin nor that of albumin is symmetrical on the acid and alkaline side of the isoelectric point. On the acid side the velocities increase rapidly with diminishing  $p_H$  to a maximum and then fall. On the alkaline side the velocities increase up to  $p_H$  6—7, then fall, and reach a constant or nearly constant value which is lower and more nearly constant in the case of gelatin. Mixtures of gelatin and albumin behave anomalously. S. S. ZILVA.

**Mechanism of plastic flow.** G. E. CUNNINGHAM (J. Physical Chem., 1931, 35, 796—814).—The water retained by clay suspensions centrifuged at different speeds varies with the centrifugal force. The effect of external pressure on the mobility of clay pastes has been quantitatively determined. With thick pastes, mobility decreases at low pressures, increases beyond its original value at intermediate pressures, and decreases again at higher pressures. Plasticity is due to the ability of the plastic material to experience a change in mobility under the influence of an applied pressure which may be independent of the shearing force. L. S. THEOBALD.

**Thermodynamic equilibrium in a static Einstein universe.** R. C. TOLMAN (Proc. Nat. Acad. Sci., 1931, 17, 153—160).

**Graphic method of calculating equilibrium in the water gas reaction.** P. MONTAGNE (Compt. rend., 1931, 192, 677—679).—An application of the graphic method previously described (cf. A., 1929, 138).

**Vapour pressure of liquids. II. Vapour pressure, Henry's constant, and osmotic pressure of concentrated solutions.** K. WATANABE (Sci. Rep. Tokyo Bunrika Daigaku, 1931, A, 1, 67—84; cf.

A., 1930, 1357).—Theoretical. A general equation is derived for the vapour pressure of a solution. This agrees with van Laar's equation for substances which satisfy the van der Waals relation. Further equations are derived for Henry's constant and for the osmotic pressure.

H. F. GILLBE.

**Spectroscopic investigation of the dissociation relations in aqueous solutions of lead and thallos halides.** H. FROMHERZ and K. H. LIH (Z. physikal. Chem., 1931, 153, 321—375; cf. A., 1930, 1234).—The extinction curves for aqueous solutions of lead perchlorate, chloride, bromide, and iodide, of the corresponding thallos salts, and for solutions containing the halides of these metals and lithium or potassium halides have been determined over a range of concentration extending from near saturation to high dilutions. The absorption curves of the lead and thallos salts in dilute pure solution represent solely the absorption of the halogen ion and the simple hydrated metal ion; contrary to the assumption of Koch (A., 1929, 1364), there is no evidence of the presence of undissociated molecules in any appreciable quantity. In solutions of lead halides of higher concentrations, however, complex ions of the type  $PbX'$  are present. The dissociation constants of the complex chloride, bromide, and iodide ions have been found to be in the ratios 2.225 : 2.066 : 1, respectively. In the case of thallos halides, ionic association is detectable only in nearly saturated solutions. In presence of alkali halides at concentrations exceeding about 4*N*, lead and thallos halides are almost completely transformed into complex ions, possibly  $PbX_4''$  and  $TlX_3''$ , respectively. As the alkali halide concentration falls, however, there is a continuous transition from these complex ions through indefinite mixtures of ions of various compositions to the ions  $Pb''$ ,  $PbX'$ , and  $X'$  in the case of lead halides, and to the simple metal and halogen ions with the thallos halides. None of the solutions affords evidence of undissociated molecules of lead or thallos salt.

R. CUTHILL.

**Behaviour of phosphate buffer mixtures with different cations.** S. M. NEUSCHLOSZ and R. P. INÁÑEZ (Biochem. Z., 1931, 232, 106—122).—The equations of Sørensen are modified. In mixtures of primary and secondary ammonium phosphate, the  $p_H$  is always smaller than for the corresponding potassium phosphate mixtures, due partly to a decrease in the activity of  $HPO_4$  ions in presence of  $NH_4$  ions and partly to the hydrolysis of the secondary ammonium phosphate. A buffer equation for ammonium phosphate mixtures is developed, and agrees closely with the values obtained. The difference in acidity of potassium and ammonium phosphate mixtures increases as the total phosphate increases and also when sodium chloride is added to the mixture. The osmotic and conductivity factors of diammonium hydrogen phosphate are smaller than for dipotassium hydrogen phosphate of the same concentration. The primary phosphates of the two bases do not show these differences.

P. W. CLUTTERBUCK.

**Apparent dissociation constants of phenylalanine and of dihydroxyphenylalanine and the apparent free energy and entropy changes of**

**certain amino-acids due to ionisation.** S. MIYAMOTO and C. L. A. SCHMIDT (J. Biol. Chem., 1931, 90, 165—178).—The titration curves of phenylalanine and dihydroxyphenylalanine have been examined and the apparent dissociation constants of a number of amino-acids in water at 25° derived. The free energy changes and the entropy changes of a large number of naturally occurring amino-acids have been calculated from the apparent dissociation constants. It is shown that no appreciable error results when concentration is used instead of activity in calculating the primary dissociation constant of aspartic acid and of glutamic acid. The values of  $K_a$  of aspartic and of glutamic acid derived from f.-p. data are compared with those calculated from a combination of electro-metric and f.-p. data.

W. O. KERMAK.

**Hydrolysis measurements in beryllium halide solutions.** M. PRYTZ (Z. anorg. Chem., 1931, 197, 103—112).—The  $p_H$  curves for 0.005—0.1*M* beryllium bromide and iodide when titrated with *M*-sodium hydroxide have been determined, and the mechanism previously suggested for the hydrolysis of the chloride and sulphate (A., 1929, 883) has been confirmed. The hydrolytic constant  $K_0$  is for the bromide  $5.9 \times 10^{-7}$  and for the iodide  $4.4 \times 10^{-7}$ . As with the sulphate and chloride, a precipitate is formed only when more than one equivalent of sodium hydroxide has been added, and the precipitate has the composition  $Be_2O_3H_2$ . The solubility product  $[Be_2O''][OH']^2$ , calculated from measurements with the bromide, is  $2.7 \times 10^{-19}$ , and from the iodide measurements is  $3.3 \times 10^{-19}$ . The final point of inflexion on the titration curve coincides exactly with the addition of two equivalents of sodium hydroxide.

H. F. GILLBE.

**Hydrolysis of zinc sulphate solutions, solubility product of hydrous zinc oxide, and composition of the latter precipitated from zinc sulphate solutions.** I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1931, 53, 832—842; cf. this vol., 585).—Identical values of  $p_H$  are obtained for 0.01—0.1*M* zinc sulphate solutions at 25° by the use of the hydrogen electrode and methyl-red. The hydrolysis constant,  $[ZnOH^+][aH^+]/[Zn^{2+}]$ , is  $2.2 \times 10^{-10}$  and thus zinc hydroxide is a strong monoacid base. The second ionisation constant is  $4.4 \pm 0.4 \times 10^{-5}$  at 25°. The  $p_H$  (6.13—6.22) of 0.05*M* zinc sulphate at 25° saturated with zinc oxide or hydroxide is independent of the origin of the latter. Titration of 0.05*M* zinc sulphate with sodium hydroxide results in the precipitation of hydrous zinc oxide at  $p_H$  6.17; the solubility at 25° is thus about  $10^{-6}$ *M*. The composition of the hydrous oxide is approximately constant during the entire precipitation and corresponds with a basic salt,  $3ZnO \cdot ZnSO_4 \cdot xH_2O$ . This substance is stable at the ordinary temperature, but at 80° it gradually becomes more basic and the  $p_H$  of the supernatant solution decreases.

J. G. A. GRIFFITHS.

**Dynamic azeotropism. II.** (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], 16, 1412—1424; cf. A., 1930, 292).—Mathematical.

C. W. GIBBY.

**Dynamic azeotropism. III.** (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], 17, 47—59; cf.

A., 1930, 1106).—Theoretical. The Gibbs-Konowalow and Duhem-Margules theorems, previously derived for ternary systems, are extended to systems with any number of components. A new form of the law of displacement of equilibrium is derived.

J. R. I. HEPBURN.

**Dynamic azeotropism. IV.** (MLLE.) G. SCHOOLS (Bull. Acad. roy. Belg., 1931, [v], 17, 191—202).—Theoretical. The generalised Duhem-Margules equation is applied first to binary systems, and then to the more general case of systems with several constituents.

A. J. MEE.

**Vapour-pressure depressions of aqueous solutions of phosphate buffer mixtures at 20.3°.** A. GROLLMAN (Biochem. J., 1931, 25, 166—168).—Data are given for *M*/15 aqueous solutions of monopotassium and of disodium phosphate, and for mixtures of these salts.

S. S. ZILVA.

**Lowering of vapour pressure of water by dissolved electrolytes.** J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1140—1160).—The relative lowering of the vapour pressure of water has been derived from the thermodynamic potentials of the two components of a binary system without introducing the conceptions of fugacity or activity:  $(p_0 - p)/p_0 x = i - \psi x^{1/2} + \rho x - \sigma x^{3/2} + \dots$ . For binary electrolytes  $i = 2$  and  $\psi$  is approximately 5 at 20°, and neither of these terms is affected by the state of association of the water. The coefficients  $\rho$ ,  $\sigma$ , etc. depend on the mutual physical influence of the two components. The equation has been tested by means of the data available in the literature for solutions of the alkali halides and of potassium nitrate for values of  $x$  (mol. fraction of solute) between 0.001 and 0.14, *i.e.*, up to the saturation concentration in some cases, and in general good agreement is found between the experimental and calculated values.

O. J. WALKER.

**Activity coefficient of a non-electrolyte in aqueous salt solutions from solubility measurements.** J. W. BELTON (Proc. Leeds Phil. Soc., 1931, 2, 178—182).—From measurements of the solubility of *N*-chloroacetanilide in solutions of sodium chloride, barium chloride, and magnesium sulphate at 25° its activity coefficient,  $f$ , has been calculated. For each salt solution  $\log f = \text{constant} \times \mu$ , provided that  $\mu$ , the ionic strength, does not exceed 4. At low salt concentrations slight deviations from this equation are, however, observed.

R. CUTHILL.

**Solubility of acids in solutions of salts. V.** Temperature coefficient of activity coefficients of benzoic acid molecule in solutions of sodium chloride, potassium chloride, and sodium benzoate. E. LARSSON (Z. physikal. Chem., 1931, 153, 466—470; cf. this vol., 431).—From measurements of the solubility of benzoic acid in solutions of the chlorides at 0.2° and 25° and in solutions of the benzoate at 0.2° the activity coefficients of the benzoic acid molecule in the various solutions have been calculated. The activity coefficient in sodium chloride solutions does not vary with the temperature, and that in potassium chloride solutions increases only slightly as the temperature rises. The activity

coefficients in sodium benzoate solutions are, however, considerably greater at 0.2° than at 18°.

R. CUTHILL.

**Solubility and activity of silver benzoate and silver nitrate in concentrated salt solutions.** E. LARSSON and B. ADELL (Z. anorg. Chem., 1931, 196, 354—363).—The solubilities at 18° of silver benzoate and acetate in solutions of sodium, potassium, and barium nitrates, and sodium acetate have been measured. The relation between the calculated activity coefficients and the ionic strengths of the solutions is in good agreement with the Debye-Hückel theory if suitable values are chosen in each case for the constants. The activity coefficients of the two silver salts in sodium and potassium nitrate solutions of the same ionic concentration are almost identical; in sodium acetate solutions the activity coefficients of both salts are strongly depressed.

H. F. GILLBE.

**Vapour pressure and heat of dilution. VII.** Vapour pressures of aqueous solutions of sodium hydroxide and of alcoholic solutions of calcium chloride. (MISS) A. M. HAYWARD and E. P. PERMAN (Trans. Faraday Soc., 1931, 27, 59—69).—The air-bubbling method has been used to determine, over wide ranges of concentration, the vapour pressures of aqueous solutions of sodium hydroxide at 30°, 45°, 60°, 70°, and 80°, and of alcoholic solutions of calcium chloride at 20°, 30°, 40°, 50°, and 60°. From these data the respective heats of dilution have been computed by means of the Kirchhoff equation, and of the Porter modification of this equation. The respective osmotic pressures were computed by the use of the perfect gas law.

F. G. TRYHORN.

**Activity coefficients and adsorption of organic solutes. I. *n*-Butyl alcohol in aqueous solution by the f.-p. method.** W. D. HARKINS and R. W. WAMPLER (J. Amer. Chem. Soc., 1931, 53, 850—859).—The depression of the f. p. of water by *n*-butyl alcohol at concentrations between 0.001 and 1.0 *M* has been determined to within 0.00001°. The activity coefficients of the alcohol at 1.0, 0.5, and 0.1 molal concentrations are 0.8227, 0.8681, and 0.9433, respectively. The application of the adsorption equation to existing surface tension data indicates that the film of the alcohol on its aqueous solutions is unimolecular, each molecule occupying an area of 23.7 sq. Å.

J. G. A. GRIFFITHS.

**Activity coefficients of the lead halides and the normal electrode potential of lead.** H. FROMHERZ (Z. physikal. Chem., 1931, 153, 376—390).—The activity coefficients of lead chloride in aqueous solution obtained from solubility and *E.M.F.* data by assuming complete ionisation have been corrected for the presence in the solutions of the  $\text{PbCl}^+$  ion (cf. this vol., 565); at concentrations up to 0.04 *M*, the new values are identical with those for barium chloride at corresponding concentrations. These new data have been used to correct the solubility product, and by combining this with the potential of the electrode  $\text{Pb}|\text{PbCl}_2(\text{solid}), \text{KCl}$  the value of 0.1274 volt is deduced for the normal electrode potential of lead at 25° referred to the hydrogen electrode. The same value is also derived from solubility and *E.M.F.*

data for lead bromide and iodide by assuming that the activity coefficients of these salts are equal to that of barium chloride in a solution of the same ionic strength. The equilibrium constants and affinities of the reactions  $\text{PbCl}' \rightleftharpoons \text{Pb}'' + \text{Cl}'$ ,  $\text{PbBr}' \rightleftharpoons \text{Pb}'' + \text{Br}'$ , and  $\text{PbI}' \rightleftharpoons \text{Pb}'' + \text{I}'$  have been calculated.

R. CUTHILL.

**Free energy of some copper compounds.** M. RANDALL, R. F. NIELSEN, and G. H. WEST (Ind. Eng. Chem., 1931, 23, 388—400).—A review of the available data relating to copper, and the oxides, sulphates, and sulphides of copper leads to the following values for the free energies of substances which are important in the thermodynamical study of the metallurgy of copper. Copper (vapour) +78,944, copper (liquid) +2282, copper (solid) 0, copper (in saturated amalgam) 0, copper (diatomic vapour) +82,565, cupric oxide (liquid) -19,469, cupric oxide (solid) -30,300, cupric hydroxide (solid) -113,766, cupric sulphide (solid) -11,755, cupric sulphate (anhydrous) -156,200, cupric sulphate monohydrate -216,962, cupric sulphate trihydrate -331,876, cupric sulphate pentahydrate -446,310, cuprous oxide (liquid) -20,230, cuprous oxide (solid) -34,990,  $\alpha$ -cuprous sulphide -19,155,  $\alpha'$ -cuprous sulphide -19,693,  $\beta$ -cuprous sulphide -19,243, cuprous sulphate (solid) -186,570.

E. S. HEDGES.

**Free energy of formation of thallium amalgams.** C. E. TEETER, jun. (J. Amer. Chem. Soc., 1931, 53, 1180—1181).—At 20°, the free energy attains a minimum at the composition  $\text{Tl}_2\text{Hg}_5$ , indicating the existence of this compound in solution.

J. G. A. GRIFFITHS.

**Hydrogen cyanide.** III. F. p. of hydrogen cyanide-water mixtures. J. E. COATES and N. H. HARTSHORNE (J.C.S., 1931, 657—665).—The f.-p. diagram is of the simple eutectic type, with a eutectic point at -23.4° and 74.5 mols. % HCN. Solutions of hydrogen cyanide in water are ideal up to concentrations of 9.1 mols. % HCN and of water in hydrogen cyanide up to 1 mol. %  $\text{H}_2\text{O}$ . The mol. wts. of the solutes are within 2% of the normal values. The water branch of the curve has a marked inflexion at -16.0° and about 35.5 mols. % HCN; corresponding with this inflexion a metastable system characterised by two liquid phases has been discovered. The critical solution temperature corresponds with -24.0° ± 0.5° and about 35.5 mols. % HCN. Two metastable solid phases have been recognised, one of which is thought to be hydrogen cyanide and the other a compound of hydrogen cyanide and water. The limited miscibility of hydrogen cyanide and water agrees with the large positive deviation from ideality shown by the partial vapour pressures.

F. J. WILKINS.

**Oxide hydrates.** XXXVII. System barium oxide-water. G. F. HÜTTIG and A. ARBES [with Z. HERRMANN and C. SLONIM] (Z. anorg. Chem., 1931, 196, 403—412).—Dehydration of moist barium hydroxide at constant (10 mm.) pressure takes place with decreasing velocity as the water content falls. The Debye diagrams indicate that the mono- and octo-hydrates of barium hydroxide possess characteristic structures, and that no hydrates of intermediate composition exist. The decomposition tem-

peratures of the octo- and mono-hydrates at 10 mm. pressure are 30° and 82—92°, respectively. The method of preparation has but little influence on the form of the dehydration curve, except when the hydroxide is formed in absence of liquid water, e.g., by the action of water vapour on anhydrous barium oxide; the decomposition temperature of the product is then about 60°. When prepared by precipitation of a barium nitrate solution with potassium hydroxide solution at 0°, barium hydroxide contains only about 0.3 mol. of water.

H. F. GILLBE.

**Fusion diagrams of highly-refractory oxides.**

III. H. VON WARTENBERG and W. GURR (Z. anorg. Chem., 1931, 196, 374—383; cf. A., 1930, 847).—Ferric oxide, contaminated with the lower oxide, melts at about 1570°; the resulting mixture of oxides vaporises rapidly at 1800° and forms a eutectic with zirconium dioxide at 1520°. Manganomanganic oxide has m. p. 1705°, and the m. p. of the eutectic mixture with zirconium dioxide is 1620°. Zinc oxide and zirconium dioxide form a eutectic at 1810°, but the former volatilises completely within a few minutes. The m. p. of cerium dioxide is above 2600°, although it vaporises markedly at 2400°, but at 2300° it becomes black and evolves oxygen; at 2500° about 33—50% of the dioxide is reduced to sesquioxide, which is soluble in zirconium dioxide, forming a eutectic at 2400°. Nickelous and cobaltous oxides have m. p. 2090° and 1935°, respectively, and do not volatilise appreciably; the eutectics with zirconium dioxide lie at 2050° and 1850°. Above 1800° titanium dioxide evolves oxygen and becomes bluish-black; the resulting mixture of oxides has m. p. 1850°, is only slightly volatile, and forms a eutectic with zirconium dioxide at 1750°. Stannic oxide commences to volatilise at 1700°, its sublimation temperature being 1800—1900°, but its m. p. could not be determined. Zirconium metasilicate begins to lose silica at 1800°, and the process is rapid at 2000°; the compound is not appreciably soluble in zirconium dioxide.

H. F. GILLBE.

**Systems carbamide-resorcinol and carbamide-pyrocatechol.** J. P. VAN DER HAMMEN (Rec. trav. chim., 1931, 50, 347—350; cf. Puschin and König, Sitzungsber. Akad. Wiss. Wien, 1928, 137, IIB, 75).—In the first system the 1:1 compound melts at 104.4° and appears to be dissociated in the liquid state. The eutectic on the resorcinol side melts at 84.2° and that on the carbamide side at 91.1°. The second system also shows a 1:1 compound, m. p. 71.3°. The eutectic on the pyrocatechol side melts at 65.9°, whilst the other melts at 67°. Part of the metastable melt line could be followed at concentrations between 35 and 45% of carbamide.

J. W. SMITH.

**Equilibrium in the iron-oxygen-hydrogen system at temperatures above 1000°.** W. E. JOMINY and D. W. MURPHY (Ind. Eng. Chem., 1931, 23, 384—387).—Mixtures of hydrogen and water vapour were passed over electrolytic iron at high temperatures for 30 min., after which the iron was quenched in water to stop the reaction and the sample was examined to see whether oxidation had occurred. By suitably controlling the ratio of hydrogen to water

vapour, this method provides a means of determining the equilibrium in the system iron-iron oxide-hydrogen-water vapour. The tests were made between 1097° and 1427°. The equilibrium data when plotted show a break in the curves at 1357°, which may be taken as the m. p. of ferrous oxide. The heat of fusion of ferrous oxide determined from these data is  $+29,000 \pm 5000$  g.-cal. per g.-mol. E. S. HEDGES.

**Reduction of manganese oxides by carbon monoxide.** E. NISHIBORI (Chikashige Anniv. Vol., 1930, 295—298).—The equilibria between carbon monoxide and manganese oxides at 780° have been determined. The gas phase contains 100% CO<sub>2</sub> until the composition of the solid approaches that of the monoxide, when the carbon monoxide content increases rapidly. Reduction beyond this stage proceeds very slowly, with about 7% CO<sub>2</sub> in the gas phase, and a substance is produced which on dissolution in sulphuric acid partly reduces the acid to hydrogen sulphide. The reaction in the reverse direction proceeds with extreme slowness. H. F. GILLBE.

**Ternary systems. IX. Sodium iodate, sodium nitrate, and water.** A. E. HILL and J. E. DONOVAN. **X. Magnesium iodate, magnesium nitrate, and water.** A. E. HILL and S. MOSKOWITZ (J. Amer. Chem. Soc., 1931, 53, 934—941, 941—946).—IX. Isotherms have been determined at 5°, 25°, and 50°. The double salt 2NaIO<sub>3</sub>·3NaNO<sub>3</sub>·15H<sub>2</sub>O exists below 9·8°.

X. The transition temperatures corresponding with  $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O} \rightarrow \text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Mg}(\text{IO}_3)_2$  are 13·3° and 57·5°, respectively. The metastability of the tetrahydrate permits of measurements of solubility beyond the transition temperatures. Isotherms for the ternary system have been determined at 5°, 25°, and 50°.

J. G. A. GRIFFITHS.

**Double decomposition in the absence of a solvent. XIV. The irreversible mutual system  $\text{Ag}_2\text{SO}_4 + \text{Tl}_2\text{Cl}_2 \rightarrow \text{Tl}_2\text{SO}_4 + \text{Ag}_2\text{Cl}_2$ .** S. I. SOKOLOV (J. Russ. Phys. Chem. Soc., 1930, 62, 2329—2335).—The m.-p. diagram for the system  $\text{Ag}_2\text{SO}_4$ — $\text{Ag}_2\text{Cl}_2$  is of the simple eutectic type, but shows a break at the transition point of silver sulphate; solid solution and compound formation are similarly absent in the system  $\text{Tl}_2\text{SO}_4$ — $\text{Tl}_2\text{Cl}_2$ . The fusion diagram for  $\text{Tl}_2\text{SO}_4$ — $\text{Ag}_2\text{SO}_4$  shows the formation of a compound,  $\text{Tl}_2\text{SO}_4 \cdot \text{Ag}_2\text{SO}_4$ , and of solid solutions. The system  $\text{Ag}_2\text{SO}_4 + \text{Tl}_2\text{Cl}_2 \rightarrow \text{Ag}_2\text{Cl}_2 + \text{Tl}_2\text{SO}_4$ , constructed on the basis of the above, is an irreversibly mutual one, with complete solubility of the components, and without singularity on the chief diagonal section.

R. TRUSZKOWSKI.

**Lowering of the ideal eutectic temperature in *n*-component systems.** K. IWASÉ and N. NASU (Chikashige Anniv. Vol., 1930, 223—227).—The eutectic temperature of an *n*-component system is lower than that of any of the possible (*n*—1)-component systems. H. F. GILLBE.

**Graphical representation of multi-component systems in phase-rule investigations.** E. JÁNEČKE (Z. anorg. Chem., 1931, 196, 337—353).—The usual graphical methods for the representation

of multicomponent systems are summarised, and new methods, which employ the equivalents of the components as the units, are described. A tetrahedral C—H—O—N diagram, showing the relationships between the principal types of organic compounds, is reproduced; compounds of similar type, such as the amines, nitriles, or amides, appear on straight lines. In systems of five elements in which simple compounds are formed between all the components there are two distinct series of four-component systems derived from the ten binary compounds; one series may be represented by five different tetrahedra and the other by ten triangular prisms. The complete representation of all possible five-component systems would require an infinite series of tetrahedra, vanishing to a point, or an infinite series of triangular prisms, which in the limit become an equilateral triangle or a straight line. The prism method is illustrated by reference to such systems as C—H—S—O—N, H—O—Br—Cl—Na, and SiO<sub>2</sub>—MgO—Al<sub>2</sub>O<sub>3</sub>—Na<sub>2</sub>O—B<sub>2</sub>O<sub>3</sub>.

H. F. GILLBE.

**Heats of combustion of some heterocyclic compounds.** M. MILONE and S. ALLAVENA (Gazzetta, 1931, 61, 75—90).—A micro-bomb has been used to determine the heats of combustion of 18 heterocyclic compounds of the furazan, azoxime, and oxadiazole types. The heats of combustion are shown to be constitutive, the moduli assigned to the furazan, azoxime, and oxadiazole rings being respectively 187, 158, and 146 kg.-cal. F. G. TRYHORN.

**Electrical conductivity at high temperatures of solutions of common salt and of concentrated sulphuric acid.** F. J. SYMON (J. Roy. Tech. Coll. Glasgow, 1931, 2, 395—401).—Apparatus is described for measurements up to 230° and pressures rising to 400 lb./in.<sup>2</sup> The temperature coefficient of the conductivity is similar for all the solutions studied, e.g.,  $\kappa_{100}/\kappa_{20}$ , 3·0—3·04, and  $\kappa_{200}/\kappa_{20}$ , 4·92—5·14. The values in the Smithsonian Tables (No. 422, 1920) appear to be in error by about 4% at 100° and 17% at 218°. Values for sulphuric acid (94—99%) at 15—50° are also recorded. For the 99% acid the mean temperature coefficient for the range 18—50° is 0·0347, the coefficients for all solutions over the range 18—26° being slightly higher (0·0289—0·0297) than those of Kohlrausch.

J. GRANT.

**Organic acids and bases in non-aqueous solutions. V. Ethyl salicylate and amines.** F. HÖLZL (Monatsh., 1931, 57, 375—382; cf. A., 1929, 59).—The electrical conductivity of mixtures of ethyl salicylate with ammonia, diethylamine, trimethylamine, ethylenediamine, benzylamine, and *p*-phenylenediamine in absolute ethyl-alcoholic solution passes through a maximum in each case at a mol. ratio of 1 : 1, indicating the formation of a compound. Aniline and *o*- and *m*-phenylenediamine do not combine with ethyl salicylate under these conditions. The results are discussed in relation to the compounds produced between phenol, pyrocatechol, and salicylic acid and the amino-compounds investigated.

E. S. HEDGES.

**Aqueous solutions of sodium aluminate. I. Electrical conductivity.** M. PRASAD, S. M. MEHTA, and N. G. JOSHI (J. Indian Chem. Soc., 1931, 7, 973—

980).—The equivalent conductivity of solutions of aluminium hydroxide in sodium hydroxide of concentration greater than  $0.25N$  is at a minimum when the mol. ratio  $Na_2O/Al_2O_3$  is 3, whence the existence of the compound  $Na_3AlO_3$  is inferred. When the sodium hydroxide used is more dilute the minimum is masked in consequence of hydrolysis.

F. L. USHER.

Electrolysis of sodium amalgams and calculation of transport numbers of sodium, potassium, lithium, barium, and bismuth in their amalgams. R. KREMANN (Monatsh., 1931, 57, 323—374).—The amalgam was placed in a long glass capillary tube, at the ends of which the electrodes were inserted. After electrolysis different portions of the amalgam were titrated with acid in order to determine the distribution of the sodium. The effect of the length and diameter of the tube and the concentration of amalgam was investigated. From measurements of the change in composition of the anode and cathode regions transport numbers for sodium, potassium, lithium, barium, and bismuth in mercury have been calculated. E. S. HEDGES.

Electrolysis of ternary alloys. R. KREMANN (Monatsh., 1931, 57, 241—252).—The electrolysis of copper-tin alloys containing different amounts of bismuth proceeds readily at  $1000^\circ$  using a c. d. of 5–6 amp./mm.<sup>2</sup> Cooled specimens after electrolysis showed an increased copper content in the cathode portion, whilst the anode portion was richer in bismuth. Changes in the metallographic structure of the alloys are illustrated by means of photomicrographs. Ternary alloys consisting of sodium amalgam containing 0.52–4.79% of tin were electrolysed in glass capillary tubes at  $240^\circ$  for 20 hrs., using a c. d. of 6 amp./mm.<sup>2</sup> Both tin and sodium accumulate at the cathode. E. S. HEDGES.

Potential of the cadmium electrode. F. H. GETMAN (J. Physical Chem., 1931, 35, 588—595).—The *E.M.F.* of the cell  $Cd|CdCl_2|Hg_2Cl_2, Hg$  has been measured at  $25^\circ$  with single crystals or massive crystalline aggregates of cadmium. Single crystals of cadmium give constant and reproducible values which are always greater than those given by the aggregates. The normal electrode potential of cadmium calculated from the *E.M.F.* of cells with electrodes of single crystals is 0.395 volt. The activity coefficients of cadmium chloride solutions now calculated are slightly less than those deduced by Lewis and Randall from the experimental data of Horsch. L. S. THEOBALD.

Effect of pressures up to 16,000 atm. on the *E.M.F.* of the Weston standard cell. T. C. POULTER, C. RICHEY, R. WILSON, and J. FULTON (Proc. Iowa Acad. Sci., 1929, 36, 304).—The shape of the curve showing increase of *E.M.F.* with pressure is affected by the material of the cell case.

CHEMICAL ABSTRACTS.

Liquid junction of dilute electrolytes. M. PLANCK (Sitzungsber. Preuss. Akad. Wiss., 1931, 7, 10 pp.).—Further mathematical treatment yields an equation which, although giving a value for the *P.D.* at the junction of a  $0.1N$ -potassium chloride solution with a  $0.1N$ -hydrochloric acid solution which accords

with the experimental value, nevertheless leads to paradoxical conclusions relating to the change of *P.D.* with time. Henderson's assumption cannot be upheld. It is shown that a linear relationship holds only when  $U_2/U_1=V_2/V_1$ ; this condition obtains for two solutions of a single electrolyte which differ only in concentration. When  $U_2=U_1$  and  $V_2=V_1$  the relation becomes logarithmic. With the aid of this relation it becomes possible to calculate the variation of the *P.D.* with time as the boundary passes into the stationary condition. For this purpose an equation has been derived which appears to be satisfactory, but it is not possible to decide whether the correct sign is obtained for the difference between the *P.D.* in the initial and the stationary states. H. F. GILLBE.

Reduction potentials of some higher benzo-*logues* of the quinones. L. F. FIESER and E. M. DIETZ. See this vol., 623.

Reaction of hydrogen peroxide with some metallic ions. I. Potential of hydrogen peroxide. II. Alleged "reduction coefficient" of a reversible hydrogen peroxide electrode. III. Effects upon the potential and the photographic action of hydrogen peroxide exerted by the presence of several metallic acids and its stabiliser as well as by changes in its concentration. S. HAKOMORI (Tech. Rep. Tôhoku, 1931, 9, 106—120, 121—144, 145—164).—I. The normal oxidation and reduction potentials, referred to the normal hydrogen electrode, of hydrogen peroxide have been calculated theoretically as 1.7693 volts and 0.6819 volt, respectively. Palladium electrodes give better reversible values in hydrogen peroxide solution than do platinum or gold electrodes.

II. The term "reduction coefficient" is applied to the relation  $C/C_0$ , where  $C$  is the concentration of the peroxide solution in which the electrode is immersed and  $C_0$  that of the part of the solution in direct contact with the electrode. It is shown that, if  $C/C_0=G$ , then  $\log G=(\varepsilon F + \frac{1}{2}\Delta F_1)/1.15RT + \log m$ , where  $\varepsilon$  is the potential of the reversible electrode at 1 atm. pressure with reference to the normal hydrogen electrode,  $\Delta F_1$  is the free energy of the reaction  $H_2+O_2=H_2O_2(aq.)$  after time  $T$ , and  $m$  is the molar concentration of the peroxide.

III. The potential of hydrogen peroxide solutions against a normal hydrogen electrode is increased by the addition of various acidic oxides of metals; for a 1:1 ratio of metal oxide to peroxide this increase is 0.0047 volt for uranium trioxide, 0.0195 volt for titania, 0.1080 volt for molybdenum trioxide, 0.3107 volt for vanadium pentoxide, and 0.4802 volt for chromium trioxide. A. R. POWELL.

Oxidation-reduction potentials of sugar solutions. R. WURMSER and J. GELOSO (Compt. rend., 1931, 192, 680—682; cf. A., 1929, 1393; 1930, 42).—To ascertain the system determining the limiting potential of a solution of dextrose, operations were carried out very slowly (*e.g.*, with  $p_H$  7 at  $20^\circ$  48 hrs. was allowed to elapse after each addition of either oxidiser or reducer). In this way a second system of normal potential  $-0.040$  volt ( $p_H$  7, at  $20^\circ$ ) designated as  $G_1 \rightleftharpoons B + nH_2$ , is found to exist in considerable quantity. The amount of dye reduced by solutions

of dextrose etc. can be deduced from the titration curves, given the normal potential of the dye.

C. A. SILBERRAD.

**Electro-capillary curve of mercury.** K. BENNEWITZ and K. KÜCHLER (Z. physikal. Chem., 1931, 153, 443—450).—As asserted by Frumkin and Obrutscheva (A., 1929, 145), the potential of mercury dropping from a capillary beneath the surface of a liquid is not the same as that of mercury at rest in contact with the same liquid, and the determination of the electro-capillary curve of mercury previously reported (A., 1927, 316) has therefore been repeated with a suitably modified technique. The maximum on the curve in the neighbourhood of 0.5 volt observed when dropping into pure very dilute mercurous nitrate solution is still present. Such additions as potassium nitrate, and probably also potassium hydroxide, cause considerable displacement of the curve. It seems fairly certain that there is a change in direction of the current at the maximum point, but in the absence of further evidence the maximum point cannot safely be regarded as corresponding with zero potential.

R. CUTHILL.

**Phase-boundary potential between quartz and solutions of electrolytes.** B. VON LENGYEL (Z. physikal. Chem., 1931, 153, 425—442).—The phase-boundary potential between quartz glass and aqueous solutions of sodium hydroxide, alkali halides, and various acids has been measured. The potential set up apparently depends solely on the adsorption of ions from the solution; no appreciable amount of ions can come from the quartz itself, and there is no evidence that a swollen surface layer on the quartz plays a part. It must be supposed that the quartz with its adsorbed ions behaves electrically like an ordinary electrode, the electrolytic solution tension depending on the concentration of adsorbed ions. As a result of the acid character of the adsorbent, the tendency is to take up positive ions, and the potential in solutions of acids is independent of the anion. In very dilute solutions of alkali salts the salt ions have little effect on the potential, but as the salt concentration increases the metal ions are adsorbed in greater and greater amount until ultimately the electrode becomes an alkali metal electrode instead of a hydrogen electrode; here also the anion has little influence on the potential. The potential in 0.01—0.1*N*-sodium hydroxide solutions seems to be determined by the sodium ions and not by the hydrogen ions. The potential in an acid solution rises as sodium hydroxide is added, passes through a maximum, and falls again, this behaviour probably being a consequence of the progressive replacement of adsorbed hydrogen ions by sodium ions.

R. CUTHILL.

**Electrokinetic potentials. VIII. Ion antagonism.** H. B. BULL and R. A. GORTNER (J. Physical Chem., 1931, 35, 700—721; cf. this vol., 435).—The surface potential at a cellulose-solution interface has been determined for aqueous solutions of the chlorides of sodium, potassium, calcium, and magnesium alone and mixed in pairs with a total cation normality equal to  $8 \times 10^{-4}$ . Except in the case of calcium and magnesium chlorides which shows a suggestion of ion antagonism, the results for the mixtures are approximately an average of those obtained with the individual

salts. Magnesium and calcium chlorides show no ion antagonism in a diluted physiological salt solution which is  $2 \times 10^{-4}N$ , and there is no antagonism which affects the electrokinetic potential between potassium chloride and sodium chloride (20:1) or between sodium chloride and calcium chloride (100:1).

L. S. THEOBALD.

**Becquerel's "electro-capillary phenomenon."** J. J. BIKERMAN (Z. physikal. Chem., 1931, 153, 451—465).—It has been shown experimentally that the theories advanced by Ostwald (A., 1890, 1354) and by Girard and Platard (A., 1924, ii, 396) to account for the effects observed when a solution of a copper salt is separated from a sodium sulphide solution by a glass membrane containing a crack are untenable, neither can the effects be attributed to diffusion or Donnan potentials. A satisfactory explanation is, however, obtained by supposing that the two solutions form, in conjunction with the copper sulphide deposited in the crack, a cell. The circuit is completed through the pores of the sulphide by the solution of the sodium salt formed by the reaction and a continuous current therefore circulates, as a result of which copper is deposited on one side of the sulphide membrane, and sulphide ions undergo the reaction  $S'' + Na_2S = Na_2S_2 + 2e$  at the other. Indirect determinations of the *P.D.* across the membrane show this explanation to be quantitative. If the membrane in the crack or the solutions are of such a nature that a current cannot circulate, no metal is deposited.

R. CUTHILL.

**Electrolytic dissolution and deposition of metals.** J. HOEKSTRA (Rec. trav. chim., 1931, 50, 339—342).—The current density-voltage curve for electrolytes generally shows a logarithmic form, the change in current with change of potential being almost zero at zero voltage. When the electrodes are scraped continuously, however, a straight line is obtained. Metallic deposition during electrolysis has also been studied photomicrographically. For most metals deposition appears to occur in films of approximately 1000 atoms thick. "Active lines" are seen on the surface of the crystals and these spread over the crystal face as deposition continues. The form and number of these active lines are modified by the applied voltage and by interruption of the current. Iron, nickel, and cobalt form exceptions to this rule, as they normally deposit in relatively thick films in nodule-like form. The results obtained are interpreted as due to adsorption phenomena.

J. W. SMITH.

**Relation between the hydrogen overvoltage and composition of brass.** M. DE K. THOMPSON (Trans. Amer. Electrochem. Soc., 1931, 59, 65—69).—Hydrogen overvoltages for alloys ranging from pure zinc to pure copper have been determined at various current densities in *N*-potassium hydroxide. The overvoltage varies linearly with the composition, except in the  $\epsilon$ -brass region, where there is a marked depression in the curve. There is no apparent relation between this curve and the *f.p.* curve for the alloys.

H. J. T. ELLINGHAM.

**Reductivity of hydrogen at certain metal surfaces in relation to the overvoltage.** G. R. HOOD and F. C. KRAUSKOPF (J. Physical Chem., 1931, 35,



786—795).—The measurement of cathodic potentials during electrolytic reduction without contamination of the electrolyte is described. The electrolytic reduction of an aqueous solution of potassium chlorate (0.493*M*) using cathodes of iron, copper, silver, nickel, platinum, cadmium, tin, or zinc has been studied. When the cathodic potential exceeds 1.5 volts electrolytic reduction is negligible, but it increases rapidly as the potential falls below this value. The results obtained by electrolytic reduction, catalytic reduction by hydrogen in the presence of platinum-black, and decomposition potential measurements are discussed in connexion with the mechanism of overvoltage.

L. S. THEOBALD.

New abnormality in the properties of aqueous solutions of cadmium salts. E. TESCHE and P. J. VAN RYSSELBERGHE (Trans. Amer. Electrochem. Soc., 1931, 59, 71—75).—Apparent current efficiencies notably greater than 100% in the electrodeposition of cadmium from its aqueous iodide solutions are shown to be due to the adsorption of cadmium iodide on the metal during deposition. Electrodeposited or even cast cadmium adsorbs notable amounts of cadmium iodide when merely dipped into solutions of the salt, and desorption occurs when the metal is transferred to water. This effect is ascribed to neutral molecules of the salt and not to complex ions, because the amount of adsorption is somewhat increased when the metal is being deposited from a methyl-alcoholic solution of cadmium iodide, but becomes practically zero when it is deposited from aqueous solutions of the complex salts  $K_2CdI_4$  and  $KCdI_3$ . Adsorption also occurs, but to a smaller extent, in the electrodeposition of cadmium from bromide solutions, and abnormally heavy deposits are obtained from nitrate solutions. From the chloride and sulphate solutions, however, pure cadmium is deposited. A tentative explanation of the difference in behaviour of the three halides is put forward. H. J. T. ELLINGHAM.

Passivity of chromium. II. E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1931, 37, 185—197; cf. this vol., 173).—Experiments on the activation of chromium by cathodic polarisation in acid solutions show that each acid requires a definite activation potential. The negative potential at which activation occurs in normal acid solutions increases in the order hydrochloric < hydrofluoric < hydrobromic < sulphuric < perchloric < orthophosphoric; thus, activation is more easily effected the smaller is the anion. The potentials for electrolytic and thermite chromium are slightly different. When the activation is effected by grinding with an emery wheel there is again a definite activation potential, which depends on the anion of the acid, and the order is the same as that given above. The experiments lead to the following deductions concerning the nature of passivity. Chromium in the passive state is covered by a network of chromic oxide molecules, which are anchored to the units of the chromium space lattice. Acids cannot dissolve the oxide film except by penetrating between the molecules, and the size of the anion is therefore all-important. As the cathodic polarisation is increased the small hydrogen ion is drawn through the oxide net-work and the electrostatically

bound anion can follow it and dissolve the oxide film, if the anion is not too large. At the corners and edges of the metal the oxide net-work is looser and anions can readily penetrate at such points, which therefore become active. A short-circuited cell is then set up, and if the potential reaches a higher negative value than the activation potential for the particular acid the whole metal will become active and dissolve. In the case of chromium at 20° this state of affairs is realised in hydrochloric acid only. The degree of polarisation may be increased also by mechanical grinding and by raising the temperature, whereupon the whole metal becomes active. E. S. HEDGES.

Cathodic behaviour of pyrites and chalcopyrite. A. MATSUBARA and J. TAKUBO (Chikashige Anniv. Vol., 1930, 311—339).—Cathodic polarisation of iron pyrites in dilute sulphuric acid causes the ionisation of one or both atoms of sulphur, which then combine with the hydrogen ions present to form hydrogen sulphide. If the material is first made the anode, subsequent cathodic polarisation gives rise to an abnormal amount of hydrogen and certain natural specimens behave similarly without previous treatment. The current yield is, in general, smaller when much hydrogen is evolved. Copper pyrites in dilute sulphuric acid is decomposed cathodically into hydrogen sulphide, cuprous sulphide, and ferrous sulphate, and, ultimately, into metallic copper; preliminary anodic polarisation produces the reverse effect of that observed with iron pyrites. Copper pyrites which yields but little hydrogen gives abnormal quantities of decomposition products. It is suggested that the fraction of the mineral which is dissolved directly by the acid exists in the solid in an ionised condition, the degree of ionisation in various specimens of copper pyrites being 0.035—0.305.

H. F. GILLBE.

Statistical treatment of reaction velocity data. I. Critical review of current methods of computation. L. J. REED and E. J. THERIAULT (J. Physical Chem., 1931, 35, 673—689).—The possibility of obtaining a consistent series for the values of *k* should be discarded as a test for the unimolecular nature of a reaction. Procedures involving least squares are inapplicable to unimolecular data and the proposed systems for the weighting of unimolecular constants cannot be used in the presence of constant errors.

L. S. THEOBALD.

Interpretation of the thermal decomposition of nitrous oxide. H. C. RAMSPERGER and G. WADINGTON (Proc. Nat. Acad. Sci., 1931, 17, 103—105).—The theories of Rice and Ramsperger (A., 1927, 833) and of Kassel (A., 1928, 372) have been applied to the data obtained for the thermal decomposition of nitrous oxide at 665°. Only two squared terms (one classical oscillator) are required to fit the data. The minimum value obtained for the critical energy for breaking the nitrogen-oxygen linking is 42,000 g.-cal.

E. S. HEDGES.

Combustion of inflammable gases by electric sparks. J. D. MORGAN (Phil. Mag., 1931, [vii], 11, 158—163).—The amount of combination produced in the flameless combustion of very dilute coal gas-air mixtures by a succession of high-tension sparks is

closely proportional to the heat energy of the discharge when the gap between the electrodes is kept constant. When the heat energy of the discharge is maintained constant the amount of combustion is proportional over a wide range to the gap. The results are consistent with the hypothesis that combustion depends on the heating of the gas by conduction.

F. G. TRYHORN.

**Flame temperatures of hydrocarbon gases.** G. W. JONES, B. LEWIS, J. B. FRIAUF, and G. ST. J. PERROTT (J. Amer. Chem. Soc., 1931, 53, 869—883; cf. Loomis and Perrott, B., 1928, 881).—The spectral line reversal method (Griffiths and Awbery, A., 1929, 534) has been applied to moist hydrocarbon-air mixtures. In qualitative agreement with calculations based on the dissociation of the products at the temperatures of the flames, mixtures containing hydrocarbon slightly in excess of that necessary to consume all of the oxygen afford the observed maximum temperatures: ethylene 1975°, propylene 1935°, butylene 1930°, propane 1925°, isobutane 1900°, butane and ethane 1895°, Pittsburgh natural gas (87% CH<sub>4</sub>) 1890°, and methane 1880°. These values are about 100° and 40—70° lower than those calculated for the unsaturated and saturated hydrocarbons, respectively, and this discrepancy may be attributed to radiation losses. Mixtures affording maximum flame temperatures contain less hydrocarbon than those affording maximum speeds of uniform movement of flame (cf. Wheeler, Coward, Payman, and others).

J. G. A. GRIFFITHS.

**Oxidation of gaseous acetaldehyde by oxygen as a typical example of the [slow] combustion of hydrocarbons.** M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1931, III, 18 pp.; cf. Bäckström, A., 1927, 737, 1151).—Acetaldehyde vapour reacts slowly with oxygen at 55—90° and 70 mm. pressure, and the reaction can be followed, except in the later stages, by measuring the diminution of pressure. The primary product is peracetic acid, which towards the end of the reaction decomposes in an irregular manner, causing an increase of pressure. With a deficit of oxygen the pressure decreases linearly with time, and the reaction stops abruptly when all the oxygen has been used; with oxygen in excess the velocity of reaction decreases with time. In both cases a period of induction is generally, but not invariably, found. The course of the main reaction is expressed by the formula  $d[P]/dt = k[A]^2/([O_2] + b)$ , in which  $P$  denotes peracetic acid and  $A$  acetaldehyde. The sequence of changes, which is considered to occur generally in the oxidation of hydrocarbons, consists essentially in the activation of an aldehyde molecule, which combines with oxygen to form an activated molecule of peracetic acid. Normally, the energy of the latter is transferred to another aldehyde molecule, but in the presence of certain substances (e.g., diphenylamine) which act as negative catalysts, the latter absorb the energy instead, and the reaction "chain" is then interrupted. There is evidence that the acetaldehyde reacts in a tautomeric form other than vinyl alcohol.

F. L. USHER.

**Mechanism of oxidation of acetaldehyde and hydrocarbons.** M. BODENSTEIN (Z. physikal.

Chem., 1931, B, 12, 151—164).—A mechanism is proposed for the slow reaction of gaseous acetaldehyde with oxygen, and shown to be applicable without essential modification to the slow combustion of hydrocarbons, the results of Spence and Kistiakowsky for the oxidation of acetylene (this vol., 313) being in particularly good agreement with the theory. In the explosive oxidation of hydrocarbons the series of reactions involved in slow oxidation appears to be initiated by reaction chains in which free atoms and radicals take part.

R. CUTHILL.

**Inflammation limits of fuels containing alcohol.** YANNAQUIS (Ann. Office Nat. Combust. liq., 1930, 5, 175—178; Chem. Zentr., 1930, ii, 3878).—The dependence of the limits of inflammation of benzene-ethyl alcohol-methyl alcohol, benzene-ethyl alcohol-petrol, and ethyl alcohol-methyl alcohol mixtures on the temperature has been studied. Partial substitution of alcohol by benzene limits the inflammability region of the ethyl alcohol-methyl alcohol mixture without affecting the temperature coefficient. Substitution of methyl alcohol by petrol has the opposite effect in both cases.

A. A. ELDRIDGE.

**Rates of intramolecular change between ammonium thiocyanate and thiocarbamide.** W. URE and T. B. EDWARDS (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 153—159).—The velocity of the opposing reactions in the system  $NH_4CNS \rightleftharpoons CS(NH_2)_2$ , has been investigated in solution over a range of concentrations and temperatures. Although the presence of side reactions is indicated, the results seem to show that the main process consists of two opposing unimolecular reactions. The reaction coefficients are evaluated for two temperatures.

W. GOOD.

**Kinetics of chlorine bleaching.** J. J. WEISS (Z. angew. Chem., 1931, 44, 102—104).—Polemical against Kauffmann (cf. B., 1930, 1062).

R. CUTHILL.

**Kinetics of chlorine bleaching and of [decomposition of] hypochlorite solutions.** J. J. WEISS (Z. Elektrochem., 1931, 37, 20—25).—The velocity data of both Foerster (A., 1917, ii, 367) and Kauffmann (B., 1930, 1062) for the decomposition of hypochlorite in alkaline solution can be accounted for by the theory that the decomposition consists of two concurrent composite reactions, viz.,  $2ClO' \rightarrow ClO_2' + Cl'$  followed by  $ClO_2' + ClO' \rightarrow ClO_3' + Cl'$ , and  $2HClO \rightarrow 2H' + 2Cl' + 2O$  followed by  $2ClO' + 2H \rightleftharpoons 2HClO$ , the first stage in each reaction determining the rate of the reaction as a whole (cf. A., 1930, 1379). In hypochlorite bleaching the active agent is not the complex ion  $HClO \cdot ClO'$  postulated by Kauffmann, but chlorine monoxide or undissociated hypochlorous acid. If it is assumed that in the bleaching of cellulose fibres the attack on the fibre itself runs parallel with the degree of swelling and that the latter is proportional to the concentration of adsorbed hydroxyl ions, it appears that the rate of attack is maximal for a certain  $p_H$  and falls rapidly with either increase or decrease of  $p_H$ . The predicted relationship between rate of attack on the fibre and  $p_H$  is, in fact, in satisfactory agreement with existing experimental data. It thus appears possible that by

suitable adjustment of the  $p_H$  the colouring matter may be rapidly destroyed without the fibre being appreciably attacked. R. CUTHILL.

**Kinetics of chlorine bleaching.** H. KAUFFMANN (Z. angew. Chem., 1931, 44, 104-105).—A reply to Weiss (cf. preceding abstract). R. CUTHILL.

**Reactions involving hydrogen peroxide, iodine, and iodate ion. III. Reduction of iodate ion by hydrogen peroxide.** H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1931, 53, 896-911; cf. this vol., 324).—The rate of the reaction at 50° in the system potassium iodate 0.0019-0.23*M*, hydrogen peroxide 0.002-2.5*M*, and perchloric acid 0.007-0.14*M* is given by the relation  $-d[IO_3^-]/dt = (i) 2.6 \times 10^{-4} [H_2O_2][IO_3^-] + (ii) 129 \times 10^{-4} [H_2O_2][IO_3^-][H^+]$  (units: min., mol., litre), which is no longer valid when  $[H^+]$  exceeds 0.14*M*. The first stages in the reduction may be  $IO_3^- + H_2O_2 \rightarrow IO_2^- + H_2O + O_2$  and  $IO_3^- + H_2O_2 + H^+ \rightarrow HIO_2 + H_2O + O_2$ . The catalytic decomposition of hydrogen peroxide is minimised by removal of iodine by means of carbon tetrachloride. The induction period is approximately independent of the concentration of hydrogen and iodate ions and inversely proportional to the concentration of hydrogen peroxide. The relation between the induction period, the slow initial reaction, and the succeeding rapid reactions is discussed. From the temperature coefficient between 30° and 60°, the energies of activation of (i) and (ii) are computed to be 27,500 and 23,500 g.-cal., respectively, and the diameter  $10^{-6}$  to  $10^{-7}$  cm. is deduced for the entities  $H_2O_2$  and  $IO_3^-$ . It is concluded that the number of ternary collisions (ii) is insufficient to afford the observed reaction velocity and hence some complex must be present. The relation between this reaction and the decomposition of hydrogen peroxide catalysed by the iodide-iodate couple is discussed. J. G. A. GRIFFITHS.

**Chemical kinetics of ionic reactions. II. Mechanism of the reaction between ferric and iodine ions.** A. KISS (Magyar Chem. Fol., 1930, 36, 49-59; Chem. Zentr., 1930, ii, 1030; cf. A., 1930, 1256).—The reaction between ferric and iodine ions is termolecular, being bimolecular with respect to iodine and unimolecular with respect to ferric ions. Hydrolysed ferric ions do not react with iodine ions. In dilute solution, the primary salt effect follows Brönsted's law of neutral salt action. The retarding effect of ferrous and sulphate ions must be regarded as a secondary salt effect. L. S. THEOBALD.

**Period of induction of the reaction between ammonium sulphide and formaldehyde solutions.** R. J. W. LE FÈVRE and (MISS) M. MACLEOD (J.C.S., 1931, 474-478).—A mixture of aqueous solutions of ammonium sulphide and formaldehyde deposits after a period of induction a white precipitate. The induction period diminishes with rise of temperature, vanishing at about 60°. F. J. WILKINS.

**Relationship of structure of hydrocarbon radical to velocity and position of equilibrium in organic reactions.** W. HEROLD and K. L. WOLF (Z. physikal. Chem., 1931, B, 12, 194-205).—It is suggested that in reactions between organic dipole molecules the effect of the radicals attached to the

polar groups may be twofold: one radical may be of such dimensions as to prevent the close approach of the other molecule to the attached polar group ("steric hindrance"), and further the probability that the polar groups will come in contact in a collision will be diminished if either group is not readily accessible from all sides ("steric screening"). The degree to which the polar group is screened may, in the case of a group with absorbent power, be determined from the amount of displacement of its absorption bands under the influence of other dipole molecules; the less is the screening the greater will be the displacement. The relationships of the velocity and position of equilibrium of reactions occurring in solution to the nature of the reactants and solvent are, in general, in satisfactory agreement with the theory. R. CUTHILL.

**Optical investigations in the system aldehyde-alcohol.** W. HEROLD and K. L. WOLF (Z. physikal. Chem., 1931, B, 12, 165-193).—Optical absorption measurements have been made with solutions of aliphatic aldehydes in water, heptane, and various alcohols. From the results the rate of formation of alcoholates and acetals from aldehydes in alcoholic solution and the position of equilibrium have been determined, the presence of free mineral acid being found not to be necessary for this reaction. In dilute alcoholic solution a large proportion of the aldehyde is converted into the semiacetal at equilibrium, but no detectable amount of the acetal is formed. As the screening of the reacting polar groups increases, the rate of reaction and the proportion of semiacetal formed at equilibrium diminish (cf. preceding abstract). The formation of a hydrate when propaldehyde is dissolved in water apparently takes place instantaneously. The optical data show that the hydrates and alcoholates of the simple aliphatic aldehydes are true valency compounds and not merely loose molecular compounds. R. CUTHILL.

**Salt and medium effects on the temperature coefficient of velocity of decomposition of diacetone alcohol.** G. M. MURPHY (J. Amer. Chem. Soc., 1931, 53, 977-981; cf. Åkerlöf, A., 1928, 716, 485, 137).—The velocity of the decomposition in 0.01-0.1*M*-sodium hydroxide, 0.05*M*-sodium hydroxide + 0-1.0*M*-sodium chloride, and 0.1*M*-sodium hydroxide in 0-60% aqueous methyl alcohol has been determined at 20°, 25°, 30°, and 35°. The temperature coefficient is independent of the concentration of sodium hydroxide alone and of that of the hydroxide-chloride mixtures. The energy of activation is computed to be 18,000 g.-cal. The temperature coefficient increases with increasing concentration of methyl alcohol. J. G. A. GRIFFITHS.

**Influence of solvent on the decomposition of trichloroacetic acid.** J. N. PEARCE and A. C. NELSON (Proc. Iowa Acad. Sci., 1929, 36, 251-260).—The decomposition of trichloroacetic acid to chloroform and carbon dioxide is unimolecular in water, aniline, and mixtures of aniline with chloroform or toluene. Measurable decomposition does not occur in methyl alcohol, ethyl alcohol, chloroform, toluene, or pyridine. The reaction is accelerated by light. Only in aniline or in aniline (87.5 mol.-%) + chloro-

form is the effect of light considered to be photo-catalytic. The velocity coefficients calculated from the heats of activation by the equations of Dushman and of Lewis are not in accord with those determined.

CHEMICAL ABSTRACTS.

**Kinetic analysis of  $\alpha$ -bromobutyric acid.** R. AHLBERG (Svensk Kem. Tidskr., 1931, 43, 69—74).—A repetition of the work of Senter and others on the hydrolysis of  $\alpha$ -bromobutyric acid (cf. J.C.S., 1909, 95, 1831; A., 1918, i, 250). The rate of hydrolysis of an aqueous solution of the barium salt at 25.2° has been studied. The results indicate that two different unimolecular reactions are involved, one of which proceeds 500 times as rapidly as the other; in two series of experiments 5% and 9%, respectively, of the acid was used in the faster reaction. The acid employed was prepared from the ordinary butyric acid of fermentation, and it is pointed out that in contradistinction to Fischer's statement such an acid is not suitable for the preparation of  $\alpha$ -bromobutyric acid where a perfectly pure product is required.

H. F. HARWOOD.

**Non-enzymic reduction of methylene-blue.** F. LIEBEN and E. MOLNAR (Biochem. Z., 1931, 232, 209—217).—Glycine does not reduce methylene-blue, but, like alanine, inhibits the deepening of the colour of the methylene-blue by dilute sodium hydroxide. The effect can be reproduced by use of an inorganic buffer. The anaerobic reducing powers of a number of carbamide and guanidine derivatives are examined. The reducing power is often increased by a CO and inhibited by a CH<sub>2</sub> group; cyclic substances reduce more quickly than the corresponding open-chain substances, and guanidine derivatives more quickly than the corresponding carbamide compounds.

P. W. CLUTTERBUCK.

**Furfuraldehyde; properties, preparation, and industrial applications.** B. GROTH (Svensk Kem. Tidskr., 1931, 43, 23—42).—A description is given of the chemical and physical properties of furfuraldehyde, and of its technical production and uses. In the production of furfuraldehyde by heating acid solutions of pentoses, the yield obtained increases with the dilution of the original solution, and at infinite dilution would coincide with the value calculated theoretically on the assumption that the reaction is unimolecular. The maximum yield is nearly independent of the temperature and  $p_H$  value of the liquid, but depends largely on the concentration of the pentose. The production of by-products appears to be a bimolecular reaction, a fairly satisfactory coefficient being obtained in this case for pentose solutions of widely different concentrations. The decomposition of furfuraldehyde was investigated by heating it in an autoclave at 150—170° with buffered solutions. The rate of decomposition increases with the hydrogen-ion concentration in solutions of  $p_H < 2$ , and with the hydroxyl-ion concentration where  $p_H > 6$ ; for the intermediate values a maximum is attained at about  $p_H$  3.5. In solutions of  $p_H < 1.5$  the reaction is unimolecular, provided that the solution does not contain large quantities of neutral salts, sugar, etc., as these considerably accelerate the rate of decomposition; in alkaline solution the reaction is possibly bimolecular.

H. F. HARWOOD.

**Instability of colloidal powders.** H. MURAOUR (Bull. Soc. chim., 1931, [iv], 49, 276—279).—A discussion between the author and de Bruin.

F. J. WILKINS.

**Influence of moisture on the rate of combustion of colloidal powders.** H. MURAOUR (Bull. Soc. chim., 1931, [iv], 49, 268—274).—The presence of moisture decreases the rate of combustion of colloidal powders, such as cellulose nitrate. It is suggested that this effect is to be attributed to the comparatively large amount of heat required to vaporise the moisture. This theory provides a satisfactory quantitative explanation of the phenomenon.

F. J. WILKINS.

**Kinetics of a type of heterogeneous reactions. Mechanism of combustion of pulverised fuel.** S. P. BURKE and T. E. W. SCHUMANN (Ind. Eng. Chem., 1931, 23, 406—413).—A mathematical treatment is given of a highly exothermic reaction between a finely-divided reacting solid suspended in a reacting fluid medium, the products of reaction being totally fluid. The theory is applied to the combustion of pulverised solid fuel, employing only fundamental physical constants, such as coefficients of thermal conduction and diffusion, and the results are in agreement with published experimental data. The theory involves the hypothesis of a stagnant film of gas surrounding the burning particle, leading to the conclusion that combustion takes place by diffusion only. The effects of pressure, temperature, density, and size of the particle, ash content, formation of carbon monoxide, reactivity of carbon, content of volatile matter, and motion of fuel particles during combustion are discussed in the light of the theory and the conclusions reached are shown to be in agreement with experimental results. The peculiar motions of the particles predicted by the theory are confirmed by photographic records.

E. S. HEDGES.

**Theory of corrosion [of metals].** E. MAASS and E. LIEBREICH.—See B., 1931, 298.

**Principles of corrosion.** G. MASING.—See B., 1931, 298.

**Corrosion of metals.** T. KUCZYŃSKI and M. SMIAŁOWSKI (Przemysł Chem., 1931, 15, 52—61, 99—104).—Duffek's method (Korrosion u. Metallsch. Beih., 1929, 32) whereby the resistance to corrosion of a metal is measured as a function of the  $P.D.$  between the metal and a mercury electrode immersed in the same solution, does not yield good results. Tödt's method (Korrosion u. Metallsch., 1929, 5, 169), depending on the measurement of the current flowing between the metal and a platinum electrode, gives better results, which are not, however, entirely trustworthy in every case. The most important factors in the corrosion of metals immersed in alkali chloride solution are the velocity of diffusion of oxygen to the cathodic parts of the metal surface, and the catalytic properties of these surfaces, depending on their ability to activate oxygen; platinum surfaces activated oxygen to a smaller extent than other metals examined, with the exception of tin. The quantity of current flowing between the metal and the platinum electrode was unaffected by the presence of quinoline, brucine, mannitol, and sodium arsenite in the solution, whilst 0.5% potassium cyanide considerably reduced

the current, acting probably as an anticatalyst. Measurements of the current flowing between a carbon cathode and a metal anode in alkali chloride solution under various conditions show that the deviations found from Ohm's law diminish with increasing density of current, and are ascribed to the resistance due to the formation of deposits on the anode. The velocity of dissolution of metals connected with a non-polarising cathode is expressed by  $I = \chi(E'_a - E_a)/C + X_x$ , where  $I$  represents density of current in amp.,  $\chi$  is the conductivity of the electrolyte,  $E'_a$  and  $E_a$  are the *P.D.* at the anode during the passage of the current and with the circuit open,  $X$  is the additional resistance due to the deposit on the anode, and  $C$  is the resistance capacity of the cell.

R. TRUSZKOWSKI.

**Mechanism of retardation of corrosion [of iron] by colloids.** W. BECK and F. VON HESSERT (*Z. Elektrochem.*, 1931, 37, 11—20).—Friend's observation (*J.C.S.*, 1921, 119, 932; 1922, 121, 466) that the rusting and corrosion of iron in water and aqueous solutions of acids are retarded by hydrophilic colloids has been confirmed, and it has been found that the protective action is a function of both the concentration and nature of the colloid. The retardation cannot, however, be explained by simple adsorption of the colloid on the metal, but seems rather to be the result of the deposition of a film of colloid on the metal by local coagulation brought about by iron ions. This view receives support from the observation that if the metal is vigorously shaken in contact with the acid solution the protective action is small or even absent.

R. CUTHILL.

**Action of oxygen on the corrosion of iron and steel in aqueous solution.** H. ENDO and S. KANAGAWA.—See *B.*, 1931, 351

**Resistance to corrosion of chromium-nickel-iron alloys [with reference to Tammann's theory of limits of resistance].** E. WELLMANN (*Z. Elektrochem.*, 1931, 37, 142—156; cf. Guertler and Ackermann, *B.*, 1928, 753).—The corrodibility of alloys of chromium, nickel, and iron has been studied in relation to composition and temperature, the attacking substances being sulphur dioxide, hydrogen sulphide, sodium hypochlorite, phenol, tartaric acid, and citric acid. Sulphur dioxide causes oxidation with liberation of sulphur, the effect being noticeable between 350° and 400° and increasing rapidly with rise of temperature in all except nickel-free alloys with 22% Cr, which are resistant below 600°. Admixture of air or steam increases the corrosion. All alloys are corroded by hydrogen sulphide above 300°, the presence of chromium affording some degree of protection at temperatures below 500°. Hypochlorite with 1% of active chlorine is without action, whilst that with 4% attacks binary alloys of iron and chromium, the chromium going into solution and the iron forming rust. Ternary alloys of the type of "V<sub>2</sub>A" steels are completely unattacked even when the hypochlorite contains iron. Aqueous phenol corrodes only binary chromium-free alloys. Chromium acts as a protective against attack by tartaric or citric acid when present in greater proportion than 12.5 at.-%.

F. L. USHER.

**Kinetics of the combination of hydrogen and oxygen; influence of iodine.** W. L. GARSTANG and C. N. HINSHELWOOD (*Proc. Roy. Soc.*, 1931, A, 130, 640—654).—The surface reaction between hydrogen and oxygen in porcelain and silica vessels was accelerated by iodine, the gas reaction was retarded at relatively high temperatures and pressures, whilst the explosion which normally occurs between certain limits of pressure was inhibited. The quantities of iodine necessary are small. Water vapour lowers the upper critical limit of the low pressure explosion region, and, if present in sufficient amount, inhibits the explosion altogether. The results of an investigation of the effect of pre-treatment of the vessel with hydrogen or oxygen agree, so far as the direction of the effect is concerned, with the experiments of Alyca and Haber (*A.*, 1930, 1255), but the magnitude of the effect is much smaller. In the region of high temperature and pressure where the inhibiting action of iodine is observed it is calculated that the efficiency of collisions with iodine in breaking chains is less than about 10<sup>-4</sup>. Commercial hydrogen contains no inhibiting substances.

L. L. BIRCUMSHAW.

**Catalytic action of hydrogen on the carbon monoxide flame.** W. E. GARNER, D. A. HALL, and F. E. HARVEY (*J.C.S.*, 1931, 641—653).—The influence of dimensions of the explosion vessel, the addition of inert gases, etc. has been studied on the position and magnitude of the step on the curves showing the relation between the radiation from the flame and the percentage of hydrogen. The position of the step is unaffected by the length or the diameter of the vessel or the direction in which the radiation is measured, which suggests that it is due to changes in the chemical phenomena occurring in the flame and not to wave phenomena set up by it. The addition of carbon monoxide or oxygen in excess to the hydrogen-free flame does not affect the position of the step and, therefore, the hypothesis put forward previously that the position of the step is determined by the relation,  $k = p_H p_{CO}$  is amended to  $k = p_H p_{CO}$ , (*cf.* *A.*, 1930, 1379).

F. J. WILKINS.

**Determination of catalytic coefficients from isocatalytic data.** H. M. DAWSON and E. SPIVEY (*Proc. Leeds Phil. Soc.*, 1931, 2, 174—177).—The catalytic activity of a mixture of a moderately strong acid with one of its salts is, for a given acid concentration, minimal for a certain salt concentration, and from the composition of this "isocatalytic" mixture and the corresponding velocity the catalytic coefficients of the undissociated acid and its anion may be calculated. Calculations of this kind have been made with data for the iodine-acetone reaction in presence of sodium acetate and acetic acid at 25°. R. CUTHILL.

**Mechanism of iron catalysis in certain oxidations.** C. V. SMYTHE (*J. Biol. Chem.*, 1931, 90, 251—265).—The results of determinations of the rate of oxidation of ferrous sulphate in presence of pyrophosphate and of metaphosphate at different hydrogen-ion concentrations confirm the view that the ferrous iron is oxidised in the form of a non-ionised complex, the effect of  $p_H$  on the oxidation being exerted only indirectly through its effect on the stability of the

complex. The catalytic effect of ferrous iron on the oxidation of organic acids such as citric acid or tartaric acid has been investigated and a detailed mechanism for the reaction is proposed.

W. O. KERMAK.

**Catalytic decomposition of sodium hypochlorite solutions. III. Promoter action of hydrated magnesium oxide in the hydrated copper oxide catalysis of sodium hypochlorite.** J. R. LEWIS (*J. Physical Chem.*, 1931, 35, 915—919; cf. A., 1928, 376).—Data showing the promoter action of hydrated magnesium oxide on the hydrated copper oxide catalysis of the decomposition of sodium hypochlorite are recorded. The maximum promoter action occurs when the ratio copper:magnesium is 1:3 or 4, but the effect disappears when this ratio is 1:8. The promoter preserves the activity of the catalyst by preventing agglomeration of the particles; this view is supported by the fact that in the catalyst most effectively promoted the colour of the hydrated copper oxide remains unchanged, which is not the case when the promoter is absent. L. S. THEOBALD.

**Autoxidation of phosphorus dissolved in carbon tetrachloride.** B. BLASER (*Ber.*, 1931, 64, [B], 614—619).—Finely-divided phosphorus suspended in carbon tetrachloride rapidly absorbs oxygen with strong phosphorescence and separation of a voluminous pale yellow precipitate. The rate of reaction depends greatly on the temperature and, apparently, on uncontrollable catalytic influences. Independently of the use of an excess of phosphorus or oxygen, the ratio P:O is very nearly 2:3 and, since the product differs completely from phosphorous oxide, the structure  $(P_2O_3)_x$  must be ascribed to it. The compound inflames immediately when brought into contact with water, but cautious decomposition of it suspended in carbon tetrachloride yields a strongly-reducing aqueous solution which has an odour of phosphine and slowly deposits a yellow precipitate of phosphorus suboxide. It is relatively stable in a vacuum at 100° and does not appear to be affected by light.

H. WREN.

**Quantum mechanics of adsorption catalysis.** M. BORN and V. WEISSKOPF (*Z. physikal. Chem.*, 1931, B, 12, 206—227).—From the point of view of quantum mechanics the function of a catalysing surface is to keep the reactants in contact long enough for the probability of their surmounting the energy hill lying between the initial and final states to reach a maximum. If the surface itself takes part chemically in the reaction, it may be supposed that there is an energy hill between the adsorbed molecule and the atom of adsorbent, which is surmounted in the course of the sojourn of the molecule on the surface, a secondary reaction thus becoming possible. Whilst it is admitted that these two processes may not be essential in every case of adsorption catalysis, and that such factors as the resolution of primary linkings under the influence of adsorption forces may often be of prime importance, quantum mechanical theory has been used to deduce the reaction velocity in an adsorbed system as a function of its mechanical properties and the properties of the adsorbent (cf. this vol., 318).

R. CUTHILL.

**Combination of carbon monoxide with oxygen at mixed oxide catalysts.** B. NEUMANN, G. KRÖGER, and R. IVANOVSKI (*Z. Elektrochem.*, 1931, 37, 121—128).—The effect of varying the composition of mixtures of manganese dioxide with cobalt oxide, nickel oxide, and silver oxide, and of silver permanganate with nickel oxide, on their catalytic activity in promoting the combination of carbon monoxide with oxygen has been studied at different temperatures. The relation between activity and composition depends on the temperature; e.g., addition of 33% of cobalt oxide ( $Co_3O_4$ ) to manganese dioxide depresses the activity of the latter at 50°, but increases it at 60°. At a given temperature the activities of the individual oxides are in the same order as their dissociation pressures. The function of the oxides is chemical, and their relative activities are not determined by the total amount of the reacting gases adsorbed.

F. L. USHER.

**Reactions at the surface of hot metallic filaments. V. Reaction  $H_2 + CO_2 \rightarrow CO + H_2O$  at the surface of platinum, platinum coated with barium oxide, and thoriated tungsten.** B. S. SRIKANTAN (*Indian J. Physics*, 1930, 5, 685—698; cf. A., 1930, 1531).—An apparatus for the investigation of electron emission from prepared filaments is described; the minimum temperature of perceptible emission obtained by extrapolation is that required to start the interaction of carbon dioxide and hydrogen on these surfaces, and for the activation of hydrogen. The effect of varying the proportions of the gases is considered. Carbon dioxide, on a barium oxide-coated platinum filament as more conducive to adsorption, is activated at a lower temperature. The temperature of oxidation of methane at the platinum surface was that of minimum electron emission. It is concluded that the activation of gases at a catalytic surface depends largely on the ability of the surface to emit electrons at that temperature.

N. M. BLIGH.

**Catalytic conversion of gases containing methane into carbon monoxide and hydrogen.** K. KELLER and W. KLEMPF.—See B., 1931, 325.

**Conversion of carbon monoxide by means of steam or air into hydrogen or nitrogen-hydrogen mixtures.** K. KELLER and W. KLEMPF.—See B., 1931, 326.

**Catalytic decomposition of carbon disulphide by steam.** B. NEUMANN and E. ALTMANN (*Z. Elektrochem.*, 1931, 37, 173—185).—The reaction between carbon disulphide and steam is catalysed by many substances. Copper, gold, and platinum catalysts, chromic oxide, and a mixture of the oxides of copper, lead, and chromium in molecular proportions are most effective at about 600° and the maximum yield of hydrogen sulphide is about 65%. Oxides of barium, calcium, magnesium, and aluminium are most effective at about 450° and the maximum yield of hydrogen sulphide is 77%. Thorium dioxide and cerium dioxide are most active at about 300° and the yields obtained are 81 and 87%, respectively. A mixture of magnesium oxide with 10% of thorium dioxide is a very active catalyst, having an optimal temperature of about 350° and giving a 98% yield.

Active carbon gives a 78% yield at 600° and the addition of oxides of magnesium, uranium, or iron does not increase the yield, but the addition of thorium dioxide increases the yield to 87% at 425°. The reaction probably takes the course (1)  $CS_2 + H_2O = COS + H_2S$ , (2)  $COS + H_2O = CO_2 + H_2S$ , and over the range 170—500° the products are as represented by (2). Below 170° the rate of decomposition of the intermediate carbon oxysulphide is greater than its rate of hydrolysis and carbon monoxide and free sulphur appear among the products. The action of the catalyst is probably to form a sulphide with the carbon disulphide vapour, which is then hydrolysed by the steam. The formation of sulphide occurs rapidly, but the subsequent hydrolysis is slow in the case of the heavy metals and more rapid in the case of the alkaline earths, particularly with the mixture of magnesium oxide and 10% of thorium dioxide.

E. S. HEDGES.

**Behaviour of the catalyst in carbon monoxide filters.** G. STAMPE and F. BANGERT.—See B., 1931, 368.

**Catalytic formation of hydrogen cyanide. V. Cerium dioxide as catalyst.** G. BREDIG and E. ELÖD [with W. KÖNIG] (Z. Elektrochem., 1931, 37, 2—11; cf. this vol., 176).—In the formation of hydrogen cyanide from carbon monoxide and ammonia in presence of cerium dioxide as catalyst it is not possible to detect the presence of cerium nitride, hydride, or carbide as an intermediate product, nor does any change occur in the crystal structure or lattice dimensions of the catalyst as a result of the reaction. Contrary to the observations of Lipski (A., 1909, ii, 478), no ammonia is produced by the reaction of metallic cerium with nitrogen and hydrogen unless oxygen is present, and even then reaction ceases when all the cerium has combined to form cerium dioxide. The activity of cerium dioxide in catalysing the formation of hydrogen cyanide runs approximately parallel with its adsorptive power for ammonia, carbon dioxide, and carbon monoxide, the adsorption of which on a given catalyst decreases in this order. It is therefore suggested that the adsorbed ammonia is highly active, perhaps even partly broken up into hydrogen and the NH group, and that similarly the adsorbed carbon monoxide is readily resolved into carbon and carbon dioxide, the formation of hydrogen cyanide occurring by reaction between this free carbon and the NH group.

R. CUTHILL.

**Catalytic addition of hydrogen chloride to unsaturated hydrocarbons.** W. J. PIOTROWSKI and J. WINKLER.—See B., 1931, 328.

**Catalytic reactions of sulphur compounds present in petroleum.** J. C. ELGIN and others.—See B., 1931, 327.

**Catalytic synthesis of methyl alcohol under pressure.** M. FLEURY.—See B., 1931, 385.

**Thermal behaviour of phenols. III. Influence of the time of heating and the nature of the accompanying gas.** A. HAGEMANN (Z. angew. Chem., 1931, 44, 221—224).—When phenol vapour is passed over a heated filament about 92% is decomposed; the condensable fraction of the product (63%)

contains about 34% of *cyclopentadiene* and 27% of naphthalene and polymerised *cyclopentadienes*, and the non-condensable fraction contains carbon monoxide 70.3% and methane 5.9%. In presence of nitrogen or hydrogen the quantity of phenol decomposed is reduced, but the yield of *cyclopentadiene* is increased, and in the case of hydrogen a considerable quantity of benzene is formed. *m*-Cresol yields *cyclopentadiene* 2.1%, benzene 14.2%, and toluene 12.8%, calculated on the cresol decomposed. A study of the influence of the rate of flow of the vapour shows that the shorter is the period of heating the higher lies the temperature of initial decomposition. At high filament temperatures the reactions involved are of a photochemical rather than a thermal type. Water vapour and, to a smaller extent, carbon dioxide favour the cracking of the primary decomposition products of pyrocatechol to a greater extent than do nitrogen and hydrogen. In presence of water vapour a 67.5% yield of butadiene has been obtained from pyrocatechol, whereas in presence of hydrogen or nitrogen the yield is only 30—33%. H. F. GILLBE.

**Effect of adding colloids to electrolytic solutions for preparing the anodic film on aluminium.** S. SETOH and A. MIYATA.—See B., 1931, 352.

**Electrochemical preparation of sodium and lead arsenates.** W. A. PLOTNIKOV and M. IVANENKO (Z. Elektrochem., 1931, 37, 88—91).—By the use of an anolyte containing 150 g. per litre of arsenious oxide as sodium arsenite and a catholyte containing 150 g. per litre of sodium hydroxide, sodium arsenate may be prepared by electrolysis with a current density of 3 amp. per dm.<sup>2</sup>; the current efficiency is 100%. The process may be rendered continuous by circulating the anolyte and removing the precipitated arsenate. Iron or nickel electrodes are satisfactory, and the diaphragm should be of asbestos cement; although nickel electrodes yield a purer product, iron has the advantage of hindering the formation of arsine. Pure lead arsenate cannot be obtained by simultaneous oxidation of sodium arsenite and anodic dissolution of lead, as the oxidation potential of arsenious oxide and the solution potential of lead differ only slightly. By using an anolyte containing 20 g. of sodium arsenite and 70 g. of sodium nitrate per litre and sufficient acetic acid for neutralisation, and as the catholyte a 30% solution of sodium nitrate, an almost theoretical yield of lead arsenate may be obtained. The anode should be of lead and the cathode of iron, and the current density 5.5—6 amp. per dm.<sup>2</sup>

H. F. GILLBE.

**Electrolytic oxidation of solutions of manganese salts in hydrofluoric acid.** L. VON PUTNOKY and B. VON BOBEST (Z. Elektrochem., 1931, 37, 156—163).—Solutions of manganous sulphate in hydrofluoric acid (4—8%), electrolysed at an anode current density of 0.01—0.04 amp. per cm.<sup>2</sup>, become at first dark brown owing to the formation of manganic fluoride, and are finally converted into permanganic acid, the yield of the latter reaching 80%. No permanganic acid is detectable in the anode liquid until all manganous ions have disappeared. Quadrivalent manganese cannot be detected at any stage of the

oxidation. Microscopic observation shows that in the initial stage the primary product at the anode is permanganic acid, which diffuses into the solution and immediately reacts with any manganous salt present to give manganic fluoride. The latter is finally directly oxidised to permanganic acid.

F. L. USHER.

**Action of electrical discharge on gaseous hydrocarbons.** S. C. LIND, B. M. MARKS, and G. GLOCKLER (Trans. Amer. Electrochem. Soc., 1931, 59, 33—40).—Determinations have been made of the amounts of hydrogen produced by the decomposition of methane, ethane, propane, and butane under the influence of high-speed electrons (125—130 kilovolts) emitted from a Slack-Lenard cathode-ray tube. The number of hydrogen molecules liberated was always about ten times the number of electrons corresponding with the filament current. Assuming that only 1% of these electrons actually enter the reaction vessel, it is estimated that the number of ion pairs produced in the gas is of the same order of magnitude as the number of molecules reacting.

H. J. T. ELLINGHAM.

**Electrolytic reduction of dicarboxylic acids.** H. NAKATA (Chikashige Anniv. Vol., 1930, 49—55).—By electrolysis of a 10% solution of oxalic acid in 2*N*-sulphuric acid with a lead anode and mercury cathode, and a current density of 8.3 amp. per dm.<sup>2</sup>, at 5—7°, an 88.3% yield of glyoxylic acid is obtained after 6 hrs. The current efficiency is about 88% during the first 2 hrs., but falls to about 37% in the later stages of the reduction. Formaldehyde does not appear among the reduction products, but dihydroxytartaric acid is probably formed. At higher temperatures (60°) the current efficiency diminishes, but the yield of glycollic acid, which is formed directly from the oxalic acid, is increased; the glyoxylic acid produced undergoes immediate reduction. In 6*N*-sulphuric acid solution at 60° the glycollic acid yield is further increased. Experiments with various electrodes show that a mercury cathode gives the best yield of glyoxylic acid and a mercury cathode the best yield of glycollic acid. The progress of the reduction in hydrochloric acid solution is almost identical with that in sulphuric acid. The current and material yield may both be raised to nearly 100% by employing a current density of 4.15 amp. per dm.<sup>2</sup> Malonic and succinic acids are not cathodically reduced in sulphuric acid solution.

H. F. GILLBE.

**Study of chemical reactions from potential energy diagrams.** A. R. OLSON (Trans. Faraday Soc., 1931, 27, 69—76).—Potential energy diagrams have been employed to discuss the molecular rearrangement of dichloroethylene. On this basis the effects of temperature, pressure, solvents, and light frequency are considered.

F. G. TRYHORN.

**Function of Br<sub>3</sub>' and I<sub>3</sub>' ions and influence of chlorine ions in oxidation reactions in light.** R. M. PURKAYASTHA (J. Indian Chem. Soc., 1931, 7, 991—996; cf. A., 1930, 718).—The velocity coefficients of the rates of photochemical reaction of mandelic acid and of lactic acid with bromine in the presence of potassium bromide at 30°, are zero-molecular. Whilst the oxidation of hydroxy-acids by bromine is

accelerated by chlorine ions in the dark, it is retarded in the light. The light reactions are zero-molecular, but the oxidation of phenyl-lactic acid appears unimolecular on account of the preponderance of the dark reaction. The function of I<sub>3</sub>' ions in photochemical oxidations by iodine is discussed.

F. L. USHER.

**Photochemical reaction between iodine and hydrogen.** N. SASAKI and K. NAKAMURA (Chikashige Anniv. Vol., 1930, 299—302).—No hydrogen iodide is produced when an equimolecular mixture of hydrogen and iodine at 1 atm. pressure and 270° is irradiated by mercury arc light from which radiation of wave-length shorter than 3500 Å. has been removed. Under the action of ultra-violet radiation, using a streaming method, atomic hydrogen is produced in the mixture, probably by the action of excited iodine molecules on the hydrogen molecules, and hydrogen iodide is then formed by combination of atomic hydrogen with molecular iodine.

H. F. GILLBE.

**Photo-reaction between hydrogen and iodine monochloride.** G. K. ROLLEFSON and F. E. LINDQUIST (J. Amer. Chem. Soc., 1931, 53, 1184—1185).—The results of Mellor and Iredale (this vol., 180) are not inconsistent with those of the authors (A., 1930, 1135).

J. G. A. GRIFFITHS.

**Photosensitised decomposition of nitrogen trichloride.** I. T. G. A. GRIFFITHS and R. G. W. NORRISH (Proc. Roy. Soc., 1931, A, 130, 591—609; cf. this vol., 179).—The decomposition of nitrogen trichloride (up to 3 mm.) in chlorine is photosensitised by chlorine, and is a zero-molecular order reaction until decomposition is almost complete, when a semi-explosive reaction occurs. The velocity of the reaction is directly proportional to the light flux absorbed by the chlorine. The quantum efficiency ( $\gamma$ ) in homogeneous blue (436 m $\mu$ ) and ultra-violet (365 m $\mu$ ) is less than 2° at low pressures of chlorine and decreases with increase of chlorine pressure to the limiting value 2.0 (approx.). The equation  $\gamma = 1/0.0038P_{Cl_2} + 2.5$  expresses the results quantitatively. No decomposition is produced by the wave-lengths 579 or 546 m $\mu$ .

L. L. BIRCUMSHAW.

**Photochemical decomposition of nitrous acid.** K. S. MURTY and N. R. DHAR (J. Indian Chem. Soc., 1931, 7, 985—990; cf. A., 1925, ii, 691).—The unimolecular velocity coefficients of the decomposition of nitrous acid by light of wave-lengths 4725, 5650, 7304, and 8500 Å. decrease in the order given. The temperature coefficient of the dark reaction increases from 1.58 (20—30°) to 2.21 (30—40°), whilst that of the light reaction falls below unity in the range 30—50°. Both these effects are explained by the reversibility of the decomposition. The velocity coefficient is proportional to the cube root of the intensity of the incident light. The reaction does not obey the law of photochemical equivalence. Quantum yields for different temperatures and wave-lengths are given.

F. L. USHER.

**Photochemical decomposition of carbonyl chloride vapour by ultra-violet radiation of different wave-lengths.** F. ALMASY and T. WAGNER-JAUREGG (Naturwiss., 1931, 19, 270).—Under similar conditions, at 20° the amount of photochemical



decomposition of highly purified carbonyl chloride at 300 mm. produced by light of 2750–3041 Å. was 1/4.2–1/8.7 that produced by the full radiation of the mercury arc lamp. At 160° no increase in decomposition was obtained using the narrower spectral region, whereas there was an increase of 1.8% in decomposition due to the full radiation. The decomposition, therefore, is caused principally by light of shorter wave-lengths (cf. Henri and Howell, A., 1930, 1088).

W. R. ANGUS.

Decomposition of potassium cobaltioxalate and sodium cobaltinitrite by light. W. V. BHAGWAT and N. R. DHAR (Z. anorg. Chem., 1931, 197, 18–28).—The temperature coefficient of the decomposition of potassium cobaltioxalate is 1.13 in sunlight, 1.85 in tungsten lamp radiation, and 3.7 in the dark, and that of sodium cobaltinitrite is 1.56 in sunlight and 2.7 in tungsten lamp radiation. Both reactions are strongly accelerated by short wave-length radiation. In sunlight the decomposition of potassium cobaltioxalate is a reaction of zero order, and the velocity is proportional to the square root of the intensity of the radiation, but in tungsten lamp radiation the linear relationship holds; the velocity coefficient in sunlight increases with increase of concentration of the solution. The quantum yield in unity in sunlight, but is less in tungsten lamp radiation; it increases with rise of temperature. The decomposition of sodium cobaltinitrite in sunlight is a semimolecular reaction, and the velocity is independent of the concentration; Einstein's law is invalid. Both reactions are unimolecular in tungsten lamp radiation. The following general equation has been derived for the velocity of a photochemical reaction:  $dx/dt = KS^n - I_0^n (1 - e^{-i(a-x)^n})/l$ , where  $S$  is the surface area exposed to radiation of intensity  $I_0$ ,  $n$  is the order of the reaction,  $i$  is the molecular absorption coefficient, and  $K$  is a constant. It is shown theoretically that, in accordance with observation,  $n$  may vary from 0 to 1 and is related inversely to the quantity of light absorbed.

When prepared by Sørensen's method potassium cobaltioxalate contains 10 mols. of water, and not 3 mols. as reported by Sørensen. The absorption spectrum of the compound exhibits pronounced maxima at 6050 and 4250 Å. H. F. GILLIE.

Chemical origin of the colour changes of silicate and quartz glasses under the influence of radium radiation. J. HOFFMANN (Z. anorg. Chem., 1931, 197, 29–51).—The production of a grey coloration when various types of glass are subjected to the action of radium radiation is a complex process and is due to both atomic and ionic changes. A blue colour is produced in silicate glasses only when trivalent manganese is present; contrary to previous reports, sodium atoms cannot cause the effect. Radium or ultra-violet radiation thus affords a sensitive reagent for the manganic ion, although the blue colour fades after a time to a stable amethyst colour. The occurrence of multi-coloured parallel lines in irradiated glasses is ascribed to phase segregation. The brown coloration of glasses ascribed by Salaquada to iron and manganese can be caused only by manganous ions. The violet coloration of quartz glass is

produced by ferrous and ferric ions in presence of titanium. H. F. GILLIE.

Relation between density, silver content, covering power, grain distribution, and grain size of developed photographic films. H. ARENS, J. EGGERT, and E. HEISENBERG (Z. wiss. Phot., 1931, 28, 356–366).—The relation  $s = -x \log(1 - ya)$  is theoretically deduced (cf. Nutting, Phil. Mag., 1913, 26, 423), where  $s$  = density,  $x$  = the number of grain layers,  $y$  = the number of grains per cm.<sup>2</sup> of a one-grain layer, and  $a$  = the mean projection of a grain, in cm.<sup>2</sup> The formula is experimentally proved for a one-grain layer. For many layers (e.g., 20) in a film, the approximation  $s = za/2.3$  is obtained, where  $z$  = the number of grains per cm.<sup>2</sup> of the whole film. The relation  $\delta = k(f/d^2)\mu^{-1}$  is calculated, where  $\delta$  = covering power,  $d$  = the density of a grain,  $\mu$  = the weight of a grain, and  $f$  is a factor dependent on the shape of the grain. Experimental results are compared; silver grains by physical development ( $d$  10.5) give  $f$  2.6, corresponding with crystalline leaflets, but by chemical development are probably spongy colloidal masses.

J. LEWKOWITSCHE.

Separate [processes in] ripening. LÜPPCRAMER (Z. wiss. Phot., 1931, 28, 350–356).—By using 50% excess of bromide at emulsification, and no ripening, an emulsion may be prepared having large grains, but with small content of sensitive nuclei; its characteristic curve is very flat.  $D_{max}$  is small and does not increase with exposure. If plates are treated with Capri-blue solution, they are sensitised and give comparatively normal curves. The ripened emulsion is normal. The grain size of the unripened emulsion is unaltered by increase of the amount of gelatin present at emulsification (the final gelatin addition being reduced in proportion). The properties of fine-grain emulsions are compared. Grain growth and the formation of sensitive nuclei may be considered separately in relation to ripening processes.

J. LEWKOWITSCHE.

Photonegative effect on [the conductivity of] silver bromide. E. A. KIRILLOV (Z. wiss. Phot., 1931, 28, 367–373; cf. A., 1929, 276).—After illumination (430 m $\mu$ ) of silver bromide, its conductivity, measured in the dark, shows at first a decrease, superseded by an increase, which, in course of time, again slowly decreases. The primary negative effect is enhanced by previous treatment with sodium nitrite (photographic sensitiser), and inhibited by picric acid (desensitiser) which causes an immediate increase of conductivity on illumination of the silver bromide. Hence photonegative sensitivity is comparable to photographic sensitivity. Measurements of the resistance of silver bromide, by a method eliminating the influence of polarisation, show that it increases markedly after illumination. J. LEWKOWITSCHE.

Different forms of silver bromide. A. REYCHLEB (Bull. Soc. chim. Belg., 1931, 40, 12–17).—By placing a glass plate in a solution of silver nitrate rendered faintly turbid with potassium bromide solution an adherent deposit of silver bromide is formed within 15–20 hrs., and the plate behaves normally as regards exposure to light and development. By immersing a filter-paper in a similar turbid solution

it is readily sensitised; the time required for exposure to light is very short, and the resulting image, after development, is clear and may be viewed from either side of the paper. The turbid solution is reduced immediately by an ordinary photographic developer, without previous exposure to light, on account of the fineness and reactivity of the silver bromide particles; this activity diminishes as the suspension ages, e.g., during deposition on the plate or paper, and it is suggested that the action of light is to arrest this ageing process or to restore the initial condition of the halide. Experiments on the addition of gelatin to a silver bromide suspension demonstrate the mutual affinity of the halide and the gelatin, and indicate that after the micelles are formed the bromide associates to produce the form which is not reduced by a developer without exposure to light.

H. F. GILLBE.

Determinations on the size-frequency distribution of residual (undevelopable) grains of a photographic emulsion. E. C. JENSEN and A. P. H. TRIVELLI (J. Franklin Inst., 1931, 211, 489—494).—An attempt to correlate exposure with the size-frequency distribution of residual grains has been unsuccessful. The log log frequency-size curves resemble parabolas, but the shape varies and shifts with the exposure in such a way as to preclude the existence of any simple relation.

J. LEWKOWITSCH.

Secondary reactions in latent image formation. Influence of free alkali halide. T. S. PRICE.—See B., 1931, 367.

Hydrolysis of acetone in ultra-violet light. M. QURESHI and N. A. TABER (Nature, 1931, 127, 522).—In the hydrolysis of acetone in ultra-violet light the velocity of reaction is directly proportional to the intensity of the incident light. Formaldehyde is also formed when an aqueous solution of acetone is exposed to the light of a quartz mercury lamp (cf. Bowen and Watts, A., 1926, 808).

L. S. THEOBALD.

Influence of wave-length in the irradiation of ergosterol. E. KISCH and T. REITER (Deut. med. Woch., 1930, 2034—2036; Chem. Zentr., 1931, i, 479).—The formation of malodorous products in the irradiation of milk and of inconstant products in that of ergosterol is avoided by using radiation of wave-length greater than 2800 Å.

A. A. ELDRIDGE.

Effect of radiation energy on the protein molecule. J. P. MISCHTSCHENKO (Strahlenther., 1928, 30, 707—719; Chem. Zentr., 1930, ii, 3787).—Sunlight decomposes protein of low mol. wt.; eventually Bach's nitrate reaction for fission products fails. Peptone, nutrose, and horse serum are unaffected. Certain proteins suffer change in the dark; the change is much more rapid in sunlight. Protein of high mol. wt. is not decomposed by X- or radium rays in the doses employed; large doses cause in fresh solutions of proteins of low mol. wt. immediate diminution, in aged solutions almost always a diminution, of fission products, whilst small doses cause in fresh solutions an increase in fission products. Experiments on extracts of organs showed that the tissues can be grouped according to their content of protein fission products.

A. A. ELDRIDGE.

Photochemical decomposition of nicotine salts. I. PLOTNIKOV and K. WEBER (Chem.-Ztg., 1931, 55, 237—239).—The decomposition of nicotine and nicotine salicylate, tartrate, and malonate solutions under the influence of prolonged exposure (up to 1 year) to sunlight, with or without catalysts (photo-active substances), has been studied. The best catalysts were dichromates, gold chloride, ferric nitrate, iodine, and chlorophyll; up to 85% decomposition was found. Experiments on tobaccos exposed to an arc lamp up to 8 days give lower and fluctuating results; the catalysts are difficult to apply in these cases.

J. LEWKOWITSCH.

Radiochemical equilibrium in mixtures of ammonia, nitrogen, and hydrogen. J. F. D'OLIESLAGER and J. C. JUNGERS (Bull. Soc. chim. Belg., 1931, 40, 75—84).—The velocity of formation and decomposition of ammonia under the influence of  $\alpha$ -rays at 24° has been investigated as a function of the pressure. The equilibrium mixture contains 4.7 vol.-%  $\text{NH}_3$  when the other gases are present in stoichiometric proportions. At constant pressure (500 mm.) the velocity of the reaction increases at first rapidly, then more slowly, and finally at an increasing rate as the concentration of the ammonia increases beyond the equilibrium point. The low value of the equilibrium concentration, compared with that calculated theoretically, is probably connected with the abnormal concentration of ammonia in the neighbourhood of each ion, due to the high dipole moment of ammonia.

H. F. GILLBE.

Solid polyiodides of potassium. N. S. GRACE (J.C.S., 1931, 594—609).—The effect of moisture on the m. p. of iodine-potassium iodide mixtures has been studied. The results suggested that potassium triiodide prepared from aqueous solution contained chemically combined water, and, moreover, that only the hydrated form was stable. This suggestion was confirmed by an investigation of the more concentrated solutions of the system iodine-potassium iodide-water which showed that at 25° the solid hydrated iodides  $\text{KI}_3 \cdot \text{H}_2\text{O}$  and  $\text{KI}_7 \cdot \text{H}_2\text{O}$  exist; no anhydrous polyiodide can be formed at this temperature. A study of the system iodine-potassium iodide-benzene indicated the formation of the solvated hepta-iodide,  $\text{KI}_7 \cdot 2\text{C}_6\text{H}_6$ .

F. J. WILKINS.

Hypothetical potassium polyiodides. W. D. BANCROFT, G. A. SCHERER, and L. P. GOULD (J. Physical Chem., 1931, 35, 764—785).—Mainly a discussion. Solid potassium tri-iodide does not occur as a stable phase at 25°; potassium iodide and iodine are the only solid phases which can be stable at this temperature. X-Ray measurements [by H. M. SOUTHWORTH] afford no evidence for the existence of potassium tri-iodide.

L. S. THEOBALD.

Chemical reactivity of the fused bases. I. Action of alkali amides on electropositive metals. W. C. FERNELIUS and F. W. BERGSTROM (J. Physical Chem., 1931, 35, 740—755).—The reactions of the electropositive elements with fused potassamide at 375—400° are, in general, similar to the same reactions in liquid ammonia at the ordinary temperature. Magnesium, calcium, and aluminium form initially the free alkali metal which colours the fused mass blue.

Magnesium, beryllium, zinc, and calcium dissolve in the amide to give compounds of the type  $M''(\text{NHK})_2, 2\text{NH}_3$  or  $M''\text{NK}, 2\text{NH}_3$ ; aluminium gives a white or grey mass insoluble in the fused mass and of indefinite composition, whilst germanium appears to be converted into a mixture of the compounds  $\text{NGe}\cdot\text{NHK}$  and  $\text{Ge}\cdot\text{NK}, \text{NH}_3$ . Mercury itself is apparently unattacked, but dissolves in the potassium which results from the slow decomposition of the amide into its elements. Cerium, thorium, cadmium (very slight), and manganese are only slightly attacked, and copper, thallium, titanium, zirconium (powder), tantalum, chromium, nickel, platinum, and iridium are not attacked after fusion for several hours. At  $400^\circ$  in fused sodium hydroxide, sodium dissolves to a slight extent, giving a blue colour to the fused mass, magnesium gives a blue colour around the strips of metal and then dissolves in a short time, whilst calcium, in an atmosphere of nitrogen, reacts to form a blue mass and ultimately a white precipitate, insoluble in the fused mass. Aluminium wire is apparently unattacked during 5 hrs.' treatment.

L. S. THEOBALD.

**Action of sulphuric acid on copper.** F. DE CHAVES (Anal. Fis. Quim., 1931, 29, 177—181).—By the action of concentrated sulphuric acid at  $55^\circ$  on copper there result, after 6 days, anhydrous cupric sulphate, free sulphur, sulphur dioxide, and a black deposit which contains Cu 69.73%, S 8.5%; the black substance yields sulphate ion on dissolution in hydrochloric acid. Its composition differs markedly from that of any natural or artificial substance previously reported, and it appears to be a more highly basic cupric sulphate than has been hitherto described.

H. F. GILLBE.

**Carbonyls of copper halides.** O. H. WAGNER (Z. anorg. Chem., 1931, 196, 364—373).—By the action of carbon monoxide on cuprous chloride and bromide at pressures up to 100—150 atm. the existence of  $\text{Cu}_2\text{Cl}_2, 2\text{CO}$  and  $\text{Cu}_2\text{Br}_2, 2\text{CO}$  has been established; the analogous iodide probably exists, but its formation takes place very slowly. Although the presence of water is not essential, it appears to have some catalytic influence on the progress of the reaction. Cuprous oxide or cyanide, or mixtures of copper and cupric sulphate, do not react with carbon monoxide. Vapour-pressure measurements show that equilibrium is established only very slowly; the vapour pressure of  $\text{Cu}_2\text{Cl}_2, 2\text{CO}$  attains 760 mm. at about  $40^\circ$  and that of  $\text{Cu}_2\text{Br}_2, 2\text{CO}$  at about  $10^\circ$ . The  $\log p-1/T$  curve is linear at temperatures above  $-20^\circ$ , and the calculated mean heats of dissociation of the chloride and bromide complexes are 9.8 and 8.2 kg.-cal., respectively. The stability of these halide compounds follows the same order as that of the copper, silver, and gold ammoniates. Analogous silver complexes could not be prepared.

H. F. GILLBE.

**Hydroxylamine as a precipitation agent.** II. J. C. ROLDÁN (Anal. Fis. Quim., 1931, 29, 158—161).—The precipitate resulting from the action of hydroxylamine on a solution of a cupric salt (A., 1930, 1547) is converted into the white form more rapidly in presence of an excess of copper, and is redissolved to a colourless solution by an excess of the reagent. Copper ferrocyanide is not formed in presence of

hydroxylamine, but a white colloidal compound is slowly precipitated and the solution becomes orange-yellow and fluorescent; ammonia destroys the fluorescence. These results vary with the quantities and order of addition of the reagents. Hydroxylamine inhibits the precipitation of uranium ferrocyanide within certain concentration limits. H. F. GILLBE.

#### Thermal decomposition of silver subfluoride.

R. SCHOLDER and K. TRAUlsen (Z. anorg. Chem., 1931, 197, 57—64).—Contrary to the report of Hettich (A., 1927, 1155), fluorine is not evolved when silver subfluoride is heated. The primary decomposition, which takes place at  $100-150^\circ$  is  $\text{Ag}_2\text{F} = \text{AgF} + \text{Ag}$ , and in presence of moisture this is followed by  $4\text{AgF} + 2\text{H}_2\text{O} = 4\text{Ag} + 4\text{HF} + \text{O}_2$ . When silver subfluoride is heated in dry nitrogen or oxygen at  $700^\circ$ , there is a slow and progressive loss of weight, amounting to about 5% after 66 hrs., which is ascribed to volatilisation of silver fluoride. The subfluoride is partly re-formed when the mass is cooled. Silver subfluoride is slightly light-sensitive. H. F. GILLBE.

#### Composition of the cyanide complex radical of metals. II. Cadmium cyanide complex.

K. MASAKI (Bull. Chem. Soc. Japan, 1931, 6, 60—64).—A simple titration method for the determination of the ratio of combined cyanide to cadmium in the complex ion has shown that the ion is probably  $\text{Cd}(\text{CN})_3^-$  at all concentrations. The constant  $K = [\text{Cd}(\text{CN})_3^-]/[\text{Cd}^{2+}][\text{CN}^-]^3$  is evaluated as  $5.4 \times 10^{17}$ .

E. S. HEDGES.

#### Principles of genetic formation of substances.

V. Chemistry and morphology of aluminium hydroxide. II, III. V. KOHLSCHÜTTER [with W. BEUTLER] (Helv. Chim. Acta, 1931, 14, 305—330, 330—354; cf. this vol., 444).—II. Three forms of aluminium hydroxide,  $\alpha$ ,  $\beta$ , and  $\gamma$ , have been recognised among the products of reaction of aluminium amalgam with water. None of these forms has a measurable solubility in conductivity water and the hydrogen-ion concentration of the liquid does not change during the reaction. The slight development of alkalinity which is observed when aluminium amalgam reacts with sodium chloride solution is due to an exchange reaction between the hydroxide and sodium chloride. Aluminium is also rendered active towards water by cathodic polarisation. The primary product of reaction of an aluminium cathode with water is  $\alpha$ -aluminium hydroxide, which undergoes further transformation into the  $\beta$ - and  $\gamma$ -forms, depending largely on the nature of the foreign substances present, and the continuance of the reaction is due to the electrostatic repulsion of the negatively-charged hydroxide from the cathode. No evidence was obtained that the activation is due to an increase in the concentration of electrons in the metal, according to the theory of Smits. Experiments are described on the precipitation of aluminium hydroxide by mixing solutions of aluminium chloride or potassium or ammonium alum with solutions of sodium hydroxide or ammonia in such concentrations that suspensions containing about 0.1 g. of aluminium hydroxide per 100 c.c. were obtained. When equivalent quantities of the reagents were mixed the suspension always had an alkaline reaction, due to exchange adsorption.

The forms of aluminium hydroxide and basic salts produced in each case are described; increasing concentrations of ammonia solution accelerate the  $\alpha$ - $\beta$  transformation. When aluminium hydroxide was precipitated in the presence of alkali chlorides the precipitate had different properties in each case, but no simple correlation with the lyotropic series of cations was apparent; the greatest difference was produced by the presence of lithium chloride and the precipitate apparently contained lithium aluminate and basic salts. Aluminium hydroxide precipitated from more concentrated solutions of the reagents was less reactive. The properties of aluminium hydroxide prepared by the action of ammonia solution on crystals of ammonium alum are described. X-Ray spectrographic examination has established the presence of bauxite lines in the spectrum from the  $\beta$ -pseudomorph, whilst the  $\gamma$ -pseudomorph gives a bayerite spectrum; electrolytically prepared aluminium hydroxide gives an amorphous spectrum. The forms of aluminium hydroxide precipitated from aluminate solutions by ageing and by the addition of reagents are described.

III. Independently of the method of preparation,  $\gamma$ -aluminium hydroxide is always observed under the microscope to be in a somatoid form. X-Ray examination shows these to consist partly of amorphous material and partly of crystalline material giving a spectrum containing the lines of bayerite. The processes of gelation and syneresis enter into the formation of these structures. The results of a microscopical study of their forms of aggregation are described.

E. S. HEDGES.

**Preparation of active aluminium chloride.** K. BODENDORF (J. pr. Chem., 1931, [ii], 129, 340).—Highly activated aluminium chloride for Friedel-Crafts reactions may be prepared *in situ* by passing dry hydrogen chloride into a boiling suspension of 5 g. of aluminium powder in 100 c.c. of benzene, toluene, or xylene, containing 1 g. of mercuric chloride and 0.5 g. of iodine as catalysts. J. W. BAKER.

**Significance of the crystallographic transformations of silica for its reactivity in the solid state.**

I. Ferric oxide with quartz, tridymite, or cristobalite. J. A. HEDVALL and P. SJÖMAN (Z. Elektrochem., 1931, 37, 130—142; cf. A., 1930, 1503).—Mixtures of finely-powdered quartz and ferric oxide, both of a high degree of purity, were heated at temperatures from 550° to 1350°, and the products examined by chemical and by X-ray analysis. No action occurs below 575°, the transition temperature of  $\beta$ - to  $\alpha$ -quartz, at and above which temperature one or more compounds are formed. A similar change takes place more rapidly in the neighbourhood of 950°, corresponding with the conversion of  $\alpha$ -quartz into cristobalite. At the higher temperature there is also formed a solid solution of ferric oxide in cristobalite, whereby the length of the unit cell is increased from 6.99 to 7.02 Å. Neither cristobalite nor tridymite reacts *per se* with ferric oxide, and the observed changes must therefore occur during the actual transition from one crystallographic form to another.

F. L. USHER.

**Volatility of silica in water vapour.** C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav.

chim., 1931, 50, 338).—The statement made previously (A., 1930, 1262) that tridymite passes into cristobalite at 395° and 300 atm. is now corrected. A small amount of cristobalite was always formed under these conditions, but the amount was independent of the duration of the experiment and may have been formed as the initial metastable product from the vapour on cooling. J. W. SMITH.

**Cerium sulphide.** PICON (Compt. rend., 1931, 192, 684—686).—Pure cerous sulphide is prepared by passing hydrogen sulphide over ceric oxide contained in a graphite boat for 1 hr. at 1000—1200°, and then for 30 min. at 1550—1600°. It is thus obtained as an apparently fused, cinnabar-red solid devoid of real crystal structure,  $d_s$  5.184. When heated in a vacuum it sinters at 2000°, and melts at 2200° with slow volatilisation and slight decomposition, which becomes rapid at 2300°. In hydrogen volatilisation and decomposition are slow even at 2400°. Chlorine at 250° converts it into cerous chloride. Oxygen above 400° and sulphur dioxide at 600° form cerous sulphate, accompanied by much ceric oxide. Water and hydrogen chloride separately have little action below 300°; together they attack it rapidly at the ordinary temperature, as also does moist bromine. Carbon dioxide at 800° reacts as follows:  $Ce_2S_3 + 4CO_2 = 3S + 4CO + 2CeO_2$ . Dilute (but not concentrated) sulphuric acid attacks it rapidly, and concentrated nitric acid forms the nitrate with no separation of sulphur. Hydrogen peroxide and potassium permanganate in the cold give cerous sulphate with some ceric oxide. It is unattacked up to 1000° by nitrogen, carbon monoxide, magnesium, sodium chloride, potassium cyanide, or the sulphides of lead, antimony, or bismuth. C. A. SILBERRAD.

**Mechanism of precipitation processes. IV. Processes in which compounds of chlorine with lead are formed.** Z. KARAOGLANOV [with D. TSCHAVDAROV] (Z. anorg. Chem., 1931, 196, 384—394).—The precipitation of lead acetate solutions by the chloride ion has been investigated; the phenomena observed resemble those which occur with the bromide ion (A., 1930, 438). Lead chloride, lead hydroxychloride, or mixtures of the two, are formed, the mechanism of the process being probably  $Pb(OAc) + Cl' \rightleftharpoons Pb(OAc)Cl$  followed by  $Pb(OAc)Cl + H_2O \rightleftharpoons Pb(OH)Cl + HOAc$ . Experiments with lead nitrate solutions show that addition of potassium acetate to a solution from which the chloride is normally precipitated causes the production of the basic salt, probably as a result of the intermediate formation of the acetatochloride from  $PbCl'$  and acetate ions. This view is confirmed by the precipitation of  $Pb(OH)Cl$  when potassium acetate solution is added to a saturated lead chloride solution. The hydroxychloride may also be obtained by addition of potassium chloride solution to a dilute solution of lead perchlorate. Lead hydroxychloride is only slightly hydrolysed by water, and its solubility (0.1—0.2 g. per litre) is markedly increased by the presence of carbon dioxide; unlike the corresponding bromine compound, it is not light-sensitive. Attempts to prepare pure lead acetatochloride were unsuccessful. Mixed halides of indefinite composition have been

prepared by the interaction of lead chloride and potassium bromide, potassium iodide, or lead bromide.

H. F. GILLBE.

**Influence of  $p_{\text{H}}$  on formation and decomposition of chloro-derivatives of ammonia.** R. M. CHAPIN (J. Amer. Chem. Soc., 1931, 53, 912—920; cf. A., 1929, 1026).—An interpretation of the stability of nitrogen trichloride towards 4—7*N*-sulphuric acid and the instability towards 2—5*N*-hydrochloric acid indicates that chlorine reacts with ammonium ion only after conversion into hypochlorous acid. Hydrogen ions, especially below a specific  $p_{\text{H}}$ , afford, by reaction with the chloro-derivatives, ammonium ions and hypochlorous acid which yields more highly-chlorinated derivatives. At  $p_{\text{H}}$  about 9, the principal reactions are  $2\text{NHCl}_2 + 4\text{OH}' \rightarrow 3\text{Cl}' + \text{ClO}' + 3\text{H}_2\text{O} + \text{N}_2$ ;  $2\text{NCl}_3 + 6\text{OH}' \rightarrow 3\text{Cl}' + 3\text{ClO}' + 3\text{H}_2\text{O} + \text{N}_2$ . With increasing dilution, and depending on the  $p_{\text{H}}$ , nitrous oxide, nitrite, and nitrate may be produced. Contrary to previous statements, oxygen is not liberated by passing chlorine into ammonia solutions.

J. G. A. GRIFFITHS.

**Decomposition of nitrates and nitrites of metals of different valencies. I. Ferrous nitrate.** C. MONTEMARTINI and E. VERNAZZA (Industria Chim., 1930, 5, 1260—1266; Chem. Zentr., 1931, i, 435).—The dehydration of ferrous nitrate hexahydrate at the ordinary temperature in an atmosphere of carbon dioxide is accompanied by evolution of nitric oxide:  $3\text{Fe}(\text{NO}_3)_2 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{OH})_3 + 5\text{HNO}_3 + \text{NO}$ . Decomposition in boiling aqueous solution in an atmosphere of carbon dioxide is at first slow with formation of a reddish precipitate; it then suddenly becomes violent and continues to completion according to the above scheme. The preliminary period is shorter for more concentrated solutions or on addition of nitric or nitrous acid, but no definite relation between concentration and the formation of nitrogen dioxide, nitrous oxide, ammonia, etc. was found. The solid product is the hydrate  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

A. A. ELDRIDGE.

**Loss of material and corrosion of apparatus during the evaporation of solutions of ammonium nitrate.** L. WASILEWSKI and W. BADZYŃSKI. —See B., 1931, 347.

**Phosphonates. II. Action of phosphine on aluminium and beryllium halides.** R. HÖLTJE and F. MEYER (Z. anorg. Chem., 1931, 197, 93—102).—Phosphine reacts with aluminium chloride if the latter be heated at 50—70°, yielding a white crystalline compound  $\text{AlCl}_3 \cdot \text{PH}_3$ , m. p. 81—83°; when heated in a vacuum it sublimes and at higher temperatures the phosphine molecule is evolved. At 34.1° the phosphine pressure is about 38 mm., and at 71°, 193 mm. At pressures up to 15 atm. no further compounds are formed. Aluminium bromide reacts readily with phosphine; the compound  $\text{AlBr}_3 \cdot \text{PH}_3$  sublimes without decomposition at 60—70°, and has m. p. 114—118°. The total vapour pressure at 63.4° is 1.6 mm., and at 83°, 8.5 mm. Aluminium bromide and its phosphonate are mutually soluble. Aluminium iodide reacts only at temperatures above 100°; the sole product is the compound  $\text{AlI}_3 \cdot \text{PH}_3$ , which has m. p. 145—150° and sublimes readily; the phos-

phine pressure at 81.7° is 4.9 mm., and at 115.1°, 30.6 mm. The stability of the phosphonates is greater than that of the analogous thiohydrates, and increases in the order chloride, bromide, iodide. Beryllium halides do not combine with phosphine even at high temperatures and pressures. Theoretical considerations are discussed.

H. F. GILLBE.

**Composition of hydrogen sulphide hydrate.** (MLLE.) A. KORVEZEE and F. E. C. SCHEFFER (Rec. trav. chim., 1931, 50, 256—260).—By applying the relation between the slopes  $dP/dT$  of the curves and the compositions of the various phases at an invariant point (cf. this vol., 430) to the quadruple point hydrate-ice-liquid-gas of the system hydrogen sulphide-water the formula  $\text{H}_2\text{S} \cdot 6\text{H}_2\text{O}$  is obtained for the hydrate.

O. J. WALKER.

**Preparation and structure of lower oxides of tungsten.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1931, 50, 343—346).—The reduction of tungstic oxide by mixtures of carbon monoxide and carbon dioxide, and of hydrogen and water vapour, at various temperatures has been investigated. Of the lower oxides of tungsten only the brown  $\text{WO}_2$  and the bluish-violet  $\text{W}_4\text{O}_{11}$  are stable, the so-called oxides of intermediate composition being either mixtures or mixed crystals. The oxide  $\text{W}_2\text{O}_5$  does not exist. The conditions for the preparation of  $\text{WO}_2$  and  $\text{W}_4\text{O}_{11}$  are given. The heats of combustion of the oxides to tungstic oxide are  $64,520 \pm 0.5\%$  g.-cal. and  $61,380 \pm 4\%$  g.-cal., respectively. These values are not in disagreement with the structural formulæ suggested by Spitzin and Kaschtanoff (A., 1927, 33).

J. W. SMITH.

**Manganous acid.** W. BILTZ [with O. RAHLFS] (Nachr. Ges. Wiss. Göttingen, 1930, 189—194; Chem. Zentr., 1931, i, 46).—The fact that natural manganese dioxide always contains basic oxide points to its acidic nature. Treatment of manganese dioxide containing water with liquid ammonia removes all the water except 1 mol. Moreover the existence of the compounds  $(\text{NH}_4)_2\text{MnO}_3$  and  $\text{NH}_4\text{HMnO}_3$  is indicated by the isothermal decomposition of the ammoniate.

A. A. ELDRIDGE.

**Rhenium.** I. NODDACK and W. NODDACK (Z. angew. Chem., 1931, 44, 215—220).—A survey of the chemical properties of rhenium and its compounds and of the detection of the metal by chemical, spectroscopic, and X-ray spectrographic methods. Details are given of the determination of rhenium in an alloy with tungsten and osmium by fusion with sodium hydroxide and nitrate, removal of the osmium as tetroxide, precipitation of the sulphides, and removal of the rhenium as heptoxide after oxidation with nitric acid. In per-rhenates the metal is most satisfactorily determined by isolation of the heptoxide, conversion into dioxide, and reduction to metal in a current of hydrogen, and in rhenium-molybdenum concentrates by fusion with alkali, precipitation of the sulphides from the solution of the mass, and isolation of the heptoxide. The preparation of per-rhenic acid, rhenium dioxide, and of derivatives of quadrivalent rhenium, and the recovery of the metal from residues and its isolation from all other metals are described in detail.

H. F. GILLBE.

**Reduction of potassium per-rhenate.** H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART (J.C.S., 1931, 666—669).—The reduction of potassium per-rhenate gives rise initially to a yellow colloidal suspension, probably of the hydrated dioxide  $\text{RcO}_2 \cdot 2\text{H}_2\text{O}$ ; this suspension finally flocculates to precipitate the hydrated dioxide. This compound may be precipitated quantitatively and dehydrated without decomposition. No evidence of the formation of intermediate products, such as rhenic acid, has been obtained. F. J. WILKINS.

**Reduction of iron oxide by carbon.** H. H. MEYER (Mitt. Kaiser Wilh.-Inst. Eisenforsch., 1930, 12, 1—5; Chem. Zentr., 1931, i, 435).—The reduction takes place in stages; there is a considerable difference in the temperature at which the reactions (in absence of oxygen) commence. The difference for ferric and ferrosiferrous oxides is 300—370° according to the form of carbon used, and that for ferrosiferrous and ferrous oxides 100°. The variation in the temperature of commencement of reduction according as wood charcoal, sugar charcoal, or coke is used is about 150°. The reduction of ferric to ferrosiferrous oxide is quantitative, and may be used for the determination of the former in mixtures of oxides. A. A. ELDRIDGE.

**Influence of  $p_{\text{H}}$  on the oxidation of ferrous sulphate.** J. CORNOG and A. HERSHBERGER (Proc. Iowa Acad. Sci., 1929, 36, 264—265).—Little ferrous sulphate was oxidised at  $p_{\text{H}}$  less than 5; in solutions buffered to  $p_{\text{H}}$  5 the degree of oxidation increased with increasing iron concentration, but at  $p_{\text{H}}$  10 it decreased with increasing iron concentration. The percentage,  $x$ , of iron oxidised by aeration of a solution of  $p_{\text{H}}$  5 in  $T$  hrs. is given by  $T = 0.032x - 0.01$ .

#### CHEMICAL ABSTRACTS.

**Reactions of iron, manganese, and calcium sulphides with the oxides of iron.** E. DIEPSCHLAG and E. HORN (Arch. Eisenhüttenw., 1930—1931, 4, 375—382; Stahl u. Eisen, 1931, 51, 329—330).—Interaction of ferrous sulphide and ferric oxide according to the equation  $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$  commences at 550° and is complete at 800—850°. Between 850 and 1100° no reaction occurs between ferrosiferrous oxide and ferrous sulphide, but at higher temperatures the reaction  $\text{FeS} + 3\text{Fe}_2\text{O}_3 = 10\text{FeO} + \text{SO}_2$  takes place, 77.5% of the iron being converted into ferrous oxide at 1220°; above 1300° a small amount of free sulphur is formed and the solid product contains traces of metallic iron. Similar reactions occur when manganous sulphide replaces ferrous sulphide, but in this case ferrous oxide is found among the reaction products at temperatures above 975°, and at 1250° 95.5% of the iron is converted into ferrous oxide. With calcium sulphide the reaction  $\text{CaS} + 3\text{Fe}_2\text{O}_3 = \text{CaO} + 6\text{FeO} + \text{SO}_2$  commences at 720°, but the lime formed combines with the excess of ferric oxide to form ferrites. The following ferrites have been prepared:  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ ,  $5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$ , and  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ , and their reactions with ferrous and calcium sulphides studied; in all cases reduction of the ferrite proceeded directly to ferrous oxide without the intermediate formation of ferrosiferrous oxide and commenced at 800° in a stream of nitrogen. The mixture  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$  reacts

with calcium sulphide at 800°, but not with ferrous sulphide below 1150°; it is suggested that this is due to the decomposition of the ferrite  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$  into  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and free lime below 800°. Ferrous sulphide is oxidised by sulphur dioxide at 800° thus,  $3\text{FeS} + 2\text{SO}_2 = \text{Fe}_3\text{O}_4 + 5\text{S}$ . A. R. POWELL.

**Iron titanates.** B. PESCE (Gazzetta, 1931, 61, 107—111).—By heating together at 900° in appropriate proportions titanium dioxide and ferrous oxalate, ilmenite and ferrous orthotitanate have been prepared. Ferric orthotitanate was obtained by heating at 1000° a mixture of titanium dioxide and ferric oxalate. Attempts to obtain metatitanates were unsuccessful. The chemical individuality of the above compounds was confirmed by an X-ray analysis. F. G. TRYHORN.

**New methods in analytical chemistry.** J. DICK (Z. anal. Chem., 1931, 83, 105—107).—Polemical. A reply to the criticism of Moser and von Zombory (cf. A., 1930, 1149). A. R. POWELL.

**Radioactivity method for investigating powdered substances.** F. BĚHOUNEK (Z. Physik, 1931, 68, 284—285).—A criticism of Šebesta's paper (this vol., 449). A. J. MEE.

**Use of Wood's light for the investigation of minerals.** F. V. LUTATI (Industria Chim., 1930, 5, 1222—1225; Chem. Zentr., 1931, i, 490).—Fluorescence reactions on illumination with light of the hydrogen discharge are described. A. A. ELDRIDGE.

**Nephelometric titrations. II. Standard solution end-point.** C. R. JOHNSON (J. Physical Chem., 1931, 35, 830—835; cf. this vol., 456).—An end-point, termed the standard solution end-point, is proposed as an alternative to the usual end-point employed in nephelometric at. wt. titrations. The chief advantages are that systems which are practically identical in composition are compared and that absolute instead of relative amounts of silver and halide ions are measured. L. S. THEOBALD.

**Micro-acidimetric studies. I.** J. MIKA (Mikrochem., 1931, 9, 143—164).—Sources of error in micro-titrations are discussed and the theory of acid-alkali titration is examined from the microchemical point of view. For micro-chemical purposes strong acids should be titrated to  $p_{\text{H}}$  4.8, thus giving a red colour to methyl-orange. The most favourable conditions of concentration and range of availability for the application of methyl-red, bromothymol-blue, phenol-red, phenolphthalein, thymolphthalein, and alizarin-yellow R as indicators for micro-titrations are given. E. S. HEDGES.

**Acidity in non-aqueous solvents. Conductimetric and electrometric titrations of acids and bases in benzene.** V. K. LAMER and H. C. DOWNES (J. Amer. Chem. Soc., 1931, 53, 888—896; cf. Walden and Gloy, A., 1930, 37).—Equivalence points in the conductimetric titration of diethylamine with trichloroacetic acid in benzene correspond with regions of minimum conductivity. Electrometric titration curves obtained with cells of the type  $\text{Pt}|\text{quinhydrone, tetraisoamylammonium iodide (sat.)}, \text{trichloroacetic acid (0.165M)}, \text{diethylamine (0.0413M)}|\text{tetraisoamyl-}$

ammonium iodide (sat.), trichloroacetic acid (0.165*M*), diethylamine ( $x$ ), quinhydrone|Pt, where  $x$  is increased by titration, are similar to those observed in strong acid-base titrations in aqueous solution. It is unlikely that the results are attributable to traces of water in the benzene. J. G. A. GRIFFITHS.

Use of the antimony-antimonous oxide electrode in the determination of the concentration of hydrogen ions and in potentiometric titrations. The Prideaux-Ward universal buffer mixture. H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1931, 458—473).—The scope of the antimony electrode as a titrimetric indicator and the extent to which the *E.M.F.* may be converted into accurate  $p_H$  values have been investigated. The values of the Prideaux-Ward universal buffer mixture have been confirmed and measured at a larger number of stages in the neutralisation, and then used to calibrate this electrode. A number of acids and bases have been titrated potentiometrically with this electrode and the  $p_K$  values calculated. The electrode has been employed successfully in the titration of hydrocyanic, sulphurous, selenious, selenic, and telluric acids which it has hitherto been impossible to titrate against the standard electrodes. The results obtained indicate that the electrode is capable of extended use in the determination of  $p_H$  values rapidly and with a moderately high degree of accuracy. F. J. WILKINS.

Measurement of hydrogen-ion concentration in unbuffered solutions. II. Application of the hydrogen electrode. III. Colorimetric method. I. M. KOLTHOFF and T. KAMEDA (J. Amer. Chem. Soc., 1931, 53, 821—824; 825—832).—II. No adsorption of cation or anion is observed when the previous experiments with platinised platinum (A., 1929, 1410) are repeated in an atmosphere of nitrogen. The preparation of a platinum electrode covered with a bright layer of the metal is described. Acids adsorbed by the electrode in presence of air are removed by water in an atmosphere of hydrogen. The electrode is easily poisoned, but gives reproducible results in unbuffered or slightly buffered solutions (cf. Beans and Hammett, A., 1925, ii, 694).

III. Pure indicators must be used. Conductimetric titration with sodium hydroxide affords evidence of their purity. The technique and corrections involved in the colorimetric determination of  $p_H$  are detailed (cf. Acree and Fawcett, A., 1930, 560). The  $p_H$  of pure water at 25° is 7.00—7.05, determined by means of isohydric bromothymol-blue and phenol-red, whilst the  $p_H$  of very dilute sodium hydroxide solutions have been determined to within 0.1 unit by means of isohydric thymol-blue and phenolphthalein. The  $p_H$  of 0.05*M*-potassium chloride, determined by means of bromothymol-blue and phenol-red, accords with the value derived by the hydrogen electrode. J. G. A. GRIFFITHS.

Buffer mixtures from secondary sodium phosphate and citric acid. K. H. SLOTTA and W. FRANKE (Ber., 1931, 64, [B], 452—454).—Determinations of the  $p_H$  values of solutions of these substances are recorded. Between the acid limits 4.0 and 7.0, the data differ by as much as 0.19 unit from those recorded previously. H. WREN.

Use of dichroic indicators for the photometric determination of hydrogen-ion concentration. H. LINSER (Biochem. Z., 1931, 230, 285—289).—Dichroic indicators are not as suitable for these determinations as indicators giving a colour-colourless change. P. W. CLUTTERBUCK.

Determination of concentration of hydrogen ions with the Hellige comparator. J. GUILLAUME (Bull. Assoc. Chim. Sucr., 1930, 47, 450—454).—The liquid to be tested, contained in a glass cell and treated with an indicator of appropriate  $p_H$  range in prescribed amount, is matched against a series of coloured glasses mounted on a rotatable disc viewed through a second glass cell containing the liquid without indicator. The series of glasses on the disc correspond with  $p_H$  values differing by 0.2 unit over the useful range of the indicator, so that  $p_H$  values can be determined to 0.1 unit with liquids not too dark. Discs with coloured glasses are supplied for a variety of indicators covering different  $p_H$  ranges. The matching of the colours is facilitated by a prism which brings the fields of view into close juxtaposition. J. H. LANE.

Determination of hydrogen in gaseous mixtures. G. N. SCHUTOV.—See B., 1931, 348.

Ebullioscopic method of determining water content of substances. S. BAKOWSKI (Rocz. Chem., 1931, 11, 49—64).—A known weight of substance is placed in an ebullioscope flask containing a known quantity of methyl alcohol or acetone, and the rise in b. p. of the solvent is determined; the water content of the azeotropic mixture in the flask is a function of the b. p. R. TRUSZKOWSKI.

Determination of hydrochloric acid in presence of hydrobromic and hydriodic acids. G. G. LONGINESCU and T. J. PIRTEA (Bul. Chim. Soc. Române Stiin., 1928, 31, 77—87).—In Field's method for the determination of chlorine, bromine, and iodine in mixtures of the three incomplete conversion of the silver salts into bromide or iodide often occurs and leads to errors. Bromide and chloride may be determined in mixtures by precipitating the halogens as silver salts from two equal volumes of the solution, determining gravimetrically the total halogen in one precipitate, and converting the other precipitate wholly into bromide by digesting the precipitate with 50 c.c. of 7% ammonia solution, adding dilute potassium bromide or hydrobromic acid solution, acidifying the solution with nitric acid, and weighing the washed and dried precipitate. The difference in weight of the precipitate of mixed silver salts and that of the converted precipitate multiplied by 3.22402 gives the weight of silver chloride in the mixed halogen precipitate. Chloride and iodide may be determined by a similar method in which the potassium bromide or hydrobromic acid is replaced by potassium iodide; the difference in weight of the two precipitates, multiplied by 1.56724, gives the amount of silver chloride in the mixed precipitate. A corresponding method is applied to mixtures of bromide and iodide in solution. A combination of the three methods may be applied for the determination of chloride, bromide, and iodide in a solution. The factors used are calculated from the theoretical

increase in weight resulting from conversion of silver chloride into bromide or iodide and of silver bromide into iodide.

A. H. EDWARDS.

**Micro-determination of iodide in common salt.** H. WERNER.—See B., 1931, 391.

**Thermal reduction of sulphur in a hydrogen atmosphere applied to the analysis of iron and steel.** Y. YAMAUCHI (Chikashige Anniv. Vol., 1930, 111—118).—Free sulphur covered with a layer of electrolytic iron is completely reduced to hydrogen sulphide by hydrogen at 600°. Barium sulphate (at 800°) and ferrous and nickelous sulphates also give quantitative yields of hydrogen sulphide if free iron is present; in absence of iron part of the sulphur escapes as sulphur dioxide. Manganous sulphate retains part of its sulphur as sulphide. Sulphur may be determined in iron and steel by reduction with hydrogen, passage of the gas through cadmium sulphate solution, and treatment of the residue with acid in a current of hydrogen in case any of the sulphur has been retained, as, e.g., with manganese steels. The method is comparatively rapid and gives trustworthy results.

H. F. GILLBE.

**Determination of small amounts of hydrogen sulphide.** W. V. HARSHMAN, D. A. MCPHERSON, and F. H. EDMISTER (J. Elisha Mitchell Sci. Soc., 1930, 46, 54—61).—A comparative study. Hydrogen sulphide produced by micro-organisms cannot yet be determined accurately.

CHEMICAL ABSTRACTS.

**Determination of hydrogen sulphide, methane, and hydrocarbon vapours in air.** E. POSNER and R. A. MELIKOVA (J. Appl. Chem., Russia, 1930, 3, 965—977).—Hydrogen sulphide is absorbed in sodium hydroxide solution; hydrocarbon vapours (other than methane, which is determined by combustion) are adsorbed on activated charcoal.

CHEMICAL ABSTRACTS.

**Nephelometric micro-determination of sulphates as barium sulphate.** CHATRON (J. Pharm. Chim., 1931, [viii], 13, 321—327; cf. Denis and Reed, A., 1927, 167).—The solution ( $p_H$  2.8) for titration (5 c.c., containing 0.0025—0.03 mg. S) is treated with 1 c.c. of a solution containing 100 c.c. of 5% aqueous gelatin, 5 g. of barium chloride, and 1 c.c. of *N*-hydrochloric acid per litre. After the first 15 min. the optical density remains constant for 24 hrs. and is proportional over a wide range to the sulphur content. It is not affected by the presence of sodium chloride, or of larger amounts of gelatin, but it increases slightly in more acid solutions.

H. E. F. NOTTON.

**Volumetric determination of sulphates by the benzidine method.** CHATRON (J. Pharm. Chim., 1931, [viii], 13, 244—253).—A reaction of  $p_H$  2.8, the presence of acetone, and the use of the benzidine hydrochloride solution of Fiske (A., 1921, ii, 556) are recommended for the precipitation of sulphate with benzidine. The technique includes filtration through sintered glass filters, washing the precipitate with 95% acetone, and titration at the b. p. following hydrolysis. An error of less than 4% is claimed.

F. O. HOWITT.

**Volumetric determination of very small quantities of ammonia, especially in sea- and fresh-**

**water.** S. K. HAGEN (Z. anal. Chem., 1931, 83, 164—175).—The water (250—350 c.c.) is distilled with magnesia or sodium hydroxide from a pyrex glass flask and the vapours are passed through a quartz condenser, the distillate (90—100 c.c.) being collected in 5 c.c. of *N*/140-hydrochloric acid and 0.5 c.c. of 96% alcohol containing 0.01% of methyl-red and 0.04% of bromothymol-blue. The solution is treated with a current of pure nitrogen for 1 hr. and then titrated with *N*/140-sodium hydroxide free from carbonate until the indicator becomes orange-yellow, treated with nitrogen for a further 20 min., and again titrated until the indicator becomes blue. The correct end-point is obtained by comparison with the colour of a buffer solution of  $p_H$  6.8 to which is added 0.5 c.c. of indicator. An allowance of 0.09 c.c. is made for the indicator and a further correction, varying from 0.6 to 3.6  $\mu$ g. of nitrogen for a total quantity of 5—500  $\mu$ g., is deducted to compensate for hydrolysis errors.

A. R. POWELL.

**Use of acridine dyes for the determination of nitrites.** W. M. RUBEL (Z. Unters. Lebensm., 1930, 60, 588—592).—The red colour produced on addition of 0.5 c.c. of a 0.1% solution of rivanol (2-ethoxy-6:9-diaminoacridine hydrochloride) to 10 c.c. of the test solution in the presence of 0.5 c.c. of hydrochloric acid (*d* 1.06) is matched against that developed in a graded series of standards containing 0.001—0.1 mg.  $N_2O_3$  in 10 c.c. The reaction, which is a diazotisation, has a limiting sensitiveness of 0.001 mg.  $N_2O_3$ , and is unaffected by sodium chloride (10%), nitrates, dextrose, lactic acid, phenol, and ammonium salts. Aldehydes and thymol suppress the colour, but to a smaller extent than in the Griess reaction, and free iodine produces a greenish-blue shade. Free ammonia inhibits the reaction by raising the  $p_H$  value, and should be neutralised. The reagent (solubility 1 in 260) is stable in the dark, and should be tested for colouring impurities by means of a nitrite-free control solution.

J. GRANT.

**Determination of nitrite and sulphite in presence of one another in salt mixtures.** E. SZABÓ.—See B., 1931, 391.

**Determination of nitrate in drinking water.** K. SCHERINGA.—See B., 1931, 420.

**Quantitative analysis of phosphoric acid. V. Colorimetric determination.** M. ISHIBASHI (Chikashige Anniv. Vol., 1930, 1—7; cf. A., 1929, 783).—To the solution is added a small quantity of a 10% solution of hydroxylamine hydrochloride, and the mixture is treated with an excess of a mixture of manganous chloride (1 mol.) and ammonium chloride (100 mols.); the  $p_H$  of the solution should be such that scarcely any precipitation results. The solution is heated to the b. p. and ammonia solution is added slowly and with stirring until precipitation is complete; the mixture is kept for 5 hrs. at the ordinary temperature in order to ensure conversion of the amorphous precipitate into crystalline manganous ammonium phosphate, which is removed and washed 2—4 times with a slightly alkaline *M*-solution of ammonium chloride containing 2 c.c. per litre of 10% hydroxylamine hydrochloride solution. The washed precipitate is treated with 4*N*-nitric acid and is



oxidised to permanganate by sodium bismuthate at 0°. The solution is removed by centrifuging, 0.5*N*-nitric acid being used for washing the residue, and is diluted to a definite volume, the permanganate content being determined colorimetrically. The permanganate concentration should be 0.001—0.0001*N*. In presence of only small quantities of phosphoric acid the precipitate consists of the normal manganous salt, and the double salt is produced only after prolonged contact with the solution; it is therefore necessary to ascertain that the precipitate is of the characteristic crystalline form before it is further treated. If the analysis is continued with the normal salt the empirical factor 0.3300 (theory 0.2997) should be used for calculation to P<sub>2</sub>O<sub>5</sub>. The error of the method is less than 2% (P<sub>2</sub>O<sub>5</sub>).  
H. F. GILLBE.

Determination of phosphates in presence of silica in boiler water. E. W. SCARRITT.—See B., 1931, 320.

Potassium permanganate as a reagent for the detection of lower oxides in phosphoric acid. J. W. SMITH (J.C.S., 1931, 528—529).—A colorimetric method for the determination of small quantities of phosphorous oxide in phosphoric oxide is sufficiently sensitive to detect the presence of 2 parts of the lower oxide in 10<sup>6</sup>.  
F. J. WILKINS.

Rapid determination of small quantities of boric acid by the intensity of the flame coloration. W. STAHL (Z. anal. Chem., 1931, 83, 340—344).—The substance is dissolved in 50 c.c. of a mixture of 100 vols. of methyl alcohol and 20 vols. of sulphuric acid (*d* 1.8); a current of air is passed through the solution at a definite rate and then into the non-luminous flame of a Bunsen. The colour so obtained is compared with that given by a solution containing a known weight of boric acid; if necessary either the standard or the test solution is diluted with more of the above acid-alcohol mixture until the flame colours match.  
A. R. POWELL.

Quantitative investigation of the boric acid-alcohol flame reaction. W. STAHL (Z. anal. Chem., 1931, 83, 268—289).—Air dried with sulphuric acid is passed under similar conditions through three solutions in parallel, and through similar capillary tubes into the air inlets of shielded micro-burners giving similar flames. The solutions contain the sample and two suitable quantities (0.1—0.01 mg.) of a standard solution of boric acid, each in 15 c.c. of a mixture of methyl alcohol and sulphuric acid (5:1) at 60°. Curves from which these optimum conditions were derived show the relation between the colour intensity of the flame, the temperature, and the water and sulphuric acid contents. The colour varies linearly with temperature (−30° to 80°), and rises to a maximum and then falls with increasing amounts of sulphuric acid. Under the above conditions, using a small apparatus, and in the presence of less than 3% of water, the colours of the flames may be matched with a sensitiveness corresponding with 0.005 mg. of B<sub>2</sub>O<sub>3</sub>, *i.e.*, double that obtained at the ordinary temperature without the use of acid. With ethyl alcohol (optimum acid concentration 1:4) the sensitiveness is 0.02 mg., but decreases rapidly in the

presence of small amounts of water, whilst with propyl alcohol it is about 0.05 mg.  
J. GRANT.

Analysis of ferrosilicon. G. H. GOODWIN.—See B., 1931, 298.

Analysis of gases and vapours which influence the rate of oxidation of phosphorus. J. TAUSZ and H. GÖRLACHER (Z. anal. Chem., 1931, 83, 81—92).—By measuring the pressure at which phosphorus starts to glow in a mixture of air or oxygen and various hydrocarbons it is possible to determine the amount of hydrocarbon vapour in the mixture by reference to graphs or tables which are given for the following substances: benzene, cyclohexane, acetylene, methylcyclohexane, ethylene, propylene, cyclohexene, isoprene, and iron pentacarbonyl.  
A. R. POWELL.

Volumetric determination of carbon dioxide in carbonates. T. HECZKO.—See B., 1931, 293.

Systematic procedure for qualitative analysis with small quantities of cations. A. SCHEINKMANN (Z. anal. Chem., 1931, 83, 176—188).—Details are given for the detection of the usual common elements of the five analytical groups using only 0.1—0.15 g. of material and making the confirmatory tests for each element with a few drops of solution only. The original must be consulted for the working directions, which comprise no novel procedures.  
A. R. POWELL.

Microscopic determination of minerals. M. BEREK (Z. Krist., 1931, 76, 396—430).—The intensity of the light reflected by anisotropic materials is calculated for both perpendicular and oblique incidence. Methods for determining the amount of the various materials in a section depend on measurement of either the degree of polarisation or the intensity of the reflected light.  
C. A. SILBERRAD.

Lithium chloroplatinate and separation of potassium from sodium and lithium by the unmodified original Fresenius method. G. F. SMITH and A. C. SHEAD (J. Amer. Chem. Soc., 1931, 53, 947—957; cf. Fresenius, A., 1877, ii, 220; 1882, ii, 1231).—Factors to which the empiricism of the Fresenius method for determining potassium may be attributed (cf. Dupré, A., 1897, ii, 232) are considered. When, instead of chloroplatinic acid, the reagent is a solution of lithium chloroplatinate prepared by conversion of lithium carbonate (twice precipitated from a solution of the hydrogen carbonate by boiling) into the chloroplatinate by means of chloroplatinic acid, the precipitated potassium chloroplatinate has the theoretical composition and is stable at 260°.  
J. G. A. GRIFFITHS.

Nickel uranyl acetate as a qualitative reagent for sodium. P. FELDSTEIN and A. M. WARD (Analyst, 1931, 56, 245—248).—This reagent compares favourably with zinc, magnesium, or cobalt uranyl acetates and gives a pale green precipitate of sodium nickel uranyl acetate, consisting of microscopic octahedral crystals. Potassium forms yellow needle-shaped crystals of potassium uranyl acetate and, in excess, prevents the formation of the sodium salt. Magnesium and ammonium salts are without effect, but lithium gives crystals isomorphous with the triple

sodium salt, and phosphate gives an entirely different precipitate. High concentrations of sodium precipitate the double sodium uranyl acetate from either the nickel or zinc reagents. The triple sodium salt has the formula  $\text{NaNi}(\text{UO}_2)_3(\text{OAc})_9, 6( ? 6.5)\text{H}_2\text{O}$ .

T. McLACHLAN.

**Toxicological detection of silver.** E. MENE-  
GHETTI (Biochem. Terap. Sperim., 1930, 17, 237—  
241; Chem. Zentr., 1931, i, 118—119).—The material  
is ignited with sodium carbonate and potassium  
nitrate, the residue being treated with nitric acid and  
evaporated to dryness. Silver is precipitated from  
an aqueous solution with hydrogen sulphide; the  
silver sulphide is evaporated with nitric acid and the  
silver determined gravimetrically as chloride.

A. A. ELDRIDGE.

**Micro-determination of calcium.** L. VELLUZ  
and R. DESCHASEAUX (Compt. rend. Soc. Biol., 1930,  
104, 976; Chem. Zentr., 1931, i, 323—324).—The use  
of organic solvents for washing the calcium oxalate  
and oxidation in the cold with  $N/150$ -permanganate  
are proposed (cf. this vol., 641).

A. A. ELDRIDGE.

**Micro-determination of calcium and mag-  
nesium in the presence of each other.** K. L.  
MALJAROV (Mikrochem., 1931, 9, 132—135).—The  
method described is specially suited for the analysis  
of magnesite, dolomite, etc. About 10 mg. of the  
material (in which calcium and magnesium are present  
only in the form of carbonates, oxides, and hydroxides  
and alkali carbonates are either absent or present only  
in traces) are ignited for 30 min. in a platinum  
crucible, cooled in a desiccator, and diluted with 60—  
80 c.c. of water, which is rapidly boiled in order to  
dissolve all the calcium oxide. The solution is filtered  
and calcium is determined in the filtrate by titration  
with 0.05—0.2*N*-sulphuric acid, using methyl-orange.  
The precipitate of magnesium oxide is dissolved in  
excess of 0.05—0.2*N*-sulphuric acid and the excess  
titrated back with standard sodium hydroxide  
solution. Iron or aluminium oxides, which may be  
present in the precipitate, are not dissolved by  
sulphuric acid of this concentration. The presence of  
calcium oxide diminishes the solubility of magnesium  
oxide in water.

E. S. HEDGES.

**Micro-determination of barium.** R. R.  
McLAUGHLIN (Biochem. J., 1931, 25, 307—309).—  
A gravimetric method capable of dealing with 20 mg.  
of barium sulphate with a loss of not more than 0.3%  
is described.

S. S. ZILVA.

**Determination of magnesium in Portland  
cement and similar materials of the use of  
8-hydroxyquinoline.** J. C. REDMOND and H. A.  
BRIGHT.—See B., 1931, 396.

**Electrolytic determination of lead as lead  
dioxide.** W. T. SCHRENK and P. H. DELANO.—  
See B., 1931, 299.

**Electrolytic separation of lead and antimony  
and its application to the determination of lead  
in tartar emetic.** E. M. COLLIN and H. J. S. SAND  
(Analyst, 1931, 56, 90—93).—The method depends on  
the fact that lead free from antimony is deposited by  
internal or external electrolysis on a copper-plated

platinum cathode from alkaline tartrate solutions  
containing quinquevalent antimony. For the analysis  
of tartar emetic the salt is dissolved in water and the  
solution treated with 3 g. of potassium hydrogen  
carbonate, then with a slight excess of iodine followed  
by 4 g. of potassium hydroxide and 2—3 g. of tartaric  
acid; electrolysis is conducted with a rotating anode  
using an external current of 3 amp. or with a zinc  
anode immersed in 10% potassium cyanide solution  
in the anode compartment of Sand's internal electro-  
lysis apparatus.

A. R. POWELL.

**Determination and separation of lead and bi-  
smuth by the filtration method.** H. T. BUCHERER  
and F. W. MEIER (Z. anal. Chem., 1931, 83, 351—  
361).—Good results for lead may be obtained by  
titrating the hot, slightly acid solution, containing  
an excess of sodium acetate, with potassium di-  
chromate or with selenious acid and determining the  
end-point by the filtration method (cf. B., 1930,  
1153). In the second case the lead is precipitated as  
white granular  $\text{PbSeO}_4$ , which settles and filters  
readily. The filtration method may also be used for  
the volumetric determination of bismuth in 0.05—  
0.08*N*-nitric acid at 70°, using selenious acid as the  
precipitant; lead does not interfere and, if present,  
may be subsequently determined with selenious acid  
after addition of sodium acetate to the solution  
without removing the bismuth selenite precipitate.

A. R. POWELL.

**Separation of bismuth from lead as oxy-  
chloride.** W. HERTEL (Metall u. Erz, 1930, 27,  
557—560; Chem. Zentr., 1931, i, 489).—The oxy-  
chloride method is more accurate than the sulphate  
method, and applicable at any bismuth content. A  
procedure for determining bismuth in lead in presence  
or absence of antimony is described.

A. A. ELDRIDGE.

**Luminescence analysis. II. Luminescence  
of white pigments.** E. BEUTEL and A. KUTZEL-  
NIGG.—See B., 1931, 403.

**Cobalticyanide and chromicyanide anions as  
precipitating agents in potentiometric volu-  
metric analysis.** L. CZAPOROWSKI and J. WIERCIEŃ-  
SKI (Rocz. Chem., 1931, 11, 95—102).—Hydrocobalti-  
cyanic acid,  $\text{H}_3\text{Co}(\text{CN})_6, 5\text{H}_2\text{O}$ , decomp. 50°, is prepared  
by saturating saturated aqueous potassium cobalti-  
cyanide with hydrogen chloride, and extracting the  
precipitate with alcohol, from which the free acid  
crystallises. The acid and its sodium or lithium  
salts are suitable reagents for the potentiometric  
titration of silver, cupric, and mercuric ions. Cupric  
sulphate should be titrated in presence of an equi-  
valent amount of sodium acetate. Cobalt can be  
determined by conversion into cobalticyanide and  
titration with standard silver or mercuric solutions;  
this method is, however, not convenient. Chromi-  
cyanides are unsuitable for potentiometric analysis,  
as the titration curve varies according to the con-  
centration of cations.

R. TRUSZKOWSKI.

**Determination of small amounts of mercury.**  
A. STOCK and H. LUX [with F. CUCUEL and F. GERST-  
NER] (Z. angew. Chem., 1931, 44, 200—206).—  
Methods of determining quantities of mercury of the

order of 0.001 mg. by deposition on a copper wire, followed by distillation, conversion into chloride, and colorimetric determination, are untrustworthy because of incomplete deposition on the copper, and subsequent loss by evaporation. The mercury is deposited from the chloride solution (10—15 c.c.) on a copper wire, using a platinum anode, then distilled and condensed in a small capillary. After washing with alcohol, the amount is determined by microscopic measurement. If the mercury is contained in a larger volume of solution than 15 c.c. it is first concentrated by precipitation as sulphide in the presence of a copper salt, and reconversion into chloride by the action of chlorine. A. KEY.

**Determination of small concentrations of mercury vapour in air.** B. L. MOLDAVSKI (J. Appl. Chem., Russia, 1930, 3, 955—964).—The mercury is combined with bromine vapour and the mercuric bromide dissolved in water.

## CHEMICAL ABSTRACTS.

**Determination of aluminium in ferrochromium and chromium.** T. R. CUNNINGHAM.—See B., 1931, 298.

**Determination of alumina in refractory clays.** R. BIAZZO.—See B., 1931, 395.

**Rhenium. II. Determination of rhenium as thallium per-rhenate.** F. KRAUSS and H. STEINFELD (Z. anorg. Chem., 1931, 197, 52—56; cf. this vol., 53).—Pure thallos per-rhenate may be prepared by adding, with stirring, a slight excess of thallos acetate or sulphate solution to a cold solution of potassium per-rhenate rendered slightly acid with acetic acid; the precipitate is collected, washed with glacial acetic acid, and dried at 140°. The compound forms white, anisotropic, apparently rhombic crystals. Its solubility is 0.085% at 10° and 0.16% at 26°, and is still lower in ethyl alcohol and dilute or concentrated acetic acid. For the determination of rhenium as thallos per-rhenate the sample (0.3—0.4 g.) is dissolved in 40 c.c. of hot water, 10 c.c. of glacial acetic acid are added, and the rhenium is precipitated by a slight excess of a solution of thallos carbonate in acetic acid. The solution is evaporated to 3—4 c.c. and after being cooled 10 c.c. of acetic acid are added and the precipitate is washed and dried. Halides must be absent. Results are somewhat low, probably as a result of volatilisation. H. F. GILLBE.

**Determination of iron in water.** O. MAYER.—See B., 1931, 320.

**Separation of iron, titanium, and aluminium in tartaric acid solution.** E. S. VON BERGKAMPF (Z. anal. Chem., 1931, 83, 345—350).—The acid tartrate solution of the metals is treated with hydrogen sulphide to reduce ferric salts, and then with ammonia and hydrogen sulphide under pressure to precipitate ferrous sulphide. The filtrate is acidified with sulphuric acid and treated cold with 6% cupferron solution to remove the titanium; the filtrate is made ammoniacal again, and the aluminium precipitated with 8-hydroxyquinoline at 70°. Vanadium interferes in the separation; zirconium is precipitated with the titanium, and beryllium with the aluminium. A. R. POWELL.

**Influence of co-ordinated groups on the central iron atom of complex iron cyanides.** O. BAUDSCH (Biochem. Z., 1931, 232, 35—49).—Benzidine and guaiacol are oxidised both by ferric and by autoxidised pentacyanoaquoferroate ions. 5-Aminouracil reacts only with the ferroate at  $pH$  3.8—8.0. Thioglycollic acid detects ferric and complex ferric ions, nitrosophenol detects ferrous ions. A reaction with dithio-oxamide is introduced for detection of pentacyanoaquoferroate ions. Ferroate is directly oxidised by 0.01N-hydrogen peroxide only in acid solutions. The reduction of ferriate to ferroate ions by a large number of substances is investigated (A., 1930, 41, 75). P. W. CLUTTERBUCK.

**Gravimetric determination of iron in organic substances.** G. SVEDENIUS (Acta paediatr., 1929, 9, 1—8; Chem. Zentr., 1931, i, 323).—The ash is dissolved in hydrochloric acid, the solution nearly neutralised with ammonia, and the iron precipitated from the filtrate by four additions at 7—8 hr. intervals of 1-nitroso- $\beta$ -naphthol, the precipitate being dried and ignited in a platinum crucible. A. A. ELDRIDGE.

**Determination of traces of chromium in steel.** W. J. AGNEW.—See B., 1931, 297.

**Determination of chromium and vanadium in ores and alloys after oxidation with perchloric acid.** H. H. WILLARD and R. C. GIBSON.—See B., 1931, 299.

**Determination of molybdenum.** H. A. DOERNER (Metal Ind., London, 1930, 37, 444—445; Chem. Zentr., 1931, i, 321).—The sample (1 g.) is fused with sodium carbonate and peroxide in an iron or nickel crucible; the hot aqueous extract is boiled for 10 min. with hydrogen peroxide and filtered. After acidification with hydrochloric acid and removal of carbon dioxide by boiling an alkali thiocyanate and zinc are added; a cherry-red colour appears in presence of molybdenum. For determination, 0.5—5 g. of finely pulverised material are digested with nitric (40 c.c.) and sulphuric (7 c.c.) acids, the soluble sulphates being dissolved by addition of water (50 c.c.). Tartaric acid (5 g.) is added and hydrogen sulphide passed; the filtrate is acidified with dilute sulphuric acid and the molybdenum sulphide collected. This is dissolved in aqua regia; the solution is neutralised with ammonia and heated with hydrochloric acid (7 c.c.), ammonium acetate (10 g.), and water (300 c.c.), lead acetate solution being added from a burette until a drop test with freshly prepared tannin solution gives no colour change. A slight excess is added, the lead molybdate being collected after heating for 30 min. and weighed as  $PbMoO_4$ . A. A. ELDRIDGE.

**Colorimetric determination of molybdenum in steel.** T. R. CUNNINGHAM and H. L. HAMNER.—See B., 1931, 297.

**Colorimetric determination of tungsten.** G. HEYNE (Z. angew. Chem., 1931, 44, 237—238).—The diluted ammoniacal solution of tungstic acid is treated with 0.5 c.c. of 10% potassium hydroxide solution, evaporated, and heated to fuming with 0.55 c.c. of sulphuric acid; if it is brown, potassium

persulphate is added. The liquid is cooled in a desiccator, treated with 1 c.c. of a solution of 10 g. of quinol in 100 c.c. of sulphuric acid, and the colour is matched with a standard solution of tungsten, for which 0.063 g.  $WO_3$  is dissolved in 25 c.c. of 10% potassium hydroxide solution, evaporated to dryness, and dissolved in sulphuric acid to make 50 c.c. (1 c.c.  $\equiv$  0.001 g. W); 0.02—0.10 c.c. of this standard solution is mixed with solution of potassium sulphate in sulphuric acid and 1 c.c. of the quinol sulphate until the colours match. The determination is unaffected by small amounts of alkalis, phosphates, or nickel, but is affected by nitrates, iron, titanium, niobium, chromates, per-rhenates, and molybdates. In presence of molybdenum, the tungsten should be determined colorimetrically by means of rhodamine B.

D. WOODROFFE.

**Reduction of tin and antimony prior to titration.** B. S. EVANS (Analyst, 1931, 56, 171—177).—Hypophosphorous acid may be employed for the reduction of stannic salts if the operation is carried out in hydrochloric acid solution (1:1) at the b. p. in an atmosphere of carbon dioxide, using mercuric chloride as a catalyst; starch, citric acid, and potassium iodide are added before titrating with 0.1N- or 0.01N-iodine solution. Antimony is reduced more rapidly and no catalyst is required, but ammonia is added in excess before titration. Lead, if present, is precipitated by sulphuric acid before reduction; with tin, cadmium, and bismuth, iodine is added to give a faint permanent blue colour to starch before the citric acid. Arsenic is reduced to the metallic state and may be filtered off. T. McLACHLAN.

**Lead reduction method for the volumetric determination of tin and the interference with it by copper and antimony.** S. G. CLARKE (Analyst, 1931, 56, 82—89).—Reduction of stannic chloride solutions by sheet lead leads to accurate results for tin provided that the reduction, cooling, and titration are carried out while a current of carbon dioxide is passed through the flask. An acidity of 50 c.c. of hydrochloric acid in a total volume of 250 c.c. and a time of reduction of 1.5 hrs. are recommended (cf. Powell, J.S.C.I., 1918, 37, 285r). When the solution contains copper boiling with lead results in the deposition of a copper-tin compound as a black, flocculent precipitate, and hence low results for tin are obtained in the titration. If the solution contains antimony this is precipitated as a flocculent black precipitate by boiling with lead, and high results are obtained for tin if titration is carried out without filtration; if, however, the precipitate is removed and the filtrate again reduced and titrated the results for tin are low, as part of the tin is precipitated with the antimony. When both copper and antimony are present in the same solution, boiling with lead precipitates an antimony-copper compound in preference to a tin-copper compound, but the tin results are still slightly low.

A. R. POWELL.

**Selenious acid method for determination of zirconium.** S. G. SIMPSON [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1931, 53, 921—933; cf. Smith and James, A., 1920, ii, 710).—Zirconium (0.12 g. of

$ZrO_2$ ) is precipitated quantitatively as the basic selenite by excess (20 c.c.) of 10% selenious acid from hot solutions (400 c.c.) containing not more than the optimum concentration, 0.6N, of hydrochloric acid or a lower concentration of nitric acid. Sulphuric acid causes very slow precipitation, affording the crystalline normal selenite which is insoluble in hot 6N-hydrochloric acid. Nitrates and chlorides do not interfere, but more than 0.5 g. of sodium sulphate prevents quantitative precipitation unless the acidity is diminished. The effect may be due to the formation of  $[ZrOSO_4 \cdot SO_4]H_2$ . Of many metallic ions investigated, only those of titanium, ceric cerium, and thorium are precipitated with zirconium (and hafnium) under the conditions adopted. 20 C.c. each of 12N-hydrochloric acid and alcohol are added to 100 c.c. of the nearly neutral solution free from phosphate, sulphate, niobium, and tantalum. The liquid is boiled, diluted to 500 c.c. and the selenites are precipitated. The precipitate is dissolved in 15 c.c. of 12N-hydrochloric acid. Thus, adsorption of vanadium and uranyl compounds is eliminated. Next, cerium and titanium are removed by the addition of 20 c.c. of 3% hydrogen peroxide followed by warming, dilution, and precipitation of zirconium (and thorium) selenite. Before the last process is repeated to remove the titanium completely, any thorium is separated quantitatively by double precipitation as oxalate from hydrochloric acid solution, sulphate being absent. The excess of oxalate is destroyed by evaporation with sulphuric acid, sulphate being eliminated by precipitation of thorium and zirconium with ammonia solution.

A rapid method for decomposing zirconium ores by fusion with sodium peroxide and sugar charcoal, and subsequent treatment for removal of niobium, tantalum, and phosphate, is detailed.

J. G. A. GRIFFITHS.

**Determination of zirconium in steel.** T. R. CUNNINGHAM and R. J. PRICE.—See B., 1931, 298.

**Detection of gold, palladium, and silver with dimethylaminobenzylidenerhodanine.** F. FEIGL, P. KRUMHOLZ, and E. RAJMANN (Mikrochem., 1931, 9, 165—173).—The tests described may be carried out in a test-tube, shaking with ether to enrich the effect at the boundary, or by the spot method on filter-paper. One drop of a silver solution with one drop of 10% potassium cyanide and one drop of alcoholic *p*-dimethylaminobenzylidenerhodanine acidified with one drop of *N*-nitric acid produces a violet coloration. The test is sensitive at a dilution of 1 in 500,000 and succeeds in the presence of 1000 times the amount of mercury, 4000 times the amount of gold, and 300 times the amount of platinum or palladium. In the absence of potassium cyanide, gold compounds even at a dilution of 1 in 500,000 give a reddish-violet coloration with the reagent. Palladium gives a violet coloration at a dilution of 1 in  $10^7$  in neutral solution and 1 in  $5 \times 10^6$  in 0.1N-acid solution. Special directions are given for the detection of palladium in the presence of platinum, iridium, silver, and gold. E. S. HEDGES.

**Potentiometric determination of iridium.** S. C. Woo and D. M. Yost (J. Amer. Chem. Soc.,

1931, 53, 884—888; cf. this vol., 435; Delépine, A., 1917, ii, 537).—The chloroiridate in hydrochloric acid solution is reduced to the chloroiridite by standard titanous chloride which must be added slowly as the electrometric end-point is approached. The sharpness of the end-point is increased by the presence of sodium chloride. The iridium content of crystalline ammonium hexachloroiridate determined by the above method, the iodometric method in which the iodine-thiosulphate end-point is determined by means of benzene, and the gravimetric method accords, within  $\pm 0.3\%$ , with the formula  $(\text{NH}_4)_2\text{IrCl}_6$ .

J. G. A. GRIFFITHS.

Conditions of precipitation of polonium; some of its complex derivatives. I. Study, by centrifugation, of the precipitation reactions of various compounds of polonium without addition of an entraining agent. M. GUILLOT (J. Chim. phys., 1931, 28, 14—41).—The chemical reactions of polonium are reviewed, with special reference to their analytical significance. In the method of determination used the precipitated polonium (or its compound) was centrifuged at 6000 revs. per min. under standardised conditions, and the polonium removed from the walls of the tube in hot acid, and finally deposited on a silver plate, the radioactivity of which was then determined by the ionisation method (1 e.s.u. =  $1.6 \times 10^{-10}$  g. of polonium). The fixation of polonium on the walls of the tube and the formation of a centrifugable precipitate are parallel phenomena. Solutions in *N*-hydrochloric acid deposit polonium, by hydrolysis of the chloride, to a negligible extent, but hydrolysis begins with 0.1*N*-solutions and is carried almost to completion in neutral solutions. In neutral or 0.01*N*-media the curves relating the residual soluble polonium and the period of centrifuging appear to correspond with normal chemical precipitation. The properties of the hydrolysis product have been investigated, and indicate the formula  $\text{O:Po}(\text{OH})_2$ . Similar experiments were carried out on the precipitation of polonium sulphide in *N*-hydrochloric acid, of polonium carbodithiodiethylamine in neutral solution, and of polonium by reduction with stannous chloride in *N*-hydrochloric acid. Satisfactory agreement exists between the results of these experiments and those hitherto studied in which precipitation is assisted by entraining agents, an insoluble, completely precipitable polonium derivative being formed, other conditions being the same, whether the entraining agent is present or absent. Entrainment may result from true syncrystallisation, due to isomorphism of the participating molecules, (1) when the polonium is in a soluble form and the entraining agent is crystalline, (2) when the polonium is insoluble and the entraining agent (a metallic compound) is insoluble in water, but soluble in and crystallisable from another neutral solvent. A compound of trivalent polonium may be totally entrained by the corresponding compound of a bivalent metal so long as both are insoluble.

J. GRANT.

Difficulty of ensuring thermal insulation with solid insulator. P. VERNOTTE (Compt. rend., 1931, 192, 340—341).—The quantity of heat passing in  $t$  sec. between the wall of the vessel in a calorimeter

in which it is evolved and the insulating medium, counting time from the beginning of the evolution, and assuming such evolution to be sudden and to raise the temperature by  $T^\circ$ ; is  $Q = 2\sqrt{kc\rho tT}/\sqrt{\pi}$  g.-cal. per  $\text{cm}^2$ , where  $k$  is the conductivity of the insulating medium,  $c$  its specific heat, and  $\rho$  the density. If the medium is asbestos  $Q$  in 30 sec. amounts to  $0.12T$  g.-cal. per  $\text{cm}^2$ , whilst the normal flow is only  $0.02T$ . The best insulator is air, and a metal cushion is better than felt (cf. following abstract).

C. A. SILBEREAD.

Simple method of measuring specific heat of a solid [beryllium] at the ordinary temperature. P. VERNOTTE and A. JEUFROY (Compt. rend., 1931, 192, 612—614; cf. preceding abstract).—The substance is suspended together with a thermometer in a thick-walled metal box in the actual place of experiment until it acquires the same temperature. The temperatures of this place and of the water in the calorimeter are such that the latter, even after the substance is dropped in, is well below that of its surroundings. The method applied to beryllium gives as the specific heat at  $13^\circ$   $0.397$  g.-cal. per g. per degree.

C. A. SILBEREAD.

Thermostats. II. Electric relay and spark in thermoregulator. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1931, 34, 94—99b).—In order to prevent sparking the current must not exceed 8 millamp. at 100 volts and 20 millamp. at 10 volts. A relay operated by smaller currents has been devised.

E. S. HEDGES.

Thermostat regulator. E. Q. ADAMS (Rev. Sci. Instr., 1931, [ii], 2, 187—188).—An inert atmosphere is maintained above the make-and-break contact of an electrically heated thermostat by means of a tungsten-mercury contact in hydrogen permanently enclosed in glass. With an auxiliary heater a temperature variation less than  $\pm 0.001^\circ$  was obtained.

N. M. BLIGH.

Simple thermostat for  $20^\circ$  with temperature control independent of the room temperature. V. ČUPR (Z. Elektrochem., 1931, 37, 129—130).—The thermostat bath is fed continuously from the water main, the feed water passing over an electrically heated spiral operated by a relay of special construction. The temperature can be maintained within  $0.02^\circ$  of the desired point. Details and diagrams are given.

F. L. USHER.

Improved Fuessner type potentiometer. M. EPPLEY and W. R. GRAY (Rev. Sci. Instr., 1931, [ii], 2, 242—249).

Thermionic valve voltmeter. F. L. HAHN (Chem. Fabr., 1931, 121).—The circuit described is intended for microchemical titrations, and differs from circuits previously described in that the compensating rheostat utilises the full voltage of the filament battery and that a reduced voltage is applied to the filament in order to improve the constancy of the null point reading.

H. F. GILLBE.

Carborundum fractionating columns. E. C. FARNHAM (J. Physical Chem., 1931, 35, 844—858).—Midgley's results (A., 1929, 673) are confirmed. The

nature, as well as the physical structure, of the material filling the column affects fractional distillation in a specific manner. Thin plates are preferable to needles. Carborundum or micaceous hæmatite is better than glass beads or silver-plated glass films for the separation of benzene and pyridine. Ferrous sulphide is also preferable to glass beads, but needle ore, a form of hæmatite, and very finely-ground carborundum are not efficient. With alcohol and water, glass is preferable to micaceous hæmatite. Selective adsorption appears to be an important factor determining the efficiency of a fractionating column.

L. S. THEOBALD.

**Laboratory distillation apparatus.** H. BURSTIN and J. WINKLER (*Chem.-Ztg.*, 1931, 55, 212).—The apparatus described was designed for the continuous vacuum distillation of oil residues, but is suitable also for the treatment of easily decomposable or foaming liquids, such as phenols and sulphonic acids, and for organic liquids containing water. It consists essentially of a heating chamber in which the liquid is vaporised as it enters through a needle valve, a dephlegmator packed with Raschig rings, and a condenser; the heating surface and vapour space are large compared with the quantity of material heated, and the latter is therefore maintained at a high temperature for only a short period.

H. F. GILLBE.

**Storage and delivery apparatus for corrosive reagents.** G. MIDDLETON (*Analyst*, 1931, 56, 236—237).—A bottle is fitted with tubes having ground-glass and internal joints, so arranged that reagents such as antimony trichloride solution or bromine may be measured accurately and rapidly without coming into contact with the air.

T. McLACHLAN.

**Apparatus for the measurement of ultra-violet light.** E. WEYDE (*Strahlenther.*, 1930, 38, 378—390; *Chem. Zentr.*, 1931, i, 115).

**Filters for the reproduction of sunlight and daylight and the determination of colour temperature.** R. DAVIS and K. S. GIBSON (*U.S. Bur. Stand. Misc. Publ.*, 1931, No. 114, 165 pp.).—"Mean sun," *i.e.*, mean noon sunlight at Washington, is adopted as a white light standard in preference to 5000° Abs., since it represents the natural conditions of use of photographic materials and is more easily obtained from incandescence lights by means of filters. A series of filters has been prepared for conversion of the light of colour temperatures between 1600° and 20,000° Abs. into mean sun with accuracy both with regard to spectral energy distribution and colour match, over the range of wave-length 360—720  $\mu$ . Filters for conversion of one colour temperature into another are also given. The filter consists of a two-compartment cell with three borosilicate crown glass windows (each 2.5 mm. thick,  $n_D$  1.51), each cell being 10 mm. thick. The two cells contain respectively (A) a solution of equal weights of copper sulphate pentahydrate and mannitol, and 30 c.c. of pyridine, in distilled water to make 1000 c.c.; (B) a solution of copper sulphate, cobalt ammonium sulphate ( $6H_2O$ ), and 10 c.c. of sulphuric acid ( $d$  1.84), in distilled water to make 1000 c.c. The unstated amounts

of the constituents vary with the purpose of the filters, which are standardised for use at 25°. A series of charts is given showing the composition of the filter, and the spectral energy distribution of the source with its filter compared with mean sun and the source and filter separately. The transmissions of the filters vary from 10 to 60%. Full investigations have been made of the permanence of the solutions and the variations due to temperature changes, impurity of materials, and other factors.

J. LEWKOWITSCH.

**Laboratory apparatus.** M. TROMBE (*Bull. Soc. chim.*, 1931, [iv], 49, 185—186).—A bubbler for washing a gas and a water bellows which works at high pressures are described.

F. J. WILKINS.

**Aërometer for the rapid determination of the density of liquids.** G. BORGER (*Münch. med. Woch.*, 1930, 77, 2019; *Chem. Zentr.*, 1931, i, 113).

**Expansion hydrometer.** E. HIEDEMANN (*Physikal. Z.*, 1931, 32, 223—225).—An apparatus for the determination of the coefficient of cubical expansion of liquids is described.

A. J. MEE.

**Hydrometer for determining the density of heavy liquids.** A. C. TESTER (*Science*, 1931, 73, 130—131).—An apparatus suitable for determining the density of liquids (5 c.c.) between 2 and 5 is described.

L. S. THEOBALD.

**Automatic constant-level device for liquid air.** R. B. SCOTT and F. G. BRICKWEDDE (*Rev. Sci. Instr.*, 1931, [ii], 2, 171—172).—An electrically controlled apparatus for automatically maintaining a constant level in a bath of liquefied gas is described, and applied to a cryostat, using liquid air as the refrigerant.

N. M. BLIGH.

**Apparatus for the evaporation of various materials in high vacua.** C. H. CARTWRIGHT and J. STRONG (*Rev. Sci. Instr.*, 1931, [ii], 2, 189—193).—The substance to be evaporated is heated electrically in an evacuated bell-jar directly connected to a charcoal container cooled by liquid air, and is directed as a molecular beam on to the surface to be coated. Most metals and some non-metals could be deposited and the thickness of the film accurately controlled.

N. M. BLIGH.

**Glass extraction apparatus.** B. L. MANJUNATH (*Mysore Univ. J.*, 1930, 4, 243—244).—The substance to be extracted is contained in a Woulff's bottle which has an additional opening at the bottom. Solvent enters as vapour through one of the upper openings, and is prevented by a condenser from escaping through the other. By means of a two-way tap it can be caused either to run straight back to the still through the bottom opening or to accumulate until it reaches a certain height, when it automatically siphons back. Most of the joints are ground, and the use of rubber connexions is minimised.

C. W. GIBBY.

**Apparatus for continuous extraction at raised temperatures.** F. WREDE (*Biochem. Z.*, 1931, 231, 173—174).—An apparatus in which at least 5 kg. of solid material can be continuously extracted with solvents at any desired temperature is described.

W. McCARTNEY.

**Filtering discs of sintered pyrex glass.** W. F. BRUCE and H. E. BENT (J. Amer. Chem. Soc., 1931, 53, 990—992).—Details for making discs and sealing them to pyrex apparatus are given. A uniform layer, 1.5—2 mm. thick, of powdered pyrex glass of appropriate grain size is placed in a cylindrical nickel mould consisting of a piece of tube 1 cm. in diameter and 1 cm. high resting on a sheet of nickel (2.5 × 2.5 cm.). The covered mould is placed for about 2 min. in a muffle at a bright red heat.

J. G. A. GRIFFITHS.

**Measurement of permeability of porous alundum discs for water and oils.** H. G. BOTSET (Rev. Sci. Instr., 1931, [ii], 2, 84—95).—The rate of flow of distilled water through a porous alundum disc decreases with time if the water has been kept in contact with glass, on account of the presence of silicic acid produced by hydrolysis of the glass. Various petroleum fractions and crude oils also show a change in rate of flow with time, due to the oxidation of unsaturated hydrocarbons to gummy substances. Permeability measurements with oils containing unsaturated substances should be carried out in an inert atmosphere.

C. W. GIBBY.

**Electrically heated muffle furnace.** T. R. BALL (J. Chem. Educ., 1931, 8, 355—357).—The top of the rectangular crucible furnace may be opened.

CHEMICAL ABSTRACTS.

**Detection of slightly cloudy liquids.** F. W. MEYER (Chem.-Ztg., 1931, 55, 146).—A lamp which assists in the examination of fine sediments and slightly cloudy liquids is described. E. DOCTOR.

**Colorimeters, spectrophotometers, and nephelometers.** C. DIGAUD (Ann. Chim. anal., 1931, [ii], 13, 1—15, 33—54, 65—74).—An account of the theory, and an extensive description of types of apparatus available, including details of commercial photo-electric cells, thermoelements, colorimeters, photometers, spectrophotometers, nephelometers, opacimeters, and diffusimeters. H. F. GILLBE.

**Plane-parallel plate refractometer.** A. H. PFUND (J. Opt. Soc. Amer., 1931, 21, 182—186).—A simple apparatus primarily for demonstration purposes is described.

**Absorption apparatus.** S. REINER (Chem.-Ztg., 1931, 55, 203).—An apparatus suitable for the study of the adsorption of solvent vapour on active material consists of a vacuum-tight H-shaped container, in the legs of which are placed bottles of solvent and adsorbent, respectively, with means for removing and replacing their stoppers without opening the vessel. H. E. F. NOTTON.

**Application of the adiabatic microcalorimeter to the measurement of heats of adsorption and of vaporisation.** W. SWIENTOSŁAWSKI and E. BARTOSZEWICZÓWNA (Rocz. Chem., 1931, 11, 78—89).—A microcalorimeter in which the galvanometer and leads from the thermocouple are placed within a recess in the thermostatic water-jacket within which the calorimeter vessel is suspended is described; in this way disturbances due to possible variations in the temperature of the environment are largely excluded. The construction of a special micro-

calorimeter vessel for the determination of heats of vaporisation and adsorption of small quantities of liquid is described. R. TRUSZKOWSKI.

**Adiabatic microcalorimeter adapted to the determination of the specific heat of solid and liquid substances.** W. SWIENTOSŁAWSKI, S. RYBICKA, and W. SOŁODKOWSKA (Rocz. Chem., 1931, 11, 65—77).—The microcalorimeter consists of a small copper or silver vessel containing the liquid under examination, and is suspended in a spherical vessel immersed in water of known invariable temperature. The substance is heated electrically, the heat supply being such that the rise of temperature amounts to 0.2—0.5° per hr. Where it is desired to determine the specific heat of a metal, the calorimeter vessel has to be made of this metal. Specific heats are determined by using two calorimeter sets, of which one has a known heat capacity. Evaporation or condensation of infinitesimal quantities of water on the calorimeter vessel gives heat effects sufficiently large to render the results inaccurate and the same applies to adsorption or desorption of gases; equilibrium should be attained in this respect before the commencement of determinations.

R. TRUSZKOWSKI.

**Prevention of foaming.** L. HART (Chemist Analyst, 1931, 20, No. 1, 9).—Foaming during steam-distillation or distillation with xylene may be prevented by addition of sodium hydrogen sulphate (3—5 g.), rosin (2—5 g.), oleic acid (5 c.c.), paraffin, mineral oil, a soluble barium or calcium salt, or amyl alcohol. CHEMICAL ABSTRACTS.

**Orsat apparatus for complete gas analysis.** ANON. (Chem.-Ztg., 1931, 55, 192).—A portable type of Orsat apparatus, comprising six absorption vessels in one wooden box and the burettes and their accessories in a second box, is described.

A. R. POWELL.

**Continuous dialyser.** H. A. AITKEN (J. Biol. Chem., 1931, 90, 161—163).—An apparatus whereby a liquid (10 c.c. or upwards) may be subjected to continual dialysis against distilled water, the dialysing water being distilled and after condensation passed inside a parchment membrane on the outside of which is the liquid which is being dialysed, is described. By means of a siphon, the water inside the membrane is returned to the distillation flask, from which it is again distilled. W. O. KERMAK.

**Spring balance for measuring the water content of snow.** G. D. CLYDE (Science, 1931, 73, 189—190). L. S. THEOBALD.

**Micro-ebullioscopic determination of mol. wt.** J. H. C. SMITH and H. W. MILNER (Mikrochem., 1931, 9, 117—122).—The apparatus consists of a boiling tube, differential thermometer, and Cottrell pump. Satisfactory results can be obtained by using as little as 3 c.c. of solvent and 5—25 mg. of solute. The apparatus has three advantages over the micro-Beckmann apparatus: (1) it does not require a supply of platinum tetrahedra, (2) a differential thermometer is substituted for the expensive micro-Beckmann thermometer, (3) more accurate readings can be obtained. Some experimental results are given. E. S. HEDGES.

**Behaviour of "indifferent" electrodes when used for the determination of oxidation-reduction potentials in the presence of hydrogen.** E. H. LEPPER and C. J. MARTIN (*Biochem. J.*, 1931, 25, 45—48).—When a phosphate mixture is poised with 0.001*M* indigo-carmin the gold electrode remains stable on substituting hydrogen for nitrogen, but when the concentration is made 0.0001*M* the potential rises by 8 millivolts. With a concentration of 0.002*M* indigo-carmin the iridium electrode shows a rise of 10 millivolts, and with a concentration of 0.0001*M* reaches almost the potential of the hydrogen electrode by the end of 30 min. In unpoised buffer solutions when hydrogen is substituted for the nitrogen which previously expelled the air, there is a negative drift of 45 millivolts of the gold electrode at the end of 1.25 hrs., whereas the iridium electrode reaches the potential corresponding with the  $p_{\text{H}}$  of the solution and remains steady at this level. The iridium

electrode gives off hydrogen when the latter is displaced by nitrogen very slowly. When, however, oxygen is passed through the solution there is a rapid fall of potential in both electrodes. At the end of 30 min. the gold electrode gives again a steady potential, whilst the iridium electrode after the first sudden fall continues to show a slow positive drift. Gold electrodes give different results from iridium electrodes during the growth of organisms when hydrogen is evolved (cf. Lopper and Martin, *Brit. J. Exp. Path.*, 1930, 11, 100), because gold is relatively insensitive to hydrogen, whereas iridium becomes charged with hydrogen from the solutions and assumes the function of a hydrogen electrode.

S. S. ZILVA.

**Replacing the telephone by a loud speaker in conductivity measurements.** L. DU NOÛY (*Nature*, 1931, 127, 441).—An arrangement is described.

L. S. THEOBALD.

## Geochemistry.

**Combined nitrogen in rain water.** C. SRIKANTIA (*Mysore Univ. J.*, 1930, 4, 195—198).—Tables showing the ammonia and nitric acid contents of rain water collected at Bangalore during nine months are given.

C. W. GIBBY.

**Content of krypton and xenon of some natural gases in Bulgaria.** N. P. PÉNTCHEV (*Compt. rend.*, 1931, 192, 691—693; cf. *A.*, 1928, 267; 1929, 1159).—As determined by the method of Moureu and Lepape (cf. *A.*, 1922, ii, 394) the amounts of krypton and xenon per 100 vols. of gases from the thermal springs at Sulu-Dervent (Momina), Hissar (Chuluja), and Kovanlik are respectively 0.00021 and >0.000013; 0.00015 and 0.000013; and 0.00025 and 0.00002. The approximate constancy of the ratio supports Moureu and Lepape's nebular hypothesis of the solar system (cf. *A.*, 1911, ii, 1134).

C. A. SILBERRAD.

**Chromiferous pyroxene from Jagersfontein, S. Africa.** H. O'DANIEL (*Z. Krist.*, 1930, 75, 575; *Chem. Zentr.*, 1931, i, 439).—The mineral contained  $\text{SiO}_2$  53.53,  $\text{Al}_2\text{O}_3$  1.30,  $\text{Cr}_2\text{O}_3$  1.96,  $\text{FeO}$  2.10,  $\text{CaO}$  22.96,  $\text{MgO}$  17.88%, corresponding with the formula  $\text{Mg}(\text{Ca}, \text{Fe})(\text{SiO}_3)_2(\text{Al}, \text{Cr})_2\text{O}_3$ . It has  $n_D^{20}$  1.6722,  $n_D^{25}$  1.6847,  $n_D^{30}$  1.7015.

A. A. ELDRIDGE.

**Tarnowitzite.** H. O'DANIEL (*Z. Krist.*, 1930, 75, 576—577; *Chem. Zentr.*, 1931, i, 439).—Tarnowitzite is a plumbiferous aragonite; the limit of lead oxide is higher than the earlier estimate of 5%.

A. A. ELDRIDGE.

**Thermal analysis of chlorite.** J. ORCEL (*Bull. Soc. Franç. Min.*, 1930, 52, 194—197; *Chem. Zentr.*, 1931, i, 438).—The heating curve for a ripidolite in air was normal, with two maxima; in a vacuum and in nitrogen the curve shows a sharp maximum, corresponding with the exothermic reaction  $2\text{FeO} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{H}_2$ , at about 780°.

A. A. ELDRIDGE.

**Andesitic bread-crust bomb from Tusnádfürdő.** V. ZSIVNY [with K. EMSZT] (*Math. Nat. Anz. Ungar. Akad. Wiss.*, 1929, 46, 277—290;

*Chem. Zentr.*, 1930, ii, 3530).—The rock of the bread-crust bomb is an amphibole andesite poor in biotite. Analysis gave  $\text{SiO}_2$  65.16,  $\text{TiO}_2$  0.44,  $\text{CaO}$  4.41,  $\text{MgO}$  2.19,  $\text{FeO}$  2.85,  $\text{Fe}_2\text{O}_3$  1.57,  $\text{Al}_2\text{O}_3$  16.13,  $\text{Na}_2\text{O}$  3.02,  $\text{K}_2\text{O}$  2.14,  $\text{SrO}$  0.08,  $\text{H}_2\text{O}$  1.52%.

A. A. ELDRIDGE.

**Eudialyte.** B. GOSSNER (*Zentr. Min. Geol.*, 1930, A, 449—450; *Chem. Zentr.*, 1931, i, 438).—Polemic (cf. Zachariassen, *Zentr. Min. Geol.*, 1930, A, 315).

A. A. ELDRIDGE.

**Optical properties of manganese-poor grünerites and cummingtonites compared with those of manganiferous members.** N. SUNDIUS (*Amer. J. Sci.*, 1931, [v], 21, 330—344).—Analyses and optical properties of the following are given: grünerites from Lake Superior, Massachusetts, and Södermanland, cummingtonite from Saude (Norway) and from Storgruvan, Persberg, kupfferite from Bajkal and Ural.

C. W. GIBBY.

**Analysis of cyrtolite for lead and uranium.** O. B. MUENCH (*Amer. J. Sci.*, 1931, [v], 21, 350—357).—A detailed account of the method used is given. 0.374% Pb and 7.29% U were found in a sample of cyrtolite rich in hafnium from Bedford, N.Y. Assuming no ordinary lead to be present, the age of the mineral is calculated to be  $373 \times 10^6$  years.

C. W. GIBBY.

**Constitution of the scapolites.** L. H. BORGSTRÖM (*Z. Krist.*, 1931, 76, 481—499; cf. *A.*, 1915, ii, 836).—By consideration of 52 analyses of scapolites it is shown that Tschermak's meionite ("oxide-meionite"),  $(\text{CaAl}_2\text{Si}_2\text{O}_8)_3\text{CaO}$ , does not exist, but that the scapolites are isomorphous mixtures of the type  $(\text{NaAlSi}_3\text{O}_8)_3\text{NaCl}$ , in which the albite molecule may be replaced by anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , and the NaCl by  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $0.5\text{Na}_2\text{CO}_3$ , or  $0.5\text{Na}_2\text{SO}_4$ , sodium and calcium replacing each other atom for atom. The components found in the scapolites are: chloro-, sulphato-, and carbonato-marialites, respectively  $\text{NaCl}, X$ ;  $0.5\text{Na}_2\text{SO}_4, X$ ; and  $0.5\text{Na}_2\text{CO}_3, X$  [ $X = (\text{NaAlSi}_3\text{O}_8)_3$ ], and carbonato-, sulphato- (sil-



vialite), and chloride-meionites,  $\text{CaCO}_3, X$ ;  $\text{CaSO}_4, X$ ; and  $\text{CaCl}_2, X$  [ $X = (\text{CaAl}_2\text{Si}_2\text{O}_8)_3$ ].

C. A. SILBERRAD.

**Titaniferous augite from Chaudrawati, Sirohi State, Rajputana.** A. L. COULSON (Rec. Geol. Survey India, 1931, 63, 448—450).—Titaniferous augite, possibly triclinic, occurs in a contact metamorphic rock between olivine-gabbro and a calcic rock near Chaudrawati. It is black, but pleochroic in thin sections (mauve and greenish-brown),  $\alpha$  1.734,  $\gamma - \alpha$  0.0024,  $\beta$  variable; dispersion  $\rho > \nu$ .

C. A. SILBERRAD.

**Sapphirine in the Vizagapatam district.** H. CROOKSHANK (Rec. Geol. Survey India, 1930, 63, 446—448).—Sapphirine has been found in several places 25 miles east of the place of first discovery (cf. Middlemiss, A., 1904, ii, 668), and is probably fairly common over most of the Eastern Ghats in the Vizagapatam district. The following additional optical properties are given:  $\alpha$  1.714,  $\beta$  1.718,  $\gamma - \alpha$  0.006;  $2V$   $62^\circ$ .

C. A. SILBERRAD.

**Tremolite from near Jasidih, Behar, India.** A. L. COULSON (Rec. Geol. Survey India, 1931, 63, 444—446).—The tremolite is pale green, with minute twin lamellae parallel to (001);  $d$  3.05;  $\alpha$  1.6029,  $\beta$  1.6175,  $\gamma - \alpha$  0.0271;  $2V$   $85^\circ 6'$ . Analysis of another sample gave  $\text{SiO}_2$  58.50,  $\text{Al}_2\text{O}_3$  2.82,  $(\text{FeO} + \text{Fe}_2\text{O}_3)$  1.60,  $\text{MnO}$  trace,  $\text{MgO}$  23.28,  $\text{CaO}$  13.58,  $\text{H}_2\text{O}$  nil, total 99.78%.

C. A. SILBERRAD.

**Trap rocks of the Chitaldrug schist belt.** C. S. PICHAMUTHU (Mysore Univ. J., 1930, 4, 210—222).—The rocks are described and the mode of their occurrence is discussed.

C. W. GIBBY.

**Ephesite (soda-margarite) from Postmasburg, South Africa.** F. C. PHILLIPS (Min. Mag., 1931, 22, 482—485).—Pink micaceous plates with the characters of margarite occur in manganese ore. Analysis by H. G. WEALL gave  $\text{SiO}_2$  29.4,  $\text{TiO}_2$  0.1,  $\text{Al}_2\text{O}_3$  50.6,  $\text{Fe}_2\text{O}_3$  0.55,  $\text{FeO}$  0.35,  $\text{MnO}$  0.1,  $\text{MgO}$  0.4,  $\text{Na}_2\text{O}$  8.65,  $\text{K}_2\text{O}$  trace,  $\text{Li}_2\text{O}$  1.5,  $\text{H}_2\text{O} + 5.3$ ,  $\text{H}_2\text{O} - 1.25$ ,  $F$  0.2, total 99.80%. The mineral is much richer in alumina than any mica and it corresponds with margarite with the calcium largely replaced by sodium, being a soda-margarite.

L. J. SPENCER.

**Grunerite from Pierrefitte, Hautes-Pyrénées, France.** H. V. WARREN (Min. Mag., 1931, 22, 477—481).—Grunerite forms a compact grunerite-schist overlying the ore-body and also occurs as needles in the lead and zinc ore. Analysis shows  $\text{FeSiO}_3$  81.4,  $\text{MnSiO}_3$  4.3,  $\text{MgSiO}_3$  10.6,  $\text{CaSiO}_3$  3.7%. The optical data for this material and for grunerite from other localities are correlated with the variations in chemical composition.

L. J. SPENCER.

**Distinction of analcime from leucite in rocks by X-ray methods.** F. A. BANNISTER (Min. Mag., 1931, 22, 469—476).—X-Ray powder photographs of analcime from Sicily and blaimorite from Portuguese East Africa give a unit cell of edge  $a$  13.70 Å. Leucite from Vesuvius is pseudo-cubic with a body-centred cell of dimensions  $a$  12.95,  $b$  13.12,  $c$  13.74 Å. It is thus possible by this method to distinguish between analcime and leucite and also both from the glassy groundmass in rocks.

L. J. SPENCER.

**Dolerite-chalk contact of Scawt Hill, Co. Antrim. Production of basic alkali-rocks by the assimilation of limestone by basaltic magma.** C. E. TILLEY and H. F. HARWOOD (Min. Mag., 1931, 22, 439—468).—The dolerite magma intruded into chalk absorbed some calcium carbonate with the production of pyroxenite, titanaugite-melilite-rocks, nepheline-dolerite, etc. Complementary to the precipitation of magnesium-rich pyroxene in the pyroxenite there was a segregation of a basic alkali residuum. Plagioclase was reabsorbed giving place to a titaniferous lime-augite rich in alumina, melilite, and nepheline. Several unusual minerals, including the new species larnite and scawtite, were formed by this interaction of dolerite magma and chalk. Analyses are given of the rocks and the pyroxenes.

L. J. SPENCER.

**Enstatite and its relation to the pyroxenes and amphiboles.** B. GOSSNER and F. MUSSGUG (Z. Krist., 1929, 70, 234—248; Chem. Zentr., 1930, ii, 1055).—Mixed crystals of bronzite and hypersthene show rhombic unit cells with  $a$  8.93 and 8.84,  $b$  18.2 and 18.23, and  $c$  5.12 and 5.20 Å. for bronzite and hypersthene, respectively. (Enstatite gives no rotation diagram.) The cell probably contains 16 mols.; space-group probably  $V_6^c$ . The pyroxenes and amphiboles are discussed in the light of X-ray measurements.

L. S. THEOBALD.

**Formula of tourmaline.** F. MACHATSCHKI (Z. Krist., 1929, 70, 211—233; 1929, 71, 45—46; Chem. Zentr., 1930, ii, 1054).—The formula  $\text{XY}_9\text{B}_3\text{Si}_6\text{H}_x\text{O}_{31}$ , where X is Ca, Na, and possibly  $\text{Mn}^{++}$ , and Y is Li, Mg, Mn, Fe, and Al, is assigned to tourmaline. Apparently, aluminium can replace some silicon by means of the replacement of Na, Si by Ca, Al or of Si, Mg by Al, Al. Rotation photographs of black tourmaline from Grundesund, Norway, give  $a$  16.02,  $c$  7.22 Å.; the hexagonal unit cell contains 3 mols.

L. S. THEOBALD.

**Heulandite.** P. GAUBERT (Bull. Soc. Franç. Min., 1930, 52, 162—194; Chem. Zentr., 1931, i, 49; cf. A., 1930, 718, 1017).—Different types of heulandite, associated with different optical properties, are produced by partial dehydration and rehydration. Differences in the speed of diffusion of various liquids into heulandite have been measured.

A. A. ELDRIDGE.

**Kleibelsbergite.** V. ZSIVNY (Math. Nat. Anz. Ungar. Akad. Wiss., 1929, 46, 19—24; Chem. Zentr., 1930, ii, 3530).—The new mineral from Felsőbánya is a basic antimony sulphate.

A. A. ELDRIDGE.

**Minerals of the clay group.** I. F. KÄSTNER and F. K. MAYER (Chem. Erde, 1931, 6, 269—274).—A discussion of clays and the weathering of felspar. X-Ray powder photographs of samples referred to as nacrite, kaolin, and montmorillonite suggest that these are mixtures.

L. J. SPENCER.

**Formularisation of silicates.** F. MACHATSCHKI (Chem. Erde, 1931, 6, 253—254).—Further discussion on the formula of tourmaline (A., 1930, 315).

L. J. SPENCER.

**Formularisation of silicates.** W. KUNITZ (Chem. Erde, 1931, 6, 255—256).—A reply to the above.

**Origin of Schaumspat and dolomite.** E. KÖHLER (Chem. Erde, 1931, 6, 257—268).—Analyses of Schaumspat (aphrite) from the dolomitic limestones and marls (Zechstein and Muschelkalk) of several localities in Thuringia show that the material consists of calcium carbonate with only traces of magnesia and ferric oxide. It is a pseudomorph of aragonite after gypsum. It can be produced artificially by the action of magnesium hydrogen carbonate solution on gypsum at 20° under carbon dioxide pressure, or with calcium hydrogen carbonate at a higher temperature (30°). Attempts to prepare dolomite by the action of magnesium sulphate solution on vaterite usually gave magnesite, but in the presence also of ammonium sulphate dolomite was formed. Dolomite-rock has been formed at certain depths in the earth's crust by the action of solutions of magnesium salts on limestone, and the calcium set free has been partly deposited as gypsum, which later became converted into aragonite, giving Schaumspat.

L. J. SPENCER.

**X-Ray examination of the modifications of calcium carbonate in gasteropod shells.** F. K. MAYER (Chem. Erde, 1931, 6, 239—252).—In the embryonic forms of land and fresh-water snails the shell in the first stages consists of vaterite, which in later stages becomes converted into aragonite, and still later partly into calcite.

L. J. SPENCER.

**Crystals of calcite from the coal mines of Hasard and of La Concorde formed by deposition on the lateral edges of scalenohedra  $d^2$ .** Crystals from Binnen, with perfectly reflecting faces, having the notation  $d$  13/11, associated with chalcedony. J. MÉLON (Bull. Acad. roy. Belg., 1931, [v], 16, 1353—1363).—Crystallographic data are recorded. Both Hasard (yellowish) and La Concorde calcite are associated with chalcopyrite and ankerite.

C. W. GIBBY.

**Mineral succession in regions of pneumatolytic-hydrothermal action.** W. KUNITZ (Z. Krist., 1931, 76, 462—463; cf. A., 1929, 965).—The order of crystallisation of minerals containing volatile

acids is discussed according to a general scheme of fractional distillation. Thus in an acid granite pegmatite the silicates first separated, followed by the phosphates, and then by carbonates, sulphides, and fluorides.

C. A. SILBERRAD.

**Crystal habit of zinc blende with special reference to vicinal forms.** G. KALB (Z. Krist., 1931, 76, 386—395).—Examination of the vicinal forms of many samples confirms the reference of zinc blende to the octahedral isoharmonic type (cf. A., 1930, 1099). It further enables all blendes to be classified minerogenetically into an older cubo-octahedral type, usually black, rarely green, yellow, or colourless, and a younger dodecahedral type, usually red (ruby blende).

C. A. SILBERRAD.

**Genetic physico-chemical theory of formation of humus, peat, and coal.** J. ZOLCINSKI (Pflanzenbau, 1930, 4, 196—228; Chem. Zentr., 1931, i, 248—249).—Humification is not a bacterial process; hydrogen peroxide and aromatic compounds, having an antiseptic action, are formed simultaneously. The physico-chemical process proceeds the more vigorously the greater is the number of double linkings in the decomposing material. All biological factors employing stored chemical energy tend to convert organic compounds into those containing double linkings which are suitable for humification. Organic compounds, particularly aromatic, containing double linkings decompose even in the dark and with exclusion of air.

A. A. ELDRIDGE.

**Soil erosion.** ANON. (Imperial Bur. Soil Sci. Tech. Comm., Nos. 5 and 16).—A comprehensive summary of existing literature and bibliography.

A. G. POLLARD.

**Occurrence and distribution of salinity in a virgin Mallee soil.** J. E. THOMAS (J. Counc. Sci. Ind. Res. Australia, 1931, 4, 12—19).—Considerable variations in both the vertical and horizontal distribution of salt in the soil are recorded and correlated with relief, soil type, and type of vegetation.

A. G. POLLARD.

## Organic Chemistry.

**Initial and other significant temperatures in the pyrolysis of pentanes and pentenes.** G. THOMSON (Abs. Theses Mass. Inst. Tech., 1931, 7, 51—53).—The decomposition temperatures of *n*- and *iso*-pentane,  $\Delta^1$ - and  $\Delta^2$ -pentene, and  $\beta$ -methyl- $\Delta^2$ -butene have been determined by heating a definite volume of the vapour at various temperatures until a temperature is attained at which appreciable expansion occurs within a prescribed period (1 hr.). By plotting the rate of expansion at this and at successively rising temperatures against temperature, and extrapolation of the resulting straight line to zero expansion the decomposition temperature is obtained. Complications arise owing to decomposition of intermediate products and, in the case of the unsaturated compounds, to polymerisation. The results indicate that the saturated branched-chain compounds are less

stable than straight-chain compounds, and that the unsaturated compounds decompose more rapidly than the saturated compounds. The stability of the olefines is the greater the nearer is the double linking to the middle of the chain. A methyl group attached to an ethylenic carbon atom is firmly bound, and the stability increases with increase of the symmetry of the molecule.

H. F. GILLBE.

**Fission and condensation of hydrocarbons. I. Ethylene.** E. BERL and W. FORST (Z. angew. Chem., 1931, 44, 193—197).—Ethylene was circulated through a porcelain tube heated at 800—900°, the heavy oils produced being precipitated electrolytically, the light oils absorbed in active carbon, and the gaseous products analysed when decomposition had ceased, usually after several hours. Up to 43% of liquid

products were obtained, their amount and the ratio of light to heavy oils being dependent on the temperature and velocity of circulation. Packing the tube with pieces of porcelain slightly increased the total yield, and also the proportion of light oil, whilst the presence of metals or metallic oxides greatly lowered the amount of liquid obtained because of their catalytic action on the decomposition of ethylene into its elements. The gaseous products were mainly lower aliphatic hydrocarbons and hydrogen, little ethylene remaining undecomposed. The liquids consist of benzene, naphthalene, anthracene, and their homologues, *cyclopentadiene* being also detected. The mechanism of reaction is stated to be primarily the formation of unsaturated radicals, which either polymerise or unite with hydrogen. A. KEY.

**Electromerides of  $\Delta^2$ -pentene.** R. H. CLARKE and E. G. HALLONQUIST (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 115—119).—The two electromerides of  $\Delta^2$ -pentene have m. p.  $-149^\circ$  (stable) and m. p.  $-144^\circ$  (metastable), respectively. A magnetic or electrostatic field had no effect on the product obtained by addition of hydrogen bromide to the metastable form. W. GOOD.

**Catalysis of polymerisation by ozonides.** R. C. HOUTZ and H. ADKINS (J. Amer. Chem. Soc., 1931, 53, 1058—1063).—Ozonised mixtures of two *diso*-butylenes accelerate the polymerisation, both at the ordinary temperature and at  $100^\circ$ , and without solvent or in toluene solution, of styrene, indene,  $\beta\gamma$ -dimethyl- $\Delta^2$ -butadiene, methylpentadiene, and furfuryl alcohol, but are inactive towards stilbene, *o*-hydroxybenzyl alcohol,  $\beta$ -methyl- $\Delta^2$ -butene, and the original mixture of octylenes from which they were prepared. With styrene (and generally) the velocity of polymerisation increases with increasing concentration of the catalyst up to 2%, a period of induction of approximately 200 hrs. being observed when only 0.5% of the catalyst is used. The catalytic activity is inherent in the original ozonides and not in any decomposition products, since the activity diminishes rapidly on keeping. J. W. BAKER.

**Oleastene, a hydrocarbon of the olive.** G. SANI (Atti R. Accad. Lincei, 1930, [vi], 12, 238—242).—*Oleastene*, ( $C_7H_{12}$ )<sub>x</sub>, b. p.  $300^\circ$  (low pressure),  $d_{17.5}^{25}$  0.8896, obtained during the separation of the cholesterol of the olive, forms an *ozonide*,  $C_{21}H_{36}O_9$ . T. H. POPE.

**Vegetable dyes. XXIX. Symmetrical lycopene formula. Perhydrolycopene.** P. KARRER, A. HELFENSTEIN, B. PIEPER, and A. WETTSTEIN (Helv. Chim. Acta, 1931, 14, 435—438; cf. A., 1930, 1627).—Degradation of lycopene with ozone gives 1.6 mols. of acetone in accordance with the "symmetrical" formula (A., 1930, 1422), which is also supported by the close agreement in physical properties between perhydrolycopene and the hydrocarbon  $C_{40}H_{62}$ , b. p.  $238$ — $240^\circ/0.3$  mm.,  $212$ — $214^\circ/0.02$  mm. (cf. A., 1929, 49), obtained from dihydrophytyl bromide by the Wurtz synthesis.

Squalene, which also possesses a symmetrical structure (cf. this vol., 333), gives 1.8 mols. of acetone under the same conditions. H. A. PREGOTT.

**Characterisation of alkyl halides and organo-magnesium halides.** A. M. SCHWARTZ and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, 53, 1063—1068).—Alcohols and their halides are readily identified and characterised by conversion into the corresponding magnesium alkyl halide and conversion of these into crystalline acid anilides by interaction with a 10% ethereal solution of phenylcarbimide. With certain branched-chain alcohols isomerisation occurs (probably during conversion into the halide); thus methylisopropylcarbinol and  $\beta\beta$ -dimethylpropan- $\alpha$ -ol both afford  $\beta\beta$ -dimethylbutyranilide. Magnesium allyl bromide affords a liquid anilide, probably impure vinylacetanilide. *d*- $\alpha$ -Bromo-octane affords only *dl*- $\beta$ -methyloctanoanilide. J. W. BAKER.

**Removal of hydrogen halide from organic halides.** C. R. NOLLER and R. DINSMORE (J. Amer. Chem. Soc., 1931, 53, 1185—1186).—The main reaction between alkyl halides and tertiary bases, especially pyridine, other than quaternary salt formation, appears to be the removal of hydrogen halide from the alkyl halide (cf. Semb and McElvain, this vol., 494). J. W. BAKER.

**Activity of the halogens in some polyhalogeno-aliphatic derivatives.** B. V. TRONOV and L. V. LADIGUINA (J. Russ. Phys. Chem. Soc., 1930, 62, 2165—2171).—Activity is least in the case of chlorine and greatest in iodine. Halogen atom in a compound of the type  $X[CH_2]_n \cdot X$  is more readily split off than in  $H[CH_2]_n \cdot X$ . In compounds of the former type, as the value of *n* increases, the activity begins to fall after an initial rise. This is attributed to two influences in the molecule. According to the theory of alternating polarity, the activity should alternately rise and fall, depending on the number of atoms separating the halogens. Counteracting this is the effect of the large effective positive charge of the halogen nucleus; under the influence of a strongly electronegative element all the atoms in the chain tend to become more electronegative. Both these forces weaken with increasing distance between the atoms, but the weakening proceeds along different lines. The force of direct action through the chain at first exceeds the periodic force, but afterwards diminishes more rapidly. E. B. UVAROV.

**Preparation of chlorinated products of acetylene.** S. LANGGUTH (Chim. et Ind., 1931, 25, 22—25).—Laboratory details, with diagrams of apparatus, are given for the preparation of *s*-tetrachloroethane and *s*-dichloroethylene from acetylene and antimony pentachloride, and for converting the tetrachloroethane into trichloroethylene with potassium hydroxide. The preparation of  $\alpha$ - and  $\beta$ -trianilinoethylene from aniline and the tetrachloride is described.

L. J. HOOLEY.

**Halogeno-compounds of the butane series.** E. MÜLLER and F. HÜTHER (Ber., 1931, 64, [B], 589—600).—*s*-Tetrachloroethane loses chlorine when boiled for a considerable time and forms  $\alpha\alpha\beta\gamma\delta\delta$ -hexachlorobutane, m. p.  $107^\circ$ , which is contained in the residues of the technical distillation of crude tetrachloroethane. Irradiation of homogeneous tetrachloroethane with ultra-violet light causes loss of hydrogen chloride instead of chlorine and production

of  $\alpha\alpha\beta\gamma\delta\delta$ -hexachloro- $\Delta^{\beta}$ -butene, m. p. 80°. Removal of 2 mols. of hydrogen chloride from  $\alpha\alpha\beta\gamma\delta\delta$ -hexachlorobutane by means of calcium hydroxide leads to the production of two stereoisomeric forms of  $\alpha\beta\gamma\delta$ -tetrachloro- $\Delta^{\alpha\gamma}$ -butadiene, b. p. 188°,  $d^{15}$  1.516, and m. p. 50°, respectively; both compounds are present in the residues obtained technically from crude trichloroethylene. Addition of chlorine to the tetrachlorobutadiene, m. p. 50°, gives  $\alpha\alpha\beta\gamma\delta\delta$ -hexachloro- $\Delta^{\beta}$ -butene, m. p. 80°, whereas the liquid tetrachloro-compound yields a liquid,  $\alpha\alpha\beta\gamma\delta\delta$ -hexachloro- $\Delta^{\beta}$ -butene, b. p. 97—98°/10 mm. Addition of bromine leads to  $\alpha\beta\gamma\delta$ -tetrachloro- $\alpha\delta$ -dibromo- $\Delta^{\beta}$ -butene, m. p. 105°, whereas the liquid modification of this compound cannot be distilled without decomposition in a vacuum.  $\alpha\beta\gamma\delta$ -Tetrachloro- $\alpha\delta$ -dinitro- $\Delta^{\beta}$ -butene, m. p. 131°, is obtained by the action of fuming nitric acid or nitrogen peroxide.  $\alpha\beta\gamma\delta$ -Tetrachlorobutadiene can under certain conditions be regenerated from its additive compounds with chlorine and bromine.

H. WREN.

Addition of gaseous hydrogen bromide to acetylene and to gaseous vinyl bromide in presence of catalysts, and to vinyl and allyl bromides in the liquid phase. J. P. WIBAUT [with P. J. HUBERS, L. S. BROUWER, C. TER BRAAK, and J. P. WEDDEPHIL] (Rec. trav. chim., 1931, 50, 313—337; cf. A., 1929, 1399).—The combination of gaseous hydrogen bromide and gaseous vinyl bromide has been carried out in a special apparatus, the relative proportions of the isomeric dibromoethanes formed being determined thermometrically and refractometrically. Although the results obtained are not always reproducible, the following generalisations may be made. Glass wool and asbestos are catalysts at 100° for the formation of ethylene bromide, whilst silica gel, bismuth and ferric bromides (without carriers) lead to ethylidene bromide. Metallic bromides on an asbestos support give mixtures of these isomerides, of variable composition, and the results are sometimes inexplicable. The effect of raising the temperature to 200° is to decrease the total yield, but to increase the proportion of ethylidene bromide. No interconversion of the two isomerides take place at 150°, with or without the above catalysts. Similar experiments with acetylene and hydrogen bromide show that the formation of dibromoethanes takes place with less ease, and it is concluded that the primary formation of vinyl bromide takes place with greater difficulty than its subsequent conversion into dibromoethanes. The formation of ethylene bromide by this process seems a practical possibility. Aqueous hydrogen bromide ( $d$  1.6—1.7) with vinyl bromide at 100° leads to ethylidene bromide, but more concentrated solutions ( $d$  1.82—1.86) give mixtures which contain 31—35% of ethylene bromide. Acetic acid solutions of hydrogen bromide, with or without the addition of metallic bromides or other contact substances, yield with vinyl bromide at 100° mainly ethylidene bromide. Acetic acid solutions of hydrogen bromide under a variety of conditions give only  $\alpha\beta$ -dibromopropane with allyl bromide, whereas in bright sunlight, liquid allyl bromide and anhydrous hydrogen bromide give mainly trimethylene bromide.

An explanation of the results, based on the hypo-

thesis of "directed absorption" of Kruyt and van Duin (A., 1921, ii, 392; 1928, 849; 1929, 1399), is offered, but it is pointed out that the results are not in agreement with the theory of alternate polarities.

J. D. A. JOHNSON.

Addition of hydrogen bromide to allyl bromide in a magnetic and electrostatic field. R. H. CLARKE and K. R. GRAY (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 111—114).—The composition of the product obtained on the addition of hydrogen bromide to allyl bromide in glacial acetic acid is greatly changed when the reaction is carried out in a magnetic field.

W. GOOD.

Catalytic hydrogenation of organic compounds over copper chromite. H. ADKINS and R. CONNOR (J. Amer. Chem. Soc., 1931, 53, 1091—1095).—Copper chromite, prepared by thermal decomposition of copper ammonium chromate, is a very effective hydrogenation catalyst, the reaction being exothermic. It is preferable to nickel, since it is much less readily deactivated, is less sensitive to sulphur and halogen poisons, and is less reactive towards a carbonyl group adjacent to benzenoid rings, reducing it only to the corresponding alcohol.

J. W. BAKER.

Catalytic hydrogenation of esters to alcohols. H. ADKINS and K. FOLKERS (J. Amer. Chem. Soc., 1931, 53, 1095—1097).—By use of a copper chromite catalyst (cf. preceding abstract) and hydrogen at 250°/220 atm., ethyl laurate, myristate, valerate, cinnamate,  $\alpha\alpha$ -dimethylpropionate, and succinate are reduced to the corresponding alcohols in 80—90% yield. Ethyl  $\gamma$ -hydroxy- $\beta\beta$ -dimethylbutyrate is reduced to the carbinol, but the molecule subsequently undergoes fission, yielding *isobutyl* and *n*-propyl alcohols.

J. W. BAKER.

Formation of methyl alcohol by the direct oxidation of methane. W. A. BONE (Nature, 1931, 127, 481).—Newitt and Haffner have obtained methyl alcohol by the interaction of oxygen and methane at 360°/100 atm. With a 9:1 mixture of methane and oxygen, the reaction is complete in a few min., 17% of the methane oxidised being recovered as methyl alcohol, 0.6% as formaldehyde, and the remainder as oxides of carbon and water vapour. No hydrogen and no trace of a peroxide is formed.

L. S. THEOBALD.

Ethylene chlorohydrin. E. D. G. FRAHM (Rec. trav. chim., 1931, 50, 261—267).—The methods of preparation of ethylene chlorohydrin already described are critically discussed. The rate of formation is increased if the ethylene and chlorine are allowed to react in dilute aqueous solutions of suitable catalysts (copper chloride 0.1—1.0%, ferric chloride 0.1%, etc.), the simultaneous formation of ethylene chloride being diminished considerably. The catalysts used facilitate the decomposition of hypochlorous acid into hydrochloric acid and oxygen, and it is therefore suggested that the formation of ethylene chlorohydrin from ethylene and chlorine in aqueous media takes place by way of ethylene oxide, which is subsequently decomposed by hydrogen chloride.

J. D. A. JOHNSON.

Configurations of secondary carbinols of the *isopropyl* and *isobutyl* series. P. A. LEVENE and

R. E. MARKER (J. Biol. Chem., 1931, 90, 669—675).—The homologous *d*-isobutylcarbinols form a series in which the values of the mol. rotations fall with increasing mol. wt., whereas in the corresponding *d*-isopropyl alcohol series (Pickard and Kenyon, J.C.S., 1912, 101, 620) the values rise; this is due to the differing distances, in the two series, of the isopropyl group from the asymmetric carbon atom. The following data are recorded, the values for  $[\alpha]_D$  being for the homogeneous state in the case of the carbinols, and in absolute alcohol in the case of the esters: *d*-methylisobutylcarbinol, b. p. 64°/60 mm.,  $n_D^{20}$  1.4100,  $[\alpha]_D^{20} +20.85^\circ$  (hydrogen phthalate,  $[\alpha]_D^{20} +55.8^\circ$ ); *d*-ethylisobutylcarbinol, b. p. 81°/60 mm.,  $n_D^{20}$  1.4171,  $[\alpha]_D^{20} +21.23^\circ$  (hydrogen phthalate,  $[\alpha]_D^{20} +24.8^\circ$ ); *d*-*n*-propylisobutylcarbinol, b. p. 80°/25 mm.,  $n_D^{20}$  1.4205,  $[\alpha]_D^{20} +12.54^\circ$  (hydrogen phthalate,  $[\alpha]_D^{20} +13.0^\circ$ ); 1-*n*-butylisobutylcarbinol, b. p. 87°/20 mm.,  $n_D^{20}$  1.4258,  $[\alpha]_D^{20} -9.48^\circ$  (hydrogen phthalate,  $[\alpha]_D^{20} -8.1^\circ$ ); *d*-*n*-isobutylamylcarbinol, b. p. 117°/40 mm.,  $n_D^{20}$  1.4302,  $[\alpha]_D^{20} +7.22^\circ$  (hydrogen phthalate,  $[\alpha]_D^{20} +11.9^\circ$ ).

A. RENFREW.

Butenols. J. VERHULST (Bull. Soc. chim. Belg., 1931, 40, 85—90).— $\Delta^2$ -Butenyl alcohol [the preparation of which by Pariselle's method (A., 1909, i, 282) is accompanied by a *by-product*  $C_7H_{12}O$ , b. p. 149—150°/745 mm.,  $d_4^{20}$  0.8570] or its acetate is not isomerised in the presence of sodium phenoxide, aniline, or other amines. If the product obtained by heating allylcarbinol, saturated with dry hydrogen chloride, in sealed tube is distilled, allyl chloride first passes over, followed by  $\gamma$ -chlorobutyl alcohol, b. p. 67—68°/15 mm.,  $d_4^{20}$  1.06218,  $n_D^{20}$  1.44464, also obtained by the action of hydrogen chloride on  $\alpha\gamma$ -dihydroxybutane.  $\Delta^2$ -Butenyl alcohol, b. p. 120—121°/755 mm.,  $d_4^{20}$  0.85306,  $n_D^{20}$  1.42976, is produced (yield, 25%) by distilling the chlorohydrin, preferably in the presence of quinoline. The 6 fractions distilled between 115° and 122° give the same *phenylurethane*, m. p. 79.4—80°. The question of the formation of geometrical isomerides is therefore open.  $\Delta^2$ -Butenyl alcohol cannot be prepared by Charon's method (A., 1896, i, 407).

A. RENFREW.

## Preparation of carbon monoxide diethylacetal.

A. E. ARBUSOV (Ber., 1931, 64, [B], 698—700).—A criticism of Scheibler's work (A., 1926, 711; 1927, 338) on the preparation of diethoxymethylene (cf. Adickes, this vol., 196).

H. WREN.

Dioxan and halogens. H. RHEINBOLDT and R. BOY (J. pr. Chem., 1931, [ii], 129, 273—277).—In agreement with Wurtz (*ibid.*, 1863, 486) the view that the compound, m. p. 65—66°, obtained by the action of bromine on dioxan is the additive compound ( $C_4H_8O_4$ ) $_2$ Br $_2$ , and not the oxonium perbromide ( $C_4H_8O_4$ ) $_2$ HBr $_3$ , as stated by Kehrman and Falke (A., 1925, i, 351), is confirmed by analysis of the corresponding additive compounds with iodine, m. p. 84—85°; iodine monochloride, m. p. 56—58°; and iodine monobromide, m. p. 65°. The iodine compound is the most stable of these derivatives.

J. W. BAKER.

Stannic halides and dioxan. H. RHEINBOLDT and R. BOY (J. pr. Chem., 1931, [ii], 129, 268—272).—Dioxan reacts with stannic chloride itself or with its

co-ordination compounds of the type  $SnCl_4 \cdot 2R$  ( $R = Et_2O, Ph \cdot CHO, AcPh, \text{ and } CHPh \cdot CHAc$ ) at 0° to give the co-ordination compound  $SnCl_4 \cdot (C_4H_8O)_2$ , similar compounds being obtained with stannic bromide and iodide. The iodine compound is very unstable.

J. W. BAKER.

Condensations [of polyhydric alcohols] with acetone in presence of phosphoric oxide. L. SMITH and J. LINDBERG (Ber., 1931, 64, [B], 505—516).—The polyhydric alcohol is kept well stirred with anhydrous acetone while a mixture of phosphoric oxide and sand or quartz powder is gradually added. The temperature is maintained between -10° and 30°, the optimum conditions being secured by keeping it as low as practicable. The upper acetone layer, containing the product of the reaction, is neutralised with anhydrous potassium carbonate and the acetone removed by distillation; mesityl oxide is formed in small amount. Ethylene glycol affords ethylene isopropylidene ether, b. p. 92—92.5°,  $d_4^{20}$  0.9458,  $n_D^{20}$  1.4009, in 50% yield and glycerol  $\beta$ -chlorohydrin yields its isopropylidene ether, b. p. 161.5—162.2° (corr.)/757 mm.,  $d_4^{20}$  1.1344,  $n_D^{20}$  1.4487, in 71% yield (calculated on the chlorohydrin consumed in the reaction). With trimethylene glycol the yield of ether is 35%. With rise of temperature the  $\alpha\beta$ -ether from glycerol appears to be mixed with increasing amount of the  $\alpha\gamma$ -isomeride. The acetonisation of arabinose (70%), rhamnose (85%), mannose (64%), galactose, laevulose (83%), and dextrose is described; the yields are recorded in parentheses. Mandelic acid condenses very readily with acetone in presence of phosphoric oxide. In the presence of hydrogen chloride, glycerol  $\alpha$ -chlorohydrin condenses with acetone about thirteen times as rapidly as the  $\beta$ -chlorohydrin, whereas in presence of phosphoric oxide the ratio is about 5.6. The isolation of glycerol  $\beta$ -monochlorohydrin from its mixture with the  $\alpha$ -isomeride is effected by acetonisation in presence of phosphoric oxide, followed by removal of the more volatile products. The residue is treated with acetone and hydrogen chloride, giving a residue containing 95% of the  $\beta$ -isomeride, which is purified by ether and finally by fractional distillation under very low pressure. Glycerol  $\alpha$ -monochlorohydrin has b. p. 119°/14 mm.,  $d_4^{20}$  1.3214,  $n_D^{20}$  1.4811,  $\eta^{20}$  1.59, whereas the  $\beta$ -monochlorohydrin has b. p. 124°/14 mm.,  $d_4^{20}$  1.3219,  $n_D^{20}$  1.4831,  $\eta^{20}$  3.00.

H. WREN.

## Partial esterification of polyhydric alcohols.

XI. Methyl ethers of glycerol. A. FAIRBOURNE, G. P. GIBSON, and D. W. STEPHENS (J.C.S., 1931, 445—458).—The five methyl ethers of glycerol (cf. Fairbourne, A., 1929, 1038, 1422; Hibbert and Whelen, *ibid.*, 908) are obtained by the methylation of sodium glyceroxides with methyl sulphate in glycerol, both  $\alpha$ - and  $\beta$ -monomethyl ethers being separable from the monomethylation product. On further methylation, the  $\beta$ -monomethyl ether yields only glycerol trimethyl ether and glycerol  $\alpha\beta$ -dimethyl ether, b. p. 100°/40 mm.,  $d_4^{20}$  1.028,  $n_D^{20}$  1.4249 (*p*-nitrobenzoate, m. p. 44°). By acetylation of the appropriate ethers,  $\beta$ -acetoxy- $\alpha\gamma$ -dimethoxypropane, b. p. 105—106°/40 mm.,  $d_4^{20}$  1.025,  $n_D^{20}$  1.413;  $\gamma$ -acetoxy- $\alpha\beta$ -dimethoxypropane, b. p. 108—109°/40 mm.,  $d_4^{20}$  1.027,

$n_D^{25}$  1.414;  $\alpha\gamma$ -diacetoxy- $\beta$ -methoxypropane, b. p. 144—145°/40 mm.,  $d_4^{25}$  1.100,  $n_D^{25}$  1.424;  $\beta\gamma$ -diacetoxy- $\alpha$ -methoxypropane, b. p. 139—140°/40 mm.,  $d_4^{25}$  1.097,  $n_D^{25}$  1.422, all hydrolysable to the parent ethers, and  $\beta\gamma$ -diacetoxy- $\alpha$ -ethoxypropane, b. p. 117—119°/10 mm.,  $d_4^{25}$  1.062,  $n_D^{25}$  1.422;  $\beta$ -acetoxy- $\alpha\gamma$ -diethoxypropane, b. p. 127—129°/60 mm.,  $d_4^{25}$  0.980,  $n_D^{25}$  1.415;  $\alpha\gamma$ -diphenoxy- $\beta$ -acetoxypropane, m. p. 33°;  $\alpha\gamma$ -di-*o*-tolylxy- $\beta$ -acetoxypropane, b. p. 204—206°/2—3 mm.,  $d_4^{25}$  1.103,  $n_D^{25}$  1.536;  $\alpha\gamma$ -di-*m*-tolylxy- $\beta$ -acetoxypropane, b. p. 215—217°/2—3 mm.,  $d_4^{25}$  1.103,  $n_D^{25}$  1.536;  $\alpha\gamma$ -di-*p*-tolylxy- $\beta$ -acetoxypropane, m. p. 49°, are obtained.  $\beta$ -Chloro- $\alpha\gamma$ -dimethoxypropane, b. p. 155—156°,  $d_4^{25}$  1.05,  $n_D^{25}$  1.42; glycerol  $\alpha\gamma$ -diisopropyl ether, b. p. 123—124°/60 mm.,  $d_4^{25}$  0.914,  $n_D^{25}$  1.418; glycidyl isopropyl ether, b. p. 137—138°,  $d_4^{25}$  0.924,  $n_D^{25}$  1.408; glycerol  $\alpha$ -monobenzyl ether, b. p. 164—166°/2—3 mm.,  $d_4^{25}$  1.130,  $n_D^{25}$  1.530, and glycerol  $\alpha\gamma$ -dibenzyl ether, b. p. 198—204°/2—3 mm.,  $d_4^{25}$  1.100,  $n_D^{25}$  1.547, are prepared from the appropriate chlorohydrins and sodium alkoxides. The method of Newman, Trikojus, and Harker (A., 1927, 40) for esterification has been modified for the synthesis of *p*-tolyl *n*-octoate, b. p. 163—165°/10 mm.,  $d_4^{25}$  0.957,  $n_D^{25}$  1.483.

G. DISCOMBE.

**Methylation of hexosemonophosphoric ester.** E. J. KING, R. R. McLAUGHLIN, and W. T. J. MORGAN (Biochem. J., 1931, 25, 310—322).—The methylation of the aldosemonophosphate of Robison's fermentation hexosemonophosphate by Fischer's method at 18° and at 60° has yielded two distinct forms of methylhexosidemonophosphate. That produced by methylation at 18° is extremely sensitive to acids. With 0.1*N*-acid at 36° it is rapidly hydrolysed, yielding a reducing hexosemonophosphoric acid. The corresponding hexoside produced by methylation at 60° is stable in the presence of 0.1*N*-acid at 37°. Its rate of hydrolysis closely resembles that of  $\alpha$ -methylglucoside under the conditions described.

S. S. ZILVA.

**Soya-bean lecithins. II. Lecithins of the  $\alpha$ -series.** Y. YOKAYAMA and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 12—14).—By fractional extraction of the brominated  $\alpha$ -lecithins of the soya bean (separated as their double salts with cadmium chloride; this vol., 401) with various solvents are isolated the bromides of palmito-linoleo-, oleo-linoleo-, dioleo-, and dilinoleo-, m. p. 113—114°,  $\alpha$ -lecithin. The structures are proved by hydrolysis to tetrabromostearic and palmitic; di- and tetra-bromostearic; dibromostearic; and tetrabromostearic acids, respectively.

J. W. BAKER.

**Isomeric isoprenesulphone. II.** E. EIGENBERGER (J. pr. Chem., 1931, [ii], 129, 312—326).—By the action of ultra-violet light (which of itself has no action) on a solution of the unimolecular isoprenesulphone *A* (A., 1930, 1405) in 0.5*N*-aqueous or alcoholic potassium hydroxide is obtained an isomeric sulphone *B*, m. p. 77.5—78° (mixed m. p. with *A* depressed to 30°), unchanged by heating at 200°, which forms no bromine additive compound even in a sealed tube at 100°, and is only slightly attacked by boiling *N*-potassium hydroxide. Oxidation with *N*-potassium permanganate (1 atom of oxygen) in neutral solution at 0° gave no crystalline products,

28% of the sulphone being recovered unchanged. The action of potassium on the sulphone *A* or *B* in anhydrous ether gives similar results, yielding the potassium salt of an unstable, readily polymerised, di-isoprenedisulphinic acid (calcium and zinc salts), most probably  $\gamma\zeta$ -dimethyl- $\Delta^{\beta\zeta}$ -octadiene- $\alpha\theta$ -disulphinic acid, since the potassium salt reacts with methyl iodide to give the corresponding dimethylsulphone, b. p. 130—140°/13—14 mm., and is oxidised with potassium permanganate (10 atoms of oxygen) at 0° giving carbon dioxide, sulphuric, formic, and oxalic acids and acetylacetone (from the acid from *B*) and, in addition, acetic and tartaric acids in the case of the corresponding acid from *A*. No succinic acid could be detected. In moist ether potassium acts on the sulphone *A* to give a mixture of potassium salts in which  $\gamma$ -methyl- $\Delta^{\beta}$ -butene- $\alpha$ -sulphinic acid, obtained by reductive fission of the di-isoprenedisulphinic acid, is probably present, since oxidation of the calcium salt with potassium permanganate affords acetone. On the basis of these results it is suggested that the *A* and *B* sulphones are stereoisomerides, being, respectively, the *cis*- and *trans*-forms relative to the double linking in the ring.

J. W. BAKER.

**Structure of thiolmethanetrissulphonic acid.** H. J. BACKER (Rec. trav. chim., 1931, 50, 268—278). Oxidation of the potassium salt of the acid described as thiolmethanetrissulphonic acid (A., 1930, 1556) by a variety of reagents leads always to the potassium salt of methanetrissulphonic acid and not of the tetrasulphonic acid. In support of the view that no thiol group is present, it is found that no mercaptides are formed with alkali, the tripotassium salt is neutral, no precipitates are given by solutions of neutral salts of lead, copper, and mercury, the precipitate with silver nitrate is white and unstable, and the substance is odourless; however, a white precipitate is given with mercuric oxide. Colour reactions and the action of heat and hydrolytic reagents appear to indicate that the substance is disulphomethanemonthiosulphuric acid,  $(\text{SO}_3\text{H})_2\text{CH}\cdot\text{S}\cdot\text{SO}_3\text{H}$ . Crystallographic data are given for the potassium, ammonium (+2H<sub>2</sub>O), and thallium (+2H<sub>2</sub>O) salts, which are isomorphous; the sodium salt (+4H<sub>2</sub>O) is described.

J. D. A. JOHNSON.

**Methylselenol.** A. BARONI (Atti R. Accad. Lincei, 1930, [vi], 12, 234—237).—Methylselenol, SeHMe, b. p. 12°/758 mm., is obtained by the action of methyl iodide on alcoholic sodium hydrogen selenide solution. The mercuric, lead, silver, copper, and bismuth derivatives were also prepared.

T. H. POPE.

**Manufacture of carboxylic acids from nitriles.** I. G. FARBENIND. A.-G.—See B., 1931, 289.

**Identification of fatty acids. I.** R. SEKA and R. H. MÜLLER (Monatsh., 1931, 57, 97—105).—A slight excess of the fatty acid is heated with *o*-phenylenediamine at 140—150°, the reaction mixture neutralised with 10% alcoholic potassium hydroxide, the alcohol evaporated, and the residue extracted with benzene. The alkylbenzimidazole so produced is purified by distillation and crystallisation. The following alkylbenzimidazoles are described: 2-*n*-propyl-, b. p. about 220°/15 mm., m. p. 152—153°

(prepared from *n*-butyric acid); 2-*n*-*amyl*-, b. p. about 250°/15 mm., m. p. 155—156°; 2-*n*-*heptyl*-, b. p. about 280°/15 mm., m. p. 139—140°; 2-*n*-*nonyl*-, b. p. about 280°/15 mm., m. p. 114—115°; 2-*n*-*undecyl*-, b. p. about 300°/15 mm., m. p. 101—193°; 2-*n*-*pentadecyl*-, b. p. about 300°/15 mm., m. p. 91—92°; 2-*n*-*heptadecyl*-, b. p. about 310°/15 mm., m. p. 90—91°; 2-*isopropyl*-, b. p. about 180°/15 mm., m. p. 223—225° (from *isobutyric acid*), and 2- $\beta$ -*methylamyl*-, b. p. about 230°/15 mm., m. p. 158—159° (from  $\beta$ -methylvaleric acid). The penta- and hepta-decyl derivatives are isolated by dissolving the reaction mixture in alcohol, removing the excess of palmitic or stearic acid as the barium salt, and crystallising the benziminazole from the mother-liquors. The m. p. of the above benziminazoles are compared with the m. p. of the corresponding fatty acid amides and anilides.

H. BURTON.

**Qualitative tests for acetic acid.** E. TSCHIRCH (Oesterr. Chem.-Ztg., 1931, 34, 38—40).—The formation of ethyl acetate, the reactions with ferric chloride and with *o*-phthalaldehyde and ammonia, and Benedict's reaction are of limited application; the ferric chloride reaction is masked by the presence of moderate amounts of sulphate. The cacodyl reaction is unsatisfactory. The blue coloration produced with iodine and lanthanous salts (cf. A., 1930, 62) is a very sensitive test for acetic acid, but inorganic salts, if present in quantity, should first be removed by extraction of the dry material with absolute alcohol (in which acetates are in general very soluble), oxalates and formates must be removed by oxidation with bromine, and if non-volatile organic acids are present in quantity, the acetic acid should be separated by distillation of the acidified solution. Benzoic acid and the homologues of acetic acid either give a similar coloration or inhibit the reaction.

H. A. PIGGOTT.

**Mechanism of the allyl transformation.** I. Reply to Burton. II. Tautomerism. C. PRÉVOST (Bull. Soc. chim., 1931, [iv], 49, 261—268; cf. A., 1928, 1211; 1929, 169, 170).—No isomerisation of crotyl trichloroacetate or its isomeride could be detected on heating in toluene for 8 hrs. at 100°; with concentrated trichloroacetic acid as solvent the esters are partly resinified and partial isomerisation occurs, affording in the one case a 75 : 25 mixture and in the other 15 : 85. In the presence of 10% of water the ratios are 55 : 45 and 30 : 70, respectively, but considerably removed from the equilibrium and accordingly Burton's theory of isomerisation is considered inadequate. With 10% of water in the trichloroacetic acid partial hydrolysis also occurs, with subsequent formation of ethers. In the action of crotyl bromide on potassium trichloroacetate isomerisation is much too slow to account for the formation of mixed esters under the conditions employed. In support of Burton's theory is the isomerisation of the esters in boiling acetic anhydride. Support for the synionic theory is adduced from the absence of anomaly among allyl compounds and the absence of isomerisation in their preparation. The high dielectric constant of acetic anhydride explains the isomerism, mesomerides in such solvents being con-

verted into desmotropes. Further evidence in support of the theory is supplied by the allelotrope of primary and secondary dichlorides obtained from  $\Delta^{\beta}$ -penten- $\alpha$ -ol and  $\Delta^{\alpha}$ -penten- $\gamma$ -ol, the chlorides being mesomeric at 140° in absence of solvent and isomerising at 175° or in presence of water at 100°. Esterification of ethylvinylcarbinol with aqueous hydrochloric acid at 0° yields 43—47% of primary chloride. Phosphorus trichloride at 45° yields 48—52% of primary chloride. The equilibrium mixture obtained after catalytic isomerisation by water at 100° contains almost equal amounts of the two chlorides, and the allelotrope at 175° under pressure in absence of solvent contains 53—55% of primary chloride and at 225°, 60—62%. These five points lie on the same curve, the desmotropic curve being thus a continuation of the mesomeric curve. Contrary to the observations with keto-enols, the influence of the medium is thus much less important than that of temperature, and the composition of the equilibrium mixture can vary widely with temperature.

R. BRIGHTMAN.

**Electrolysis of trifluoroacetic acid and its salts.** F. SWARTS (Bull. Acad. roy. Belg., 1931, [v], 17, 27—28).—Electrolysis of 4*N*-solutions of trifluoroacetic acid or its sodium salt with current density 0.2 amp./cm.<sup>2</sup> yields *hexafluorethane*, a colourless gas, b. p.  $-79 \pm 0.5^{\circ}$ /760 mm., m. p.  $-106.3^{\circ}$ . The vapour pressure at the triple point is 234 mm.

J. R. I. HEPBURN.

**Transformation of oleic into elaidic acid by sulphur.** II. G. RANKOV (Ber., 1931, 64, [B], 619—621; cf. A., 1930, 65).—Oleic acid is converted to the extent of 50% into elaidic acid, m. p. 44.4° (corr.),  $n_D^{20}$  1.4308, when heated with 1% of sulphur at 200—220° in an open or closed vessel or in a current of carbon dioxide. If 3% of sulphur is employed, a crystalline compound of higher m. p. in which sulphur is present is also formed.

H. WREN.

**Selective hydrogenation of unsaturated acids and their constitution.** II. *isolinoleic acid of silkworm pupæ.* Y. INOUE and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 15—18).—Oxidation of the methyl ester of *isolinoleic acid*, isolated from the oil of silkworm pupæ, with potassium permanganate in acetone affords oxalic, hexoic, and azelaic acids. After partial reduction with hydrogen and a palladium-barium sulphate catalyst in tetrahydronaphthalene, similar oxidation affords nonoic and azelaic acids. Hence, like linoleic acid, *isolinoleic acid* is also  $\Delta^{\alpha}$ -octadecadienoic acid, the two being stereoisomerides. Oxidation of partly reduced *isolinoleic acid* with alkaline potassium permanganate gives the dihydroxystearic acids, m. p. 130° and m. p. 100°, stearic acid, and elaidic acid, and the last-named is concluded to be the main constituent of the partly reduced acid. Since on partial reduction and subsequent oxidation linoleic acid affords the dihydroxystearic acid of m. p. 130° and oleic acid, this evidence suggests that around the  $\alpha$  double linking linoleic and *isolinoleic acids* are *cis*- and *trans*-forms, respectively, a view which is supported by the observation that linoleic acid is hydrogenated much more rapidly than is *isolinoleic acid*.

J. W. BAKER.

Polymerisation of methyl esters of higher saturated fatty acids. VI. Hydrogenation of polymerised products. VII. Hydrogenation of linseed oil and of the methyl ester of liquid fatty acids of linseed oil. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 127—129, 130—136).—VI. The polymeride obtained by heating the methyl ester of a higher unsaturated fatty acid at 290—300° for 25 min. in hydrogen and removal of the methyl monocarboxylate, does not depolymerise when catalytically hydrogenated, alone at 180—200° for 5—7 hrs., or in glacial acetic acid at 90° for 2½—3½ hrs. The saponification value and mol. wt. remain unaltered, but the iodine value falls. The amount of hydrogen absorbed is greater than that calculated from the decrease in the iodine value. The excess of hydrogen is probably used in rupturing the 4-membered carbon ring.

VII. The acetone-soluble and acetone-insoluble fractions of linseed oil, polymerised by heating for 5 hrs. at 290—300° in hydrogen, were saponified, and the monocarboxylic acids were removed. The mol. wts. of the residues were not altered by catalytic hydrogenation. By hydrogenating, in glacial acetic acid, the liquid fatty acids separated from the distillates, a product is formed the iodine value of which is not greatly reduced, although the calculated amount of hydrogen has been absorbed. Further, stearic acid (m. p. 69—70°) can be crystallised from the hydrogenated product of the liquid fatty acids of the acetone-insoluble fraction. Hydrogenation appears to rupture the intermolecular 4-membered carbon ring. The stearic acid obtained by Bauer and Hugel (B., 1925, 250) from the hydrogenated product of the acetone-insoluble fraction of perilla oil was probably formed in this way.

Similar results are obtained by catalytically hydrogenating the distillate and residue (after shaking with 99% methyl alcohol) from the vacuum distillation of the polymerised methyl ester of liquid fatty acids of linseed oil. A. RENFREW.

Separation of glycerides. XVI—XVIII. B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 9—11).—XVI. [With Y. MASUDA.] By fractional extraction of the brominated bone oil of the common finbock (*Balanoptera physalus*) with various solvents are isolated the bromides of *dilinolenoleno-*, m. p. 65°, *clupanodonolinolenoleno-*, m. p. 132°, *stearolinoleo-*, *stearo-oleo-*, and *stearolinolenoleno-zoomarin*; *clupanodonoarachidonoleno-*, m. p. 95°, and *arachidonolinolenoleno-*, m. p. 145°, *-olein*; *linolenoleno-*, and *oleo-dizoomarin*; *linoleodiolein*; *triarachidonin*, m. p. 218°; and  $C_{22}H_{42}O$ -*clupanodono-linolenin*, m. p. 123°.

XVII. [With S. OE and U. NISHIMOTO.] From the skin are similarly isolated:  $C_{18}H_{32}O$ -*linolenoleno-*, m. p. 122°,  $(C_{13}H_{27}O)_2$ , m. p. 148°, *celoleo-linoleo-*, m. p. 172°, and *tri-*, m. p. 192° (decomp.), *-stearidonin*; *distearidonozoomarin*, m. p. 168° (decomp.); triolein and (?) *dierucolinolein bromides*.

XVIII. [With R. YONEDA and U. NISHIMOTO.] From the internal organs are obtained the bromides of *clupanodono-C<sub>22</sub>H<sub>33</sub>O-*, m. p. 105°, and  $C_{22}H_{35}O$ -?, m. p. 98°, *-linoleuin*; *clupanodono-stearidonozoomarin*, m. p. 193°; *diarachidonogadolein*, m. p. 220° (decomp.); and *linoleodizoomarin*. J. W. BAKER.

“Rhodanometry” of tung oil. J. VAN LOON (Z. Unters. Lebensm., 1930, 60, 320—327).—When sufficient excess of reagent was used  $\beta$ -elæostearic acid gave a thiocyanogen-iodine value of 91.7, which is one third of the ordinary iodine value. (A suggested formula for the compound formed is given.) On storage in carbon dioxide for several days the acid gave low values unless a large excess of reagent was present. This is attributed to polymerisation.  $\alpha$ -Elæostearic acid had a thiocyanogen-iodine value slightly above that of the  $\beta$ -isomeride. The theory is advanced that an unknown acid is present in the product. The thiocyanogen-iodine value of the  $\alpha$ -acid is also lowered by polymerisation and oxidation.  $\Delta^8$ -Octadienoic acid, which has two double linkings similarly situated to two of those in elæostearic acid, gave the theoretical iodine value of 181, using Wijs' iodine or Kaufmann's bromine method, when an excess of 200—300% of halogen was present; the thiocyanogen-iodine value was 107.0—108.4. It is concluded that two isomerides are present which behave differently towards the thiocyanogen reagent. The thiocyanogen-iodine value of various tung oils unaltered by storage varied from 90.9 to 94.8, being much higher than the highest value (81) which corresponds with a mixture of glycerides of oleic and  $\alpha$  (or  $\beta$ )-elæostearic acids with 5% of saturated acids. It is concluded that a hitherto unknown acid,  $\gamma$ -elæostearic acid,  $C_{18}H_{30}O_2$ , is present which adds thiocyanogen corresponding with two double linkings. Tung oil must contain about 15.5% of this substance. This conclusion is confirmed by the thiocyanogen-iodine values found for the total fatty acids. W. J. BOYD.

I. Constitution of the hydroxyoleic acid from ergot oil. II. Fission products of ricinoleic acid ozonide. H. MATTHES and O. H. KÜRSCHNER (Arch. Pharm., 1931, 269, 88—101, 101—104).—I. The hydroxyoleic acid from ergot oil has the same chemical and physical constants as ricinoleic acid. It may be reduced through the corresponding bromo-oleic acid to stearic acid, is quantitatively oxidised by permanganate to two isomeric trihydroxystearic acids, and is, accordingly, chemically homogeneous. When ozonised, it gives results identical, except in the particulars mentioned below, with those obtained by Haller and Brochet (A., 1910, i, 216) for ricinoleic acid. The ozonides and ozonide peroxides of the ergot acid and its ethyl ester are viscous liquids, the crystalline products previously described being their hydrolysis products. The sodium hydrogen sulphite additive products of  $\eta$ -aldehydo-octoic acid and its ethyl ester are non-crystalline. The  $\beta$ -hydroxynonoic acid obtained together with traces of a liquid acid, (?)  $C_8H_{16}(OH)CO_2H$ ,  $[\alpha]_D^{20} -7.7^\circ$ , from the ozonides, has m. p. 49.5—50.5°, b. p. 186°/17 mm.,  $[\alpha]_D^{20} -17.7^\circ$ , not  $+2.5^\circ$  as previously given. It is only partly dehydrated at 230—240°/760 mm. By heating with hydrochloric acid and subsequently with alcoholic potassium hydroxide it gives a  $\Delta^2$ -nonenoic acid which has an abnormally low iodine value, but is identified by its ozonisation to heptoic acid and carbon dioxide. II. The ozonisation products of ricinoleic acid are identical in all respects with those of the ergot acid. The two are therefore identical.

H. E. F. NOTTON.



**Reactions of malonic esters with formaldehyde.**  
 II. K. N. WELCH (J.C.S., 1931, 653—657; cf. A., 1930, 452).—By aid of the method of integration of fractional parts (Noyes, A., 1896, ii, 158) the initial reaction between malonic ester and formaldehyde is shown to be of the second order at  $p_H$  4.9, whilst the reaction velocity is inversely proportional to the hydrogen-ion concentration. Piperidine has a profound effect on the reaction velocity at  $p_H$  4.9, methylamine has a similar but temporary effect, whilst ammonia and triethylamine are without effect. The results are explained by Lapworth's theory (A., 1930, 571), but the reaction takes a different course in the presence of piperidine. G. DISCOMBE.

**Course of addition of sodium enol-alkylmalonic and -alkylcyanoacetic esters to unsaturated esters.** A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, 53, 1150—1172).—The course of addition of the sodium enol of alkylmalonic esters to  $\alpha\beta$ -unsaturated esters agrees with the law of chemical neutralisation (A., 1900, i, 321), and in agreement, also, in the addition of the sodium enols of alkylmalonic ester to ethyl fumarate, the alkyl group migrates so that the addenda are alkyl and  $\cdot\text{C}(\text{CO}_2\text{Et})\text{C}(\text{ONa})\text{OEt}$ . Thus in marked contrast to the formation of ethyl pentane- $\beta\gamma\delta\delta$ -tetracarboxylate (acid, m. p. 166°) by methylation of ethyl butane- $\beta\gamma\delta\delta$ -tetracarboxylate [described by Michael (A., 1901, 123) as the  $\alpha\beta\gamma\gamma$ -compound (acid, m. p. 176°)] formed by addition of ethyl sodiomethylmalonate to ethyl fumarate, ethyl butane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, b. p. 180°/3 mm. [obtained by methylation of ethyl propane- $\alpha\beta\gamma\gamma$ -tetracarboxylate (acid, m. p. 153°), and hydrolysed to butane- $\alpha\beta\gamma\gamma$ -tetracarboxylic acid, m. p. 170°], is converted by an ethereal suspension of dry sodium methoxide and methyl iodide into ethyl fumarate and the enol of ethyl sodiomethylmalonate, which is methylated to ethyl dimethylmalonate. Similarly, ethyl pentane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, b. p. 180°/3 mm. (acid, m. p. 177°), obtained by ethylation of ethyl propane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, is unchanged by treatment with cold sodium ethoxide and methyl iodide, whereas ethyl pentane- $\alpha\alpha\beta\gamma$ -tetracarboxylate (*loc. cit.* described as the  $\alpha\beta\gamma\gamma$ -compound) [acid, m. p. 179° (decomp.)] is readily methylated to ethyl hexane- $\beta\beta\gamma\delta$ -tetracarboxylate (acid, m. p. 170°), the ethyl group migrating during the addition. In the addition of the sodium enols of alkylcyanoacetic esters to ethyl crotonate the addenda are, similarly, alkyl and  $\cdot\text{C}(\text{CN})\text{C}(\text{ONa})\text{OEt}$  (cf. Thorpe, J.C.S., 1900, 77, 923). Thus ethyl  $\alpha$ -cyanopropionate condenses with ethyl crotonate in alcoholic sodium ethoxide to give ethyl  $\gamma$ -cyano- $\alpha\beta$ -dimethylglutarate, b. p. 145—148°/3 mm. (50% yield) [together with an ester, b. p. 182°/3 mm., which gives a ketonic compound, b. p. 50—120°/10 mm. (semicarbazone, m. p. 224°), on hydrolysis, the possible cyclic structure of which is discussed], which is apparently a stereoisomeride of the cyano-ester obtained by addition of ethyl sodiocyanoacetate to ethyl tiglate (this vol., 67), since it is hydrolysed by 20% potassium hydroxide to  $\gamma$ -cyano- $\alpha\beta$ -dimethylglutaric acid, b. p. 145—148°/3 mm., hydrolysed by concentrated hydrochloric acid to give only a trace of  $\alpha\beta$ -dimethylglutarimide and, mainly, a liquid cyano-

acid, further hydrolysed to *trans*- $\alpha\beta$ -dimethylglutaric acid. Complete hydrolysis of the original cyano-ester with 20% potassium hydroxide affords a  $\gamma$ -methylbutane- $\beta\delta\delta$ -tricarboxylic acid, m. p. 142°, not identical, but probably stereoisomeric, with the corresponding product in the ethyl tiglate condensation. Ethyl sodioethylmalonate does not add to ethyl crotonate, but with ethyl sodio- $\alpha$ -cyanobutyrate the latter affords ethyl  $\gamma$ -cyano- $\beta$ -methyl- $\alpha$ -ethylglutarate, b. p. 153°/3 mm. (33% yield) (together with an ester, b. p. 160—165°/3 mm.), hydrolysed by potassium hydroxide to the corresponding cyano-acid, m. p. 147°, further converted by boiling hydrochloric acid into a mixture of *cis*- and *trans*- $\beta$ -methyl- $\alpha$ -ethylglutarimides, m. p. 92° (main product) and 102°, both hydrolysed to the same *cis*- $\beta$ -methyl- $\alpha$ -ethylglutaric acid, m. p. 88°. Complete hydrolysis of the original cyano-ester with alkali gives  $\beta$ -methylpentane- $\alpha\alpha\gamma$ -tricarboxylic acid, m. p. 143°. Similar addition of ethyl sodiocyanoacetate to ethyl  $\alpha$ -ethylcrotonate gives a stereoisomeride, b. p. 154°/4 mm., of ethyl  $\gamma$ -cyano- $\beta$ -methyl- $\alpha$ -ethylglutarate, hydrolysed by alcoholic potassium hydroxide to a cyano-acid, m. p. 132°, which with concentrated hydrochloric acid gives only a trace of the mixed glutarimides, the main product being the syrupy  $\gamma$ -cyano- $\beta$ -methyl- $\alpha$ -ethylbutyric acid, completely hydrolysed to *trans*- $\beta$ -methyl- $\alpha$ -ethylglutaric acid. Complete hydrolysis of the original cyano-ester affords a  $\beta$ -methylpentane- $\alpha\alpha\gamma$ -tricarboxylic acid, m. p. 141°. For comparison, ethyl  $\gamma$ -cyano- $\beta$ -methylglutarate was ethylated to ethyl  $\gamma$ -cyano- $\beta$ -methyl- $\gamma$ -ethylglutarate, b. p. 152°/4 mm., similarly hydrolysed to the corresponding cyano-acid, m. p. 139°, which with concentrated hydrochloric acid gives a very small quantity of the glutarimides and, mainly, a liquid cyano-acid (?  $\gamma$ -cyano- $\beta$ -methyl-*n*-hexoic acid) hydrolysed to *trans*- $\beta$ -methyl- $\alpha$ -ethylglutaric acid. Complete hydrolysis of the parent cyano-ester affords a liquid  $\beta$ -methylpentane- $\alpha\gamma\gamma$ -tricarboxylic acid, further hydrolysed to a mixture of *cis*- and *trans*- $\beta$ -methyl- $\alpha$ -ethylglutaric acid. These additive reactions appear to take place with selective synthesis of one of the stereoisomeric forms. Addition to the  $\gamma$ -carbon atom of  $\beta\gamma$ -unsaturated esters or nitriles has not been found possible, addition occurring to the  $\alpha\beta$ -form with migration of hydrogen. Thus ethyl sodio-cyanoacetate or  $\alpha$ -cyanopropionate and allyl cyanide afford ethyl  $\alpha\gamma$ -dicyano- $\beta$ -methylbutyrate, b. p. 160°/3 mm., and ethyl  $\alpha\gamma$ -dicyano- $\beta$ -methyl-*n*-valerate, b. p. 152°/3 mm., respectively. With ethyl  $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoate and ethyl sodiocyanoacetate is obtained ethyl  $\gamma$ -cyano- $\beta$ -benzylglutarate, b. p. 193°/3 mm., hydrolysed to  $\beta$ -benzylpropane- $\alpha\gamma\gamma$ -tricarboxylic acid, m. p. 158° (possibly identical with the acid, m. p. 146°, obtained by Vorländer and Strunck, A., 1906, i, 362), and methylated to ethyl  $\gamma$ -cyano- $\beta$ -benzyl- $\gamma$ -methylglutarate, b. p. 194°/3 mm., from which  $\beta$ -benzylbutane- $\alpha\gamma\gamma$ -tricarboxylic acid, m. p. 177°, and  $\beta$ -benzyl- $\alpha$ -methylglutaric acid, m. p. 139°, are obtained. Similarly, condensation of ethyl sodiomethylmalonate with ethyl  $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoate affords ethyl  $\beta$ -benzylbutane- $\alpha\alpha\gamma$ -tricarboxylate, b. p. 197°/3 mm., hydrolysed by alkali to  $\beta$ -benzylbutane- $\alpha\alpha\gamma$ -tricarboxylic acid, m. p. 197°, and its stereoisomeride, m. p. 118°, converted, respectively, by loss of carbon dioxide, into two forms, m. p.

139° and m. p. 137°, of  $\beta$ -benzyl- $\alpha$ -methylglutaric acid, the former being identical with the acid obtained above. For comparison  $\alpha$ -phenylpropaldehyde was condensed with malonic acid to give  $\gamma$ -phenyl- $\Delta^{\beta}$ -pentenoic acid, the ethyl ester, b. p. 156°/10 mm., of which {obtained together with ethyl  $\gamma$ -phenyl- $\Delta^{\beta}$ -butene- $\alpha$ -dicarboxylate, b. p. 175—182°/10 mm. [acid, m. p. 151° (decomp.)]} condenses with ethyl sodiocyanoacetate to give ethyl  $\alpha$ -cyano- $\beta$ -( $\alpha'$ -phenylethyl)glutarate, b. p. 198°/3 mm., hydrolysed to  $\beta$ -( $\alpha'$ -phenylethyl)-propane- $\alpha\alpha$ -tricarboxylic acid, m. p. 162°, which affords  $\beta$ -( $\alpha'$ -phenylethyl)glutaric acid, m. p. 88°, when heated. The mechanism of the retrograde Michael reaction is also discussed on the basis of the authors' views. J. W. BAKER.

**Ethyl methylenedimalonate.** K. N. WELCH (J.C.S., 1931, 673—674).—Ethyl methylenedimalonate is prepared by the interaction of paraformaldehyde and ethyl malonate in presence of alcoholic potassium hydroxide at the temperature of the water-bath. A yield of more than 90% (cf. A., 1930, 452) is obtained by destroying the catalyst with alcoholic hydrogen chloride before the ester is isolated.

G. DISCOMBE.

**$\alpha\beta\gamma$ -Trimethylglutaric acids.** F. E. RAY (J. Amer. Chem. Soc., 1931, 53, 1174—1175).—Crystalline  $\gamma$ -methylpentane- $\beta\beta\delta$ -tricarboxylic acid, m. p. 144—145°, decomposes into  $\alpha\beta\gamma$ -trimethylglutaric acid, m. p. 134° (A., 1928, 394), so that it cannot be identical with  $\gamma$ -methylbutane- $\beta\beta\gamma$ -tricarboxylic acid, m. p. 145°, as suggested by Michael and Ross (this vol., 67).

J. W. BAKER.

**$\alpha\beta\gamma$ -Trimethylglutaric acids.** A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1931, 53, 1175—1176).—A reply to Ray (preceding abstract).

J. W. BAKER.

**Glutaconic acids. XXII. Optically active  $\alpha\gamma$ -dimethylglutaconic acid.** T. H. MCCOMBS, J. PACKER, and J. F. THORPE (J.C.S., 1931, 547—560).—The peculiarities of glutaconic acids can be explained as a consequence of geometrical isomerism and three-carbon tautomerism (A., 1926, 820). *trans*-(normal)- $\alpha\gamma$ -Dimethylglutaconic acid can be resolved by repeated fractional precipitation of its *strychnine* salt from acetone solution, the *l*-acid having m. p. 132.5—133.5°,  $[M]_D^{25}$  —100°, *strychnine* hydrogen salt, m. p. 208—209° (decomp. and resolidifying with m. p. 260—263°). Partial resolution is effected by refluxing the *r*-acid with *strychnine* in a small quantity of acetone, whilst *strychnine* or *brucine* in excess of boiling acetone displaces the equilibrium *l*-acid  $\rightleftharpoons$  *d*-acid in favour of the *l*-acid. Impure specimens of the *d*-acid are described.

G. DISCOMBE.

**Action of ozone on aldehydes.** F. G. FISCHER, H. DÜLL, and J. L. VOLZ (Annalen, 1931, 486, 80—94).—The ozonisation of undiluted aldehydes gives a mixture of the corresponding acid and peracid with the former in excess, the whole of the oxygen of the ozone being used, thus  $2R\cdot CHO + O_3 \rightarrow R\cdot CO_2H + R\cdot CO_3H$  and  $3R\cdot CHO + O_3 \rightarrow 3R\cdot CO_2H$ ; the "aldehyde peroxides" of Harries and his collaborators appear to be mixtures of acid, peracid, and unchanged aldehyde. The second "nonylaldehyde peroxide," m. p. 73°, is actually *dihydroxynonyl peroxide* (cf.

Riehe, "Alkylperoxide und Ozonide," 1931). *Dihydroxyheptyl peroxide* has m. p. 68—69°.

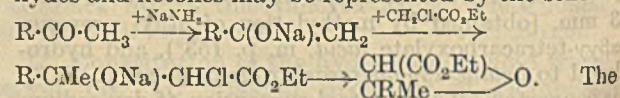
Ozonisation of an aldehyde in solution results in considerably more oxidation than is accounted for by the ozone used; this is not due to the action of oxygen alone, and the oxidation of aldehydes (by oxygen) is not catalysed by the acids or peracids. The ozone, therefore, must be regarded as the catalyst, and it is suggested that an ozonide is formed intermediately, which, in addition to decomposition according to the above equations, can react with oxygen as follows:  $R\cdot CHO, O_3 + O_2 \rightarrow R\cdot CO_3H + O_3$ . A similar behaviour is shown by olefinic substances in solution.

H. A. PIGGOTT.

**Decomposition of aliphatic aldehydes by the Friedel-Crafts reaction.** K. BODENDORF (J. pr. Chem., 1931, [ii], 129, 337—339).—By addition of aliphatic aldehydes (1 mol.) to a suspension of aluminium chloride (1.2 mols.) in a large excess of benzene saturated with dry hydrogen chloride at 0° are obtained 50% yields of the corresponding diarylparaffins, the by-products being alkylbenzenes and resinous material. Thus from the appropriate aldehyde are obtained  $\alpha\alpha$ -diphenyl-ethane, *n*-propane, and *n*-butane, and  $\alpha\alpha$ -diphenyl- $\beta$ -methyl-*n*-propane.

J. W. BAKER.

**Condensation of ketones and aldehydes with ethyl chloroacetate.** B. N. RUTOVSKI and N. A. DAJEV (Ber., 1931, 64, [B], 693—698, and J. Russ. Phys. Chem. Soc., 1931, 62, 2161—2164).—The reaction of ethyl chloroacetate with aliphatic aldehydes and ketones may be represented by the scheme



The preparation of the sodium derivative of acetone and its conversion into ethyl dimethylglycidate, together with the preparation of the last-named compound from acetone, sodium, and ethyl chloroacetate in the presence of ether, are described. Ethyl methylglycidate is obtained from acetaldehyde. With aromatic ketones and aldehydes condensation may occur through the medium of metallic ketyls or ester enolates. The successive action of benzaldehyde and ethyl chloroacetate on powdered sodium suspended in ether gives benzyl alcohol, phenylacetaldehyde, and  $\alpha$ -chlorocinnamic acid; if the ether is replaced by toluene, the yield of  $\alpha$ -chlorocinnamic acid is considerably increased. The sodium derivative of benzophenone and ethyl chloroacetate in ether afford benzhydrol and ethyl diphenylglycidate.

H. WREN.

**Interaction of citronellaloxime and acetic anhydride.** J. ZIMMERMANN (Rec. trav. chim., 1931, 50, 283—286).—Citronellaloxime and acetic anhydride give the corresponding nitrile, amide, tarry material, and a base not identified. Hydrolysis of the nitrile with 0.5*N*-alcoholic potassium hydroxide leads to 7.1% of the amide. The determination of citronellal in crude specimens by the method of Dupont and Labaune (A., 1912, i, 880) is therefore impracticable.

J. D. A. JOHNSON.

**Enolic derivative of  $\beta$ -hydroxypropaldehyde; preparation of glyceraldehyde.** H. O. L. FISCHER,

L. AHLSTRÖM, and H. RICHTER (Ber., 1931, 64, [B], 611—614).—The action of *p*-toluenesulphonyl chloride and pyridine on  $\alpha\gamma$ -benzylideneglycerol affords  $\alpha\gamma$ -benzylideneglyceryl  $\beta$ -*p*-toluenesulphonate, m. p. 125° (yield 86.7%), transformed by distillation with powdered potassium hydroxide into benzylidene- $\Delta^{\alpha}$ -propene- $\alpha\gamma$ -diol,  $\text{CH} \begin{array}{c} \text{CH}_2\text{O} \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{O} \end{array} \text{CHPh}$ , b. p. 72—75°/0.1 mm.,  $d_{20}^{25}$  1.126,  $n_D^{20}$  1.5408. Oxidation of the last-named compound with perbenzoic acid in chloroform at 0° followed by hydrolysis of the product with 12.5% acetic acid affords glyceraldehyde, m. p. 142°. Benzylidene- $\Delta^{\alpha}$ -propene- $\alpha\gamma$ -diol is hydrogenated in presence of palladised barium sulphate to benzylidenepropene- $\alpha\gamma$ -diol, m. p. 49.5°, hydrolysed to trimethylone glycol. H. WREN.

**Condensation between aliphatic esters and ketones.** S. G. POWELL and K. H. SEYMOUR (J. Amer. Chem. Soc., 1931, 53, 1049—1051).—Reaction through the methylene group could not be detected in condensation between esters and ketones of the type  $\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{R}$  under the conditions of Claisen and Ehrhardt (A., 1889, 850) and modifications thereof. Thus  $\beta\delta$ -diketohexane is obtained from ethyl acetate and methyl ethyl ketone or from ethyl propionate and acetone;  $\gamma\epsilon$ -diketo-*n*-octane from ethyl propionate and methyl *n*-propyl ketone or from ethyl butyrate and methyl ethyl ketone; and  $\gamma\epsilon$ -diketo- $\beta$ -methyl-*n*-hexane from ethyl acetate and methyl isopropyl ketone or from ethyl isobutyrate and acetone.

J. W. BAKER.

**Relation of the structure of ketones to their reactivity and affinity in acetal formation.** II. G. J. PFEIFFER and H. ADKINS (J. Amer. Chem. Soc., 1931, 53, 1043—1048).—Re-determination of the amount of ethyl formate present in a mixture of this substance with alcohol, ethyl orthoformate, a ketone, and its acetal by Carswell and Adkins' method (A., 1928, 274) shows that the ratio of carbon monoxide formed to the ethyl formate,  $3\text{H}\cdot\text{CO}_2\text{Et} + 4\text{Na} = 2\text{CO} + \text{MeONa} + 3\text{EtONa}$ , is independent of the amounts of ethyl orthoformate and ketone acetal present, but is a function of the amount of sodium ethoxide and of the amount and nature of the ketone. The presence of sodium ethoxide presumably facilitates the reactions,  $\text{H}\cdot\text{CO}_2\text{Et} + \text{Me}_2\text{CO} = \text{EtOH} + \text{COMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$  and  $\text{H}\cdot\text{CO}_2\text{Et} + \text{Ph}_2\text{CO} = \text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{Et}$ , between the ketone and ethyl formate. The amount of ethyl formate equivalent to a given volume of carbon monoxide has been determined. The extent of acetal formation under the conditions previously used (0.136% alcoholic hydrogen chloride at 25°), with acetone, acetophenone, benzophenone, methyl ethyl, methyl  $\beta$ -phenylethyl, methyl neopentyl, diisopropyl, methyl *tert*-butyl, ethyl *tert*-butyl, isopropyl *tert*-butyl, and di-*tert*-butyl ketones, is found to be 94.8, 86.2, 33.7, 90.1, 89.1, 84.0, 65.4, 50.1, 36.2, 25.8, and 17.2%, respectively. The corresponding values of the equilibrium coefficient  $k_E \times 10^2$  are given. In general, substitution of one of the hydrogen atoms of the methyl groups in acetone results in a decrease in the amount of acetal formed. J. W. BAKER.

**Preparation of telluroketones.** R. E. LYONS and E. D. SCUDDER (Ber., 1931, 64, [B], 530—532; cf.

A., 1927, 449).—Telluroketones are prepared by the action of hydrogen telluride, from aluminium telluride and hydrochloric acid, on a cooled mixture of the requisite ketone and concentrated hydrochloric acid. *Dimethyl telluroketone*, b. p. 55—58°/10—13 mm.,  $d_4^{20}$  0.8578,  $n_D^{20}$  1.48825, *methyl ethyl telluroketone*, b. p. 63—66°/9—10 mm.,  $d_4^{20}$  0.8711,  $n_D^{20}$  1.5055, *diethyl telluroketone*, b. p. 69—72°/8—11 mm.,  $d_4^{20}$  0.8821,  $n_D^{20}$  1.5480, and the unstable dipropyl telluroketone are described. Benzil and benzophenone do not appear to react.

H. WREN.

**Dioximes.** LXXIII. G. PONZIO and G. BERTINI (Gazzetta, 1931, 61, 51—59).—Chloro-derivatives of the type  $\text{R}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{Cl}$  are converted into the corresponding cyano-derivatives when an ethereal solution is added slowly to ice-cold aqueous potassium cyanide solution. The product is isolated, after acidification, by extraction with ether. Chloro-oximinoacetone yields *cyano-oximinoacetone*, m. p. 84° [*benzoyl* derivative, m. p. 138—139°; *phenylhydrazone*, m. p. 177° (decomp.)]. Methylchloroglyoxime yields *methylcyanoglyoxime*, m. p. 154—155° (+2H<sub>2</sub>O) and m. p. 164—165° (anhydrous) [*nickel* salt (+2H<sub>2</sub>O); *diacetyl* derivative, m. p. 92—93°; *dibenzoyl* derivative, m. p. 236—237°; *peroxide*, an oil], which is also obtained by the action of hydroxylamine on cyano-oximinoacetone. The interaction of hydroxylamine and methylcyanoglyoxime yields  *$\alpha$ -amino- $\alpha\beta$ -trioximinobutane*, m. p. 170—172° (decomp.) (*nickel* salt), which is converted by acetic anhydride into *2-*c*-amino-3-acetoximinoacetyl-furazan*, m. p. 137—138°. Hydrolysis of the last-named compound yields *2-amino-3-acetyl-furazanoxime*, m. p. 199—200° (*benzoyl* derivative, m. p. 168—169°), from which, or its acetyl derivative, there is obtained by complete hydrolysis *aminoacetyl-furazan*, m. p. 96—97° [*benzoyl* derivative, m. p. 136—137°; *semicarbazone*, m. p. 242—243° (decomp. from 210°); *phenylhydrazone*, m. p. 142—143°]. R. K. CALLOW.

**Oxidative decomposition of sugars.** X. **Formation of methylglyoxal from sugars and related substances under the action of hydrogen peroxide.** XI. **Formation of phenols.** XII. **Formation of higher fatty acids.** K. BERNHAUER (Biochem. Z., 1931, 230, 484—492, 493—500, 501—504).—X. [With H. TSCHINKEL.] Under the action of hydrogen peroxide sugars and related substances (especially  $\gamma$ -methylglucoside) in acid solution and in presence of ferrous sulphate yield methylglyoxal, whereas in absence of ferrous sulphate considerable amounts of acids (chiefly formic) are formed.

XI. [With J. NEPP.] The formation of phenols on fusion of various sugars and related substances with potassium hydroxide is comparatively investigated. By the action of potassium formate on phenol, salicylic and *m*-hydroxybenzoic acids, and on pyrocatechol, protocatechuic acid were obtained.

XII. [With J. NEPP.] When lactic acid and sugars are autoclaved with potassium hydroxide, formic, acetic, and propionic but not higher acids are formed.

P. W. CLUTTERBUCK.

**Cellobiosan and cellulose.** K. HESS and E. GARTHE (Naturwiss., 1930, 18, 180).—The observ-

ations of Freudenberg (A., 1930, 198) are ascribed to unsuitable experimental conditions. B. LEVIN.

**Æsculin.** R. SEKA and P. KALLIR (Ber., 1931, 64, [B], 622—627).—Æsculin, m. p. 204°,  $[\alpha]_D^{25}$  —38.5° in pyridine, is transformed by diazomethane in methyl alcohol into *æsculin methyl ether*, m. p. 225°, hydrolysed by 2.5% sulphuric acid to *æsculetin monomethyl ether*, m. p. 185°. The last-named compound is identified as 6-hydroxy-7-methoxycoumarin by the following method. *p*-Aminoguaiacol hydrochloride is warmed with sulphuric acid until the hydrogen chloride is completely expelled, and the resulting solution is diluted with water, diazotised, and boiled, thus giving 2:5-dihydroxyanisole, m. p. 79°, in 41.7% yield. Treatment of this compound in ether with zinc chloride, hydrogen cyanide, and hydrogen chloride leads to the isolation of 2:5-dihydroxy-4-methoxybenzaldehyde, m. p. 206° (decomp.) (*phenylhydrazone*, m. p. 166°), transformed by acetic anhydride and sodium acetate into 6-acetoxy-7-methoxycoumarin, hydrolysed to 6-hydroxy-7-methoxycoumarin, m. p. 184.5°.

Treatment of *æsculetin* with diazomethane followed by fractional extraction of an ethereal solution of the product with 0.1N-alkali hydroxide leads to the isolation of 6:7-dimethoxycoumarin, m. p. 144°, and 6-hydroxy-7-methoxycoumarin, m. p. 184—185° (*benzoate*, m. p. 211°); the isomeric 7-hydroxy-6-methoxycoumarin does not appear to be produced.

H. WREN.

**Strophanthin.** XIX. Dehydrogenation of *strophanthidin* and *gitoxigenin*. W. A. JACOBS and E. E. FLECK (Science, 1931, 73, 133—134).—Preliminary details of the fractionated products obtained after dehydrogenation of *strophanthidin* and *gitoxigenin* with selenium are recorded.

L. S. THEOBALD.

**Isolation of phytosterolin from wheat embryo.** N. NAKAMURA and A. ICHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 137—141).—The insoluble material separated from the oil obtained by extracting air-dried wheat embryo powder with ether gives phytosterolin (Power and Salway, J.C.S., 1913, 103, 399, 1022), m. p. 285—290° (*acetate*, m. p. 168° uncorr.,  $[\alpha]_D$  —22.4° in chloroform; *benzoate*, m. p. 198° uncorr.,  $[\alpha]_D$  +17.24° in chloroform), hydrolysed to phytosterol and dextrose.

A. RENFREW.

**Bacterial decomposition and constitution of starch.** H. PRINGSHEIM (Woch. Brau., 1931, 48, 73—78, 83—86).—A lecture.

**Cellulose butyrate.** G. VON FRANK and H. COHN (Cellulosechem., 1931, 12, 68—70).—Cellulose butyrate, giving on hydrolysis 65—66% of butyric acid, and therefore intermediate in composition between the di- and tri-esters, is obtained by first steeping cellulose in 80—95% aqueous formic acid for 24 hrs. at the ordinary temperature, then esterifying with butyric anhydride, butyric acid, and zinc chloride, and finally removing the formyl group by hydrolysis with 93% butyric acid. The product sinters at 172°, becomes clear at 208°, and begins to decompose at 225°. It is soluble in the usual solvents, forming highly viscous solutions. In the form of films

or fine threads it has a much lower tensile strength and greater plasticity than cellulose acetate.

H. A. PIGGOTT.

**Preparation of cellulose nitrate with mixtures of nitric and phosphoric acids.** E. BERL and G. RUEFF (Cellulosechem., 1931, 12, 53—62).—An expanded description of results already published (cf. this vol., 203). The maximum content of nitrogen in the product (14.14%, corresponding with the pure trinitrate) is obtained with nitric and phosphoric acids in the ratio 1:1, the value falling more rapidly with excess of nitric acid on account of hydrolysis; under suitable conditions a product containing 11.3% N can be obtained with an acid mixture containing only 0.8% of nitric acid and 4.85% of water.

H. A. PIGGOTT.

**Chemical composition of wood of the red beech (*Fagus sylvatica*).** E. SCHMIDT (Cellulosechem., 1931, 12, 62—67).—Delignification of the wood of the red beech (and other deciduous trees) by chlorine dioxide yields the partly decomposed "skeletal substances" of the cell-wall, from which may be isolated by treatment with alkali of successively increasing concentrations an easily soluble xylan, a polymeric carboxylic acid, a sparingly soluble xylan, and cellulose. The stoichiometric ratio of 1:3 is found for the xylose anhydride in the sparingly soluble xylan and the glucose anhydride in the cellulose. If deacetylation be avoided by the use of milder conditions, a further ratio of 1:1 for the acetyl group and xylose anhydride is observed. These proportions are constant, and unaffected by the age or habitat of the tree. The water-soluble products from this degradation contain decomposition products of the lignin and the "galactose constituents," *i.e.*, products that may be regarded as built up from *d*-galactose and its simple transformation products. The view is advanced that the skeletal substance, which forms about 78% of the cell-wall, is a compound of ester type derived from the four constituents isolated by chlorine dioxide treatment, physically incorporated with the lignin and the galactose constituents, the proportion of lignin increasing somewhat with the age of the tree.

H. A. PIGGOTT.

**Determination of choline and acetylcholine; decomposition of acetylcholine.** L. LEMATTE, G. BOINOT, E. KAHANE, and (MME.) M. KAHANE (J. Pharm. Chim., 1931, [viii], 13, 371—385).—Methods for the gravimetric determinations of choline and acetylcholine with either phosphotungstic or silicotungstic acid are described and also a method by which a measure of the decomposition of the acetylcholine may be calculated from the weight of the ignited precipitate.

E. H. SHARPLES.

**Salts of glycine.** J. V. DUBSKÝ and A. RABAS (Coll. Czech. Chem. Comm., 1931, 3, 135—154).—Aqueous solutions of the zinc salt of glycine deposit 21% of the zinc as hydroxide when heated at 65—70°, and 32% when boiled, during 2 hrs. Further precipitation occurs when the filtrate is boiled with sodium carbonate solution. Precipitation of zinc hydroxide in the former cases is prevented by addition of glycine. The following *salts* are described

(GH = glycine):  $G_2Zn, 3GH, H_2O$ , decomp.  $245^\circ$ ;  
 $ZnSO_4, GH, 5H_2O$ , m. p.  $82^\circ$ , decomp.  $320^\circ$ ;  
 $HCl, G_2Cu, CuCl_2$ , decomp.  $190^\circ$ ;  
 $CuCl_2, 2GH, 2HCl, 2H_2O$ , m. p.  $96^\circ$ , decomp.  $120^\circ$ .

J. D. A. JOHNSON.

**Identity of Fischer's "glycylglycinecarboxylic acid" and carbamidodiacetic acid.** R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], 49, 318—324).—The isomeric "glycylglycinecarboxylic ester," m. p.  $146-148^\circ$ , obtained by Fischer (A., 1901, i, 675; 1902, i, 350; 1903, i, 607) is ethyl carbamidodiacetate, yielding hydantoin-3-acetic acid when boiled with hydrochloric acid. Esterification of the residue from the alkaline hydrolysis of  $\alpha$ -carbethoxyglycylglycine ester, m. p.  $87^\circ$ , yields ethyl hydantoin-3-acetate, and since hydrolysis of  $\alpha$ -carbethoxyglycylglycine ester, m. p.  $87^\circ$ , with hydrochloric acid yields glycine hydrochloride or with alcoholic hydrochloric acid ethyl aminoacetate, m. p.  $144^\circ$ , hydrochloric acid has no isomerising action, but only decomposes  $\alpha$ -carbethoxyglycylglycine ester into glycine. Accordingly, isomerisation of the latter must occur in its alkaline hydrolysis and not later. The true glycylglycinecarboxylic acid has not been isolated. Since the two terminal carbethoxy-groups in  $\alpha$ -carbethoxyglycylglycine ester are not equivalent, tautomerism of the type  $-CO \cdot NH- \rightleftharpoons -C(OH) \cdot N-$  is suggested, although the final result represents a more profound transformation, probably in accordance with the tendency of organic molecules to assume the most symmetrical form.

R. BRIGHTMAN.

**Isomerisation of Fischer's "carbethoxydiglycylglycine ester."** V. CERCHEZ (Bull. Soc. chim., 1931, [iv], 49, 324—328; cf. preceding abstract).— $\alpha$ -Carbethoxydiglycylglycine ester, m. p.  $160-161^\circ$ , on hydrolysis yielded a small amount of the acid, m. p.  $206^\circ$  (decomp.), not identical with carbamidodiacetic acid, and the existence of diglycylglycinecarboxylic acid is regarded as probable. On esterification this acid yielded an ethyl ester of m. p.  $149-150^\circ$ . There appears to be no analogy in the isomerisation of diglycylglycinecarboxylic acid and of glycylglycinecarboxylic acid.

R. BRIGHTMAN.

**Decomposition of cystine and cysteine during irradiation.** F. LIEBEN and E. MOLNAR (Biochem. Z., 1931, 230, 347—352).—In diffused daylight cystine is decomposed in alkaline and cysteine in acid medium in presence of a sensitiser such as hæmatoporphyrin. The decomposition proceeds readily without addition of sensitiser when the substances are irradiated with ultra-violet light. Addition of tryptophan of irradiated cystine does, but of cysteine does not, decrease its Voisenet colour reaction. Investigation of the action of diffused daylight on the reduction of methylene-blue by cysteine showed that the reduction times in the light and dark tests increase with decreasing  $pH$ , and the difference between the reduction times of light and dark tests also increases.

P. W. CLUTTERBUCK.

**Glutathione. V. Spontaneous cleavage of glutathione in aqueous solution.** H. L. MASON (J. Biol. Chem., 1931, 90, 25—32).—When glutathione is kept in an aqueous solution at  $37-62^\circ$  it

undergoes cleavage into pyrrolidonecarboxylic acid and cysteinylglycine. With Sullivan's test for cysteine, cysteinylglycine gives a purplish-red colour resembling, but not identical with, that given by cysteine. The view put forward by Meldrum and Dixon (cf. A., 1930, 803) on the basis of a positive Sullivan test, that glutathione is frequently contaminated with cysteine and that this latter compound is responsible for autoxidation, is considered to be erroneous, the contaminant being probably cysteinylglycine. Erepsin does not attack glutathione, but hydrolyses the cysteinylglycine after the glutamyl radical has been split off as pyrrolidonecarboxylic acid.

W. O. KERMACK.

**Constitution of so-called cyanoacetoacetic ester and a disputed synthesis of citric acid.** G. FAVREL and C. PRÉVOST (Bull. Soc. chim., 1931, [iv], 49, 243—261).—Chlorination of ethyl acetoacetate always yields the  $\alpha$ -chloro-derivative, and Haller and Held's ester (A., 1882, 1280; 1889, 588; 1891, 171; 1892, 697) consisted entirely of the  $\alpha$ -chloro-ester. Ethyl  $\gamma$ -chloroacetoacetate obtained by Lespieau's method with potassium cyanide yields 80—90% of ethyl succinosuccinate, m. p.  $127-128^\circ$ , and not the  $\gamma$ -cyanoacetoacetate. Haller and Held's B derivative, b. p.  $142-144^\circ/43-45$  mm., also obtained from pure ethyl  $\alpha$ -chloroacetoacetate and aqueous potassium cyanide in 32% yield (minimum), has no enolic structure, since it gives no coloration with ferric chloride. With alcohol and hydrochloric acid about 50% of ethyl  $\alpha$ -chloroacetoacetate is regenerated. No trace of ethyl acetonedicarboxylate was detected but 40% of an acid,  $C_5H_7O_2Cl$ , m. p.  $147-149^\circ$  (m. p.  $105-106^\circ$ , hydrated), also obtained by the action of potassium cyanide on ethyl  $\alpha$ -chloroacetoacetate in presence of hydrochloric acid or sulphuric acid, which is regarded as  $\alpha$ -chloropropion- $\beta$ -ol- $\alpha$ - $\beta$ -dicarboxylic acid.

The structure,  $\begin{matrix} CH(CO_2Et) \\ | \\ CMe(CN) \end{matrix} \rightarrow O$ , is accordingly assigned to the B compound of Haller and Held. Hydrolysis of this cyano-glycidic ester with 4N-potassium hydroxide and precipitation of the potassium as sulphate yields a syrup which decomposes at  $160^\circ$ , yielding traces of hydrogen cyanide, carbon dioxide, formaldehyde, acrylonitrile, and a little water. The hydration product,  $CN \cdot CMe(OH) \cdot CH(OH) \cdot CO_2H$ , is obtained by addition of a slight excess (1%) of sulphuric acid in neutralising after hydrolysis with potassium hydroxide as a syrup, stable below  $140^\circ$ , slow decomp. at  $145-160^\circ$ , decomp. at  $185^\circ$ , hydrolysed by potassium hydroxide to ammonia and a dicarboxylic acid. Hydrolysis of the cyanoglycidic ester at  $70^\circ$  with 0.25N-potassium hydroxide affords a methyltartaric acid, m. p.  $100^\circ$  (lead and silver salts), which with copper sulphate, ferric salts, resorcinol and sulphuric acid, and  $\beta$ -naphthol and sulphuric acid gives reactions resembling those of tartaric acid. The acid  $Ac \cdot CH(OH) \cdot CO_2H$ , obtained by hydrolysis of ethyl O-acetyl- $\alpha$ -hydroxyacetoacetate, by addition of hydrogen cyanide and hydrolysis yields a similar methyltartaric acid. None of these compounds is capable of yielding citric acid, as claimed by Haller and Held. The mobility of the  $\alpha$ -halogen in  $\alpha$ -halogeno-ketones is contrary to the feeble mobility which would be

expected, and the mobility of the halogen is regarded as affording an index of complex reactions appearing with the ketonic group, double decomposition and replacement of the halogen by a fresh radical being usually abnormal.

R. BRIGHTMAN.

**Structure of the glutaconic acids and esters.** I. **Cyanoglutaconic esters.** G. A. R. KON and H. R. NANJI (J.C.S., 1931, 560—575).—The  $\alpha$ -cyanoglutaconic esters form equilibrium mixtures of the  $\alpha\beta$ - and  $\alpha\gamma$ -forms. Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate (Rogerson and Thorpe, *ibid.*, 1905, 87, 1685) forms a potassium compound from which by the action of benzoic acid or hydrogen chloride in non-polar solvents is obtained *ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 178—180°/22 mm.,  $d_4^{20}$  1.0918,  $n_D^{20}$  1.47409, converted by sodium ethoxide into the equilibrium mixture containing about 23% of its  $\alpha\beta$ -isomeride, and yielding on alkylation with the corresponding alkyl halide *ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 162°/14 mm.,  $d_4^{20}$  1.0456,  $n_D^{20}$  1.46619, and *ethyl  $\alpha$ -cyano- $\gamma$ -benzyl- $\beta$ -methyl- $\Delta^{\alpha}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 213°/15 mm.,  $d_4^{20}$  1.0997,  $n_D^{20}$  1.51800, both yielding the equilibrium ester with sodium ethoxide. *Ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 154°/9 mm.,  $d_4^{20}$  1.0729,  $n_D^{20}$  1.46916, is obtained by decomposing the potassium derivative of ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethylglutaconate with benzoic acid in ether. *Ethyl  $\alpha$ -cyano- $\alpha$ -methyl- $\Delta^{\beta}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 160—161°/16 mm.,  $d_4^{20}$  1.0662,  $n_D^{20}$  1.45543, and its  $\alpha$ -ethyl analogue, b. p. 158—160°/11 mm.,  $d_4^{20}$  1.0503,  $n_D^{20}$  1.5323, are obtained by alkylation of ethyl sodio- $\alpha$ -cyanoglutaconate with methyl and ethyl iodides, whilst *ethyl  $\alpha$ -cyano- $\alpha\gamma$ -dimethyl- $\Delta^{\beta}$ -propene- $\alpha\gamma$ -dicarboxylate*, b. p. 176—177°/22 mm.,  $d_4^{20}$  1.0729,  $n_D^{20}$  1.46818, is obtained by similar alkylation of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate, and with sodium ethoxide yields *ethyl  $\alpha$ -cyano- $\alpha\gamma$ -dimethylcrotonate*, b. p. 103°/12 mm. Attempts to apply Linstead and May's iodometric method (A., 1927, 1167) to these esters under standard conditions were partly successful.

G. DISCOMBE.

**Constitution of acid amides and thioamides.** A. HANTZSCH (Ber., 1931, 64, [B], 661—667).—Comparison of the ultra-violet absorption of trichloroacetamide, trichloroacetpiperidine, and the ether  $\text{CCl}_3\cdot\text{C}(\text{OMe})\cdot\text{NH}$  in methyl alcohol, water, and chloroform establishes the close similarity of the two last-named compounds and shows that the equilibrium  $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2 \rightleftharpoons \text{CCl}_3\cdot\text{C}(\text{OH})\cdot\text{NH}$  is displaced extensively towards the right in chloroform and further in water. The curve for benzamide in alcohol is almost identical in its most characteristic portion with that of benzimino ethyl ether and markedly different from that of benzdimethylamide; benzamide is almost completely dissolved as the iminohydrin  $\text{Ph}\cdot\text{C}(\text{OH})\cdot\text{NH}$ . Comparison of the b. p. of the amides, methylamides, dimethylamides, and iminoethers shows that the two first-named types exist mainly in the iminohydrin form  $\text{R}\cdot\text{C}(\text{OH})\cdot\text{NH}$  and  $\text{R}\cdot\text{C}(\text{OH})\cdot\text{NMe}$ . The anomalies in the b. p. of the "amides and methylamides" are attributed to association caused by the presence of the hydroxyl groups and consequent greater difficulty in passing into the unimolecular condition. The b. p.

is essentially the temperature of decomposition of the dimolar or more highly associated iminohydrin into the unimolecular form.

In all solvents the absorption spectrum of thioacetamide is so similar to that of thioacetpiperidine and different from that of the thioether,  $\text{CH}_3\cdot\text{C}(\text{SEt})\cdot\text{NH}$ , that it is regarded as exclusively or almost exclusively present in chloroform or ether as the true thioamide  $\text{CH}_3\cdot\text{CS}\cdot\text{NH}_2$  and only to a minor extent as the iminothioether in water. Similar conclusions are reached for xanthamide and its derivatives. The optical results are confirmed cryoscopically, since xanthdiethylamide and the thioether,  $\text{OEt}\cdot\text{C}(\text{SMo})\cdot\text{NH}$ , are unimolecular in benzene, whereas xanthamide becomes partly associated with increasing concentration owing to the action of the thiol groups developed in the equilibrium  $\text{OEt}\cdot\text{CS}\cdot\text{NH}_2 \rightleftharpoons \text{OEt}\cdot\text{C}(\text{SH})\cdot\text{NH}$ .

H. WREN.

**So-called imido- and amido-chlorides, the salts of nitriles and acid amides, and the chemistry of the transformation of nitriles into acid amides.** A. HANTZSCH (Ber., 1931, 64, [B], 667—678).—Preparative work combined with measurements of mol. wt. and observations of the optical behaviour of nitriles and amides in concentrated sulphuric acid leads the author to the following conclusions. The additive products from hydrogen halides and nitriles are identical with the products obtained from amides and phosphorus pentachloride and regarded hitherto as imide chlorides,  $\text{R}\cdot\text{CCl}\cdot\text{NH}$ , and amide chlorides,  $\text{R}\cdot\text{CCl}_2\cdot\text{NH}_2$ . They are actually nitrilium salts, the former being monohalides,  $[\text{R}\cdot\text{C}\equiv\text{NH}]\text{Cl}$ , and the latter dihalides,  $[\text{R}\cdot\text{C}\equiv\text{NH}]\text{Cl}_2$ , in which the second acid molecule is not structurally combined. All these compounds decompose spontaneously or when treated with water into hydrogen halide and nitrile, which may pass secondarily into the amide. Determinations of mol. wt. in absolute sulphuric acid show the nitriles to be present as completely dissociated sulphates,  $[\text{R}\cdot\text{C}\equiv\text{NH}]\text{SO}_4\text{H}$ . A solid *sulphate* has been obtained from triphenylacetone nitrile; the datum that this nitrile is converted by sulphuric acid into a dissociated cyanide,  $\text{CPh}_3\cdot\text{CN}'$ , and exhibits "polarity isomerism" is erroneous. Acid amides are similarly dissolved by concentrated sulphuric acid to dissociated sulphates which absorb light more strongly than the corresponding nitriles. The salt formation weakens the absorption of the aliphatic nitriles and amides, whereas that of the aromatic analogues is strengthened by the chromophoric benzene residue. The aromatic compounds are optically almost completely identical with the compounds of the benzimino-ethers,  $[\text{Ar}\cdot\text{C}(\text{OEt})\cdot\text{NH}_2]\text{SO}_4\text{H}$ , and therefore contain iminohydrinium salts,  $[\text{Ar}\cdot\text{C}(\text{OH})\cdot\text{NH}_2]\text{SO}_4\text{H}$ , in harmony with the observation that the free primary "acid amides" are preponderatingly iminohydrins,  $\text{R}\cdot\text{C}(\text{OH})\cdot\text{NH}$ . Since the true tertiary acid amides,  $\text{Ar}\cdot\text{CO}\cdot\text{NR}_2$ , form the analogously constituted dialkyliminohydrinium salts,  $[\text{Ar}\cdot\text{C}(\text{OH})\cdot\text{NH}_2]\text{SO}_4\text{H}$ , isomeric acylammonium salts,  $[\text{Ar}\cdot\text{CO}\cdot\text{NH}_2]\text{SO}_4\text{H}$  and  $[\text{Ar}\cdot\text{CO}\cdot\text{NMe}_2\text{H}]\text{SO}_4\text{H}$ , do not exist. The heats of dissolution of the nitriles and amides in sulphuric acid are essentially the heats of formation of their salts, and since those of the amides are much greater than those of the corresponding nitriles

the latter are much weaker base anhydrides than the former. The exothermal transformation of nitrilium sulphate into iminohydrinium sulphate occurs slowly but completely at the ordinary temperature. In aqueous solution the conversion of nitrile into amide is not a consequence of the catalytic acceleration of the addition of water by the acid, since addition of acid to the nitrile is the primary change; the nitrilium salts pass by addition of water into acid amides or, more accurately, into iminohydrinium salts, which are hydrolysed to "acid amides" and acids or to their hydroxonium salts:  $[R \cdot C \equiv NH]X + H \cdot OH \rightarrow [R \cdot C(OH) \cdot NH_2] \cdot X + nH_2O \rightarrow R \cdot C(OH) \cdot NH + [H(OH_2)_n] \cdot X$ . The processes occur in accordance with the author's chemical theory of acids, the strength of which is determined by their differing tendency towards salt formation. The strongest acids have their most marked action as such and are weakest as their ions in aqueous solution. Their so-called catalytic action depends on their salt formation. They are weakest in dilute aqueous solution, since they are then present exclusively as hydroxonium salts. The increase in activity with rise of temperature in aqueous solution depends on increasing decomposition into water and acid.

The following compounds are prepared, generally by the action of the hydrogen halide on the nitrile dissolved in anhydrous ether or benzene: *dihydrochlorides* of cinnamionitrile and *p*-toluonitrile; *monohydrobromides* of trichloroacetonitrile, phenylacetonitrile, and cinnamionitrile; *dihydrobromides* of benzonitrile, *p*-toluonitrile, acetonitrile, and trichloroacetonitrile; *dihydroiodides* of *p*-toluonitrile, phenylacetonitrile, and acetonitrile. All are very unstable.

H. WREN.

**Preparation of bisacetamide hydrochloride and its use as an acetylating agent.** H. STEPHEN (J.C.S., 1931, 672—673).—Bisacetamide hydrochloride (yield 66%) and acetonitrile are obtained from thionyl chloride and dry ethereal acetamide. On fusion of equimolecular proportions of bisacetamide hydrochloride and the hydrochloride of an aromatic primary amine, acetylation of the base occurs with formation of small quantities of an amidine. The reaction probably involves the intermediate formation of acetyl chloride and diacetamide (cf. Brunner and others, A., 1927, 867).

G. DISCOMBE.

**Structure of the carbamide molecule.** L. EBERT (Ber., 1931, 64, [B], 679—681).—In reply to Devoto (A., 1930, 1358), it is pointed out that analysis of the dielectric polarisation of aqueous solutions affords no valid evidence of an unusually strongly polar form of the carbamide molecule. The crystalline structure of carbamide can be reconciled only with the symmetrical diamide formula. In thiocarbamide the two amido-groups are strictly equivalent.

H. WREN.

**Nitroso- and oximino-ferropentacyanides derived from nitroprusside.** L. CAMBI [with A. CAGNASSO and T. RICCI] (Gazzetta, 1931, 61, 3—13).—The formation of highly-coloured complex compounds, probably of the general formula  $K_4[(CN)_5Fe \cdot NO \cdot CRR']$ , has been demonstrated when a further series of compounds with mobile hydrogen atoms able to react

with nitrous acid to form nitroso- or oximino-derivatives are treated with potassium nitroprusside and potassium methoxide in methyl alcohol (cf. A., 1914, i, 967; 1927, 346; 1930, 905). Spontaneous isomerisation to the less highly-coloured compounds,  $K_4[(CN)_5Fe \cdot O \cdot N \cdot CRR']$ , takes place, and hydrolysis with dilute sulphuric acid then yields the oximino-compounds. In this way the oximino-derivatives of nitroethane, ethyl cyanoacetate, phenylacetonitrile, and *p*-nitrophenylacetonitrile have been obtained. Indole yields the compound  $K_4[(CN)_5Fe \cdot NO \cdot C_8H_7N]$ . Spectrographic data for the highly-coloured compounds from acetone, acetylacetone, acetophenone, pyruvic acid, indole, and nitrosobenzene show a general resemblance.

R. K. CALLOW.

**Preparation of tri-*n*-alkylbismuthines.** W. C. DAVIES, I. NORVICK, and W. J. JONES (Bull. Soc. chim., 1931, [iv], 49, 187—194).—When a solution of bismuth chloride in ether is added to about 6 mols. of magnesium *n*-propyl bromide in an atmosphere of hydrogen, the mixture finally decomposed with ammonium chloride, and distilled in vacuum, *tri-n-propylbismuthine*, b. p. 86—87°/8 mm.,  $d_4^{20}$  1.621, is obtained together with a little hexane. *Tri-n-butylbismuthine*, b. p. 124°/7 mm.,  $d_4^{20}$  1.456, and *tri-n-amylbismuthine*, b. p. 157—158°/7 mm.,  $d_4^{20}$  1.381, are similarly obtained. With a smaller proportion of Grignard reagent, by-products are obtained, magnesium amyl bromide (3 mols.) with bismuth chloride (1 mol.) affording a greenish liquid, b. p. 165—185°/6 mm.,  $d_4^{20}$  1.67. The trialkylbismuthines oxidise readily in air and no methiodides could be prepared.

R. BRIGHTMAN.

**Autoxidation of cyclohexene.** H. N. STEPHENS (Ber., 1931, 64, [B], 637—638).—The author's experiments (A., 1928, 401) show that the product obtained by Zelinski and Borissov (A., 1930, 1422) is not the simple cyclohexene peroxide, but probably a mixture of complex products of which the main component is a higher polymeride of the peroxide.

H. WREN.

**Oscillating, puckered, centroid model for the benzene ring.** M. L. HUGGINS (J. Amer. Chem. Soc., 1931, 53, 1182—1183).—Recent chemical and X-ray evidence may be explained by the author's electronic model for benzene (A., 1922, i, 928) if the tetrahedra are sufficiently distorted and there is a frequent or continuous oscillation between such a puckered form and its mirror image.

J. W. BAKER.

**Effect of substituents on certain physical properties of benzene picrate.** O. L. BARIL and E. S. HAUBER (J. Amer. Chem. Soc., 1931, 53, 1087—1091).—The *picrates* of the following aromatic hydrocarbons and their derivatives have been prepared by gently melting an equimolecular mixture of picric acid and the compound, and cooling to determine the f. p. (recorded after each) of the compound so formed: toluene, 88.2°; ethyl-, 96.6°, and propyl-, 103.5°, -benzene; *o*-, 88.5°, *m*-, 90—91.5°, and *p*-, 90.5°, -xylene; hemimellitene, 89.5°; pseudocumene, 96—97°; mesitylene, 96.6°; 1 : 2 : 3 : 4-tetra-, 92—95°; penta-, 131°, and hexa-, 170°, -methylbenzene; phenol, 83.1°; pyrocatechol, 122°; resorcinol, 89—90°; quinol, 115—117°; pyrogallol, 128—129°; hydroxy-

quinol, 96°; phloroglucinol, 101—103°; *o*-, 88°; *m*-, 61.6°, and *p*-, 64—65°, -cresol; orcinol, 92°; 1:2:4-, 83.8°, 1:3:2-, 50—53°, and 1:4:2-, 81—82°, -xylenol; 1-, 140—141°, and 2-, 115—116°, -methyl-; 1-, 97.4°, and 2-, 69—70°, -ethyl-; 1-, 140—141°, and 2-, 89—90°, -propyl-; 1-, 104—105°, and 2-, 71—73°, -butyl-; 1:4-, 139—140°, and 2:6-, 141—142°, -dimethyl-; 1:2:6-trimethyl-, 121—122°, -naphthalene;  $\alpha$ -, 188.5°, and  $\beta$ -, 155.5°, -naphthol; anthracene, 138°; hexamethylanthracene, 203°; phenanthrene, 132.8°; acenaphthene, 160.5°; stilbene, 90—91°; fluorene, 77°; and pyrene, 220°. The colour of the picrate is deepened and the f. p. raised by substitution of methyl groups into benzene, the side-chain, or naphthalene, whilst the colour is deepened but the f. p. lowered by introduction of hydroxyl groups into benzene.

J. W. BAKER.

**Induction of the reaction between chlorine and benzene by ethylene.** T. D. STEWART and M. H. HANSON (J. Amer. Chem. Soc., 1931, 53, 1121—1128).—In homogeneous solution in benzene the ratio of total chlorine reacting to ethylene reacting varies from 1.7 to 2.2 when the chlorine concentration varies between 0.3 and 0.42*M*, and the ethylene concentration changes from the initial value 0.042*M* to zero, but in one experiment in which the initial ethylene concentration was 0.013*M*, the value was as high as 10. A large amount of benzene substitution occurs even at high concentrations, the ethylene having a low induction efficiency. When ethylene is passed into a benzene solution of chlorine in the dark, benzene hexachloride (mixture of stereoisomerides in which the  $\alpha$ -form, m. p. 157°, predominates) is formed, comparatively little substitution occurring. Under these conditions the mol. ratio of total chlorine reacting to total ethylene reacting varies from 2 to 11, being the greater the lower is the partial pressure of the ethylene. These results are provisionally explained on the basis of chain mechanisms for both the ethylene-chlorine and benzene-chlorine reactions, the latter being induced by, and acting as an inhibitor of, the former. No evidence of a Friedel-Crafts type of reaction between the (assumed) intermediate activated ethylene chloride and benzene could be detected, nor is any benzophenone formed when ethylene is introduced into a mixture of benzene, benzoyl chloride, and chlorine.

J. W. BAKER.

**Magnesium phenyl fluoride.** H. GILMAN and L. L. HECK (J. Amer. Chem. Soc., 1931, 53, 377—378).—When fluorobenzene is treated with activated magnesium-copper alloy in ether during 18 months at the ordinary temperature, magnesium phenyl fluoride is formed.

H. BURTON.

**Velocity of nitration of certain derivatives of the benzene series by nitric acid in nitrobenzene solution.** B. V. TRONOV and G. J. BER (J. Russ. Phys. Chem. Soc., 1930, 62, 2337—2345).—The effect of substituents in the nucleus on the velocity of nitration varies at different stages of the reaction.

E. B. UVAROV.

**Nitration of benzene by ethyl nitrate in the presence of catalysts.** B. V. TRONOV and N. C. SIBGATULLIN (J. Russ. Phys. Chem. Soc., 1930, 62,

2267—2272).—Aluminium chloride is the best catalyst in this reaction. An explanation of the mechanism of the catalyst is based on the formation of a complex salt between the catalyst and ethyl nitrate.

E. B. UVAROV.

**Nitration of *m*-dichlorobenzene.** H. S. JOIS and B. L. MANJUNATH (Mysore Univ. J., 1930, 4, 239—240; cf. Dann, A., 1930, 79).—Nitration of *m*-dichlorobenzene by Nietzki and Schedler's method (A., 1897, i, 464) gives mainly 1:3-dichloro-4:6-dinitrobenzene (I). The mixture of dinitro-derivatives formed (cf. Davies and Hickox, J.C.S., 1922, 121, 2649) consists of I and 1:3-dichloro-2:4-dinitrobenzene, m. p. 70—71°; separation is best effected by Dann's method (*loc. cit.*).

H. BURTON.

**Reactions of nitrosulphonyl chlorides. II. Separation of nitrosulphonyl chlorides by means of hydrazine hydrate.** W. DAVIES, F. R. STORRIE, and S. H. TUCKER (J.C.S., 1931, 624—629).—The method of Dann and Davies (A., 1929, 921) has been extended to the nitrobenzenesulphonyl chlorides. A mixture of *o*- and *p*-nitrobenzenesulphonyl chlorides gives with hydrazine hydrate at 35° *o*-nitrobenzenesulphinic acid and *p*-nitrobenzenesulphonhydrazide, m. p. 150—152° (decomp.). The *o*- and *m*-nitrobenzenesulphonyl chlorides at 50° yield *o*-nitrobenzenesulphinic acid, and the *m*- and *p*-sulphonyl chlorides at 55° form *p*-nitrobenzenesulphinic acid. The mixture of the three isomerides is separated by removing the *o*-nitro-isomeride as sulphinic acid, and the resulting mixture separated at 40—45°. 2-Chloro-5-nitro-*p*-toluenesulphonyl chloride and 2-chloro-6-nitro-*p*-toluenesulphonyl chloride were separated in the same way at 60°. 2:4-Dinitrobenzenesulphonhydrazide, m. p. 110° (decomp.), is prepared at -10°. Nitrobenzenesulphonhydrazides form hydrazones with aldehydes and ketones. *p*-Nitrobenzenesulphonhydrazones of acetone, m. p. 169—171°; benzaldehyde, m. p. 142—144°; piperonal, m. p. 189—190°; *o*-nitrobenzenesulphonhydrazides of acetone, m. p. 147—148° (decomp.); piperonal, m. p. 177—179° (decomp.). *m*-Nitrobenzenesulphonhydrazones of acetone, m. p. 148—150° (decomp.); methyl ethyl ketone, m. p. 124—125° (decomp.); benzaldehyde, m. p. 150—151° (decomp.); piperonal, m. p. 173—175° (decomp.), are described. The reactivities of the isomeric chloro-nitrobenzenes towards sodium disulphide is shown to be in the order *o,p* > *m* (Sprung, A., 1930, 759).

G. DISCOMBE.

**Preparation of *o*-chlorotoluene from toluene-*p*-sulphonyl chloride.** L. McMASTER and J. CAROL (Ind. Eng. Chem., 1931, 23, 218—219).—*o*-Chlorotoluene is obtained in 90% yield by chlorinating toluene-*p*-sulphonyl chloride at 70—80° in presence of antimony trichloride as catalyst [cf. G.P. 133,000 (A., 1903, i, 331); iron is unsatisfactory], and hydrolysing the *o*-chlorotoluene-*p*-sulphonyl chloride formed first with 10% and then with 80% sulphuric acid.

H. A. PIGGOTT.

**Chlorination of *o*- and *p*-nitrotoluenes.** 3:4:6-Trichloro-2-nitrotoluene and 2:6-dichloro-4-nitrotoluene. L. F. LEVY and H. STEPHEN (J.C.S., 1931, 76—79).—Chlorination of *o*-nitrotoluene in presence of antimony pentachloride gives 3:4:6-*tri*-



*chloro-2-nitrotoluene*, m. p. 93—94°, identified by conversion on nitration into 3:4:6-trichloro-2:5-dinitrotoluene, m. p. 229.5° (Seelig, A., 1887, 362). It is reduced by stannous chloride and hydrochloric acid to 3:4:6-trichloro-*o*-toluidine, m. p. 89° (*acetyl*, m. p. 199°, and *benzoyl* derivative, m. p. 230°). Chlorination of *p*-nitrotoluene beyond the monochloro-stage is slow and gives 2:6-dichloro-4-nitrotoluene, m. p. 63—64°, the orientation of which depends on its reduction to 2:6-dichloro-*p*-toluidine, m. p. 55° (*acetyl*, m. p. 215°, and *benzoyl*, m. p. 179°, derivatives), identified by difference, and nitration to 2:6-dichloro-3:4-dinitrotoluene, m. p. 130°, the reduction product of which has the properties of an *o*-diamine.

H. A. PIGGOTT.

**Fluorination of organic compounds. I.**  
**Action of lead tetrafluoride on organic compounds.** O. DIMROTH and W. BOCKEMÜLLER (Ber., 1931, 64, [B], 516—522).— $\alpha\alpha$ -Diphenylethylene reacts with lead tetra-acetate and anhydrous hydrogen fluoride (4 mols.) in chloroform at 0° with production of  $\alpha\beta$ -difluoro- $\alpha\alpha$ -diphenylethane, m. p. 66°, b. p. 135—145°/14 mm. (slight decomp.). Reaction does not proceed smoothly, a portion of the material being unchanged and a portion resinified. Excess of hydrogen fluoride increases the resinification, which appears characteristic of fluorination. Treatment of  $\alpha\alpha$ -diphenylethylene with 40% aqueous hydrofluoric acid and lead tetra-acetate gives deoxybenzoin. With alcoholic potassium hydroxide  $\alpha\beta$ -difluoro- $\alpha\alpha$ -diphenylethane yields  $\beta$ -fluoro- $\alpha\alpha$ -diphenylethylene, m. p. 93.5°. Addition of fluorine does not occur with stilbene, cinnamic acid, ethyl cinnamate, and *p*-benzoquinone. Anisole and quinol dimethyl ether absorb two atoms of fluorine from lead tetrafluoride, but do not undergo substitution; a portion of the material remains unchanged, whilst the remainder is converted into a resin free from fluorine. Acetanilide is transformed into *p*-fluoroacetanilide in 10% yield. Fluoro-derivatives of anthracene, phenanthrene, or naphthalene could not be obtained; the last-named substance appears to be polymerised and oxidised.

H. WREN.

**Fluorination of organic compounds. II.**  
**Action of aryl iododifluorides on organic compounds.** W. BOCKEMÜLLER (Ber., 1931, 64, [B], 522—530; cf. preceding abstract).— $\alpha\alpha$ -Diphenylethylene does not react with aryl iododifluorides in chloroform or nitrobenzene at the ordinary temperature. In the presence of a little anhydrous hydrogen fluoride or silicon tetrafluoride formation of  $\alpha\beta$ -difluoro- $\alpha\alpha$ -diphenylethane occurs in 60% yield, accompanied by production of oily material which evolves hydrogen fluoride when distilled and of non-distillable, dark resin. The fluorine appears to abstract a portion of the hydrogen from the hydrocarbon, and the resulting unsaturated residues undergo condensation or fluorination. In the presence of a trace of moisture, deoxybenzoin is produced by the "hydrogen fluoride process." The optimal conditions for the reaction are thorough cooling, exclusion of moisture, and a not excessive amount of hydrogen fluoride or silicon tetrafluoride.  $\alpha\alpha$ -Diphenyl- $\Delta^{\alpha}$ -propene is smoothly transformed into  $\alpha\beta$ -difluoro- $\alpha\alpha$ -diphenylpropane, b. p. 115—120°/2 mm. Stilbene,  $\alpha$ -methylstilbene, anthracene,

and phenanthrene give resins or oils containing fluorine from which individual substances cannot be isolated. Phenanthrene and phenyl iododifluoride, in absence of hydrogen fluoride or silicon tetrafluoride, give a very unstable molecular compound. Diethylaniline is transformed into *p*-fluorodiethylaniline, b. p. 214°/atmospheric pressure, and tetraethylbenzidine, m. p. 89.5—90°.

Iodosobenzene is converted by a solution of potassium hydrogen fluoride in 40% hydrofluoric acid into phenyl iododifluoride. The following iododifluorides are prepared analogously: *p*-tolyl, m. p. 107—109° (decomp.); *m*-nitrophenyl, m. p. 115° (slight decomp. after softening at 113°); *p*-nitrophenyl, m. p. 173.5° (decomp.); *p*-chlorophenyl, m. p. 99°. H. WREN.

**Isolation of an intermediate form during an acetylene isomerisation.** M. BOURGUEL (Compt. rend., 1931, 192, 686—688).—The conversion of  $\alpha$ -phenyl- $\Delta^{\alpha}$ -propinene (I) into  $\alpha$ -phenyl- $\Delta^{\beta}$ -propinene (II) by potassium hydroxide and the reverse reaction under the influence of sodamide lead to the intermediate formation of the sodium derivative of a hydrocarbon, b. p. 72°/17 mm.,  $d_4^{20}$  0.939,  $n_D^{20}$  1.5642, inactive to cuprous chloride, and not hydrated by sulphuric acid and mercuric salts, converted by sodamide into I and by potassium hydroxide above 40° into II. On atmospheric oxidation it yields  $\alpha$ -phenylpropane- $\alpha\beta$ -dione, adds two atoms of iodine, reduces mercuric acetate to mercury, polymerises to a resin at 60°, and is hydrogenated to  $\alpha$ -phenylpropane.

G. DISCOMBE.

**Acenaphthenesulphonic acids. I. Derivatives of acenaphthene-3-sulphonic acid.** K. DZIEWOŃSKI, B. GRÜNBERG, and (Mlle) J. SCHOENŃWNA (Bull. Acad. Polonaise, 1930, A, 518—528).—Acenaphthene is converted by chlorosulphonic acid at 125—130° into its 3-sulphonic acid (A., 1924, i, 1178) and 3:3'-diacenaphthylsulphone, m. p. 230—232°, converted by oxidation with potassium dichromate and acetic acid into the compound  $(O \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} C_{10}H_5)_2SO_2$ ,

m. p. above 420°. Sodium acenaphthene-3-sulphonate [*aniline* salt, m. p. 284—286° (decomp.)] reacts with sulphorus pentachloride to give the corresponding sulphonyl chloride, m. p. 113—114°, reduced by zinc dust in moist ether to acenaphthene-3-sulphinic acid, m. p. 148—149°, and by zinc dust and dilute sulphuric acid to 3-thiolacenaphthene, m. p. 68° (*picrate*, m. p. 117°; coloured lead and mercury salts). This is oxidised by air in alcoholic ammonia to diacenaphthyl 3:3'-disulphide, m. p. 141—142°, and reacts with sodium chloroacetate in alkaline solution to give acenaphthyl-3-thiolacetic acid, m. p. 142° (*sodium* salt). Reduction of either the " $\alpha$ " (amide, m. p. 237—238°, not 137° as given in error) or " $\beta$ " 5-bromoacenaphthenesulphonic acids (A., 1930, 600) with zinc dust and 35% sodium hydroxide or with sodium amalgam in alcoholic solution affords the same acenaphthene-3-sulphonic acid, so that the  $\alpha$  and  $\beta$  acids are 5-bromoacenaphthene-3- and -8-sulphonic acids. The  $\alpha$ -sulphonyl chloride is reduced by zinc dust and dilute sulphuric acid to 5-bromo-3(or 8)-thiolacenaphthene, m. p. 59—60° (lead and mercury salts), converted as above into 5:5'-dibromodiacenaphthyl 3:3'(or 8:8')

disulphide, m. p. 147—148°, and 5-bromoacenaphthyl-3(or 8)-thiolacetic acid, m. p. 154—156°.

J. W. BAKER.

**Anthracene derivatives.** IV. E. DE B. BARNETT and F. C. MARRISON (Ber., 1931, 64, [B], 535—541; cf. this vol., 341).—Phthalic anhydride is condensed with *o*-xylene to *o*-3:4-dimethylbenzoylbenzoic acid, which is reduced by ammonia and activated zinc dust to *o*-3:4-dimethylbenzylbenzoic acid, m. p. 136°. Treatment of the benzoylbenzoic acid with concentrated sulphuric acid yields a mixture of 2:3-dimethylantraquinone, m. p. 210°, and 1:2-dimethylantraquinone, m. p. 156° (not completely free from the 2:3-isomeride). 2:3-Dimethylanthrone, m. p. 158°, is obtained from the anthraquinone and tin and hydrochloric acid in presence of glacial acetic acid or from the benzylbenzoic acid and 80% sulphuric acid at 100°. 2:3-Dimethylanthranyl acetate has m. p. 171°. With magnesium methyl iodide, 2:3-dimethylanthrone affords 2:3:9-trimethylanthrane, m. p. 125°, in poor yield. 9-Benzyl-2:3-dimethylanthrane, m. p. 149°, is transformed by bromine in carbon disulphide into 10-bromo-9-benzyl-2:3-dimethylanthrane, m. p. 158°, which is unchanged by piperidine in boiling chloroform. The following derivatives of 2:3-dimethylanthrone are described: 10-bromo-, m. p. 125—128° (decomp.); 10-piperidino-, m. p. 174° after softening, which gives a dark orange colour with alkali; 10-anilino-, m. p. about 186° (decomp.) according to the rate of heating; 10-*p*-dimethylaminophenyl-, m. p. 235° (decomp.); 10-methoxy-, m. p. 102° (10-methoxy-2:3-dimethylanthranyl acetate, m. p. 109°); 10-phenyl-, m. p. 207° after becoming red (10-phenyl-2:3-dimethylanthranyl acetate, m. p. 168°). 9-Methoxy-10-phenyl-2:3-dimethylanthrane, m. p. 151°, is obtained from 10-phenyl-2:3-dimethylanthrone, potassium hydroxide, and methyl *p*-toluenesulphonate in boiling alcohol. 10-Phenyl-2:3:9-trimethylanthrane, m. p. 119°, and 10-phenyl-9-benzyl-2:3-dimethylanthrane, m. p. 163°, are described. Reduction of 2:3-dimethylanthrone with zinc dust and ammonia yields 2:3-dimethylanthrane, m. p. 252°, converted by bromine in carbon disulphide into 9:10-dibromo-2:3-dimethylanthrane, m. p. 207°. H. WREN.

**Polycyclic aromatic hydrocarbons.** II. Non-existence of 1:2:7:8-dibenzanthracene. III. Derivatives of 1:2:5:6-dibenzanthracene. IV. Condensed derivatives of 1:2-benzanthracene. J. W. COOK (J.C.S., 1931, 487—489, 489—499, 499—507).—II, III. The 1:2:7:8-dibenzanthracene of Clar (A., 1929, 435) and of Fieser and Dietz (*ibid.*, 1055) obtained by the pyrolysis of 2-methyl-1:1'-dinaphthyl ketone is identical with 1:2:5:6-dibenzanthracene (I). Carcinogenic substances derived from 1:2:5:6-dibenzanthracene are described. Dinaphthyl ketones are obtained by the Friedel-Crafts reaction, and submitted to pyrolysis at 440—450°. 2:4'-Dimethyl-1:1'-dinaphthyl ketone, m. p. 120—121°, yields I on pyrolysis; 2:6-dimethyl-1:1'-dinaphthyl ketone, m. p. 162—163°, and 2:6:4'-trimethyl-1:1'-dinaphthyl ketone yield 3'-methyl-dibenzanthracene, whilst 2:7-dimethyl-1:2'- and 2:7-dimethyl-1:1'-dinaphthyl ketones, m. p. 113.5—114.5° and 161—162°, respectively, and 4:7:2'-trimethyl-

1:1'-dinaphthyl ketone (an oil) yield 2'-methyl-1:2:5:6-dibenzanthracene, m. p. 256—257.5°, the trimethyl ketones by demethylation at the position  $\alpha$  to a closed ring (A., 1930, 903). 1:2:5:6-Dibenzanthraquinone (Clar, *loc. cit.*) is converted by Grignard reagents into 9:10-dihydroxy-9:10-dialkyl-9:10-dihydro-1:2:5:6-dibenzanthracenes (dimethyl compound, m. p. 245—250°; di-*n*-butyl, m. p. 214—215°; dibenzyl, m. p. 249—251°), reduced, according to conditions, to 9:10-dialkyl-1:2:5:6-dibenzanthracenes [dimethyl, m. p. 205.5—206.5°; di-*n*-butyl, m. p. 143.5—144.5°; dibenzyl compound, m. p. 195—201° (decomp.)] or to 9:10-dialkyl-9:10-dihydrodibenzanthracene (cis-dimethyl compound, m. p. 207—209°, trans-dimethyl, m. p. 277—278°). By reduction of I with sodium in amyl alcohol an octahydro-derivative, m. p. 188—190°, is obtained. 4-Benzoyl-1:6-dimethylnaphthalene, m. p. 77—78°, is described.

The high-boiling constituents of coal tar contain chrysene, a substance m. p. 153—156°, with fluorescence similar to that of the product from tetrahydronaphthalene and aluminium chloride, and a mixture of substances oxidisable to quinones.

IV. Unsubstituted carcinogenic hydrocarbons are described (cf. above). By pyrolysis of 4:4'-di- $\alpha$ -naphthoyl-3:3'-dimethyldiphenyl, m. p. 159.5—160.5°, 1:2:1':2'-dibenz-6:6'(or 7:7')-dianthryl, m. p. above 310° (decomp.), is formed, whilst 5-(2'-methyl-1'-naphthoyl)hydrindene (an oil) yields 5:6(or 6:7)-cyclopenteno-1:2-benzanthracene, m. p. 199—200°, 3-(2'-methyl-1'-naphthoyl)acenaphthene, m. p. 184—185°, forms phenanthra-accenaphthene, m. p. 231—232°, 2-(2'-methyl-1'-naphthoyl)fluorene, m. p. 169—170°, yields 2:3-phenanthra-3':2'(or 1':2')-fluorene, m. p. 302—304°, 3-(2'-methyl-1'-naphthoyl)-phenanthrene, m. p. 341—343°, forms 2':3'-phenanthra-2:3-phenanthrene, m. p. 341—343°, with an isomeric hydrocarbon, m. p. 245—248°; and 1-(2'-methyl-1'-naphthoyl)anthracene (an oil), forms 2':3'-phenanthra-1:2-anthracene, m. p. 281—282° (decomp.). 1-Benzoyl-5-(1'-naphthoyl)-2:6-dimethylnaphthalene, m. p. 206—208°, and 1-benzoyl-5-(2'-naphthoyl)-2:6-dimethylnaphthalene, m. p. 222—223°, both yield 4:5-benz-10:11-(1':2'-naphtha)chrysene, m. p. 435—440° (decomp.). 2-Methyl-5':6':7':8'-tetrahydro-1:2'-dinaphthyl ketone, m. p. 122.5—123.5°, from tetrahydronaphthalene and 2-methyl-1-naphthoyl chloride, on pyrolysis loses hydrogen and forms 1:2:5:6-dibenzanthracene. G. DISCOMBE.

**Fluosilicates of organic bases.** II. C. A. JACOBSON (J. Amer. Chem. Soc., 1931, 53, 1011—1015).—By the method previously used (A., 1929, 57) the characteristically crystalline fluosilicates of *o*-tolidine (AB), m. p. 268—269° (0.013);  $\alpha$ -, m. p. 218° (decomp.) (0.1504), and  $\beta$ -, m. p. 263.3° (0.0816), -naphthylamine; *m*-nitroaniline, m. p. 200° (0.1210); diphenylamine, m. p. 169° (2.4492); *m*- (AB), m. p. 243—244° (0.065), and *p*- (AB) (decomp.) (0.014), -phenylenediamine; ethylaniline, m. p. 165.3° (0.979); nitrosodiphenylamine, m. p. 124.5° (decomp.) (0.84); *p*-aminoazobenzene, m. p. 220° (decomp.) (0.187); and *p*-aminobenzoic acid, m. p. 240—245° (0.91), have been prepared. All these are of the type

AB<sub>2</sub> except where otherwise indicated. The figures in parentheses are the solubilities in 95% alcohol at 25°.

J. W. BAKER.

**p-Bromoanilides of isobutyric and isovaleric acids.** M. KUEHN and S. M. McELVAIN (J. Amer. Chem. Soc., 1931, 53, 1173—1174).—By a modification of Robertson's method (J.C.S., 1919, 115, 1210) *p*-bromo-*isobutyric*, m. p. 150—151° (lit., m. p. 128°), and *iso-valeric*, m. p. 128—129°, *anilides* are prepared.

J. W. BAKER.

**Action of amines on 2-substituted semicarbazones.** J. CHAPMAN and F. J. WILSON (J.C.S., 1931, 507—514; cf. A., 1928, 1247).—Those 2-substituted semicarbazones which decompose at moderate temperatures to give hydrazones and cyanic acid afford, when heated with an amine, hydrazones and substituted carbamides, the latter arising from the action of the amine on the cyanic acid. Others more stable to heat give 2:4-disubstituted semicarbazones, which may react with further quantities of amine, yielding hydrazones and substituted carbamides. Acetone-2-phenylsemicarbazone heated at 140—145° gives acetophenonylhydrazone and cyanuric acid. Acetophenonylhydrazone and *s*-disubstituted carbamides were obtained from the interaction of acetone-2-phenylsemicarbazone and benzylamine, aniline, *p*-toluidine,  $\beta$ -phenylethylamine, and *n*-heptylamine. Benzylamine gave also some monobenzylcarbamide, whilst aniline and *p*-toluidine gave small quantities of *solids*, m. p. 133° and 162°, respectively. Acetophenone-2-phenylsemicarbazone (m. p. 126°) and aniline gave acetophenonylhydrazone and *s*-diphenylcarbamide. Benzaldehyde-2-benzylsemicarbazone yielded with aniline benzaldehyde-4-phenyl-2-benzylsemicarbazone; with *p*-toluidine *benzaldehyde-4-p-tolyl-2-benzylsemicarbazone*, m. p. 172°; and with benzylamine *benzaldehyde-2:4-dibenzylsemicarbazone*, m. p. 124°, together with *s*-dibenzylcarbamide. Benzaldehyde-2-methylsemicarbazone gave with aniline benzaldehyde-4-phenyl-2-methylsemicarbazone, and with benzylamine *s*-dibenzylcarbamide, *benzaldehyde-4-benzyl-2-methylsemicarbazone*, m. p. 106°, a substance C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>, m. p. 207°, and (by prolonged action) a substance C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>, m. p. 63°.

A. A. LEVI.

**Effects of substituents in the formation of thiocarbanilides.** L. C. RAFFORD and G. M. McNULTY (Proc. Iowa Acad. Sci., 1929, 36, 269).—The presence of a methyl group *meta* to the amino-group diminishes the velocity of reaction of monoacetyl-*p*-phenylenediamine with carbon disulphide by about 33%; if either or both *m*-positions are occupied by bromine atoms the reaction does not take place. An *o*-bromine atom also causes inhibition. The acetyl group could not be removed from the thiocarbanilides produced.

CHEMICAL ABSTRACTS.

**Monoacetylation and monodiazotisation of diphenylene [2:4'-diaminodiphenyl].** C. FINZI (Gazzetta, 1931, 61, 33—42).—When 2:4'-diaminodiphenyl in aqueous alcohol is treated with acetic anhydride the diacetyl derivative formed is accompanied by 2-amino-4'-acetamidodiphenyl, m. p. 176—177°, the constitution of which has been proved by its conversion into 4-acetamido-, 4-amino-, and 4-hydroxy-

diphenyl, successively, and also into 4'-acetamido-2-hydroxydiphenyl, m. p. 199°, 4-amino-2-hydroxy-, and 2-hydroxy-diphenyl, successively. Monodiazotisation, on the other hand, yields the 2-diazonium compound, for the product may be converted either into 4'-amino-2-hydroxy- and 2-hydroxy-diphenyl, successively, or into 4-amino- and 4-hydroxy-diphenyl, successively.

R. K. CALLOW.

**Catalytic reduction of benzidine.** F. BALAŠ and P. ŠEVČENKO (Coll. Czech. Chem. Comm., 1931, 3, 171—176).—Hydrogenation of benzidine in presence of colloidal platinum gives *perhydrobenzidine* (4:4'-diaminodicyclohexyl), m. p. 59°, b. p. 120°/0.8 mm. (*dihydrochloride*, decomp. 290°; *dipicrate*, decomp. 247°), in small yield.

J. D. A. JOHNSON.

**Molecular compounds of hydroxyazo-compounds with acid halides.** W. M. FISCHER and A. TAURINSCH (Ber., 1931, 64, [B], 236—239).—All hydroxyazo-compounds yield adducts with the chlorides and bromides of carboxylic and inorganic acids in ether, benzene, light petroleum, or carbon disulphide. The molecular compounds of many of the azo-derivatives of phenols are solvatised by these media; in these cases the adducts can be prepared without use of solvent. Azo-hydrocarbons and alkylated and acylated hydroxyazo-compounds do not yield molecular compounds, so that the formation from the hydroxy-compounds appears due to the residual valency of the hydrogen atom of the hydroxyl group. The compounds are formed most readily when the hydroxyl group is in the *para*-position to the azo-complex, less readily when it is in the *ortho*-position. The presence of a substituent in the *para*-position in the non-hydroxylated nucleus appears to impede reaction. The adducts are remarkably stable towards air. In benzene, they appear to be dissociated almost completely into their components. The following individuals are described, the ratio of the components (hydroxyazo-compound:halide) being given in parentheses: *p*-benzeneazophenol-acetyl chloride (1:1), m. p. 172°; *propionyl chloride* (1:1), m. p. 162°; *isovaleryl chloride* (1:1), m. p. 165°; *benzoyl chloride*, (1:1), m. p. 166°; *phenylacetyl chloride* (1:1), m. p. 166°; *p*-nitrobenzoyl chloride (1:2), m. p. 177°; *bromoacetyl chloride* (2:3), m. p. 165°; *oxalyl chloride* (2:1), m. p. 175°; *phthalyl chloride* (2:1), m. p. 166°; *carbonyl chloride* (5:2), m. p. 165°; *acetyl bromide* (4:5), m. p. 165°; *benzoyl bromide* (1:2), m. p. 158°; *sulphuryl chloride* (2:1), m. p. 138°; *thionyl chloride* (2:1), m. p. 173°; *phosphorus trichloride* (3:1), m. p. 173°; *phosphoryl chloride* (3:1), m. p. 165°; *benzeneazo-o-cresol-acetyl chloride* (1:1), m. p. 175°; *propionyl chloride* (2:3), m. p. 172°; *benzoyl bromide* (1:2), m. p. 166°; *carbonyl chloride* (2:1), m. p. 167°; 4-*p*-nitrobenzeneazophenol-acetyl chloride (3:2), m. p. 164°; *benzoyl bromide* (2:3), m. p. 146°; *benzeneazo-p-cresol-benzoyl bromide*, unstable; *p*-nitrobenzeneazoresorcinol-*propionyl chloride* (1:1), m. p. 158°; *benzoyl bromide* (1:2), m. p. 131°; *p*-tolueneazosalicylic acid-*propionyl chloride* (1:1), m. p. 205°; *benzoyl bromide* (1:1), m. p. 210°; *benzeneazo- $\alpha$ -naphthol-acetyl chloride* (2:1), m. p. 183°; *propionyl chloride* (2:1), m. p. 193°; *benzoyl*

bromide (4:3), m. p. 183°; *-thionyl chloride* (4:1), m. p. 187°; *-tin tetrachloride* (2:1), m. p. 248°; *benzeneazo-β-naphthol-benzoyl bromide* (1:1), m. p. 126°; *4-α-naphthaleneazophenol-acetyl chloride* (1:1), m. p. 148°; *-propionyl chloride* (1:1), m. p. 155°; *-benzoyl bromide* (1:2), m. p. 146°; *4-β-naphthaleneazophenol-propionyl chloride*, m. p. 165°. The behaviour of *α-naphthaleneazo-α-naphthol*, *α-naphthaleneazo-β-naphthol*, 2:4:6-tribromobenzeneazo-β-naphthol, *o-nitrobenzeneazo-α-naphthol*, and 2:4-dinitrobenzeneazo-β-naphthol has been investigated qualitatively.

H. WREN.

**Carbylamines. XVII. Reactions with nitroso-derivatives.** M. PASSERINI [with N. ZITA] (*Gazzetta*, 1931, 61, 26–33).—Interaction of 1-nitroso-β-naphthol with phenylcarbylamine in benzene yields no crystalline product, but with *p*-carbylaminoazobenzene there is formed, with evolution of carbon monoxide and dioxide, *carbonyl-α-amino-β-naphthol-p-benzeneazoanil*, m. p. 241–243° (decomp.). This is reduced by brief treatment with tin and hydrochloric acid to the *p-aminoanil*, m. p. 220–221° (darkens) (*benzylidene* compound, m. p. 205–208°) (by-product, m. p. 165°), but when the reaction is prolonged hydrolysis occurs with the formation of *carbonyl-α-amino-β-naphthol* and a basic by-product, m. p. 92–95° (decomp.). The *p-aminoanil* yields *p*-phenylenediamine when fused with potassium hydroxide.

Reaction between *p*-carbylaminoazobenzene and 2-nitroso-α-naphthol yields di-*p*-benzeneazophenylformamidine, formyl-*p*-aminoazobenzene, and a dark-coloured material of high m. p.

R. K. CALLOW.

**Constitution of normal diazotates.** A. HANTZSCH and E. STRASSER (*Ber.*, 1931, 64, [B], 655–660; cf. A., 1930, 1032).—A refutation of the formula advanced by Angeli (A., 1930, 1428) for the normal diazotates.

H. WREN.

**2-Phenyl-1-methylcyclohexanol and its transformations.** S. I. SERGIEVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1930, 62, 2187–2192).—The action of sulphuric acid on 2-phenyl-1-methylcyclohexanol, b. p. 131–132°/8 mm.,  $d_4^{20}$  1.0283, gives 2-phenyl-1-methylcyclohexane, b. p. 115–118°/12 mm.,  $d_4^{20}$  0.9699 (oxide, b. p. 136–138°/19 mm.,  $d_4^{20}$  1.0266; 2-phenyl-1-methylcyclohexanediol, b. p. 139–140°/2.02 mm). The product of the pinacolin rearrangement of the glycol gives two *semicarbazones*, m. p. 226–227° (decomp.) and m. p. 172–175°; sulphuric acid treatment of these gives two *ketones*, an oil, b. p. 137–140°/16 mm., and a crystalline substance, m. p. 51.5°.

E. B. UVAROV.

**Thermal behaviour of phenols. III.** A. HAGEMANN.—See this vol., 577.

**Nitration of phenol and the rôle of nitrous acid.** A. V. KARTASHEV (*J. Russ. Phys. Chem. Soc.*, 1930, 62, 2129–2160).—A definite initial temperature dependent entirely on the solvent and concentration of nitric acid is required. The reaction in ethyl acetate solution proceeds in two stages, a deepening in colour being followed by a rise in temperature. At the commencement of the second stage there is a slight fall in temperature attributed to a simultaneous

endothermic reaction. Nitrous acid is essential to commence the reaction, but acts as a positive catalyst only within certain temperature limits, outside which it hinders nitration and gives rise to a small amount of a green solid the nature of which was not established. The whole reaction between nitric acid and phenol is stated to proceed thus:  $\text{HNO}_3 \rightarrow \text{HNO}_2 + \text{O}$ ;  $\text{PhOH} + \text{HNO}_2 \rightarrow \text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{H}_2\text{O}$ ;  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{HNO}_3 \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} + \text{HNO}_2$ .

E. B. UVAROV.

**Halogenated nitrophenols. II. Preparation of 2-chloro-3-nitrophenol from phenacetin.** H. VAN ERP (*J. pr. Chem.*, 1931, [ii], 129, 327–336).—The action of 15% nitric acid on phenacetin (A., 1930, 1176) gives 12% of the 2-nitro-derivative in addition to the 3-nitro-compound. The latter is converted by sodium chlorate and acetic acid into 2-chloro-3-nitrophenacetin, m. p. 184.5° (together with an *N*-chlorinated substance, decomp. 130°, separated by its solubility in chloroform), hydrolysed by concentrated sulphuric acid to 2-chloro-3-nitro-*p*-aminophenol, m. p. 165.5°, and by dilute sulphuric acid to 3-chloro-2-nitro-*p*-phenetidine, m. p. 74°. This is converted successively into 2-chloro-3-nitrophenetole and 2-chloro-3-nitrophenol, both identical with the specimens previously obtained (*loc. cit.*), but the ether depressed the m. p. of 5-chloro-3-nitrophenetole, m. p. 47°, prepared for comparison by the action of potassium carbonate, potassium ethyl sulphate, and glycerol on the corresponding phenol.

J. W. BAKER.

**Condensations of dimethylolcarbamide with derivatives of benzene and naphthalene.** H. DE DIESBACH, O. WANGER, and A. VON STOCKALPER (*Helv. Chim. Acta*, 1931, 14, 355–368).—Prolonged interaction of 1 mol. of dimethylolcarbamide (*s*-dihydroxydimethylcarbamide) (I) (Einhorn and Hamburger, A., 1908, i, 141) with 2 mols. of *o*-nitrophenol in acetic and sulphuric acids at 15–20° gives *α*-3-nitro-4-hydroxybenzyl-*γ*-hydroxymethylcarbamide, decomp. 128° without melting, or a mixture of *s*-di-(3-nitro-4-hydroxybenzyl)carbamide, m. p. 216°, a dinitrodihydroxydiphenylmethane, m. p. 228°, and (?) polymeric dinitrodihydroxydiphenylmethane, m. p. 200° (cf. G.P. 76,490), according to the amounts of acids used. Equimolecular quantities of *p*-nitrophenol and I in sulphuric acid afford *α*-5-nitro-2-hydroxybenzyl-*γ*-hydroxymethylcarbamide, m. p. 181°; with 2 mols. of the phenol in sulphuric and acetic acids, *s*-di-(5-nitro-2-hydroxybenzyl)carbamide, m. p. 198°, results. *p*-Cresol condenses with I in 60% alcohol saturated with hydrogen chloride forming *s*-di-(2-hydroxy-5-methylbenzyl)carbamide, m. p. 165–167°; when an excess of *p*-cresol is used in more dilute alcohol, an equimolecular compound of the carbamide and cresol is obtained. The following carbamides are prepared (usually in presence of acetic and sulphuric acids): *s*-di-(3-nitro-2-hydroxy-5-methylbenzyl)-, m. p. 229–230° (equimolecular compound, m. p. 223–224°, with 3-nitro-*p*-cresol); *s*-di-(3-nitro-4-methoxybenzyl)-, m. p. 223°; *s*-di-(4-hydroxy-3-carboxybenzyl)-; *s*-di-(2:4-dihydroxybenzyl)-; *s*-di-(*p*-acetamidobenzyl)-, m. p. 242° (decomp.), and *s*-di-(5-acetamido-2-methylbenzyl)carbamide, m. p. 270°. Quinol condenses with I in cold, dilute hydrochloric acid forming

*methylenebis*-2 : 5-*di*hydroxybenzylcarbamide (II),  $[(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}]_2\text{CH}_2$ , probably formed thus:  $2(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}\rightarrow\text{II}+\text{CH}_2\text{O}+\text{H}_2\text{O}$ . Dissolution of II in moist acetone and evaporation of the solution in a vacuum gives a compound, probably

$[(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}]_2\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$ , which when heated at 105—110° loses 1 mol. of water forming the *isopropylidene* derivative of II,

(?)  $[(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}]_2\text{C}\cdot\text{CMe}_2$ .

Condensation of *N*-methylolchloroacetamide with 3-hydroxy-2-naphthoic acid in alcohol saturated with hydrogen chloride gives 3-*hydroxy*-4-*chloroacetamidomethyl*-2-*naphthoic acid*, m. p. 239—240°; 3-*hydroxy*-4-*benzamidomethyl*-2-*naphthoic acid*, m. p. 219—220°, is prepared similarly using *N*-methylolbenzamide. 1-Hydroxy-2-naphthoic acid is converted similarly into 1-*hydroxy*-4-*chloroacetamidomethyl*-2-*naphthoic acid*, m. p. 219—220°, and 1-*hydroxy*-4 : 8(?)*di*(*benzamidomethyl*)-2-*naphthoic acid*, m. p. 219°. Hydrolysis of 1-chloroacetamidomethyl-β-naphthol (Einhorn, A., 1906, i, 245; 1908, i, 608) with boiling hydrochloric acid gives mainly di-(2-hydroxy-α-naphthyl)methane, also formed when 1-aminomethyl-β-naphthol (*loc. cit.*) is boiled with sodium hydroxide solution. β-Naphthol and I condense in 50% alcohol saturated with hydrogen chloride forming *s*-*di*-(2-*hydroxy*-α-*naphthylmethyl*)*carbamide*, m. p. 205°, converted by boiling hydrochloric acid into αβ-*di*-(2-*hydroxy*-α-*naphthyl*)ethane. *s*-*Di*-(2-*hydroxy*-3-*carboxy*-α-*naphthylmethyl*)*carbamide*, m. p. 264—265° (ethyl ester, m. p. 261°), prepared from 3-hydroxy-2-naphthoic acid (and the ethyl ester), is hydrolysed by alcoholic hydrochloric acid to αβ-*di*-(2-*hydroxy*-α-*naphthyl*)ethane-3 : 3'-*carboxylic acid* (+H<sub>2</sub>O), m. p. 295°.

Equimolecular quantities of α-naphthol and I in 50—70% alcohol saturated with hydrogen chloride give α-(1-*hydroxy*-β-*naphthylmethyl*)-γ-*hydroxymethyl**carbamide*, m. p. 211° (decomp.), oxidised by alkaline potassium permanganate to 1-hydroxy-2-naphthoic acid and hydrolysed by hydrochloric acid to αβ-*di*-(1-*hydroxy*-β-*naphthyl*)ethane, anhydrous and +2H<sub>2</sub>O, not melted at 330° [*diacetate* (+H<sub>2</sub>O), m. p. 178°, m. p. (anhydrous) 278°]. When the above condensation is effected with 2 mols. of α-naphthol, a substance, C<sub>36</sub>H<sub>32</sub>O<sub>5</sub>N<sub>4</sub>, probably derived from 2 mols. of I and 3 mols. of α-naphthol, is produced. *s*-*Di*-(4-*hydroxy*-3-*carboxy*-α-*naphthylmethyl*)*carbamide*, m. p. 239°, obtained together with other products from 1-hydroxy-2-naphthoic acid and I, is hydrolysed to αβ-*di*-(4-*hydroxy*-3-*carboxy*-α-*naphthyl*)ethane, m. p. 266°. In many of the above condensations small amounts of diarylmethane derivatives are produced.

The production of ethane derivatives by hydrolysis of the condensation products of dimethylolcarbamide and naphthol derivatives is compared with the formation of such derivatives in the anthraquinone series (cf. this vol., 226). The amido-groups appear to be eliminated, not as ammonia but as nitrogen.

H. BURTON.

Acyl derivatives of *o*-aminophenol. VI. C. B. POLLARD and R. E. NELSON (J. Amer. Chem. Soc., 1931, 53, 996—1001).—From the *O*- and *N*-acyl derivatives of *o*-aminophenol the diacyl derivatives have been prepared by the action of the appropriate

acyl chlorides, of which one was always phenylacetyl chloride, whilst the other was varied, and the *N*-acyl derivative, obtained by hydrolysis of the product with 10% potassium hydroxide, was identified to ascertain the effects of the relative acidity and mol. wt. of the acyl groups in determining any rearrangement during hydrolysis. No rearrangement occurs on hydrolysis of *o*-phenylacetamidophenyl *n*-butyrate, m. p. 91—92°, *o*-*n*-butyramidophenyl phenylacetate, m. p. 46—48°, or *o*-*n*-valeramidophenyl phenylacetate, m. p. 71—72°; of the products *o*-*n*-butyramidophenol, m. p. 80—81°, is new. Hydrolysis of *o*-phenylacetamidophenyl *n*-valerate, m. p. 80—82°, affords a mixture of *o*-phenylacetamidophenol (65%) and *o*-valeramidophenol (35%), whilst *o*-carbomethoxyamidophenyl phenylacetate, m. p. 105—106°, gives a 50% mixture of *o*-phenylacetamido- and *o*-carbomethoxyamido-phenol. Rearrangement occurs in all the following cases: *o*-phenylacetamidophenyl acetate, m. p. 101—102°; *o*-acetamidophenyl phenylacetate, m. p. 99—100°; *o*-phenylacetamidophenyl propionate, m. p. 98—99°; *o*-propionamidophenyl phenylacetate, m. p. 71—72°; *o*-phenylacetamidophenyl monochloroacetate, m. p. 113—114°; *o*-phenylacetamidophenyl benzoate, m. p. 110—111°; and benzamidophenyl phenylacetate, m. p. 108—109°, all give *o*-phenylacetamidophenol, m. p. 149—150°, on hydrolysis: *o*-phenylacetamidophenyl isovalerate, m. p. 87—88°, and *o*-isovaleramidophenyl phenylacetate, m. p. 56—57°, both give *o*-isovaleramidophenol: *o*-phenylacetamidophenyl *m*-chlorobenzoate, m. p. 146—148°, and *o*-(*m*-chlorobenzamido)phenyl phenylacetate, m. p. 150—152°, both give *o*-(*m*-chlorobenzamido)phenol, m. p. 156—158°: *o*-(*m*-bromobenzamido)phenyl phenylacetate, m. p. 157—159° (isomeride could not be obtained), gives *o*-(*m*-bromobenzamido)phenol, m. p. 180°: *o*-carbethoxy-, m. p. 62—63°, and *o*-carbobutoxy-, m. p. 72—73°, -amidophenyl phenylacetate each give the corresponding *o*-carbalkoxyamidophenol.

J. W. BAKER.

Derivatives of 3-amino-4-methoxytoluene.

L. C. RAIFORD and O. GROSZ (Proc. Iowa Acad. Sci., 1929, 36, 268).—6-Bromo-3-amino-4-methoxytoluene (*N*-acetyl and benzoyl derivatives) has been prepared.

CHEMICAL ABSTRACTS.

Bromine derivatives of certain mixed ethers and some of their reactions. L. C. RAIFORD and L. H. HOWLAND (J. Amer. Chem. Soc., 1931, 53, 1051—1057).—Fission of various tri-, and penta-bromophenyl alkyl ethers has been investigated by the following methods: (1) heating with phosphorus tribromide in acetic acid with gradual addition of the calculated amount of water; (2) as in the previous method but heated in a sealed tube at 135—150°; (3) addition of bromine to a benzene solution of the ether containing iodine as a catalyst, and (4) keeping a mixture of the ether, excess of bromine, and 1% of aluminium bromide at the ordinary temperature. Of these (2) is the most generally effective, whilst with (4) the percentage of phenol formed depends largely on the alkyl radical present in the ether. The observation (Raiford and Birosel, A., 1929, 923) that phenyl allyl ether is converted by excess of bromine in chloroform into 2 : 4-dibromophenyl

$\beta\gamma$ -dibromopropyl ether is confirmed by the following observations. 2:4-Dichloro-, b. p. 144—145°/25 mm. (prepared by Claisen's method, A., 1913, i, 1175, from 2:6-dichlorophenol and allyl bromide), and 2:6-dibromo-, b. p. 132—133°/10 mm., -phenyl allyl ether are similarly brominated to 2:4-dichlorophenyl, b. p. 188°/10 mm., and 2:6-dibromophenyl, m. p. 48—49°,  $\beta\gamma$ -dibromopropyl ether, respectively, whilst 3:5-dibromophenyl allyl ether, b. p. 145°/10 mm., is converted into 2:3:4:5-tetrabromophenyl  $\beta\gamma$ -dibromopropyl ether, m. p. 96°. Thus when any two of the *ortho* and *para* positions in a phenyl allyl ether are substituted by bromine no further bromination of the nucleus occurs under the conditions used. Pentabromophenyl allyl ether, m. p. 167—168°, is similarly converted into pentabromophenyl  $\beta\gamma$ -dibromopropyl ether, m. p. 122—123°. Phenyl allyl ethers containing two or more bromine atoms in the nucleus could not be rearranged to the corresponding phenols by heat. The phenyl  $\alpha\beta$ -dibromopropyl ethers are very hygroscopic and are converted by the action of alcoholic potassium hydroxide into phenyl propargyl ethers and thus are obtained: 2:4-dichloro-, liquid (silver salt); 2:4-, m. p. 65° (silver, cuprous, and mercuric salts), and 2:6-, m. p. 58—60° (silver salt), -dibromo-; and 2:4:6-tribromo-, m. p. 136—137° (silver, cuprous, and mercuric salts), -phenyl propargyl ether.

J. W. BAKER.

Synthesis of pharmacologically important amines. II.  $\beta$ -Arylethylamines from aromatic aldehydes and carboxylic acids. K. KINDLER (Arch. Pharm., 1931, 269, 70—78).—High yields of  $\beta$ -arylethylamines are obtained from  $\alpha$ -acetoxyarylacetonitriles only when the reaction is completed as rapidly as possible by gradual addition of the nitrile in acetic acid to palladium-black in sulphuric and acetic acids in presence of hydrogen at 3—4 atm. By this means  $\beta$ -*p*-anisylethylamine (95% of the theoretical yield) (I) is obtained from  $\alpha$ -acetoxy-*p*-anisylacetonitrile, m. p. 38—39°, and  $\beta$ -3:4-methylenedioxyphenylethylamine (75%) (II),  $\beta$ -3:4-dimethoxyphenylethylamine (80%) (III), and  $\beta$ -3:4-methylenedioxy-5-methoxyphenylethylamine (73%) from the corresponding nitriles. *p*-Anisoyl cyanide is hydrogenated, similarly, to I. Although these  $\beta$ -arylethylamines are not obtainable by the usual technique of the Hofmann process, I, II, and III are formed in 90%, 77%, and 73%, respectively, of the theoretical yield when the requisite  $\beta$ -arylpropionamides are dissolved in alkaline potassium hypochlorite solution at 0° to form the *N*-chloroamide and the product is added slowly to boiling 50% aqueous potassium hydroxide.

H. E. F. NOTTON.

Diphenyl ether series. II. Preparation and structure of some sulphonic acids and related derivatives. C. M. SUTER (J. Amer. Chem. Soc., 1931, 53, 1112—1116).—The structure of diphenyl ether-4:4'-disulphonic acid obtained by sulphonation of diphenyl ether is proved by bromination of its barium salt in aqueous solution first to 4-bromodiphenyl ether-4'-sulphonic acid (isolated as its sodium salt; *p*-toluidine salt, m. p. 245—247°) and then further to 4:4'-dibromodiphenyl ether (Le Fèvre and others, A., 1927, 66G). Diphenyl ether is converted

by chlorosulphonic acid in acetic acid or by 95% sulphuric acid and acetic anhydride into its 4-sulphonic acid [*p*-toluidine salt, m. p. 221—222°; *sulphonyl chloride*, b. p. 205—207°/12 mm., m. p. 45—46°; amide, m. p. 128—129° (lit. m. p. 88°)] identical with the product obtained by Quilico (A., 1928, 407) and also converted by bromination into 4:4'-dibromodiphenyl ether. Attempts to prepare 4-hydroxydiphenyl ether by fusion of the monosulphonic acid with alkali were unsuccessful. 4-Bromodiphenyl ether is converted by 95% sulphuric acid at 100° into its 4'-sulphonic acid and by chlorosulphonic acid into the 4'-sulphonyl chloride, m. p. 81—82° (also by bromination of diphenyl ether-4-sulphonyl chloride: amide, m. p. 131—132°; anilide, m. p. 108—109°). Excess of chlorosulphonic acid converts diphenyl ether into its 4:4'-disulphonyl chloride, m. p. 128—129° (diamide, m. p. 158—160°). Diphenyl ether-4-sulphonyl chloride is reduced by sodium sulphite to the unstable 4-sulphinic acid, darkens above 180°, and by zinc dust and sulphuric acid to 4-thiodiphenyl ether, b. p. 178—180°/20 mm., m. p. 19—22°, oxidised by iodine to the disulphide, m. p. 47—48°.

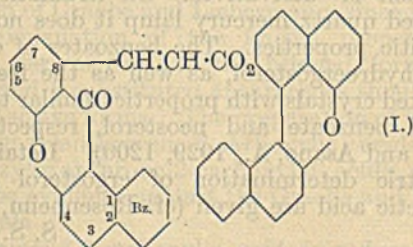
J. W. BAKER.

Substitution products of 2-nitro- and 2-acetamido-diphenyl ethers, and the corresponding diphenylene oxides. H. McCOMBIE, W. G. MACMILLAN, and H. A. SCARBOROUGH (J.C.S., 1931, 529—537).—Nitration of 2-acetamidodiphenyl ether with nitric acid, *d* 1.42, gives 5-nitro-2-acetamidodiphenyl ether, m. p. 180°, hydrolysed by alcoholic hydrochloric acid to 5-nitro-2-aminodiphenyl ether, m. p. 116°, which on diazotisation and treatment with 50% sulphuric acid gives 2-nitrodiphenylene oxide. Further nitration of 5-nitro-2-acetamidodiphenyl ether with more concentrated acid gives 5:4'(?)-dinitro-2-acetamidodiphenyl ether, m. p. 190°, from which 5:4'(?)-dinitro-2-aminodiphenyl ether, m. p. 192°, is obtained on hydrolysis as above. 2-Chloro-2'-nitrodiphenyl ether (from the condensation of *o*-chloronitrobenzene and potassium *o*-chlorophenoxide) on reduction and acetylation gives 2-chloro-2'-acetamidodiphenyl ether, m. p. 104°. This by a similar series of reactions gives 2-chloro-5'-nitro-2'-acetamido-, m. p. 142°, 2-chloro-5'-nitro-2'-amino-, m. p. 125°, 2-chloro-4(?) : 5'-dinitro-2'-acetamido-, m. p. 176°, and 2-chloro-4(?) : 5'-dinitro-2'-amino-diphenyl ether, m. p. 202°. 2:5-Dichloronitrobenzene condenses with sodium phenoxide to 4-chloro-2-nitrodiphenyl ether, b. p. 211°/20 mm., reduced to 4-chloro-2-aminodiphenyl ether, b. p. 215°/20 mm., m. p. 44° (hydrochloride, m. p. 192°). This when diazotised and treated with 50% sulphuric acid gives 3-chlorodiphenylene oxide, m. p. 106°. Chlorination of 2-nitrodiphenyl ether gives 4-chloro-2'-nitrodiphenyl ether (also from potassium *p*-chlorophenoxide and *o*-chloronitrobenzene), reduced to 4-chloro-2'-aminodiphenyl ether (hydrochloride, m. p. 181°; acetyl, m. p. 99°, diacetyl derivative, m. p. 106°), giving 3-chlorodiphenylene oxide when treated as above. From the monoacetyl derivative by the methods described above 4-chloro-5'-nitro-2'-acetamido-, m. p. 203°, 4-chloro-5'-nitro-2'-amino-, m. p. 123°, and 4-chloro-2(?) : 5'-dinitro-2'-acetamidodiphenyl ether, m. p. 198°, and 3-chloro-7-nitrodiphenylene oxide, m. p. 226°, were prepared. Potassium

*p*-chlorophenoxide condenses with 2:5-dichloronitrobenzene to 4:4'-dichloro-2-nitrodiphenyl ether, reduction of which yields 4:4'-dichloro-2-aminodiphenyl ether (*hydrochloride*, m. p. 145°; *acetyl derivative*, m. p. 109°; 3:6-dichlorodiphenylene oxide, m. p. 190°). Nitration of the above acetyl derivative gives 4:4'-dichloro-5-nitro-2-acetamido-, m. p. 159°, and 4:4'-dichloro-2'(?):5-dinitro-2'-acetamido-diphenyl ether, m. p. 212°. Bromination of 5-nitro-2-acetamidodiphenyl ether or nitration of 4'-bromo-2-acetamidodiphenyl ether gives 4'-bromo-5-nitro-2-acetamidodiphenyl ether, m. p. 208°, hydrolysed to 4'-bromo-5-nitro-2-aminodiphenyl ether, m. p. 133°, which is deaminated to give 4'-bromo-3-nitrodiphenyl ether. 5-Bromo-2-aminodiphenyl ether by the diazotisation method gives 2-bromodiphenylene oxide, m. p. 120°. Similarly, 4-bromo- or 4'-bromo-2-aminodiphenyl ether gives 3-bromodiphenylene oxide, also obtained by direct bromination of diphenylene oxide; further bromination of this gives 3:6-dibromodiphenylene oxide, m. p. 195°, also obtained from 4:4'-dibromo-2-aminodiphenyl ether. 4':5-Dibromo-2-aminodiphenyl ether gives 2:6-dibromodiphenylene oxide, m. p. 176°. 4-Chloro-4'-bromo-2-nitrodiphenyl ether is obtained by bromination of 4-chloro-2-nitrodiphenyl ether, or by synthesis from potassium *p*-bromophenoxide and 2:5-dichloronitrobenzene. Interaction of iodine monochloride with 2-nitrodiphenyl ether gives 4-iodo-2'-nitrodiphenyl ether, m. p. 86° (*dichloride*, m. p. 96°), reduced to 4-iodo-2'-aminodiphenyl ether (*hydrochloride*, m. p. 219°; *acetyl derivative*, m. p. 115°; *diacetyl derivative*, m. p. 94°). A. A. LEVI.

**Substitution in resorcinol derivatives. Bromo-derivatives from  $\beta$ -resorcyraldehyde and their orientation.** M. S. IYENGAR and H. S. JOIS (Mysore Univ. J., 1930, 4, 199—201).—Treatment of 5-nitro-2:4-dimethoxy-benzaldehyde or -benzoic acid with bromine in acetic acid containing a little iodine gives 6-bromo-4-nitroresorcinol dimethyl ether, m. p. 140—141°. 4-Bromo-6-nitroresorcinol 1-methyl 3-ethyl ether, m. p. 119—121°, is obtained similarly from 5-nitro-4-methoxy-2-ethoxy-benzaldehyde or -benzoic acid. H. BURTON.

**Oxidation of  $\beta$ -dinaphthol.** A. RIECHE and K. JUNGHOLT (Ber., 1931, 64, [B], 578—589).— $\beta$ -Dinaphthol (25 g.) in aqueous alkaline solution is oxidised by potassium ferricyanide (90 g.) at 70—80° within 30 min. to the *hydroxydinaphthylene oxide ester* of 1:2-benzoxanthone-8-acrylic acid (I), m. p. 248° (also +C<sub>6</sub>H<sub>6</sub> and +C<sub>6</sub>H<sub>5</sub>Cl), hydrolysed by concentrated, aqueous alcoholic potassium hydroxide to



hydroxydinaphthylene oxide and 1:2-benzoxanthone-8-acrylic acid, m. p. 256° (decomp.) (*sodium salt*). The acid may also be prepared directly by the oxidation

of  $\beta$ -dinaphthol with potassium ferricyanide or potassium permanganate; it affords an unstable tetrabromo-compound and adds 2 mols. of iodine chloride. It is oxidised by alkaline permanganate to 1:2-benzoxanthone-8-carboxylic acid, m. p. 263—264° (*sodium salt*), also prepared by the oxidation of  $\beta$ -dinaphthol in alkaline solution with potassium permanganate. It is prepared synthetically by condensing tetrachlorophthalic anhydride with  $\beta$ -naphthol in presence of *s*-tetrachloroethane and aluminium chloride to 3:4:5:6-tetrachloro-2-2'-hydroxy-1'-naphthoylbenzoic acid, which under the influence of alkali passes into 5:6:7-trichloro-1:2-benzoxanthone-8-carboxylic acid, m. p. 297° (also +AcOH, m. p. 301°), catalytically reduced in presence of palladised calcium carbonate to 1:2-benzoxanthone-8-carboxylic acid. Alternatively, tetrachlorophthalic anhydride and  $\beta$ -naphthyl methyl ether are condensed to 3:4:5:6-tetrachloro-2-2'-methoxy-1'-naphthoylbenzoic acid, m. p. 204° and m. p. 222° after re-solidification, reduced to 1:2-benzoxanthone-8-carboxylic acid. H. WREN.

**Synthesis of ethylpyrogallol.** F. MAUTHNER (J. pr. Chem., 1931, [ii], 129, 281—284).—Reduction of trimethylgallacetophenone (A., 1910, i, 680) by Clemmensen's method affords 3:4:5-trimethoxyethylbenzene, b. p. 149°/12 mm., hydrolysed by boiling hydriodic acid (*d* 1.96) to 3:4:5-trihydroxyethylbenzene, m. p. 86—87°. Reduction of 3:4:5-trimethoxybenzoyl chloride (prepared from the acid) with hydrogen and palladised barium sulphate in toluene affords 3:4:5-trimethoxybenzaldehyde (Späth, A., 1919, i, 548), which by treatment with amalgamated zinc and hydrochloric acid gives only resinous products. J. W. BAKER.

**$\beta$ -2:4:5-Trimethoxyphenylethylamine, an isomeride of mescaline.** M. P. J. M. JANSEN (Rec. trav. chim., 1931, 50, 291—312).—An account of syntheses of substances related to mescaline, with which  $\beta$ -2:4:5-trimethoxyphenylethylamine (I) is similar in pharmacological action. *p*-Methoxyphenylpropionhydrazide, m. p. 129° (*anisylidene derivative*, m. p. 134.5°), is converted through the azide into methyl and ethyl  $\beta$ -*p*-methoxyphenylethylcarbamate, m. p. 63—64° and 49.5°, respectively, and *s*-di- $\beta$ -*p*-methoxyphenylethylcarbamide, m. p. 162°. Hydrolysis of the last two compounds gives  $\beta$ -*p*-methoxyphenylethylamine. Asarone on ozonolysis to asaraldehyde (2:4:5-trimethoxybenzaldehyde) (II) gives as by-product 2:5-dimethoxybenzoquinone. Reduction of 2:4:5-trimethoxycinnamic acid with sodium amalgam gives 2:4:5-trimethoxyphenylpropionic acid, m. p. 98° (*methyl ester*, m. p. 52°, b. p. 325—327°), the corresponding hydrazide, m. p. 114° (*anisylidene derivative*, m. p. 153.5°), being converted by the Curtius reaction into ethyl  $\beta$ -2:4:5-trimethoxyphenylethylcarbamate, m. p. 63—64° (and a by-product, m. p. 180°, *s*-di-2:4:5-trimethoxyphenylethylcarbamide), hydrolysed by concentrated hydrochloric acid to I, which was also obtained from  $\beta$ -2:4:5-trimethoxyphenylpropionamide, m. p. 130°, by the Hofmann reaction. Asaraldehyde condenses with nitromethane to 2:4:5-trimethoxy- $\omega$ -nitrostyrene, m. p. 127—128° (red and yellow forms), which is re-

duced chemically or electrolytically to I. I was also obtained by decarboxylation of 2:4:5-trimethoxyphenylalanine, m. p. 226° (decomp.) [lit. 217° (decomp.)], obtained from 2:4:5-trimethoxybenzylidenehydantoin, m. p. 274—276 (lit. 274°), through 2:4:5-trimethoxybenzylhydantoin.

J. D. A. JOHNSON.

[Action of aminoacetal on pyrogallolsulphonic acid.] O. HINSBERG and R. MAYER (Ber., 1931, 64, [B], 702).—The compound obtained from pyrogallolsulphonic acid and aminoacetal (A., 1927, 1071) has the composition  $C_6H_4 \begin{matrix} \text{SO}_2 \cdot O \\ \text{---} \\ \text{CH} \cdot \text{CH}_2 \cdot \text{NH}_2 \end{matrix}$

H. WREN.

**Ready methylation of alcoholic hydroxyls.** K. VON AUWERS (Ber., 1931, 64, [B], 533—534).—Readiness of etherification is shown, not only by benzyl alcohol (cf. von Braun and others, this vol., 85), but also by benzhydrol, triphenylcarbinol, and hydroxybenzyl alcohols containing several bromine atoms or methyl groups in the molecule. Since the halogen atom in the corresponding halides is unusually reactive, it follows that the union of the halogen atom or hydroxyl group with the hydrocarbon residue is feeble and that etherification is represented by the scheme:  $R \cdot \text{CH}_2 \cdots \text{OH} + \text{HOR}' = R \cdot \text{CH}_2 \cdots \text{OR}' + \text{H}_2\text{O}$ . In von Braun's experiments, methyl sulphate is regarded as becoming partly hydrolysed; in the presence of the alkali hydroxide, the methyl alcohol etherifies the benzyl alcohol.

H. WREN.

**p-Tolylallylcarbinol.** A. KARTASCHEV (J. Russ. Phys. Chem. Soc., 1930, 62, 1883—1884).—p-Tolylallylcarbinol, synthesised by the Grignard reaction, using allyl iodide and p-tolylaldehyde, has b. p. 236—242° (decomp.), 194°/160 mm., 149—150°/42 mm.  $d_{20}^{25}$  0.99071. Attempts to synthesise phenylallylcarbinol using benzaldehyde and allyl iodide were unsuccessful. Apart from benzaldehyde, aldehydes and ketones gave satisfactory results.

E. B. UVAROV.

**Propargyl ethers of phenol.** C. D. HURD and F. L. COHEN (J. Amer. Chem. Soc., 1931, 53, 1068—1077).—Phenyl phenylethynyl ketone, m. p. 65—66° (Nef, A., 1900, i, 20, gives m. p. 53—55°), is also prepared from phenylpropiolyl chloride by conversion into ethyl phenylpropiolate and treatment of this with 1 mol. of magnesium phenyl bromide. Triphenylpropargyl alcohol is best prepared by Nef's method (*loc. cit.*), but the yield may be increased to 65—70% by careful purification of the initial reaction materials. Methylacetylene reacts with magnesium ethyl bromide in ether to give ethane and magnesium methylethynyl bromide which, with acetone, affords trimethylpropargyl alcohol ( $\beta$ -methyl- $\Delta^{\gamma}$ -pentinen- $\beta$ -ol), b. p. 75—77°/15 mm.,  $n_D^{20}$  1.4193, in 47% yield, together with some of its dehydration product  $\beta$ -methyl- $\Delta^{\beta}$ -penten- $\Delta^{\gamma}$ -inene  $\text{CH}_2 \cdot \text{CMe} \cdot \text{C} \cdot \text{CMe}$ , b. p. 75—77°,  $n_D^{20}$  1.4002.  $\gamma$ -Methylpropargyl alcohol, b. p. 137—140°,  $n_D^{20}$  1.4497, was obtained by Yvon's method (A., 1925, i, 514). 1-Phenylethynylcyclohexan-1-ol, b. p. 166—169°/14 mm., m. p. 58—60°, is obtained by the action of sodium phenylacetylde on cyclohexanone and hydrolysis of the product with dilute hydrochloric acid, whilst  $\alpha$ - $\gamma$ -diphenyl- $\alpha$ -(p-dimethylamino-

phenyl)propargyl alcohol, m. p. 144—145°, is similarly obtained from p-dimethylaminobenzophenone. Three of these alcohols are converted into their chlorides by the action of phosphorus trichloride in ether or benzene and thus are obtained: triphenyl-, trimethyl- ( $\beta$ -chloro- $\beta$ -methyl- $\Delta^{\gamma}$ -pentinene), b. p. 57—61°/47 mm.,  $n_D^{20}$  1.4143, and  $\gamma$ -methyl- ( $\alpha$ -chloro- $\Delta^{\beta}$ -butinene), b. p. 81—84°, -propargyl chloride. These are converted either by the action of sodium phenoxide or by refluxing with phenol and potassium carbonate in acetone into the corresponding ethers and thus are prepared: phenyl triphenyl-, m. p. 90—90.5°, trimethyl-,  $n_D^{20}$  1.3408, and  $\gamma$ -methyl-, b. p. 123—126°/25 mm.,  $n_D^{20}$  1.3894, -propargyl ether. Pyrolysis of the triphenylpropargyl ether at 310° affords phenol and

9-phenylethynylfluorene  $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > \text{CH} \cdot \text{C} \cdot \text{CPh}$ , m. p. 98—100°, identical with a specimen synthesised either by the action of sodium phenylacetylde on 9-chlorofluorene, or by interaction of 9-hydroxyfluorene and phenylacetylene in the presence of concentrated sulphuric acid in dry ether at 5—10°. Decomposition of the trimethylpropargyl ether occurs at 160°, giving  $\beta$ -methyl- $\Delta^{\beta}$ -penten- $\Delta^{\gamma}$ -inene (above), phenol, and much tarry material. Decomposition of the  $\gamma$ -methylpropargyl ether at 215—220° affords mainly a tarry product, probably a trimeride, and only a trace of phenol. J. W. BAKER.

**Combinations among certain dye radicals.** M. REBEK (Coll. Czech. Chem. Comm., 1931, 3, 155—170).—The interactions of 2:4:2':4':2'':4''-hexanitrotriphenylmethane and 2:4:6:2':4':6'-hexanitrodiphenylamine with the base of crystal-violet in acetone and nitrobenzene solutions, of piperidine with hexanitrotriphenylmethane, and of p-nitrodiphenylamine with the base of crystal-violet in acetone have been followed by conductivity measurements. The compounds hexanitrotriphenylmethane—crystal-violet base+3 mols. acetone and hexanitrodiphenylamine—crystal-violet base+1 mol. acetone, which are considered to be true dye salts, were isolated. These compounds (free from acetone) exhibited identical absorption spectra in the yellow and green.

J. D. A. JOHNSON.

**Occurrence of  $\alpha$ -dihydroergosterol as an impurity in yeast-ergosterol.** R. K. CALLOW (Biochem. J., 1931, 25, 87—94).— $\alpha$ -Dihydroergosterol has been isolated by fractionation of the benzoates from yeast-ergosterol followed by a process of partial bromination which destroys the ergosterol preferentially. It has been identified and characterised by the preparation of derivatives. On irradiation by an unscreened quartz mercury lamp it does not acquire antirachitic properties. The benzoates of ergosterol and  $\alpha$ -dihydroergosterol, as well as the free sterols, form mixed crystals with properties similar to those of neosteryl benzoate and neosterol, respectively (cf. Wieland and Asano, A., 1929, 1200). Details for the colorimetric determination of ergosterol with trichloroacetic acid are given (cf. Rosenheim, A., 1929, 359). S. S. ZILVA.

**Purification of ergosterol.** R. K. CALLOW (Biochem. J., 1931, 25, 79—86).—Distillation of ergosterol and recrystallisation of ethyl ergosteryl



carbonate are unsatisfactory methods for purifying ergosterol, and recrystallisation from alcohol-benzene (2 : 1) does not invariably yield a pure product. A high degree of purity is, however, attained by benzoylation of ergosterol, recrystallisation of the benzoate, which is trimorphic, from ethyl acetate at 37°, and hydrolysis. There is no variation in the properties of purified yeast-ergosterol from different sources and no evidence of the existence of natural isomerides (cf. Bills and Cox, A., 1930, 84, 1286). When ergosterol is kept over a dehydrating agent in air it takes up five atoms of oxygen. This oxidation is rapid with distilled material but also takes place with recrystallised hydrated material after an induction period.

S. S. ZILVA.

**Constitution of cholesterol. XIV. Cholesterylbenzoin.** E. MONTIGNIE (Bull. Soc. chim., 1931, [iv], 49, 274—275).—When cholesterol is heated with benzoin in chloroform at 50° in presence of hydrogen chloride *O*-cholesterylbenzoin, m. p. 117° (bromide, m. p. 96—97°; phenylhydrazone, m. p. 104°; oxime, m. p. 125°; semicarbazone, m. p. 143°), is obtained, converted by boiling with alcoholic potassium hydroxide into cholesterol, potassium benzoate, and benzyl alcohol, and by nitric acid into benzil and nitrocholesterol. Reduction in alcohol with zinc and hydrogen chloride affords cholesterol and deoxybenzoin.

R. BRIGHTMAN.

**Nitration of benzoic acid in magnetic and in electrostatic fields.** R. H. CLARK and R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 121—124).—No change outside experimental error was found in the proportion of mononitrobenzoic acids obtained by nitration of benzoic acid when the nitration was carried out in a magnetic or in an electrostatic field.

W. GOOD.

**Detonation of benzoyl peroxide.** S. S. NAMETKIN and L. S. KITCHKINA (J. Russ. Phys. Chem. Soc., 1930, 62, 2193—2194).—A case of spontaneous detonation of benzoyl peroxide is reported.

E. B. UVAROV.

**Preparation of *N*-*o*-chlorobenzoyl-*o*-chlorobenzenesulphonamide.** R. WERTHEIM (J. Amer. Chem. Soc., 1931, 53, 1172—1173).—This compound, m. p. 154—155°, is obtained by the action of *o*-chlorobenzoyl chloride on *o*-chlorobenzenesulphonamide at 180—190°.

J. W. BAKER.

**Optical activity of derivatives of anthracene.** H. GOUDET (Helv. Chim. Acta, 1931, 14, 379—396).—Armstrong's formula (Proc. C.S., 1890, 101) for anthracene is preferred to the usual bridged representation of Graebe and Liebermann, since it offers a better explanation of the known properties of anthracene derivatives. If the bridged formula is correct,  $\alpha$ - and  $\beta$ -substituted anthracenes should exist in optically active forms. The preparation of inactive 9(or 10)-benzylanthracene-2-carboxylic acids from active benzyloxanthrone-2-carboxylic acids is considered to be evidence against the Graebe and Liebermann formula.

Anthraquinone-2-carboxylic acid is reduced with sodium hyposulphite in ammonium carbonate solution in a current of carbon dioxide, and the resultant solution treated with benzyl chloride and sodium

hydroxide, whereby two benzyloxanthrone-2-carboxylic acids, (a) m. p. 227° and (b) m. p. 210°, are obtained; these are separable owing to their differing solubilities in benzene. These acids are resolved by brucine into the corresponding *l*-acids, (a)  $[\alpha]_D^{20} - 71.5^\circ$  in alcohol (brucine salt, m. p. 176°,  $[\alpha]_D^{20} - 42.8^\circ$  in chloroform) and (b)  $[\alpha]_D^{20} - 81^\circ$  in alcohol (brucine salt, m. p. 219°,  $[\alpha]_D^{20} - 74.8^\circ$  in chloroform), which when reduced with zinc dust and ammonia afford optically inactive benzyloxanthrone-2-carboxylic acids, (a) m. p. 264° and (b) m. p. 238°. Intermediate benzyloxanthranol-carboxylic acids could not be isolated. The possibility of racemisation occurring through the use of an alkaline reducing agent is noted.

Reduction of sodium anthraquinone-2-sulphonate with aqueous sodium hyposulphite and treatment of the product with ethyl bromide, sodium hydroxide, and a small amount of iodine gives sodium 9 : 10-diethoxyanthracene-2-sulphonate. Anthrahydroquinone-2-carboxylic acid is converted by ethyl bromide and potassium hydroxide solution into a mixture of 9 : 10-diethoxyanthracene-2-carboxylic acid, m. p. 180°, and ethyloxanthrone-2-carboxylic acid, m. p. 210° (benzoyl derivative, m. p. 355°). The last-named acid is reduced by zinc and ammonia to 9(or 10)-ethylanthracene-2-carboxylic acid, m. p. 187°.

H. BURTON.

**Asymmetric syntheses. IX. Preparation of optically active substituted glycollic acids from *l*-menthyl and *l*-bornyl  $\alpha$ -naphthoylformates.** A. MCKENZIE and P. D. RITCHIE (Biochem. Z., 1931, 231, 412—422).—*l*-Menthyl  $\alpha$ -naphthoylformate, m. p. 88.5—89°,  $[\alpha]_D^{25} - 23.8^\circ$  in ethyl alcohol, prepared by passing hydrogen chloride through a hot mixture of  $\alpha$ -naphthoylformamide and menthol, undergoes mutarotation in propyl and isobutyl alcohols provided that mineral acids are absent, equilibrium being reached in 12—14 hrs. When magnesium phenyl bromide acts on the ester a mixture of the *l*-menthyl esters of *d*- and *l*-phenyl- $\alpha$ -naphthylglycollic acids is formed. This mixture contains more of the second acid than of the first and hence on hydrolysis yields *l*-phenyl- $\alpha$ -naphthylglycollic acid. *l*-Methyl- and -ethyl- $\alpha$ -naphthylglycollic acids can be prepared in a similar way. From  $\alpha$ -naphthoylformamide and *l*-borneol, *l*-bornyl  $\alpha$ -naphthoylformate, m. p. 69.5—70.5°,  $[\alpha]_D^{20} - 23^\circ$  in benzene, is prepared and from this ester, which likewise undergoes mutarotation in ethyl alcohol, *l*-methyl- $\alpha$ -naphthylglycollic acid is obtained by Grignard synthesis.

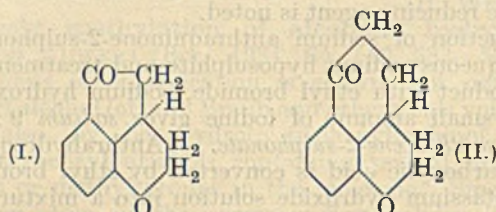
W. MCCARTNEY.

**Action of hydroxylamine on ethyl phthalimide-*N*-carboxylate.** N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, 62, 2203—2208).—The action of potassium phthalimide on ethyl chlorformate gives ethyl phthalimide-*N*-carboxylate, m. p. 86°, which reacts with hydroxylamine giving phthaloylhydroxylamine, m. p. 230° (potassium salt; silver salt; ethyl, m. p. 103°, and acetyl derivative, m. p. 181°).

E. B. UVAROV.

**Attempted synthesis of a tricyclic system present in morphine.** R. H. MANSKE (J. Amer. Chem. Soc., 1931, 53, 1104—1111).—Ethyl phenylsuccinate (improved details for preparation given) is reduced by sodium and alcohol to  $\beta$ -phenylbutane- $\alpha$ -*d*-

diol, b. p. 165°/4 mm. (*bisphenylurethane*, m. p. 113°), converted by dry hydrogen bromide in acetic anhydride into  $\alpha\delta$ -*dibromo- $\beta$ -phenylbutane*, b. p. 173—175°/16 mm. This with aqueous-alcoholic sodium cyanide affords the dinitrile, b. p. 190—200°/4 mm., hydrolysed without purification to  $\beta$ -*phenylglutamic acid*, m. p. 146°. This with phosphorus pentachloride gives the acid chloride, which with aluminium chloride in carbon disulphide affords 1-*keto-1:2:3:4-tetrahydronaphthalene-4-acetic acid* (not obtained pure but probably contaminated with the isomeric keto-acid), together with 4:9-*diketo-1:2:3:4-tetrahydroacenaphthene* (I), m. p. 149°. Similarly, ethyl



$\beta$ -phenylglutarate is converted successively into  $\gamma$ -*phenylpentane- $\alpha$ -diol*, b. p. 174°/4 mm. (*bisphenylurethane*, m. p. 112—113°),  $\alpha\epsilon$ -*dibromo- $\gamma$ -phenylpentane*, b. p. 177—182°/16 mm. (converted by aqueous-alcoholic sodium phenoxide into  $\alpha\epsilon$ -*diphenoxy- $\gamma$ -phenylpentane*, m. p. 72°), the dinitrile, b. p. 200—215°/4 mm., and  $\gamma$ -*phenylpimelic acid*, m. p. 83—84°. This is similarly converted into  $\beta$ -(1-*keto-1:2:3:4-tetrahydronaphthyl-4*-)*propionic acid*, m. p. 108—109° (*methyl ester*), together with the tricyclic *dione* (II), m. p. 111° [*dioxime*, m. p. 253—254° (decomp.)].  $\beta$ -Phenylglutaric acid is converted by treatment through the (isolated) acid chloride into  $\alpha$ -*hydrindone-3-acetic acid*, m. p. 155° (*methyl ester*, m. p. 54°, b. p. 175—180°/18 mm.). Ethyl  $\delta$ -phenoxyvalerate is reduced by sodium and alcohol to  $\epsilon$ -phenoxyamyl alcohol (75% yield), whilst similar reduction of a specimen of ethyl  $\gamma$ -phenoxybutyrate which contained  $\gamma$ -phenoxybutyronitrile gave  $\delta$ -phenoxybutylamine and  $\gamma$ -*phenoxybutyr- $\delta$ -phenoxybutylamide*,  $\text{CH}_2(\text{OPh})\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{OPh}$ , m. p. 94—95°. All m. p. are corrected. J. W. BAKER.

**Condensation of aromatic aldehydes with phenylacetone nitrile.** (MISS) T. DE KIEWIET and H. STEPHEN (J.C.S., 1931, 639—640; cf. A., 1889, 597).—Condensation of hydroxy- and methoxybenzaldehydes with phenylacetone nitrile in presence of sodium ethoxide or alkali gives derivatives of cinnamone nitrile (except *o*-hydroxyaldehydes, which give coumarins) (cf. A., 1904, i, 893). The following are described; 2:4-*dimethoxy*, m. p. 95°; 3:4-*dimethoxy*, m. p. 88°; 4-*hydroxy-2-methoxy*, m. p. 195°; 2-*methoxy-4-acetoxy*, m. p. 158°, and 4-*hydroxy-2-methoxy- $\alpha$ -phenylcinnamone nitrile*, m. p. 99°; 8-*methoxy-3-phenylcoumarin*, m. p. 155.5°. A. A. LEVI.

**cycloPropene series. I. Diphenylcyclopropenedicarboxylic acid.** S. F. DARLING and E. W. SPANAGEL (J. Amer. Chem. Soc., 1931, 53, 1117—1120).—Methyl  $\gamma$ -nitro- $\alpha\gamma$ -diphenylethylmalonate (Kohler and Barrett, A., 1926, 849) is converted by sodium methoxide and bromine in methyl alcohol into the corresponding  $\alpha$ -*bromomalonate*, m. p. 117—

118°, converted by heating with methyl-alcoholic potassium acetate into *methyl 2-nitro-2:3-diphenylcyclopropane-1:1-dicarboxylate*, m. p. 129°. This is converted, with loss of nitrous acid, by boiling with methyl-alcoholic sodium methoxide into *methyl 2:3-diphenyl- $\Delta^2$ -cyclopropene-1:1-dicarboxylate*, m. p. 140—142° (cf. Kohler and Darling, A., 1930, 933), the structure of which is proved by oxidation of the corresponding dicarboxylic acid, m. p. about 190° (decomp.; see below), with alkaline potassium permanganate, dibenzoylmethane being formed. The cyclopropene acid is converted by bromine in carbon tetrachloride into 2:3-*dibromo-2:3-diphenylcyclopropane-1:1-dicarboxylic acid*, m. p. 194—195° (decomp.), and when heated above its m. p. it is converted not into the corresponding monobasic acid but into the lactone, m. p. 149—151°, of 3-*hydroxy-2:3-diphenylcyclopropanecarboxylic acid*, m. p. 146—148°, which is obtained by hydrolysis of the lactone with aqueous methyl-alcoholic potassium hydroxide, and is only slightly attacked by ozone. No benzoin, which would result from ozonolysis of the other possible structure for the lactone,  $\begin{matrix} \text{CPh}\cdot\text{CHPh} \\ \text{CH}\text{---CO} \end{matrix} > \text{O}$ , could be detected. J. W. BAKER.

**Action of cyanoacetic acid on triphenylcarbinol. Syntheses of  $\alpha$ -cyano- $\beta\beta\beta$ -triphenylpropionic and *N*-triphenylmethylmalonamic acids.** R. FOSSE (Bull. Soc. chim., 1931, [iv], 49, 159—173; cf. A., 1907, i, 764).—The "isomeric" substance, B, m. p. 175° (decomp.), obtained with  $\alpha$ -cyano- $\beta\beta\beta$ -triphenylpropionic acid, m. p. 155° (decomp.), when triphenylcarbinol is heated with cyanoacetic acid is now shown to be *N*-triphenylmethylmalonamic acid, since on fusion at 220° it is converted into acet-triphenylmethylamide, m. p. 211°, also obtained from triphenylcarbinol and acetamide at 210—240°, and hydrolysed by 90% sulphuric acid to triphenylcarbinol, ammonia, and acetic acid. The structure of  $\alpha$ -cyano- $\beta\beta\beta$ -triphenylpropionic acid is confirmed by its conversion at 160—170° into  $\alpha$ -cyano- $\beta\beta\beta$ -triphenylethane, m. p. 140° (also obtained by heating triphenylcarbinol and cyanoacetic acid at 110—115°), hydrolysed to  $\beta\beta\beta$ -triphenylpropionic acid, m. p. 178—179° (*silver salt*). R. BRIGHTMAN.

**Action of hydrogen peroxide on 6:7-benz-2:3-diketo-2:3-dihydrothionaphthen in sodium hydroxide solution.** R. STOLLÉ and W. BADSTÜBNER (J. pr. Chem., 1931, [ii], 129, 309—311).—This compound (A., 1925, i, 1146) is converted by 3% hydrogen peroxide in sodium hydroxide solution into 1:1'-*dinaphthyl disulphide-2:2'-dicarboxylic acid*, m. p. 156°. With alkali this titrates normally as a dibasic acid, but with excess of alkali the reaction is:  $2[\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})\cdot\text{S}]_2 + 8\text{KOH} = \text{C}_{10}\text{H}_6(\text{CO}_2\text{K})\cdot\text{SO}_2\text{K} + 3\text{C}_{10}\text{H}_6(\text{CO}_2\text{K})\cdot\text{SK} + 6\text{H}_2\text{O}$ . J. W. BAKER.

**Syntheses in the cyclobutanol series. L. BLANCHARD** (Bull. Soc. chim., 1931, [iv], 49, 279—309).—When *s*-dibromohydrin or chlorobromohydrin is first converted into ethers, the condensation with ethyl sodiomalonate yields cyclobutane derivatives without difficulty, formation of ethylene oxides being avoided. Thus,  $\alpha\gamma$ -dibromo- $\beta$ -amyloxypropane, obtained from magnesium butyl bromide and chloro-

methyl  $\alpha$ -dibromopropyl ether, yields 45—50% of ethyl 3-amyloxy-cyclobutane-1:1-dicarboxylate, b. p. 175/12 mm.,  $d^{15}$  1.011,  $n_D$  1.44361 (free acid; copper salt, +H<sub>2</sub>O; chloride, b. p. 143—145°/15 mm.; amide, m. p. 177.5°; amide, m. p. 175°). The chloride condenses with carbamide to give amyloxy-cyclobutanespirobarbituric acid, m. p. 222—223°,

$C_5H_{11}O \cdot CH \left\langle \begin{array}{c} CH_2 \\ CH_2 \end{array} \right\rangle C \left\langle \begin{array}{c} CO \cdot NH \\ CO \cdot NH \end{array} \right\rangle CO$ . At 120°, 3-amyloxy-cyclobutane-1:1-dicarboxylic acid is converted into 3-amyloxy-cyclobutane-1-carboxylic acid, b. p. 164—166°/10 mm.,  $d$  1.003,  $n_D$  1.45412 (silver salt; amide, m. p. 131—132°; chloride, b. p. 100—120°/14 mm.). The corresponding methoxyhalogenopropanes are less suitable for the condensation owing to the proximity of their b. p. to that of the corresponding alcohol. Purification of ethyl 3-methoxy-cyclobutane-1:1-dicarboxylate, b. p. 130°/10 mm.,  $d^{13}$  1.076,  $n_D$  1.441, obtained from  $\alpha$ -chloro- $\gamma$ -bromo- $\beta$ -methoxypropane, is difficult owing to the presence of the formal,  $CH_2Cl \cdot CH(OMe) \cdot CH_2 \cdot CH(CO_2Et)_2$ , b. p. 157°/13 mm.  $\alpha$ -Chloro- $\gamma$ -bromo- $\beta$ -amyloxypropane and ethyl sodiomalonate yield ethyl 3-amyloxy-methoxy-cyclobutane-1:1-dicarboxylate, b. p. 190—195°/18 mm.,  $d^{14}$  1.04,  $n_D$  1.44481, together with a residue, b. p. 210—240°/18 mm. The corresponding acid and its copper salt are described. Acid hydrolysis converts the acid into amyl alcohol, amyl formal, b. p. 250°,  $d^{15}$  0.843, and 3-hydroxy-cyclobutane-1:1-dicarboxylic acid, m. p. 125° (barium salt, +3H<sub>2</sub>O). The amyl and methyl ethers of this acid and the amyl ether of ethyl 3-hydroxy-1-cyanocyclobutane-1-carboxylic acid show an abnormal molecular refraction attributed to the double linking, e.g.,  $>C=C=O$ , in conjunction with the cyclobutane ring.

Treatment of chloromethyl  $\alpha$ - $\gamma$ -dibromoisopropyl ether with methyl alcohol yields methyl chloromethyl ether and  $\alpha$ - $\gamma$ -dibromohydrin, the methoxymethyl ether first formed being decomposed by the hydrogen chloride liberated. Addition of chloromethyl amyl ether to epichlorohydrin yields the same formal as that obtained by the action of magnesium ethyl bromide on  $\alpha$ - $\gamma$ -dichlorohydrin, to form the intermediate  $(CH_2Cl)_2 \cdot CH \cdot OMgBr$ , followed by reaction with chloromethyl amyl ether, and accordingly in the former case opening of the oxide ring must occur thus:  $CH_2Cl \cdot CH \cdot CH_2$ . The following formals have

been prepared by this method: methoxymethyl  $\alpha$ -dichloroisopropyl ether, b. p. 80—81°/11 mm.,  $d^{18}$  1.237,  $n$  1.45412; ethoxymethyl  $\alpha$ -dichloroisopropyl ether, b. p. 90—91°/12 mm.,  $d^{17}$  1.182,  $n$  1.44912, and amyloxy-methyl  $\alpha$ -dichloroisopropyl ether, b. p. 133—135°/19 mm.,  $d^{18}$  1.09,  $n$  1.4506. The chloromethyl methyl ether, b. p. 60°, and ethyl ether, b. p. 80°, are not readily obtained pure; chloromethyl amyl ether, b. p. 150°, 50—55°/18 mm., is obtained in 87% yield by saturating amyl alcohol with hydrogen chloride and adding trioxymethylene. Ethoxymethyl  $\alpha$ -chloro- $\gamma$ -bromoisopropyl ether, b. p. 110—112°/20 mm.,  $d^{22}$  1.409,  $n$  1.46954 (from bromomethyl ethyl ether, b. p. 107°), amyloxy-methyl  $\alpha$ -chloro- $\gamma$ -bromoisopropyl ether, b. p. 142—144°/20 mm.,  $d^{13}$  1.277,  $n$  1.46856, and ethoxymethyl  $\alpha$ -chloro- $\gamma$ -iodoisopropyl ether, b. p. 124—125°/18 mm.,  $d^{18}$  1.6528,  $n$  1.50882 (from iodomethyl

ethyl ether, b. p. 70°/70 mm.), are similarly obtained. Methoxymethyl  $\alpha$ -chloro- $\gamma$ -amyloxyisopropyl ether, b. p. 118°/12 mm.,  $d^{15}$  1.01,  $n$  1.43587, is obtained from epiamyline and methyl chloromethyl ether.

When a mixed formal, e.g., amyloxy-methyl  $\alpha$ -chloro- $\gamma$ -bromoisopropyl ether, is heated at 170°, a mixture of the symmetrical formals, amyloxy, and  $\alpha$ -chloro- $\gamma$ -bromoisopropyl formal is obtained. Chloromethyl ethers and the corresponding alcohol also give a symmetrical formal if the hydrochloric acid formed is eliminated with a sparingly soluble hydroxide, e.g., magnesium hydroxide. The following have been obtained thus from the corresponding hydrins: methylene bis- $\alpha$ -dichloroisopropyl ether, m. p. 51°; methylene bis- $\alpha$ -chloro- $\gamma$ -bromoisopropyl ether, m. p. 54—55°; methylene bis- $\alpha$ -chloro- $\gamma$ -iodoisopropyl ether, m. p. 60°; methylene bis- $\alpha$ - $\gamma$ -dibromoisopropyl ether, m. p. 68—69°. Methyl  $\alpha$ -chloro- $\gamma$ -bromoisopropyl ether condenses with ethyl sodiomalonate giving ethyl  $\delta$ -chloro- $\gamma$ -methoxybutanedicarboxylate, b. p. 157°/13 mm.,  $d^{13}$  1.135,  $n_D$  1.44682, in 30% yield. In presence of iodine the ester yields on bromination 70% of ethyl  $\delta$ -chloro- $\alpha$ -bromo- $\gamma$ -methoxybutanedicarboxylate, b. p. 178—180°/13 mm.,  $d^{15}$  1.393,  $n_D$  1.47544. Attempts to prepare the  $\delta$ -chloro- $\gamma$ -hydroxy-ester failed, but hydrolysis with 50% hydrochloric acid yields  $\delta$ -chloro- $\gamma$ -methoxybutanedicarboxylic acid (barium salt).

R. BRIGHTMAN.

Use of tetramethylene dibromide in synthetic formation of closed carbon chains. L. J. GOLDSWORTHY (J.C.S., 1931, 482—486).—Treatment of tetramethylene dibromide (improved preparation) with ethyl sodiomalonate gives ethyl cyclopentane-1:1-dicarboxylate. With ethyl sodioethanetetracarboxylate, ethyl cyclohexane-1:1:2:2-tetracarboxylate is obtained, converted by heat into *cis*- and *trans*-hexahydrophthalic acid. The products of the action of tetramethylene dibromide on ethyl sodiopropantetracarboxylate are ethyl cyclopentane-1:1-dicarboxylate and the polymeride of ethyl methylenemalonate.

A. A. LEVI.

Synthesis of *m*-glucosidoxybenzaldehyde. F. MAUTHNER (J. pr. Chem., 1931, [ii], 129, 278—280).—*m*-Tetra-acetylglucosidoxybenzaldehyde (best prepared by the action of tetra-acetylglucosidyl bromide on *m*-hydroxybenzaldehyde in acetone with addition of 9% aqueous sodium hydroxide below 16°) is readily hydrolysed to *m*-glucosidoxybenzaldehyde, m. p. 160—161°, by 2.5% aqueous ammonia in the cold, although unsatisfactory results are obtained with barium hydroxide. It is not identical with picrin (A., 1914, i, 195).

J. W. BAKER.

New *p*-bromophenacyl esters. S. G. POWELL (J. Amer. Chem. Soc., 1931, 53, 1172).—By Reid and Judefind's method (A., 1920, i, 480) are obtained *p*-bromophenacyl  $\alpha$ -dimethylpropionate, m. p. 76.5°, isohexoate, m. p. 77.3°, *n*-, m. p. 69.2°, and iso-, m. p. 75.5°, heptoate, and *n*-nonoate, m. p. 63.5°.

J. W. BAKER.

Oximes of  $\alpha\beta$ -unsaturated ketones and the Beckmann rearrangement. A. H. BLATT (J. Amer. Chem. Soc., 1931, 53, 1133—1141).—The stable oxime of benzylideneacetophenone, obtained from the ketone by the action of hydroxylamine in the presence of alkali, is not the *anti*-oxime as stated

by Henrich (A., 1911, i, 650), but is 3:5-diphenylisooxazoline,  $\text{CH}_2 \begin{matrix} \text{CPh} \\ \text{N} \\ \text{CHPh} \end{matrix} \text{O}$ , since it gives no methane with magnesium methyl iodide. The following evidence shows that the labile oxime of benzylideneacetophenone (and of the  $\alpha\beta$ -unsaturated ketones studied) is not the *syn*-form as suggested by Henrich (*loc. cit.*), but is the *anti*-form, the Beckmann rearrangement to cinnamanilide involving a *trans*-migration. Benzylidene-*o*-chloroacetophenone is converted by hydroxylamine hydrochloride in boiling aqueous alcohol into its *anti*-oxime, m. p. 110—124° even when carefully purified, converted by a Beckmann change into cinnam-*o*-chloroanilide, m. p. 136—137°, but unchanged by prolonged heating with alcoholic potassium hydroxide which would be expected to convert it into a benzisooxazole if it possessed the *syn*-configuration. Similarly benzylidene-*p*-bromoacetophenone affords its *anti*-oxime, m. p. 138—150° (cf. above), not converted into the isooxazoline with alcoholic potassium hydroxide, giving cinnam-*p*-bromoanilide, m. p. 191°, by a Beckmann rearrangement, and converted by bromine in chloroform into a dibromide, m. p. 155° (decomp.). This is converted, with loss of hydrogen bromide, either by alcoholic alkali or by heating either alone or in acetic acid into 3-*p*-bromophenyl-5-phenylisooxazole,  $\text{CH} \begin{matrix} \text{C}(\text{C}_6\text{H}_4\text{Br})\text{N} \\ \text{CPh} \end{matrix} \text{O}$ , m. p. 178—179°, identical with a specimen prepared by the action of alcoholic hydroxylamine hydrochloride and potassium hydroxide on the dibromide of benzylidene-*p*-bromoacetophenone. This ring closure is explicable only on the *anti*-configuration for the oxime. The *anti*-oximes are not intermediates in the formation of the isooxazolines, since the *anti*-oximes of dypnone and benzylidene-*p*-bromoacetophenone are unaltered by further treatment with hydroxylamine hydrochloride and excess of alkali. The isooxazolines are not formed by 1:4-addition of hydroxylamine to the unsaturated ketones followed by ring closure, since dypnone affords 3:5-diphenyl-5-methylisooxazoline (also obtained from the *anti*-oxime by rearrangement with concentrated sulphuric acid) and not the isomeric compound  $\text{CH} \begin{matrix} \text{CPhMe} \text{NH} \\ \text{CPh} \end{matrix} \text{O}$ , since the product is inert towards the Grignard reagent. Similarly benzylidene-*p*-bromoacetophenone affords 3-*p*-bromophenyl-5-phenylisooxazoline,  $\text{CH}_2 \begin{matrix} \text{C}(\text{C}_6\text{H}_4\text{Br})\text{N} \\ \text{CHPh} \end{matrix} \text{O}$ , m. p. 138—139° (also obtained by the action of concentrated sulphuric acid on the *anti*-oxime), oxidised by chromic oxide in glacial acetic acid at 80° to the isooxazole, m. p. 178—179° (above). The rearrangement of the *anti*-oximes into isooxazolines under the influence of sulphuric acid is the best method of preparing these derivatives, and may involve halochromic salt formation by the oxime followed by rearrangement of the cation in the strongly acid medium to yield a more basic product. J. W. BAKER.

**Action of phenol on benzoyldiphenylmethyl bromide.** C. F. KOELSCH (J. Amer. Chem. Soc., 1931, 53, 1147—1150).—The product of the interaction of phenol and phenyl diphenylbromomethyl

ketone is not phenylbenzoin monophenyl ether as stated by Schuster (A., 1930, 1576), but phenyl diphenylmethyl ketone, identical with a specimen prepared by Orékhov's method (A., 1919, i, 272), *p*-bromophenol also being formed. This is confirmed by fission of the resulting ketone into potassium benzoate and diphenylmethane with hot alcoholic potassium hydroxide; its conversion by acetic anhydride and a few drops of concentrated sulphuric acid at 60—70° into triphenylvinyl acetate; and by the formation, on treatment with magnesium phenyl bromide, of  $\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol, m. p. 232—233° (Schuster, *loc. cit.* described it as benzopinacone monomethyl ether, m. p. 219°), which is hydrolysed by alcoholic potassium hydroxide to diphenylmethane and benzophenone.

J. W. BAKER.

**Synthesis of antiseptic derivatives of indan-1:3-dione.** II. Interaction of alkylmalonyl chlorides with *p*-tolyl methyl ether. T. K. WALKER, A. J. SUTHERS, L. L. ROE, and H. SHAW (J.C.S., 1931, 514—520; cf. this vol., 487).—Interaction of *p*-cresol, or its methyl ether, and suitably substituted malonyl chlorides in presence of aluminium chloride gives 4-hydroxy-7-methylindan-1:3-dione, m. p. 258° (50% yield), and the following derivatives of this compound: 2-methyl-, m. p. 253° (sinters 243°); 2-ethyl- (III), m. p. 197°; 2:2-diethyl-, m. p. 199—200°; 2-*n*-propyl-, m. p. 187° (theoretical yield); 2-*n*-butyl-, m. p. 165° (theoretical yield); 2-*n*-amyl-, m. p. 146° (29% yield); 2-*n*-hexyl-, m. p. 136° (31% yield); 2-*n*-heptyl-, m. p. 124° (50% yield); 2-*iso*-propyl-, m. p. 224° (16% yield); 2-*isobutyl*-, m. p. 152.5° (47% yield); 2-*isoamyl*-, m. p. 142° (44% yield). 4-Methoxy-7-methyl-2:2-diethylindan-1:3-dione (oily) with aluminium chloride gave III. Improved conditions for carrying out the condensation are described. Ferric chloride can be used in place of aluminium chloride.

The substances are graded in order of antiseptic activity, maximum efficiency being obtained with *n*-heptyl and *n*-hexyl derivatives. Branched-chain compounds are less effective. A. A. LEVI.

**Fluorene series. Synthesis of two ketones: 2-fluoryl methyl ketone and 2:7-fluoryl dimethyl diketone.** K. DZIEWOŃSKI and J. SCHNAYDER (Bull. Acad. Polonaise, 1930, A, 529—535).—Fluorene condenses with acetyl chloride in the presence of aluminium chloride in carbon disulphide solution to give 2-fluoryl methyl ketone, b. p. 323—328°/20 mm., m. p. 132° (phenylhydrazone, m. p. 216—218°; oxime, m. p. 196—197°), and 2:7-fluoryl dimethyl diketone (2:7-diacetylfluorene), m. p. 182—184° (phenylhydrazone, m. p. 233—235°; dioxime, m. p. 258°). 2-Fluoryl methyl ketoxime is converted by a Beckmann change when heated with dry hydrogen chloride in acetic anhydride and acetic acid solution in a sealed tube at 100° into 2-acetamidofluorene, m. p. 192—193°, hydrolysed by heating with 6% hydrochloric acid to 2-aminofluorene, m. p. 127—129°. Oxidation of 2-fluoryl methyl ketone with potassium dichromate and acetic acid converts it into fluorenone-2-carboxylic acid, identical with a specimen prepared from fluorenone-1:7-dicarboxylic acid (Bamberger and Hooker,

A., 1885, i, 905). Similarly, the dioxime of the diketone is converted into 2:7-diacetamido-, m. p. 274°, hydrolysed to 2:7-diamino-, m. p. 162—163°, fluorene. J. W. BAKER.

**Formation of chloranil from aromatic compounds, and use of the reaction in analysis.** R. P. P. COLMANT (Ann. Soc. Sci. Bruxelles, 1931, [B], 51, 27—39).—About 130 aromatic compounds were tested for the formation of chloranil, by heating with hydrochloric acid, *d* 1.08, and potassium chlorate on a water-bath. Neither benzene nor its halogeno-, nitro-, azo-, or sulphonic derivatives, nor those containing groups linked by carbon to the nucleus give chloranil, but the compound is given by benzene substituted by the amino-group and its alkyl or acyl derivatives, the hydrazine group, the pyrazole group, and the hydroxyl group and its ethers. The presence of a single active group makes the reaction possible. If more than two substituents are present, one of which is an alkylated chain, no chloranil is formed. When two active substituents are present they must be in the *p*-position if reaction is to take place. With more than two active substituents no chloranil is formed. The analytical application of the reaction is exemplified by tests on the reduction products of nitro-compounds. The introduction into phenol or aniline of any inactive substituent decreases the yield of chloranil. In phenols the nitro-group decreases the yield more than the carboxyl group, which in turn reduces the yield more than the methyl group. For aniline the order is reversed. *p*-Amino-derivatives give greater yields than *o*-amino-derivatives, but *o*-phenol derivatives give greater yields than *p*-phenol derivatives. Phenol ethers give smaller yields than phenol. Cresol ethers give no chloranil. A. RENFREW.

**Reduction potentials of some higher benzo-logs of the quinones.** L. F. FIESER and E. M. DIETZ (J. Amer. Chem. Soc., 1931, 53, 1128—1133).—The normal reduction potentials of 1:2-benzanthra-, 1:2:7:8- and 1:2:5:6-dibenzanthra-, 1:2-(3-methylbenz)-1:2:5:6-dibenzanthra-, 5:6- and 6:12-chryso-, 12-hydroxy- and 12-ethoxy-5:6-chryso-, 1:2-benz-3:4-anthra-, and picene-quinones have been determined, generally by catalytic reduction and potentiometric titration of the reductant with a suitable oxidising agent; the values are, respectively, 0.228, 0.264, 0.268, 0.257, 0.465, 0.392, 0.391, 0.418, 0.430, and 0.474 ± 0.01 volt. The significance of these results is discussed and the potentials of benz- and dibenz-anthraquinones lend support to the *o*-quinonoid theory of the structure of anthracene (cf. Fieser and Ames, A., 1927, 1198), and are not readily harmonised with the *p*-linking structure which is a symmetrical structure. Contrary to the assumption of Beschke and Diehm (A., 1911, i, 889) the stable *o*-quinonoid structure of hydroxyamphichrysoquinone is the one possessing the higher reduction potential, and this compound thus forms an exception to the rule (*loc. cit.*) that when a quinone can exist in two tautomeric forms the one with the lower potential will be the stable form. J. W. BAKER.

**New *p*-2-carboxybenzoylbenzenesulphonic acids and the corresponding anthraquinone**

**compounds.** I. GUBELMANN, H. J. WEILAND, and O. STALLMANN (J. Amer. Chem. Soc., 1931, 53, 1033—1036).—Nitration of *p*-2-carboxybenzoylbenzenesulphonic acid (as its sodium salt) with mixed acids at 15—35° affords *p*-(4-nitro-2-carboxybenzoyl)benzenesulphonic acid (I) (as its sodium salt), converted by heating in 25% oleum at 150° into 2-nitroanthraquinone-7-sulphonic acid. This is converted by sodium chlorate in boiling hydrochloric acid solution into 7-chloro-2-nitroanthraquinone, m. p. 251—252°, reduced by sodium sulphide in alkaline solution to the corresponding 2-amino-derivative, m. p. 302—303°. Reduction of the original nitrosulphonic acid (I) with iron and glacial acetic acid affords *p*-(4-amino-2-carboxybenzoyl)benzenesulphonic acid, similarly converted into 2-aminoanthraquinone-7-sulphonic acid, which on heating with ammonia and arsenic acid at 180° gives 2:7-diaminoanthraquinone, converted into the corresponding dihydroxy- and diacetoxy-derivatives in the usual manner. J. W. BAKER.

**Chlorination of derivatives of *o*-methylbenzophenone.** H. DE DIESBACH and P. DOBBELMANN (Helv. Chim. Acta, 1931, 14, 369—378; cf. A., 1925, i, 1435).—Treatment of *o*-methylbenzophenone with chlorine at 120° during 24 hrs. gives mainly 10:10-dichloro-9-anthrone (cf. Thörner and Zincke, A., 1878, 231). The product formed after 2 hrs. contains 2 atoms of chlorine per mol., and is not converted into anthraquinone when moistened and then kept in a vacuum (whereby hydrogen chloride is eliminated); boiling with alcohol, however, leads to the formation of anthraquinone and *o*-benzoylbenzoic acid. Chlorination at 180° during 4 hrs. gives a quantitative yield of 10:10-dichloro-9-anthrone, which is probably formed by loss of hydrogen chloride from the intermediate trichloromethyl derivative. 4-Chloro-2'-methylbenzophenone, b. p. 194°/14 mm., from *o*-toluoyl chloride and chlorobenzene in presence of aluminium chloride, is converted by chlorine at 130° into 3:10:10-trichloro-9-anthrone, m. p. 137°, which when boiled with alcohol gives 2-chloroanthraquinone. 2:5-Dichloro-2'-methylbenzophenone, b. p. 203°/13 mm., m. p. 63.5°, from *o*-toluoyl chloride and *p*-dichlorobenzene, does not undergo ring closure when chlorinated, probably owing to a steric hindrance effect; the resulting trichloromethyl derivative is converted by dissolution in sulphuric acid into 2:5-dichlorobenzophenone-2'-carboxylic acid. Condensation of benzoyl chloride and *p*-chlorotoluene gives 2-chloro-5-methylbenzophenone, m. p. 35—36° (cf. Heller, A., 1913, i, 631), and liquid products containing 5-chloro-2-methylbenzophenone, since chlorination of these at 180° gives some 2:10:10-trichloro-9-anthrone, m. p. 162° (the 2-chloro-derivative is not convertible into an anthrone). 4-Chloro-*o*-toluidine is converted by the usual method into 4-chloro-2-cyanotoluene, m. p. 48°, hydrolysed by 70% sulphuric acid to 4-chloro-*o*-toluic acid, m. p. 168°. The chloride of this acid and benzene in presence of aluminium chloride and carbon disulphide give 5-chloro-2-methylbenzophenone, b. p. 191°/12 mm., m. p. 41°, chlorinated to 2:10:10-trichloro-9-anthrone. 2:4-Dichloro-5-methylbenzophenone, b. p. 202—203°/12 mm., m. p. 78°, from

2 : 4-dichlorotoluene and benzoyl chloride, is chlorinated at 180° to the *monochloromethyl* derivative, which after treatment with sulphuric acid at 35° and subsequent oxidation with alkaline potassium permanganate affords 2 : 4-dichlorobenzophenone-5-carboxylic acid, m. p. 167°. Chlorination of 2 : 5-dibenzoyl-*p*-xylene in a small amount of trichlorobenzene at 140—150° gives slightly impure 2 : 5-dibenzoyl-1 : 4-di(trichloromethyl)benzene, m. p. 205.5°, which when heated in nitrobenzene or trichlorobenzene at 180° passes into 7 : 7 : 14 : 14-tetrachloro-5 : 12-diketopentacene, decomp. 200° without melting.

Chlorination of 2 : 5-dimethylbenzophenone at 180° gives mainly 2-chloromethyl-5-trichloromethylbenzophenone, which when moistened and then kept in a vacuum eliminates 1 mol. of hydrogen chloride, and is converted by water at 150° into 2-hydroxymethylbenzophenone-5-carboxylic acid, m. p. 198—200°. When the above tetrachloro-derivative is heated with alcohol for several days, unexpectedly 2-trichloromethylanthraquinone, m. p. 154°, is produced. This is converted by sulphuric acid at 35° into anthraquinone-2-carboxylic acid, and when boiled with nitrobenzene affords di-2-anthraquinonylacetylene, also formed when the trichloromethyl derivative is treated with amyl-alcoholic sodium hydroxide; reduction with alkaline hyposulphite gives  $\alpha\beta$ -di-2-anthraquinonylethylene.

H. BURTON.

**Morpholquinone.** L. F. FIESER (Ber., 1931, 64, [B], 701—702).—Fuller details are given of the synthesis of morpholquinone from 3-hydroxyphenanthrene (cf. A., 1929, 567).

H. WREN.

[Action of aluminium chloride on *o*-dihydroxybenzil.] P. K. BRASS (Ber., 1931, 64, [B], 700—701; cf. Brass and others, A., 1930, 1589).—The synthesis of morpholquinone by Fieser (A., 1929, 567) has been overlooked.

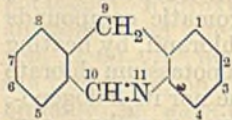
H. WREN.

**Reaction of aromatic 1 : 4-diketoneoximes occurring in place of the Beckmann transformation.** IV. Benzoylenemorphanthridone and benzoylenemorphanthridine. R. SCHOLL and J. MÜLLER [with J. DONAT] (Ber., 1931, 64, [B], 639—655; cf. this vol., 488).—Oximation of 1-arylanthraquinones leads to 1-arylanthraquinone-9-oximes (I), probably mixed with small amounts of easily removed isomerides. Dehydration of the oximes to the benzoylenemorphanthridones (II) takes place by loss of water probably through the intermediate compounds of the type III. The production

is a consequence of an isomerisation of the oximes into anthraquinone-9-anil-1-carboxylic acids,

$C_6H_4 \left\langle \begin{array}{c} CO \\ C(NPh) \end{array} \right\rangle C_6H_3 \cdot CO_2H$ ; the reaction occurs in place of the normal Beckmann transformation of quinoneoximes.

It is proposed to designate the structure IV by the name "morphanthridine," partly by reason of its relationship to phenanthridine and partly of its kinship to Knorr's morphine formula.



(IV.)

Benzoylenemorphanthridone III (anhydro-compound of phenyl anthraquinonyl ketoxime) is converted by fusion with potassium hydroxide into anthraquinoneanil-*o*-carboxylic acid,

$C_6H_4 \left\langle \begin{array}{c} CO \\ C(N \cdot C_6H_4 \cdot CO_2H) \end{array} \right\rangle C_6H_4$ , m. p. 222° (after softening) (very readily converted by acids into anthraquinone and anthranilic acid), 1 : 2-phthalyl-acridone, not molten below 350°, and acridone, m. p. 349—350°.

Anthraquinoneanil-*o*-carboxylic acid is obtained synthetically from *ms*-dibromoanthrone and anthranilic acid in boiling toluene. It is mainly unchanged by concentrated sulphuric acid at 80—90° and converted into anthraquinone and anthranilic acid at 130—140°; treatment of its chloride with aluminium chloride in benzene gives anthraquinone and *o*-aminobenzophenone.

Anthranol-1-carboxylic acid, m. p. 248° varying with the rate of heating, is converted by bromine in boiling chlorobenzene into 9-bromoanthrone-1-carboxylic acid,  $C_6H_4 \left\langle \begin{array}{c} CO \\ CHBr \end{array} \right\rangle C_6H_3 \cdot CO_2H$ , decomp. 225°

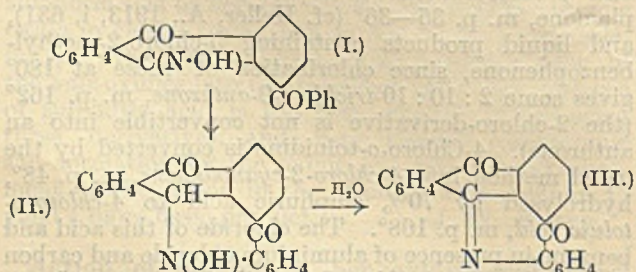
when rapidly heated, transformed by aniline in benzene into 9-anilinoanthrone-1-carboxylic acid, m. p. indef. 160—163°. The last-named compound does not give benzoylenemorphanthridone when treated with nitrobenzene containing hydrogen chloride. It is converted by potassium ferricyanide in alcoholic alkaline solution followed by very cautious addition of acetic acid into anthraquinone-9-anil-1-carboxylic acid, m. p. 171—172° (decomp.), readily hydrolysed to aniline and anthraquinone-1-carboxylic acid; attempts to transform it into benzoylenemorphanthridone were unsuccessful.

Protracted ebullition of anthraquinone and hydroxylamine in alcoholic alkaline solution gives anthraquinonemonoxime in only 2.5% yield; this may be increased to about 50% if anthraquinol is used as initial material. The application of the method to the production of 1-benzoylanthraquinone-9-oxime is described.

[With E. STIX.] Benzoylenemorphanthridone is converted by sodium amalgam in boiling absolute alcohol and repeated crystallisation of the product from alcohol into benzoylenemorphanthridine, m. p. 218°.

H. WREN.

**Constitution of amyriins.** H. DIETERLE (Arch. Pharm., 1931, 269, 78—87).— $\alpha$ -Amyrin (cf. Horrmann, A., 1930, 216; Vesterberg, A., 1922, i, 825) is oxidised by chromic and acetic acids in a current of steam to carbon dioxide, acetone,  $\alpha$ -amyrone [hydrazone, m. p. 252° (decomp.)], and a ketone,  $C_{21}H_{34}O$ ,



of anthraquinone-1-carboxyarylides or anthraquinone-1-carboxylic acid and arylamines with aqueous or alcoholic hydrochloric acid at an elevated temperature

m. p. 89—90° ( $[\alpha]_D^{20} + 123.2^\circ$  (all rotations in chloroform) (*hydrazone*, m. p. 224°).  $\alpha$ -Amyrin has therefore a side-chain of nine carbon atoms which contains an isopropyl group. With boiling nitric acid ( $d$  1.46) it yields substances,  $C_{20}H_{27}(NO_2)_2(CO_2H)_3$ , m. p. 171°, ( $[\alpha]_D^{20} + 29.6^\circ$ , and  $C_{20}H_{29}(NO_2)_2(CO_2H)_3$ , m. p. 185—186°, ( $[\alpha]_D^{20} + 54.3^\circ$ . The former is reduced by zinc dust and acetic acid to the corresponding diamine, m. p. 196°. The oily ozonide of  $\alpha$ -amyrin yields when heated an acid,  $C_{20}H_{36}(CO_2H)_2$ , ( $[\alpha]_D^{20} + 88.0^\circ$ , and when treated with water an acid,  $C_{20}H_{33}(CO_2H)_3$ , ( $[\alpha]_D^{20} + 104.5^\circ$ . Both acids are saturated. Dehydrogenation of  $\alpha$ -amyrin with selenium gives hydrocarbons,  $C_{21}H_{36}$ , m. p. 184°, ( $[\alpha]_D^{20} + 41.7^\circ$ ;  $C_{14}H_{22}$ , b. p. 140°/15 mm., ( $[\alpha]_D^{20} + 34.6^\circ$ , and  $C_{14}H_{14}$ , b. p. 170°/15 mm. (*picrate*, m. p. 134°).  $\alpha$ -Amyrin is not isomerised by boiling formic or hydrobromic acid, but  $\beta$ -amyrin yields a formate, m. p. 210°, which is hydrolysed to  $\gamma$ -amyrin,  $C_{30}H_{50}O$ , m. p. 145°, ( $[\alpha]_D^{20} + 42^\circ$ . This is dehydrated by phosphorus pentachloride to  $\gamma$ -amyrene,  $C_{30}H_{48}$ , ( $[\alpha]_D^{20} + 54.1^\circ$ .  $\alpha$ -Amyrin is reduced by hydriodic acid to amyrene,  $C_{30}H_{50}$ , b. p. 120°/15 mm., ( $[\alpha]_D^{20} + 44.9^\circ$ .  
H. E. F. NOTTON.

**Cannabis indica resin.** II. R. S. CAHN (J.C.S., 1931, 630—638).—The active principle of *Cannabis indica* resin (hashish etc.) is contained in a high-boiling resin, from which cannabinol (I), trinitrocannabinol (II), a hydrocarbon (III), and nitrocannabinolactone (IV) (cf. A., 1930, 913) have been prepared. The statements of Wood, Spivey, and Easterfield (J.C.S., 1899, 75, 20) on the isolation of I are confirmed. "Crude cannabinol" is ether-soluble, b. p. about 265°/25 mm., and yields when treated with acetyl chloride in pyridine a crystalline *acetylcannabinol*,  $C_{21}H_{25}O_2Ac$ , m. p. 75°, which on hydrolysis affords pure cannabinol, b. p. 263°/20 mm. (uncrystallisable). The cannabinol unless prepared from the acetyl derivative is a mixture. Nitration of cannabinol with cold fuming nitric acid yields II, oxidised by hot nitric acid to IV. II forms a *methyl ether*, m. p. 150°, most conveniently prepared with dry methyl iodide and silver oxide, in absence of a solvent, and hydrolysed by warm pyridine and a little water, showing that methylation occurs at the hydroxyl group; the *benzenesulphonyl* derivative of II has m. p. 196—197°. II contains two benzene nuclei, one in the residue giving IV, the other carrying two nitro-groups and a phenolic hydroxyl group. The objection of Bergel (A., 1930, 1431) to the structure previously proposed for IV (*loc. cit.*) is refuted. The main constituent of III is probably *n*-nonacosane.

F. R. SHAW.

[Constituents of] **euphorbium resin.** L. SCHMID and M. K. ZACKERL (Monatsh., 1931, 57, 177—200).—The light petroleum extractive of the resin is hydrolysed with alcoholic alkali, the alkaline solution added to 30—40% alcohol, and the euphorbone purified further by various solvents. Euphorbone can only be obtained crystalline from benzene (in which it is very soluble) or light petroleum (b. p. 20—50°; from which it separates with m. p. 67—68°). When euphorbone of m. p. 67—68° is heated at 40°/high vac. it becomes amorphous (m. p. 70—114°). The more fusible form can be isolated directly from the

resin by extraction with light petroleum. The carbon content of euphorbone varies from 79 to 83% according to the number of crystallisations. Euphorbone gives an ill-defined acetate, m. p. 96°, a *benzoate*, m. p. 118° (*dibromo*-derivative), and an *anisate*, m. p. 159—160° (hydrolysed by alcoholic alkali to the original material, m. p. 67—68°). Catalytic hydrogenation of euphorbone affords a *hydroeuphorbone*, m. p. 109° (*acetate*, m. p. 99°). Aldehydic substances are obtained by ozonolysis of euphorbone, which is probably a mixture.

Euphorbol, probably  $C_{26}H_{48}O$ , m. p. 118°, extracted from the resin by Bauer and Schenkel's method (B., 1929, 137), gives an *anisate*, m. p. 159°, which appears to be identical with euphorbone anisate. Euphorbol acetate gives an amorphous *dibromide*.  
H. BURTON.

**Optical activity and polarity of substituent groups.** XVII. *l*-Menthyl hydrogen naphthalate, its alkali salts, and methyl ester. H. G. RULE and A. McLEAN (J.C.S., 1931, 669—672).—Sodium menthoxide and naphthalic anhydride yield *l*-menthyl hydrogen naphthalate, m. p. 141° (solidifies and remelts at about 271°) (*sodium*, *potassium*, and *lithium* salts, and *l*-menthyl methyl naphthalate, m. p. 96.5—97° (slight decomp.) (from the silver salt and methyl iodide). With the exception of the methyl ester all are unstable even at the ordinary temperature. The rotatory powers for the methyl and hydrogen esters in benzene and acetonitrile for different wavelengths are given (the free hydrogen ester has a high dextrorotation in benzene); that of the hydrogen ester in methyl alcohol ( $[M]_{5401}^{20} - 383^\circ$ ,  $c=4$ ) falls to small positive values in the form of the salts, the depressions being in the order  $K > Na > Li$ .  
F. R. SHAW.

**Optically active  $\alpha$ -pinenes.** F. H. THURBER and R. C. THIELKE (J. Amer. Chem. Soc., 1931, 53, 1030—1032).—Optically pure specimens of *d*-, b. p. 155—156°/760 mm., ( $[\alpha]_D^{20} + 51.14^\circ$ ,  $d^{20}$  0.8591,  $n_D^{20}$  1.4663; *l*-, b. p. 155—156°/760 mm., ( $[\alpha]_D^{20} - 51.28^\circ$ ,  $d$  0.8590,  $n_D^{20}$  1.4662; and *dl*-, b. p. 155—156°/760 mm. ( $[\alpha]_D^{20}$  0.00,  $d^{20}$  0.8592,  $n_D^{20}$  1.4664,  $\alpha$ -pinene are prepared by the action of dimethylaniline on their nitroschlorides (preparation described), *d*-, m. p. 89.5°, ( $[\alpha]_D^{20} + 396.2^\circ$ ; *l*-, m. p. 90.0°, ( $[\alpha]_D^{20} - 366.8^\circ$  in benzene; and *dl*-, m. p. 115°. Contrary to statements in the literature, the pinenes are converted normally into *d*-, ( $[\alpha]_D^{20} + 33.52^\circ$ , *l*-, ( $[\alpha]_D^{20} - 33.24^\circ$ , in 1% alcoholic solution, and *dl*-, all m. p. 132°,  $\alpha$ -pinene hydrochloride, respectively. J. W. BAKER.

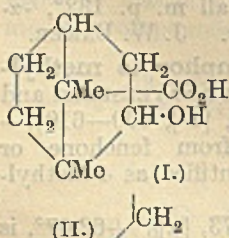
**Degradation of 4-methylcamphor to methylisocamphoronic acid.** M. BREDT-SAVELSBERG and J. BUCHKREMER (Ber., 1931, 64, [B], 600—610).—The methylcamphor derived from fenchone or camphor (A., 1919, i, 125) is identified as 4-methylcamphor.

Fenchone, b. p. 190°,  $d_4^{20}$  0.9473, ( $[\alpha]_D^{20} + 62.07^\circ$ , is converted by a small excess of magnesium methyl iodide into *tert*-methylfenchol, b. p. 88—89°/12 mm., m. p. 61°, ( $[\alpha]_D^{20} + 5.14^\circ$  in ethyl alcohol, transformed by acetic anhydride at 150° into a mixture of hydrocarbons  $C_{11}H_{18}$  from which optically inactive 4-methylisobornyl acetate, b. p. 106—107°/12 mm., is obtained by means of glacial acetic and sulphuric acids.

4-Methylisoborneol, m. p. 192—193° (phenylurethane, m. p. 102—103°), is oxidised by potassium dichromate and sulphuric acid to 4-methylcamphor, m. p. 168° (semicarbazone, decomp. 255—257°; oxime, m. p. 132—133°). Boiling sulphuric acid (*d* 1.18) converts the oxime into 5-methyl- $\alpha$ -campholenonitrile, b. p. 115—118°/18 mm.,  $d_{20}^{25}$  0.9217,  $n_D^{25}$  1.47221, hydrolysed to 5-methyl- $\alpha$ -campholenic acid,

$\begin{array}{l} \text{CH}-\text{CH}_2 \\ \text{CMe}-\text{CMe}_2 \end{array} > \text{CMe}-\text{CH}_2-\text{CO}_2\text{H}$ , b. p. 150—151.5°/12 mm., m. p. 36.5—37°,  $d_{20}^{40}$  0.9841,  $n_D^{40}$  1.64982 (ammonium salt; corresponding amide, m. p. 99—100°). Successive treatment of methyl- $\alpha$ -campholenic acid with permanganate in alkaline solution and chromic acid and sulphuric acid gives methylisocamphoronic acid,  $\text{CO}_2\text{H}-\text{CMe}_2-\text{CMe}(\text{CH}_2-\text{CO}_2\text{H})_2$ , m. p. 180—182° (decomp.) (barium and monohydrated silver salts), and methylisoketocamphoric acid [silver and barium salts; corresponding dilactone,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , m. p. 240—242°, and the compounds  $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_3$ , decomp. 224—225°, and  $\text{C}_{13}\text{H}_{22}\text{O}_4\text{N}_6$ , m. p. 244—245° (decomp.), formed therefrom with one and two mols. of semicarbazide, respectively]. [*iso*Ketocamphoric acid is transformed by acetyl chloride into a similar dilactone,  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , m. p. (indef.) 180—185°.] The dilactone is oxidised by alkaline hypobromite to methylisocamphoronic acid. H. WREN.

$\pi$ -Camphor derivatives. II. Identity of dihydroteresantallic acid with  $\pi$ -apocamphane-7-carboxylic acid. T. HASSELSTRÖM (J. Amer. Chem. Soc., 1931, 53, 1097—1103).—The structure of teresantallic acid (Ruzicka and Liebe, A., 1926, 400) is confirmed by the following observations. Methyl teresantalate is converted by 90% formic acid into the lactone of 2-hydroxy- $\pi$ -apocamphane-7-carboxylic acid (I), which is obtained by hydrolysis of the lactone with 2% sodium hydroxide and has the carboxyl group in the bridge and not in the ring, both products being identical with those obtained by Semmler and Bartelt (A., 1907, i, 1062). Oxidation of the hydroxy-acid with alkaline permanganate affords the corresponding 2-*keio*- $\pi$ -apocamphane-7-carboxylic acid (ketodihydroteresantallic acid), m. p. 269—270°,  $[\alpha]_D^{25}$  —55° in 10% alcohol solution, the semicarbazone, m. p. 204—205°, of which is reduced by Wolff's method to dihydroteresantallic acid identical with  $\pi$ -apocamphane-7-carboxylic acid (II) previously synthesised (Ann. Acad. Fenn., 1929, 30, 12). The mixed (probably stereoisomeric) methyl chlorodihydroteresantalates obtained by



Rupe and Tomi's method (A., 1917, i, 138) are reduced by aluminium amalgam and moist ether, followed by sodium and alcohol, to dihydroteresantalol, oxidised by potassium dichromate and sulphuric acid to dihydroteresantalol, further oxidised by alkaline potassium permanganate to dihydroteresantallic acid identical with the specimen obtained above. Teresantalol is converted by a saturated methylalcoholic solution of anhydrous hydrogen chloride in a freezing mixture into a mixture of solid and liquid chlorodihydroteresantalol, the solid product being re-

duced by sodium and alcohol to dihydroteresantalol. Such side reactions as are here observed may be due either to the formation of stereoisomerides or to a rearrangement of the teresantalene to the santene skeleton. J. W. BAKER.

Action of substituted aromatic amines on camphoric anhydride. Rotatory powers of some disubstituted camphoranilic acids. M. SINGH and D. SINGH (J.C.S., 1931, 478—482).—In presence of sodium acetate, from camphoric anhydride and the appropriate amine are obtained: 2':3', m. p. 190—192°, 2':6', m. p. 236—238°, 2':5'-dimethyl-, m. p. 203—204°, 5'-nitro-2'-methoxy-, m. p. 162—163°, 4'-nitro-2'-methoxy-, m. p. 185—186°, 5'-nitro-2'-methyl-, m. p. 220—221°, 3'-nitro-4'-methyl-, m. p. 204—205°, 2'-nitro-4'-methyl-, m. p. 187°, and 4'-nitro-2'-methyl-camphoranilic acids, m. p. 229—230°. Nitration of the corresponding acids gives 4'-chloro-2'-nitro-, m. p. 204—205°, 4'-bromo-2'-nitro-, m. p. 212°, (Wootton, J.C.S., 1910, 97, 405, gives m. p. 204—206°, and describes it as 3'-nitro-), 2':6'-dinitro-4'-methoxy-, m. p. 228—229°, and 2':6'-dinitro-4'-ethoxy-camphoranilic acids, m. p. 189—190°. The rotatory power of these acids in different solvents has been examined, and it is shown that, in accordance with Rule's statement (A., 1924, ii, 645), groups of like polarity reinforce, and of opposite polarity neutralise, each other when they are in the *p*-position with respect to each other. A nitro-group in the *o*-position causes considerable rise in the rotatory power, accompanied by reversal of sign. F. R. SHAW.

Solubility of salts of camphorcarboxylic acid. M. PICON (J. Pharm. Chim., 1931, [viii], 13, 185—196, 233—243, and Bull. Soc. chim., 1931, [iv], 49, 399—423; cf. Brühl, A., 1903, i, 4).—The solubility in water and organic solvents of the following camphorcarboxylates is discussed: sodium, calcium, magnesium, zinc, neodymium, cerium, normal (monohydrate and anhydrous) and basic copper, gold, lead, bismuth, uranyl. F. O. HOWITT.

$\alpha$ -Carboxycamphocean- $\beta$ -acrylic and - $\beta$ -propionic acids. Synthesis of  $\beta$ -homocamphor. F. SALMON-LEGAGNEUR (Compt. rend., 1931, 192, 748—750).—Camphoceanaldehydic acid (Bredt, A., 1917, i, 560) by successive action of thionyl chloride and methyl alcohol gave the methyl ester, b. p. 135—136°/12 mm. (semicarbazone, m. p. 184°). This with ethyl bromoacetate gave methyl ethyl  $\alpha$ -carboxycamphocean- $\beta$ -acrylate, m. p. 52—53°,  $[\alpha]_D^{25}$  —92.2° in methyl alcohol, hydrolysis of which gave the acid, m. p. 174—176°,  $[\alpha]_D^{25}$  +58.8° in methyl alcohol. This was reduced in presence of platinum oxide to  $\alpha$ -carboxycamphocean- $\beta$ -propionic acid, m. p. 150—151°,  $[\alpha]_D^{25}$  +38.1° in methyl alcohol, the lead or thorium salt of which, when heated, gave  $\beta$ -homocamphor, m. p. 202—204°,  $[\alpha]_D^{25}$  +111.2° in methyl alcohol (oxime, m. p. 104—105°; semicarbazone, m. p. 245°). A. A. LEVI.

Structure of nitrofuran and the mechanism of nitration in the furan series. B. T. FREURE and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, 53, 1142—1147).—The nitrofuran obtained by the action of nitric and acetic acids on furan is not the 3-nitro-



derivative (Marquis, A., 1905, i, 224), but is 2-nitro-furan (microcrystallographic examination by McCLELLAN), also obtained by decarboxylation of 5-nitrofuroic acid (Hill and White, A., 1902, i, 388). Nitration of methyl furoate affords a nitroacetate, m. p. 96.3° (corr.) (together with an unidentified oil), which is converted by warm pyridine into methyl 5-nitrofuroate, m. p. 81.6° (corr.) (Marquis, *loc. cit.* gives m. p. 78.5°), and is probably the acetate of either the 2:3-,  $\begin{matrix} \text{CH(OAc)-CH(NO}_2\text{)} \\ \text{CH}=\text{C(CO}_2\text{Me)} \end{matrix} \text{O}$ , or the corresponding 2:5-additive product of the ester and nitric acid. Such addition is tentatively suggested as the mechanism of nitration of furan derivatives, the observation that no intermediate nitroacetates can be isolated in the nitration of the free acid being explained by the greater lability of these intermediates.

J. W. BAKER.

**Stability of the furan nucleus.** N. A. ORLOV and V. V. TISCHTSCHENKO (J. Russ. Phys. Chem. Soc., 1930, 62, 2243—2248).—When coumarin is passed through a tube heated at 860°, coumarone is obtained; xanthone at 880° gives diphenyl ether; dimethylpyrone gives a tar with a furan reaction, carbon monoxide being evolved in each case. These reactions show the stability of the furan nucleus at high temperatures.

E. B. UVAROV.

**Condensation of ketones with resorcinol.** II. R. N. SEN, N. C. CHATTOPADHYA, and S. C. SENGUPTA (J. Indian Chem. Soc., 1930, 7, 997—1006).—A mixture of the ketone (1 mol.) and resorcinol (2 mols.) is heated until molten and treated with hydrogen chloride after addition of anhydrous zinc chloride at 180—190°. The condensation products are all coloured and possess dyeing properties in varying degree, although a quinonoid formulation appears impossible. Thus benzophenone and resorcinol afford 4:4-diphenyl-2:3-5:6-dihydroxybenzopyran,

$\text{OH-C}_6\text{H}_4 \left\langle \begin{matrix} \text{O} \\ \text{CPh}_2 \end{matrix} \right\rangle \text{C}_6\text{H}_4\text{-OH}$ , m. p. 125—127° (dipotassium salt; dibromo-derivative, m. p. 175°; dibenzoyl compound). Fluorenone affords the substance  $\text{C}_{25}\text{H}_{16}\text{O}_3$ , m. p. 220° (chloroacetyl compound, m. p. 182°), and benzil yields 4-phenyl-4-benzoyl-2:3-5:6-dihydroxybenzopyran, m. p. 215° (dipotassium salt). The following compounds are analogously obtained: 4-phenyl-4-trihydroxyphenyl-2:3-5:6-dihydroxybenzopyran, not molten below 280°, from trihydroxybenzophenone; 4-phenyl-4-methyl-2:3-5:6-dihydroxybenzopyran, m. p. 152° (from acetophenone) (dibromo-derivative, m. p. 160°; dibenzoyl compound, m. p. 115°); 4:4-dimethyl-2:3-5:6-dihydroxybenzopyran, m. p. 165°, from acetone (dibromo-derivative, m. p. 153°); the substance  $\text{C}_9\text{H}_{16} \left\langle \begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} \right\rangle \text{O}$ , m. p. 200°, from camphor (dipotassium salt; dibenzoyl compound, m. p. 120°; dibromo-derivative, not molten below 280°); the compound  $\text{C}_6\text{H}_{10} \left\langle \begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} \right\rangle \text{O}$ , softening and decomposing at 213°, from cyclohexanone (dipotassium and barium salts; dibenzoyl derivative, softening at 202—203°; dibromo-compound, not molten below 280°); the substance  $\text{C}_{11}\text{H}_{12}\text{N}_2 \left\langle \begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} \right\rangle \text{O}$ , m. p. 150°, from antipyrine

(dibromo-derivative, m. p. 190°). cycloHexanone and pyrogallol give the compound  $\text{C}_6\text{H}_{10} \left\langle \begin{matrix} \text{C}_6\text{H}_2(\text{OH})_2 \\ \text{C}_6\text{H}_2(\text{OH})_2 \end{matrix} \right\rangle \text{O}$ , unchanged below 280° (tetrapotassium and dibarium salts). With resorcinol (1 mol.), phenanthraquinone affords the compound  $\text{C}_6\text{H}_4 \left\langle \begin{matrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{matrix} \right\rangle \text{C} \left\langle \begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} \right\rangle \text{O}$ , m. p. 160° (dibenzoyl derivative, m. p. 148°), whereas 2 mols. of the phenol give the substance (I) unchanged below 290° (tetra-benzoyl derivative, m. p. 173°; tetrapotassium salt).

H. WREN.

**Fluoran derivatives.** II. Mixed hydroxy-fluorans and their bromo-derivatives. III. Di- and tetra-methylfluorans and their nitro-derivatives. M. DOMINIKIEWICZ (Rocz. Chem., 1931, 11, 103—112, 113—123).—II. 6-Hydroxyfluoran gives a 7-nitro-, m. p. 140° (decomp.), and a 5:7-dibromo-, m. p. 189°, -derivative. 6-Hydroxyfluoran-4-, -3-, and -2-carboxylic acids, all decomp. 360°, are prepared by condensation, respectively, of 2-, 3-, and 4-hydroxybenzoic acid with 2:4-dihydroxybenzoyl-*o*-benzoic acid. 5:7-Dibromo-6-hydroxy-1:2- and -3:4-phenylenefluoran, m. p. 175° and 172°, are prepared by bromination of the appropriate phenylenehydroxy-fluorans. 3:6-Dihydroxy-1:2-phenylenefluoran, m. p. 294° (4:5:7-tribromo-derivative, m. p. 308°), and 4:6-dihydroxy-2:3-phenylenefluoran, m. p. above 350°, are prepared by condensation with dihydroxybenzoyl-*o*-benzoic acid, respectively, of naphthoresorcinol and 1:2-dihydroxynaphthalene. 6-Hydroxy-1:2- and -3:4-pyridinofluoran, m. p. 285° and above 360° (5:7-dibromo-derivatives, m. p. 307° and above 360°), are prepared by condensation with dihydroxybenzoyl-*o*-benzoic acid, respectively, of 6- and 8-hydroxyquinoline. The mercuri-acetate and -hydroxy-derivatives of the pyridine derivatives have a bactericidal action equal to that of phenol in equivalent concentrations. The above products are dyes of the fluorescein type, whilst the bromo-derivatives correspond with the eosins.

III. 2:3:6:7-, 2:4:5:7-, and 1:3:6:8-Tetramethylfluoran, m. p. 269°, 271°, and 275°, respectively, are prepared by condensing *o*-4-, *m*-4-, and *m*-5-xenol with phthalic anhydride, whilst *p*-2-xenol yields 3:6-dihydroxy-1:4:6:8-tetramethylphthalophenone, m. p. 285—287°. The following are described: 4-nitro-2:7-dimethyl-, m. p. 206° (decomp.), 4:5-dinitro-2:7- and -3:6-dimethyl-, m. p. 302° and 210° (decomp.), 2:4:5:7-tetranitro-3:6-dimethyl-, m. p. 330° (decomp.), 1:8-, 3:6-, and 1:6-dinitro-2:4:5:7-tetramethyl-, m. p. 188°, 335°, and 255° (decomp.), 4:5-dinitro-1:3:6:8-tetramethyl-, m. p. 195° (decomp.), 2:4:5:7-tetranitro-1:3:6:8-tetramethyl-, m. p. 344° (decomp.), and 4:5-dinitro-2:3:6:7-tetramethyl-fluoran, m. p. 340° (decomp.).

R. TRUSZKOWSKI.

**Constitution of tea-tannin.** M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 155—159; cf. A., 1930, 1295).—Tea-tannin on methylation gives a heptamethyl derivative,

$C_{22}H_{11}O_3(OMe)_7(+\frac{1}{2}H_2O)$ ,  $[\alpha]_D^{25} -135^\circ$  in acetone. Oxidation gave gallic acid trimethyl ether and veratric acid. The trimethyl ether of galloyl chloride condensed with tetramethyl-tea-catechin (A., 1929, 934) gave *tetramethyl-tea-catechin galloate trimethyl ether*,  $C_{22}H_{11}O_3(OMe)_7$ , m. p.  $140^\circ$ , the absorption spectrum of which is identical with that of heptamethyl-tea-tannin. The demethylated product resembles tea-tannin. A. A. LEVI.

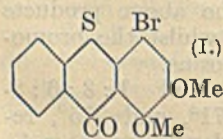
**Attempted asymmetric synthesis of sulphur compounds.** B. K. MENON and P. C. GUHA (Ber., 1931, 64, [B], 544—546).—2-Methyltetrahydrothiophen, b. p.  $130^\circ/685$  mm., is converted by *l*-menthyl bromoacetate into the ester,

$\begin{matrix} CH_2 \cdot CH_2 \\ | \quad | \\ CH_2 \cdot CHMe \end{matrix} > SBr \cdot CH_2 \cdot CO_2 C_{10}H_{19}$ , m. p.  $107^\circ$ ,  $[\alpha]_D^{25} +43.4^\circ$  in alcohol, which yields an optically inactive product after removal of the *l*-menthyl group.

Propyl mercaptan is converted by ethyl bromoacetate and subsequent hydrolysis into *propylthiolacetic acid*, b. p.  $244-245^\circ/685$  mm. The corresponding *brucine* salt, m. p.  $114^\circ$ , is transformed by ethyl iodide into *propylthiolacetic acid* and *brucine ethiodide*.

H. WREN.

**Derivatives of 1:2-dihydroxythioxanthone.** A. A. LEVI and S. SMILES (J.C.S., 1931, 520—527).—4-Bromoveratrole and chlorosulphonic acid give 4-bromoveratrole-5-sulphonyl chloride (analysed as the *amide*, m. p.  $236^\circ$ ), which is converted (a) into veratrole-4-sulphonamide, (b) by vigorous reduction into the thiol, which oxidises to *diveratryl 4-disulphide*, m. p.  $94^\circ$ , (c) by sodium sulphite into 4-bromoveratrole-5-sulphinic acid, m. p.  $122^\circ$ , which with hydriodic acid gives *di-4-bromoveratryl 5-disulphide*, m. p.  $118-119^\circ$ . The thiol derived from the sulphonyl chloride with 2-bromobenzoic acid affords 2-bromo-4:5-dimethoxy-2'-carboxydiphenyl sulphide, m. p.  $211-212^\circ$ , which by dehydration gives 4-bromo-1:2-dimethoxythioxanthone (I), m. p.  $159-160^\circ$ , identical with the product from 4-bromoveratrole and



2-thiolbenzoic acid. 5-Bromoguaiacol condenses with 2-thiolbenzoic acid to form 4-bromo-2-hydroxy-1-methoxy-, m. p.  $208^\circ$ , methylated to give I, and demethylated to 4-bromo-1:2-dihydroxy-thioxanthone, m. p.  $212^\circ$ . I is hydrolysed to 4-bromo-1-hydroxy-2-methoxythioxanthone, m. p.  $191^\circ$  (*diacetoborate*), also obtained by the condensation of 4-bromoguaiacol and 2-thiolbenzoic acid. 1-Hydroxy-2-methoxy-, m. p.  $173-174^\circ$  (*diacetoborate*), from creosol, yields 1:2-dimethoxy-4-methylthioxanthone, m. p.  $125^\circ$  (*dihydrochloride*). Oxidation with hydrogen peroxide gives 4-bromo-1-hydroxy-2-methoxy-, m. p.  $243^\circ$ , 1-hydroxy-2-methoxy-4-methyl-, m. p.  $190^\circ$  (*diacetoborate*, m. p.  $222^\circ$ ), 1:2-dimethoxy-4-methyl-, m. p.  $154^\circ$ , 4-bromo-1:2-dimethoxy-, m. p.  $165^\circ$  (by methylation of the corresponding 1-hydroxy-derivative), and 1:2-dimethoxy-thioxanthone dioxide, m. p.  $246^\circ$  (by oxidation of I). 2-Thiolbenzoic acid and *p*-cresol condense to 4-hydroxy-1-methyl-, m. p.  $245^\circ$ ; and 1-hydroxy-4-methyl-thioxanthone, m. p.  $160^\circ$  (*diacetoborate*, m. p.  $236^\circ$ ), is formed by (a) hydrolysis of 1-methoxy-, (b) diazotisation of 1-amino-4-methyl-

thioxanthone, and (c) the condensation of *p*-tolyl carbonate with 2-thiolbenzoic acid, in small yield.

Study of the basic character of these substances supports the chelate structure previously assigned to the cations of the 1-methoxy-compounds (A., 1929, 934). The relative stabilities of diacetoborates derived from 1-hydroxy-compounds follow in similar order to those of salts of 1-methoxythioxanthenes, and corroborative evidence is adduced from the characters of the dioxides. In the presence of other methoxyl groups, the process of demethylation of 1-methoxy-groups is easily accomplished and is selective. F. R. SHAW.

**Configuration of the doubly-linked tervalent nitrogen atom. IV. Resolution of  $\beta$ -methyltrimethylene dithiolcarbonate carboxyphenylhydrazone.** W. H. MILLS and B. C. SAUNDERS (J.C.S., 1931, 537—546).—With the object of obtaining an optically active compound, the molecular dissymmetry of which could be due only to the non-planar arrangement of the valencies of a doubly-linked tervalent nitrogen atom, the 2'-carboxyphenylhydrazone of  $\beta$ -methyltrimethylene dithiolcarbonate (I) has been prepared and examined.  $\beta$ -Methyltrimethylene dibromide is converted by sodium trithiocarbonate into  $\beta$ -methyltrimethylene trithiocarbonate, m. p.  $74^\circ$ , which when boiled with phenylhydrazine in alcohol gives  $\beta$ -methyltrimethylene dithiolcarbonate phenylhydrazone, m. p.  $89^\circ$ , and when boiled with methyl phenylhydrazine-*o*-carboxylate, m. p.  $48^\circ$  (from methyl anthranilate), affords the methyl ester of I, m. p.  $91.5-93^\circ$ , from which the free acid I, m. p.  $202^\circ$ , is obtained. Trimethylene trithiocarbonate, m. p.  $80^\circ$ , and trimethylene dithiolcarbonate *o*-carboxyphenylhydrazone, m. p.  $212^\circ$  (methyl ester, m. p.  $139-140^\circ$ ), are similarly prepared.

I is resolved by quinine into the *d*-, m. p.  $199^\circ$ ,  $[\alpha]_{5461}^{17} +12.4^\circ$  in chloroform (sodium salt,  $+10.6^\circ$ ; quinine salt, m. p.  $184-185^\circ$ ,  $[\alpha]_{5461}^{17} -255^\circ$  in chloroform), and *l*-isomerides, m. p.  $199^\circ$ ,  $[\alpha]_{5461}^{17} -12.8^\circ$  in chloroform. The active compounds possess considerable optical stability, solutions in chloroform showing an induction period of several days before racemisation occurs; in acid and alkaline media racemisation occurs on boiling. The structure of the compound is discussed and the conclusion reached that it must be represented by

$\begin{matrix} H \\ | \\ Me > C < \begin{matrix} CH_2 \cdot S \\ CH_2 \cdot S \end{matrix} > C : N \cdot NH \cdot C_6H_4 \cdot CO_2H \end{matrix}$ . The acid differs from its salts and esters in being bright yellow, and is doubtless an internal ammonium salt,  $CHMe < (CH_2 \cdot S)_2 > C : N \cdot NH_2 \cdot C_6H_4 \cdot CO_2^-$ . The optical stability may be accounted for by co-ordination between the hydrogen atom of the NH group and one of the sulphur atoms, but this could not determine the displacement of the group  $\cdot NH \cdot C_6H_4 \cdot CO_2H$  from the median plane of the cyclic residue on which dissymmetry depends, nor give stable optical activity associated with the asymmetry acquired, in consequence, by the sulphur atom. F. R. SHAW.

**Derivatives of the pyrrolidine ring.** N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, 62, 2209—2215).—Racemic proline was prepared by hydrolysis of gelatin with sulphuric acid and precipit-

ated as the copper salt. Action of acetic anhydride on its amide gave the *amide* of *N*-acetylproline, m. p. 178—180°; the *acetyl* derivative of the latter, m. p. 142°, and the *nitrile* of *N*-acetylpyrrolidine were prepared by further action of acetic anhydride. 2-Pyrrolidylmethylamine, b. p. 50°/7 mm., was prepared by reducing the nitrile, whilst reduction of proline-amide gave 2-pyrrolidylcarbinol, b. p. 110°/7 mm.

E. B. UVAROV.

**Catalytic reduction of pyrrole and its derivatives. Preparation of 2-pyrrolidylmethylamine and proline.** N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, 62, 2216—2225).—The reductions were carried out by passing hydrogen through a solution in glacial acetic acid and absolute alcohol, using platinum oxide and ferric chloride as catalyst. Reduction of 2-pyrrolmethylamine gave 2-pyrrolidylmethylamine, b. p. 50°/7 mm.; pyrrole-2-carboxylic acid gave proline. The use of palladium oxide gave poor yields.

E. B. UVAROV.

**Action of nitrous acid on 2-pyrrolmethylamine and 2-pyrrolidylmethylamine.** N. I. PUTOCHIN (J. Russ. Phys. Chem. Soc., 1930, 62, 2226—2234).—Action of nitrous acid on 2-pyrrolmethylamine and 2-pyrrolidylmethylamine gives pyridine and piperidine respectively.

E. B. UVAROV.

**Local anaesthetics in the pyrrole series. II.** F. F. BLICKE and E. S. BLAKE (J. Amer. Chem. Soc., 1931, 53, 1015—1025).—Various analogues of novocaine, stovaine, and  $\beta$ -eucaine have been synthesised and their anaesthetic action has been investigated qualitatively. Potassium pyrrole reacts with  $\beta$ -chloroethyl acetate (from ethylene chlorohydrin and acetyl chloride) to give the *acetate*, b. p. 222—225°/740 mm., hydrolysed to  $\beta$ -(1-pyrrolyl)ethyl alcohol, b. p. 110—113°/12 mm. [*benzoate* (I), m. p. 53—55°; *p*-nitrobenzoate, m. p. 92—94°, reduced with hydrogen at 4 atm. and a platinum oxide catalyst in alcohol, to the *p*-amino-benzoate (II), m. p. 87—88°; and 2-pyrrolylcarboxylate (III), m. p. 73—74°; all prepared by the action of the appropriate acyl chloride on the potassium derivative of the alcohol].  $\beta$ -Chloroethyl *p*-aminobenzoate with pyrrolidine in a sealed tube at 115—120° affords  $\beta$ -(1-pyrrolidyl)ethyl *p*-aminobenzoate (IV). Similarly from  $\gamma$ -chloropropyl acetate, b. p. 168—173° (lit. b. p. 160—166°; from trimethylene chlorohydrin and acetyl chloride), is prepared  $\gamma$ -(1-pyrrolyl)propyl alcohol, b. p. 229—231°/743 mm. [*acetate*, b. p. 127—135°/13 mm.; *benzoate* (V), b. p. 165—170°/5 mm. (probably not pure); *p*-nitrobenzoate, m. p. 68—70°, reduced to the *p*-aminobenzoate (VI), m. p. 114—116°; and 2-pyrrolylcarboxylate, m. p. 69—70°], whilst  $\gamma$ -chloropropyl *p*-aminobenzoate, m. p. 86—87° (from trimethylene chlorohydrin and *p*-aminobenzoic acid), is converted into  $\gamma$ -(1-pyrrolidyl)propyl *p*-aminobenzoate (VIII), m. p. 84—85°. Of these novocaine analogues, I—VIII, all but I and V produce local anaesthesia in alcoholic solution, but aqueous solutions of the hydrochlorides of IV and VIII are without action. Stovaine may be conveniently prepared by interaction of the potassium derivative of dimethylaminomethylethylcarbinol with benzoyl chloride, the 2-pyrrolylcarboxylate, m. p. 194—195° (IX), of the carbinol being similarly prepared. Chloromethylmethylethylcarbinol is con-

verted by heating with pyrrolidine in a sealed tube at 115—120° into the oily 1-pyrrolidylmethylethylcarbinol (oily benzoate, X). Ethyl chloroacetate and potassium pyrrole give ethyl 1-pyrrolylacetate, b. p. 110—115°/16 mm. (free acid, m. p. 94—95°), converted by the appropriate Grignard reagent into 1-pyrrolyl-methyl-, b. p. 86—88°/2—3 mm., and -diethyl-, b. p. 108—116°/1 mm., -carbinol. Similarly, from ethyl  $\beta$ -bromopropionate is prepared ethyl  $\beta$ -(1-pyrrolyl)propionate, b. p. 119—122°/14 mm. (acid, m. p. 62—64°), and hence 1-pyrrolylethyl-diethylcarbinol, b. p. 125—128°/4—5 mm. Of these stovaine analogues both the free bases IX and X and their hydrochlorides are local anaesthetics. Diacetoneamine hydrogen oxalate can be reduced directly to 4-hydroxy-2 : 2 : 6-trimethylpiperidine, separated into the stable and unstable forms and these methylated as described by Harries (A., 1919, i, 131). The methylated stable and labile forms are each converted through their potassium derivatives into their 4-2-pyrrolylcarboxylate, m. p. 106—107° and 106—107°, respectively (mixed m. p. 80—83°; *picrate* of stable form, m. p. 192—193°). Of these the stable form is active and the labile form is inactive as a local anaesthetic. Thus the local anaesthetic action of these derivatives is retained by substitution of the 2-pyrrolylcarboxylate for the benzoate or *p*-aminobenzoate, and by replacement of the dimethyl- or diethyl-amino-group by the 1-pyrrolyl or 1-pyrrolidyl nuclei. Improved details for the preparation of intermediates in the synthesis of pyrrolidine are given.

J. W. BAKER.

**Preparation of 2-alkylpiperidines. I. 2-Amylpiperidine.** A. FRANKE and W. PRODINGER (Ber., 1931, 64, [B], 542—543).— $\alpha$ -Dibromodecane, obtained from  $\alpha$ -oxidodecane and saturated hydrobromic acid at 100°, is converted by treatment with *p*-toluenesulphonamide and potassium hydroxide in boiling alcohol into 2-amylpiperidine isolated as the chloroplatinate, m. p. 117° after softening at 114°.

H. WREN.

**Interaction of sulphonates and sulphonamides with piperidine.** F. BELL (J.C.S., 1931, 609—615).—In contrast to the mononitro-compounds, the scission of 2 : 4-dinitrophenyl *p*-toluenesulphonate with piperidine gives (a) 2 : 4-dinitrophenol and *p*-toluenesulphonylpiperidine and, at the same time, (b) 2 : 4-dinitro-1-phenylpiperidine. 2 : 4-Dinitrophenol is not an intermediate, since it forms a stable piperidine salt, m. p. 171°, and pyridine salt, m. p. about 85°. The reaction (b) seems to require the intermediate production of an additive compound in which the nitro-group loses its normal electrical character. Disulphonamides (including dinitro-compounds) react with piperidine to give the monosulphonamides, and the mechanism of this change is discussed. Nitroamines react with difficulty, if at all, with *p*-toluenesulphonyl chloride in pyridine, but the corresponding nitrosulphonamides are easily converted into disulphonamides, *di*-*p*-toluenesulphon-2 : 4-dinitroanilide, m. p. 217°, and 3 : 5-dinitro-4-*p*-toluenesulphonamidodiphenyl, m. p. 249°, being formed. 3 : 5-Dibromo-4-*p*-toluenesulphonamidodiphenyl, m. p. 196°, is obtained from the corresponding disulphonamide and piperidine. Although polynitrophenols

are usually converted into the chloro-compounds by the action of *p*-toluenesulphonyl chloride (cf. Ullmann, A., 1908, 525), sulphonates are probably intermediate products. The following are described: *piperidine picrate*, m. p. 150° (*piperidine* compound, m. p. about 135°), *picrylpyridinium-p-toluenesulphonate*, m. p. 197°, *pyridine* salt of 3:5:4'-trinitro-4-hydroxydiphenyl, m. p. 198°, and *piperidine* salt of *p*-toluenesulphon-*p*'-nitroanilide, m. p. 138°.

F. R. SHAW.

**Pyridine bases from tar.** M. P. OPARINA (Ber., 1931, 64, [B], 562—569).—Fractional distillation of the mixture of bases followed by treatment of the fractions with picric acid leads to the isolation of 4-methyl-, 2:6-, 2:5-, and 2:4-dimethyl-, 2:4:6-, 2:3:6-, 2:3:5-, and 2:4:5-trimethyl-pyridine. The following observations appear to be new: 2:3:5-trimethylpyridine, b. p. 183—185°,  $d_4^{25}$  0.9377 (*chloroplatinate*, m. p. 227—228°; *chloroaurate*, m. p. 146—147°), oxidised to pyridine-2:3:5-carboxylic acid, m. p. 307—308°; 2:3:6-trimethylpyridine, b. p. 173—174°,  $d_4^{25}$  0.9299 (*picrate*, m. p. 146°; *chloroplatinate*, m. p. 228°; *chloroaurate*, m. p. 146—147°), oxidised to (?) 2-methylpyridine-3:6-dicarboxylic acid, m. p. 247° (decomp.) (*silver* salt), and pyridine-2:3:6-tricarboxylic acid, m. p. 245° (decomp.); 2:4:5-trimethylpyridine, b. p. 188—190° (*picrate*, m. p. 159—160°; *chloroplatinate* (+2H<sub>2</sub>O), m. p. 191—192° (decomp.); *chloroaurate*, m. p. 107—108°), oxidised to 4-methylpyridine-2:5-dicarboxylic acid, m. p. 237° (*silver* salt), and pyridine-2:4:5-tricarboxylic acid (+2H<sub>2</sub>O), m. p. 242° (*silver* salt).

H. WREN.

**Condensation of mixtures of aldehydes and ketones with ammonia in presence of aluminium hydroxide as contact substance.** M. P. OPARINA (Ber., 1931, 64, [B], 569—577).—Passage of a mixture of acetone (1 mol.) and paracetaldehyde (2 mols.) with excess of ammonia over aluminium oxide in a coppered tube at 340—350° leads to the formation of 2:4-dimethylpyridine (*picrate*, m. p. 181°); the production of 2:6-dimethylpyridine could not be detected. Formaldehyde (1 mol.) and acetone (2 mols.) give 2:6-dimethylpyridine with a small proportion of the 2:4-isomeride. 2:3:6-Trimethyl- and (?) 2:3:5:6-tetramethyl-pyridine are obtained from molar proportions of acetone, methyl ethyl ketone, and formaldehyde; the tetramethyl base is the main product from methyl ethyl ketone (2 mols.) and formaldehyde (1 mol.). Acetaldehyde (2 mols.) and methyl ethyl ketone (1 mol.) afford 2:3:4-trimethylpyridine. The base is prepared synthetically in the following manner:  $\gamma$ -methylpentane- $\beta\delta$ -dione is condensed with ethyl cyanoacetate and ammonia to 3-cyano-2-hydroxy-4:5:6-trimethylpyridine, m. p. 304—305°, which is converted by boiling sulphuric acid into 2-hydroxy-4:5:6-trimethylpyridine, m. p. 252° (*potassium* salt), reduced by zinc dust to 2:3:4-trimethylpyridine in poor yield. The hydroxy-compound is therefore transformed by phosphorus pentachloride into 2-chloro-4:5:6-trimethylpyridine, b. p. 118—119°/20 mm., m. p. 49° (*picrate*, m. p. 105°), reduced by hydriodic acid at 180° or by the acid and zinc dust at 40° to 2:3:4-trimethylpyridine, b. p. 192—193°,  $d_4^{25}$  0.9566 (*picrate*, m. p. 164.5°; *chloro-*

*platinate*, m. p. 259°; *chloroaurate*, m. p. 182—183°). Oxidation of the base with potassium permanganate gives pyridine-2:3:4-tricarboxylic acid (+1.5H<sub>2</sub>O), m. p. 249° (*trimethyl* ester, m. p. 101—102°), and 2-methylpyridine-3:4-dicarboxylic acid, m. p. (indef.) 260—268° (anhydride, m. p. 118—119°). Successive treatment of 2:3:4-trimethylpyridine with 30% formaldehyde and nitric acid ( $d$  1.4) affords 3-methylpyridine-2:4-dicarboxylic acid, m. p. 216—217°. The preparation of 4-methylpyridine-2:3-dicarboxylic acid, m. p. 190°, is incidentally described. H. WREN.

**Polyhalogenated ketones of indole.** G. SANNA (Gazzetta, 1931, 61, 60—74).—Dichloroacetyl chloride and the magnesium derivative of 2-methylindole give 3-dichloroacetyl-2-methylindole, m. p. 195°. The chlorine is feebly reactive. The compound is unaffected by boiling water. A (?) *diacetate* is obtained after prolonged boiling with alcoholic potassium acetate solution, and the *dibromo*-compound, m. p. 178°, is slowly formed by the action of alcoholic potassium bromide. The action of potassium iodide is slow and incomplete. Boiling 5% potassium hydroxide solution yields 2-methylindole-3-glycollic acid, m. p. 90° (decomp.) (*barium* salt; *silver* salt, m. p. 247°), converted by fusion into 3-(2-methyl)indolylcarbinol, m. p. 196°. When heated with ammonia at 100° in a sealed tube it yields 2-methylindole-3-carboxylamide, m. p. 218°.

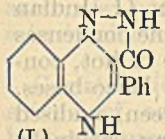
3-Trichloroacetyl-2-methylindole, m. p. 167°, is obtained from the magnesium derivative of 2-methylindole and trichloroacetyl chloride. It is very slowly attacked by boiling aqueous potassium hydroxide. Alcoholic potassium hydroxide yields 2-methylindole-3-carboxylic acid, m. p. 186° (decomp.). Potassium bromide or ammonia solutions have no action.

The m. p. of the chlorinated 3-acetylindoles show a variation with the number of chlorine atoms parallel with that of the m. p. of the chlorinated acetophenones. R. K. CALLOW.

**Methoxylated 2-phenyl-4-quinolones (4-hydroxy-2-phenylquinolines).** R. SEKA and W. FUCHS (Monatsh., 1931, 57, 52—62).—Various improvements in the Just method (A., 1886, 149, 161) of preparing ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate are described, and used in the synthesis of hydroxymethoxyphenylquinolines. Treatment of benz-*p*-anisidine with phosphorus pentachloride at 70—75° and distillation of the mixture gives the corresponding iminochloride, b. p. 220°/20 mm., m. p. 63—64° (80.6% yield), which with dry ethyl sodiomalonate in ether at 100—120° affords 26.5% of the theoretical amount of ethyl 4-hydroxy-6-methoxy-2-phenylquinoline-3-carboxylate, m. p. 245°. The free acid (+H<sub>2</sub>O), m. p. 235°, when heated in a vacuum gives 4-hydroxy-6-methoxy-2-phenylquinoline, m. p. 287°. The iminochloride from anis-*p*-anisidine and ethyl sodiomalonate in ether at 80—90° afford ethyl 4-hydroxy-6-methoxy-2-anisylquinoline-3-carboxylate, m. p. 265—266°, converted by way of the free acid, m. p. 252°, into 4-hydroxy-6-methoxy-2-anisylquinoline, m. p. 295°. Quinoline derivatives could not be prepared by the above method from the benzoyl and anisoyl derivatives of 3:5-dimethoxyaniline, 3:4:5-

trimethoxybenzanilide, or *benz-3:4:5-trimethoxyanilide*, m. p. 138-5°.

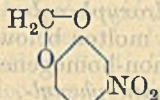
Treatment of ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, prepared as above from the imino-chloride from benzanilide, with phosphorus pentachloride in phosphoryl chloride, removal of the phosphoryl chloride in a vacuum, and treatment of the residue with ammonia and hydrazine gives 4-hydroxy-2-phenylquinoline-3-carboxylamide, m. p. 208°, and the compound (I), m. p. 317°, respectively.



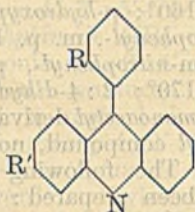
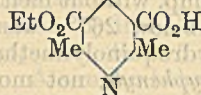
(I.)

H. BURTON.

**Stereochemistry of derivatives of diphenyl and its analogues.** F. LIONS (J. Amer. Chem. Soc., 1931, 53, 1176-1179).—Attempts to resolve the methosulphate of 2-(*o*-carboxyphenyl)pyridine-3-carboxylic acid, derivatives of 4-phenylpyridine of



(I.)



(II.)

type I, and acridine derivatives of type II (R=Cl or Me; R'=H or Me) have proved unsuccessful.

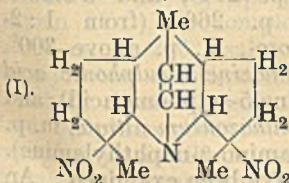
J. W. BAKER.

**Carbazole derivatives.** E. GHIGI (Gazzetta, 1931, 61, 43-46).—The compound (revised m. p. 100°) obtained by the action of sulphuric acid on  $\beta$ -tetralonephenylhydrazone (A., 1930, 787) is 3:4-benzo-1:2-dihydrocarbazole, since distillation over lead oxide yields 3:4-benzocarbazole.  $\beta$ -Tetralonephenylhydrazone and zinc chloride in alcohol may give either 3:4-benzo-1:2-dihydrocarbazole or 1:2-benzocarbazole, m. p. 229° (picrate, m. p. 185-186°; acetyl derivative, m. p. 289-290°), also obtainable by dehydrogenating 1:2-benzo-3:4-dihydrocarbazole.

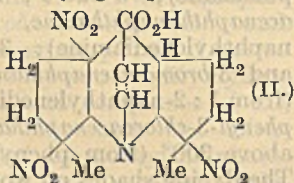
R. K. CALLOW.

**Nitrogen compounds in petroleum distillates.**

**III. Structure of a hydroaromatic base  $C_{16}H_{25}N$ .** W. C. THOMPSON and J. R. BAILEY (J. Amer. Chem. Soc., 1931, 53, 1002-1011).—The "naphthenic" base  $C_{16}H_{25}N$ , b. p. 278.2°/746 mm.,  $d_4^{20}$  0.9391,  $n_D^{20}$  1.5129 (picrate, m. p. 151°; hydrogen sulphate, m. p. 196°; hydrochloride, m. p. 251°; nitrate +  $H_2O$ , m. p. 79°, and anhydrous, m. p. 141°; chloroplatinate, decomp. 240°; methiodide, softens at 250°, decomp. without melting; zinc chloride, m. p. 171°, and mercuric chloride, m. p. 157.5°, double salts), isolated from the crude kerosene distillate of California petroleum (A., 1930, 788) contains no *N*-alkyl group, could not



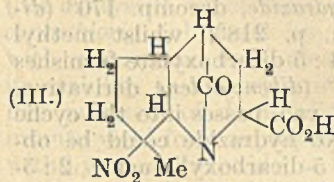
(I.)



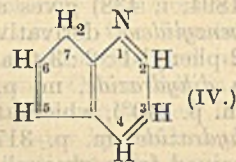
(II.)

be brominated, dehydrogenated, or reduced, and is very stable towards alkaline permanganate. Oxid-

ation with nitric acid at 170° gives the following products: 3:5-dinitro-3:5:8-trimethyldecahydro-4:8-ethylenopyrindacine (I), m. p. 116.5° (picrate, m. p. 231°); 3:5:7a-trinitro-3:5-dimethyldecahydro-4:8-ethylenopyrindacine-8-carboxylic acid (II), m. p. 347° (decomp.); 7-nitro-7-methyloctahydro-1:4-ketopyrindine-3-carboxylic acid (III), m. p. 189-190°

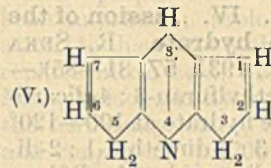


(III.)

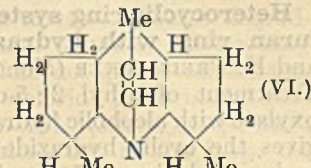


(IV.)

(decomp.); and pyridine-2:4:5-tricarboxylic acid. The nomenclature is derived from the parent com-



(V.)



(VI.)

pounds pyridine (IV) and pyrindacine (V). The structure VI is chosen for the naphthene base  $C_{16}H_{25}N$ , from various possible structures. J. W. BAKER.

**Conversion of compounds of the carbamidodiacetic acid type into the hydantoin-3-acetic acid type and the inverse process.** R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], 49, 309-318).—Contrary to the assertion of Gränacher and Landolt (A., 1928, 74) the nature of the alkali used does not affect the position at which the ring is ruptured in hydantoin-3-acetic acid. With ammonia or with alkali hydroxide rupture always occurs between positions 3 and 4, yielding carbamidodiacetic acid or derivatives. Thus ethyl hydantoin 3-acetate, m. p. 120°, with concentrated aqueous ammonia at 0° affords mainly ethyl carbamidodiacetamide, decomp. begins at 240°, m. p. 260° with carbonisation, and a little hydantoin-3-acetamide, m. p. 225-226°, whilst heating with *N*-sodium hydroxide gives a 66% yield of carbamidodiacetic acid, m. p. 230° (decomp.) (sinters at 200-210° when heated slowly), converted on esterification into ethyl carbamidodiacetate, m. p. 147-148°, and not into ethyl glycyglycinecarboxylate, m. p. 87° (Fischer, A., 1902, i, 350), as assumed by Gränacher and Landolt. Hydrolysis with 3% barium hydroxide also affords carbamidodiacetic acid.

When refluxed with alcoholic hydrogen chloride ethyl carbamidodiacetate gives ethyl hydantoin-3-acetate, also obtained by esterifying hydantoin-3-acetic acid (from ethyl carbamidodimalonate). Water at 170-180° converts hydantoin-3-acetic acid and carbamidodiacetic acid or their esters into carbon dioxide and glycine (cf. Wessely and John, A., 1928, 530).

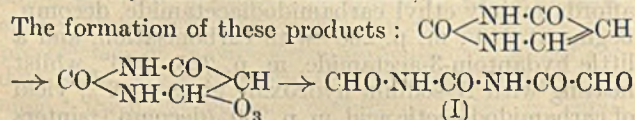
R. BRIGHTMAN.

**Heterocyclic ring systems. III. Ring closure reactions of heterocyclic *o*-dicarboxylic acids.** R. SEKA and H. PREISSECKER (Monatsh., 1931, 57, 71-80; cf. A., 1925, i, 57, 1298).—The behaviour of various heterocyclic *o*-dicarboxylic esters towards hydrazine is investigated. Ethyl 2:5-diphenyl-

furan-3 : 4-dicarboxylate and hydrazine hydrate at 100—120° give a cyclic *hydrazide*; ethyl 2 : 5-dimethyl- and 2 : 5-diphenyl-pyrrole-3 : 4-dicarboxylates and hydrazine hydrate (containing a little alcohol) at 140—150° afford cyclic *hydrazides*, decomp. 359° after charring at 295° and m. p. 324°, respectively. Ethyl pyrazolinedicarboxylate (von Pechmann, A., 1894, i, 438) gives a *dihydrazide*, decomp. 170° (*dibenzylidene* derivative, m. p. 218°), whilst methyl 2-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate furnishes a *dihydrazide*, m. p. 225° (*dibenzylidene* derivative, m. p. 240°), which at 235°/vac. passes into the cyclic *hydrazide*, m. p. 317°. No hydrazide could be obtained from glyoxaline-4 : 5-dicarboxylic acid; 2 : 5-dimethylfuran-3 : 4-dicarboxylic acid is decomposed by treatment with hydrazine hydrate. H. BURTON.

**Heterocyclic ring systems. IV. Fission of the furan ring with hydrazine hydrate.** R. SEKA and H. PREISSECKER (Monatsh., 1931, 57, 81—85).—Treatment of ethyl 2 : 5-dimethylfuran-3 : 4-dicarboxylate with alcoholic hydrazine hydrate at 100—120° gives the cyclic hydrazide of 3 : 6-dimethyl-1 : 2-dihydropyridazine-4 : 5-dicarboxylic acid (cf. Bülow, A., 1904, i, 272). The same compound (*tetra-acetyl* derivative, m. p. 140°; *tetrabenzoyl* derivative, m. p. 190°) is also obtained from ethyl  $\alpha'$ -diacetylsuccinate and hydrazine hydrate. H. BURTON.

**Pyrimidines. CXX. Action of ozone on uracil. CXXI. Action of ozone on some derivatives of uracil.** T. B. JOHNSON and R. B. FLINT (J. Amer. Chem. Soc., 1931, 53, 1077—1081, 1082—1087).—CXX. Ozonolysis of uracil gives mainly *formylglyoxylcarbamide* (I), m. p. 162° (with phenylhydrazine it gives either formylphenylhydrazine or a substance, decomp. 221°, according to conditions), and oxaluric acid (II), whilst traces of an unidentified pyrimidine, and complete degradation products, carbamide, oxalic and formic acids, are also obtained.



CXXI. Ozone attacks a suspension of 4-methyl- and 4-phenyl-uracil in acetic acid to give *acetyl*-, m. p. 150° (64% yield), and *benzoyl*-, m. p. 168° (with phenylhydrazine gives the same substance, decomp. 221°, as was obtained with formylglyoxylcarbamide), *-glyoxylcarbamide*, together with traces of carbamide and oxalic acid. Thymine gives formylcarbamide (40% yield); 5-bromouracil gives parabanic acid, whilst 5-nitouracil gives this acid and oxaluric acid. 5-Bromo-1 : 3-dimethyluracil affords *dimethyloxaluric acid*, m. p. 124—125°. Carbamide and oxalic acid are also formed in each case. J. W. BAKER.

**2 : 2'-Dipyridyl from pyridine by catalytic dehydrogenation under pressure.** J. P. WIBAUT and H. D. T. WILLINK (Rec. trav. chim., 1931, 50, 287—290).—Pyridine when heated at 320—325° in presence of nickel during 5—6 hrs. gives 2 : 2'-

dipyridyl [14—20% (pure) on the pyridine transformed]. J. D. A. JOHNSON.

**Triphenylmethane dyes derived from quinoline, tetrahydroquinoline, diphenylamine, and carbazole.** R. N. SEN and B. N. SEN (J. Indian Chem. Soc., 1930, 7, 965—972).—Quinoline condenses with aromatic aldehydes in the presence of hot, concentrated hydrochloric acid, giving leuco-bases, analogous in constitution to malachite-green, oxidised by lead peroxide to the corresponding carbinols. Since 6-nitroquinoline fails to react, it is assumed that the hydrogen atom attached to the 6-carbon atom suffers replacement. Tetrahydroquinoline behaves analogously and its residue appears to exert a stronger auxochromic influence than that of quinoline. The following diquinolylmethanes are described : *phenyl*-[*chloroplatinate*, m. p. 230° (decomp.); *picrate*, m. p. 199°]; *p-methoxyphenyl*-; *o-hydroxyphenyl*-, m. p. 157—160°; *p-hydroxyphenyl*-, not molten below 263°; *p-nitrophenyl*-, m. p. 108°, and non-homogeneous *o*- and *m-nitrophenyl*-, *p-dimethylaminophenyl*-, m. p. 168—170°; 2 : 4-*dihydroxyphenyl*-, not molten below 240° (*monoacetyl* derivative, decomp. without melting; *diacetyl* compound, not molten below 267°; *disilver* salt). The following ditetrahydroquinolylmethanes have been prepared : *m-hydroxyphenyl*-, not molten below 256°; *m-nitrophenyl*-, m. p. 212° (decomp.); *furfuryl*-, decomp. without melting; *p-methoxyphenyl*-; *o-hydroxyphenyl*-, m. p. 163—164°; *p-hydroxyphenyl*-, m. p. 255°; *p-dimethylaminophenyl*-; 2 : 4-*dihydroxyphenyl*-, not molten below 253°. *Di-1-methyltetrahydroquinolylmethane* and *phenyldi-1-methyltetrahydroquinolylmethane*, m. p. 100° after softening at 90°, have been prepared. The following dyes are obtained from diphenylamine or carbazole : *di-p-anilinotriphenylmethane* and its *disulphonic acid*; *di-p-methylanilinotriphenylmethane*, m. p. 144—146°; *phenyldicarbazolylmethane*, not molten below 260°; *phenyldi-1-methylcarbazolylmethane*, m. p. 148° after softening at 140°; *di-p-anilinodiphenylmethane*; *di-p-methylanilinodiphenylmethane*; 4' : 4''-*dianilino-2-hydroxytriphenylmethane*; 4' : 4''-*dianilino-3-4-methylenedioxytriphenylmethane*. H. WREN.

**Dyes derived from acenaphthenequinone. II. Azine and azonium derivatives.** S. K. GUHA (J.C.S., 1931, 582—586).—The following were prepared by condensing 3-chloro- and 3-bromo-acenaphthenequinones with *o*-diamines : 3-*chloro*-, m. p. 278°, and 3-bromo-acenaphthaphenazine, m. p. 272° (from *o*-phenylenediamine); 3-*chloro*-, m. p. 256°, and 3-bromo-acenaphthatholazine, m. p. 270° (from 3 : 4-tolylenediamine); 3-*chloro*- and 3-bromo-acenaphthaphenazine (do not melt; from 2 : 3-diaminophenazine); 3-*chloro*-, m. p. 274°, and 3-bromo-acenaphthanaphthazine, m. p. 266° (from 1 : 2-naphthylenediamine); 3-*chloro*-, m. p. above 300°, and 3-bromo-acenaphthanaphthazine-5'-sulphonic acid (from 1 : 2-naphthylenediamine-5-sulphonic acid); and *phenyl-3-chloroacenaphthanaphthazonium nitrate*, m. p. above 300° (from phenyl-1-amino- $\beta$ -naphthylamine). The dyeing shades on wool have been examined. An improved method for preparing 3-bromoacenaphthenequinone is described. F. R. SHAW.

**Reaction of aliphatic iminoethers with hydrazine.** W. OBERHUMMER (Monatsh., 1931, 57, 106—111).—Prolonged treatment of formiminoether hydrochloride with dry ethereal hydrazine gives 25—30% of the theoretical amount of 1-amino-1 : 3 : 4-triazole, also produced from the ether hydrochloride and a hydrazine salt in alcohol. H. BURTON.

**Constitution of bile pigments. III. Derivatives of coproporphyrin I, and synthesis of hydroxypyromethenes.** H. FISCHER and W. FRÖWIS (Z. physiol. Chem., 1931, 195, 49—80; cf. A., 1924, i, 319).—An improved method of preparation of methyl 5-bromo-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionate (I; cf. A., 1926, 1261) is described. The bromine is readily replaced by aniline, giving methyl 5-anilino-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionate, m. p. 145° (complex copper salt, m. p. 120°; hydrobromide, m. p. 186°), but with methylamine in methyl alcohol 5-bromo-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionmethylamide (II), m. p. 212° (decomp.), and with ammonia the -3 : 4'-dipropionamide, decomp. 260—270°, are produced. The bromine atom in II is replaced by methyl-alcoholic potassium hydroxide, giving 5-methoxy-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionmethylamide, m. p. 225°. A similar behaviour towards methyl-alcoholic alkali is shown by I, the product, after re-esterification with methyl sulphate, being methyl 5-methoxy-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionate (III), m. p. 88°. With silver acetate in acetic acid, however, the 5-hydroxy-compound, m. p. 180°, is produced; this is readily obtained from III by fusion with resorcinol, or by complete demethylation with methyl-alcoholic sodium methoxide at 170—180°, followed by re-esterification with methyl sulphate; the last process leads to the same result when applied to I. The 5-hydroxy-compound may be detected by the deep violet coloration it gives with acidified aqueous diazobenzenesulphonic acid. Coproporphyrin is produced from III by the action of hydrogen bromide in acetic acid at 170—180°, and a colourless, readily oxidised substance, possibly the methane, by reduction with sodium amalgam. 5-Methoxy-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyromethene, m. p. 70°, is readily prepared from the bromo-compound, and gives the corresponding 5-hydroxy-compound, m. p. 243°, on fusion with resorcinol.

The mother-liquors from the preparation of 5-bromo-4 : 3' : 5'-trimethylpyromethene-3 : 4'-dipropionic acid (*loc. cit.*) after long keeping contain coproporphyrin I, which may be isolated as its tetraethyl ester; this porphyrin also appears to be formed in small yield from the methene and concentrated sulphuric acid. Fusion of I with citric acid gives, in addition to coproporphyrin I, a little coproporphyrin IV. The complex cobalt, m. p. 270°, and silver, m. p. 286°, salts of coproporphyrin I tetramethyl ester are described; they are readily hydrolysed by dilute aqueous alkali to complexes of the free porphincarboxylic acid, of which the silver complex is readily re-esterified by methyl sulphate. Potassium cyanide and acetic acid regenerate the ester from its silver complex; ferrous acetate in acetic acid replaces the silver with formation of

*coprohæmin tetramethyl ester*, m. p. 245°, converted in the usual way, and possibly also by silver acetate, into the *hæmatin*, m. p. 215°. The cobalt salt, m. p. 316°, decomp. 320—325°, of isouroporphyrin II octamethyl ester is described.

Long exposure of a colloidal aqueous solution of coproporphyrin to bright sunlight gives a *chlorin* (not analysed), which behaves differently from normal *coprochlorin* (obtained by reduction of the hæmin with sodium and amyl alcohol) on reduction and in its stability to atmospheric oxygen. Other chlorin-like products of doubtful identity are obtained in minute yield from coproporphyrin ester by oxidation with hydrogen peroxide, or by reduction to the leuco-compound (zinc and acetic acid) and oxidation of this with ferric chloride.

The preparation of dinitrocoproporphyrin has been improved; prolonged nitration causes degradation to hæmatic anhydride. Sodium nitrite may replace nitric acid, but offers no special advantage. Methyl-alcoholic hydrogen chloride gives in the cold the *tetramethyl ester*, m. p. 191° (*silver*, m. p. 240°, and *copper*, m. p. 200°, salts), but at the b. p. the *tetramethyl ester* of a *nitrodihydroxyporphyrin*, m. p. 206° (*copper salt*, m. p. 245°), is formed (cf. Hilger, A., 1926, 189). Reduction gives coproporphyrin and a *mononitro-derivative* (isolated as *tetramethyl ester*, m. p. 204°), which also appears to be formed by incomplete nitration. Coproporphyrin tetrahydrazide (A., 1928, 1384; the *iron salt* is very sensitive to atmospheric oxidation) is converted by nitrous acid into the *tetrazide*, decomp. 90° (explodes), which with boiling methyl alcohol gives the *tetramethylurethane*, m. p. 190°. H. A. PIGGOTT.

**Porphyryns. XXVII. Mechanism of the introduction of iron into porphyryns and isolation of crystalline hæms.** H. FISCHER, A. TREIBS, and K. ZEILE (Z. physiol. Chem., 1931, 195, 1—27).—The introduction of iron into porphyryns by ferrous salts in absence of air is unaccompanied by evolution of hydrogen or by reduction of the solvent or porphyrin, even when the latter is readily reducible; thus derivatives of mesoporphyrin are completely absent from the product of interaction of ferrous salts with protoporphyrin. The products obtained are not hæmins, however, but ferrous compounds in which two pyrrole nuclei are linked by an atom of iron (>N·Fe·N<). The spectra of their solutions are almost indistinguishable from those of the corresponding hæmins, but differences are more readily observed in their "powder spectra." These new complex salts, for which the name "hæm" is proposed, are readily converted by mineral acids into the original porphyrin and a ferrous salt, and are readily oxidised, even by air, particularly in presence of chloride ions, to the hæmin, the order of ease of oxidation being ætio- < meso- < proto-hæm, and combine with pyridine to form hæmochromogens. The final property is shown in a much smaller degree by hæmins, which, however, readily combine with pyridine in the presence of reducing agents.

The hæms are necessary intermediates in the formation of hæmins, and ferric chloride is unable to convert mesoporphyrin ester into the hæmin under

the usual conditions (in presence of acetic acid and an alkali acetate) if a stream of air is passed through the solution; in the absence of the air stream, and particularly in presence of a little ferrous salt, hæmin formation is rapid and complete. Reduction of hæmins by ferrous salts in acid solution regenerates the porphyrin, owing to the decomposition of the intermediately formed hæm by the free acid. A further consequence of the ready reversibility of hæm formation is the need of the presence of sodium acetate or a similar salt in preparing hæmins by interaction of ferric chloride and a porphyrin, but alternative methods of removing the hydrochloric acid produced, e.g., use of boiling butyric acid in an open vessel as solvent, are equally effective. The presence of 3 atoms of active hydrogen in hæmin, determined by Zerevitinov's method, and the formation during the reaction of ionic chlorine, are due to reduction to hæmochromogen, which may be detected spectroscopically; this conclusion is confirmed by the value of 0.3 observed with mesoester-hæm and 1.2 with dimethylhæmatin.

Crystalline *ætio*-, *proto*-, *meso*-, and *mesoester-hæms* are readily prepared from the porphyrin and ferrous acetate in acetic acid solution in a current of pure nitrogen. The last forms with pyridine a crystalline hæmochromogen, which is relatively stable to atmospheric oxidation and contains 2 mols. of base, one of which is lost at 55°, and the other only on oxidation to the hæmatin (in chloroform). A substance, m. p. 230°, apparently the acetoxhæmin, is found in the mother-liquors from the preparation of mesoesterhæm. The oxidation of mesoporphyrin-ester with ferric chloride and potassium ferricyanide gives the corresponding *xanthoporphinogen*, m. p. 295°, readily reconverted into the original porphyrin by reduction. The occasional formation of a crystalline form of protohæmin, which shows parallel extinction, is reported. H. A. PIGGOTT.

**Chlorophyll formation.** K. NOACK and W. KIESSLING (Z. angew. Chem., 1931, 44, 93—96).—Protophæophytin (from gourd skins) is converted by 30% methyl-alcoholic hydrogen chloride into a trimethyl ester (I),  $C_{36.37}H_{42}O_6N_4$  (3 OMe groups), m. p. 234—235° (absorption spectrum: bands at 637—630, 593—576, 558—549, and 525—507 in order of increasing intensity), hydrolysis of which or of the parent phytin affords protophæophorbide,  $C_{34.35}H_{38}O_6N_4$  (1 OMe group). Reduction of methylphæophorbide with iron and 80% formic acid affords methylprotophæophorbide,  $C_{35.36}H_{38}O_5N_4$  (2 OMe groups), but reduction of chlorophyll itself always involves fission of the phytol group, the main product being an alkali-soluble substance, spectrally identical with methylprotophæophorbide, both of which give the same trimethyl ester I. The view that phylloerythrin is an acid anhydride receives support from the observation that it is hydrolysed in isopropyl alcohol by 10% aqueous potassium hydroxide to a free carboxylic acid,  $C_{33.34}H_{34}O_5N_4$ , the absorption spectrum of which (bands at 632—624, 585—569, 550—539, and 517—500, in order of increasing intensity) is very similar to that of I; this acid is of the blood-porphyrin type, and gives, with diazo-

methane, a trimethyl ester, m. p. 232—233°, spectrally identical with the acid and probably isomeric with I. The structural and biological inter-relationships of these products are discussed. The protochlorophyll series of derivatives must be photo-oxidisable to the corresponding derivatives of the chlorophyll series, and is related to the latter by the deficiency of one oxygen atom. The formation of phylloerythrin in animals involves deoxidation of chlorophyll, combination with fission of magnesium, hydrolysis and anhydride formation, this compound forming a physiological bridge between the leaf and blood colouring matters. J. W. BAKER.

**Dehydrogenation of chlorophyll and the mechanism of photosynthesis.** J. B. CONANT, E. M. DIETZ, and S. E. KAMERLING (Science, 1931, 73, 268).—Methyl phæophorbide *a* is oxidised by potassium molybdicyanide in pyridine and acetone solution to the corresponding dehydrophæophorbide which yields the same hydrolysis products with hot alkali as allomerised phæophorbide. These results support the view (this vol., 368) that the allomerisation of chlorophyll is essentially a dehydrogenation. The mechanism for photosynthesis now suggested can be represented by the scheme: dark reaction, chlorophyll + CO<sub>2</sub> + enzyme → dehydrochlorophyll + dextrose + water, and light reaction, dehydrochlorophyll + light + water → chlorophyll + oxygen. L. S. THEOBALD.

**Ring closure of *o*-thiocarbamidobenzoic acids. Isomerism.** T. N. GHOSH (J. Indian Chem. Soc., 1930, 7, 981—984).—Anthranilic acid condenses with phenylthiocarbimide in boiling alcohol with formation of 2-thio-4-keto-3-phenyl-1:2:3:4-tetrahydroquinazoline, m. p. above 300° (corresponding disulphide,  $C_{28}H_{18}O_2N_4S_2$ , m. p. 250—252°), the intermediate *o*-thiocarbamidobenzoic acid not being isolable. The corresponding -3-*p*-tolyl-, m. p. 310°, -3-*o*-tolyl-, m. p. 268—270° (disulphide, m. p. 215° after shrinking at 200°), -3-1':3':4'-xylyl-, m. p. 259—260°, and -3-allyl-, m. p. 206—207°, compounds are similarly prepared. 2-Thio-4-keto-3-phenyl-1:2:3:4-tetrahydroquinazoline is converted by concentrated sulphuric acid at 125—130° into 2-anilino-6-keto-4:5-benzo-1:3-thiazine, m. p. 184—185°, also prepared from *o*-phenylthiocarbamidobenzoic acid. 2-*p*-Toluidino-6-keto-4:5-benzo-1:3-thiazine, m. p. 235°, is similarly obtained. Boiling hydrochloric acid (*d* 1.19) transforms 2-thio-4-keto-3-allyl-1:2:3:4-tetrahydroquinazoline into 2-allylamino-6-keto-4:5-benzo-1:3-thiazine, m. p. 115° (hydrochloride, m. p. 231—232°), whereas with concentrated sulphuric acid a compound, m. p. 207°, results in very small yield. H. WREN.

**Thiodiazines. VII. Condensation of ethyl chloroacetate with thiosemicarbazides.** P. K. BOSE and B. K. NANDI (J. Indian Chem. Soc., 1930, 7, 961—964).—Thiodiazines are prepared from ethyl chloroacetate and the requisite thiosemicarbazide (1:1) in boiling alcohol. Their acetylation is effected with boiling acetic anhydride containing a little pyridine and their methylation with methyl iodide and methyl-alcoholic potassium hydroxide. The following compounds are described: 2-amino-5-



*hydroxy-1:3:4-thiodiazine*, m. p. 284° (decomp.) (acetyl derivative, m. p. 205°; benzoyl compound, m. p. 260°; adduct with phenylthiocarbimide, m. p. 195°); *2-methylamino-5-hydroxy-1:3:4-thiodiazine*, m. p. 282° (decomp.) (acetyl derivative, m. p. 198°; non-crystalline methyl compound); *2-ethylamino-5-hydroxy-1:3:4-thiodiazine*, m. p. 225° (acetyl derivative, m. p. 169°); *2-isobutylamino-5-hydroxy-1:3:4-thiodiazine*, m. p. 210° (acetyl derivative, m. p. 199°; methyl compound, m. p. 135°); *2-anilino-5-hydroxy-1:3:4-thiodiazine*, m. p. 184° (acetyl, m. p. 172°, and methyl, m. p. 265°, derivatives); *2-o-toluidino-5-hydroxy-1:3:4-thiodiazine*, m. p. 183° (acetyl derivative, m. p. 210°); *2-p-toluidino-5-hydroxy-1:3:4-thiodiazine*, m. p. 195° (acetyl derivative, m. p. 218°).

H. WREN.

**Lupinine.** C. SCHÖPF, E. SCHMIDT, and W. BRAUN (Ber., 1931, 64, [B], 683—691; cf. A., 1928, 1144).—The mixture of (—)-lupinic and (+)-epilupinic ester obtained by the successive oxidation and esterification of lupinine is converted by boiling hydrochloric acid mainly into (—)-lupinic acid and (+)-epilupinic ester hydrochloride; hydrolysis with boiling alkali hydroxide permits the isolation of (+)-epilupinic acid hydrochloride, m. p. 233—235°,  $[\alpha]_D^{25} +27.2^\circ$  in methyl alcohol. The hydrochloride is transformed by ethereal magnesium phenyl bromide into the carbinol,  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}(\text{CPh}_2 \cdot \text{OH}) \cdot \text{CH}_2$ , m. p. 170—171°, which yields two methiodides, m. p. 250—252° (decomp.) and (+H<sub>2</sub>O), m. p. 140° (decomp.). The possibility of stereoisomerism appears to be conditioned by the passage of nitrogen from the tervalent to the co-ordinatively quadrivalent state (contrast Winterfeld, this vol., 370). The ketone  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHBz} \cdot \text{CH}_2$  (*loc. cit.*) [preparation given from (—)-lupinyl chlorid, benzene, and aluminium chloride] yields an amorphous methiodide (corresponding methopicate, m. p. 153—154°) which is very readily transformed by 20% sodium hydroxide into the base  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CBz} \cdot \text{CH}_2$ , b. p. 143—145°/1 mm. [*picrate* (anhydrous), m. p. 142—143°, (monohydrated), m. p. 120—121°], catalytically hydrogenated to the dihydro-base (*picrate*, m. p. 159—160°). The ease with which the Hofmann degradation occurs is typical of β-amino-ketones. Confirmation is thus afforded to Karrer's formula for lupinine.

The work of Winterfeld and Holschneider (*loc. cit.*) is criticised in detail. Re-examination of lupinene, m. p. 68—69°, and its benzoyl derivative fails to give evidence of non-uniformity.

H. WREN.

[Lupinene.] K. WINTERFELD (Ber., 1931, 64, [B], 692—693; cf. this vol., 370).—A reply to Schöpf and others (preceding abstract). The isolation of 2-methylpyridine-6-carboxylic acid and the acid C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>N was effected from a sample of lupinene, m. p. 63—65°, but not from that of m. p. 68—69°.

H. WREN.

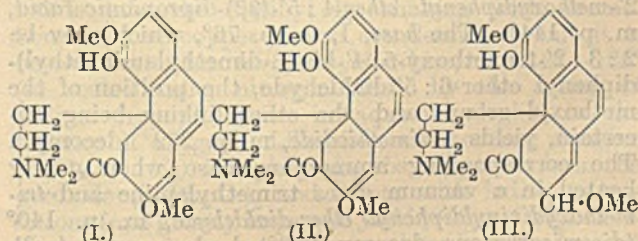
**Reactions of harmine.** O. FERNÁNDEZ and F. E. RAUBICH (Anal. Fís. Quím., 1931, 29, 74—76).—The following reactions are sensitive and characteristic. (i) Harmine is oxidised to *m*-nitroanisic acid by

evaporation with nitric acid. By reduction with stannous chloride, diazotisation, and addition of an ammoniacal solution of β-naphthol a purple coloration is obtained. (ii) Harmine is reduced by sodium and amyl alcohol to tetrahydroharmine, and water is added. The addition of *p*-nitrobenzenediazonium chloride solution gives a carmine-red coloration, whilst a hydrochloric acid solution of vanillin gives a permanganate-purple coloration. R. K. CALLOW.

**Sinomenine and disinomenine.** XXIII. Identity of β-tetrahydrodeoxycodeine and dihydrothebacodine. K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1931, 6, 33—39).—The identity of *d*-dihydrothebacodine (Speyer and Siebert, A., 1921, i, 685), dehydroxytetrahydrocodeine, and deoxytetrahydrosinomenine (deoxydemethoxydihydrosinomenine) (Kondo and Ochiai, A., 1930, 625) is supported by experiments on the reduction of sinomenine and its derivatives by various methods. Only the one substance corresponding with the above was isolated. Further, the de-*N*-methyl base and the nitrogen-free substance obtained from deoxytetrahydrosinomenine melt at the same temperatures as the corresponding products from dihydrothebacodine. The name "dihydroeuthetbainan" is proposed in place of "dihydrothebainan" suggested by Kondo and Ochiai (*loc. cit.*), since the methylaminoethyl side-chain is probably differently linked from that in thebainone.

A. A. LEVI.

**Sinomenine and disinomenine.** XXV. Three different sinomeninemethines. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1931, 6, 79—87; cf. A., 1926, 1160).—The Hofmann degradation of sinomenine has been re-examined. Sinomenine methiodide with 2% sodium hydroxide gives sinomenine-achromethine (I) (*N*-methylsinomeninium base, *loc. cit.*), m. p. 179°,  $[\alpha]_D^{25} +72.58^\circ$  in chloroform [methiodide, m. p. 212°,  $[\alpha]_D^{25} -33.00^\circ$  in water; *hydriodide*, m. p. 115—118° (not sharp); *oxime*, loses water at 120°, decomp. 204—205°]. This substance slowly changes into sinomenine-roseomethine (β-methylsinomeninemethine, *loc. cit.*) (II), m. p. 163°,  $[\alpha]_D^{25} +135.70^\circ$  in chloroform (methiodide, m. p. 276°,  $[\alpha]_D^{25} -48.26^\circ$  in water), also obtained from sinomenine methiodide and cold 5% sodium hydroxide. The achromethine with cold 10% sodium hydroxide gives sinomenine-violeomethine (α-methylsinomeninemethine, *loc. cit.*) (III), m. p. 172—173°,  $[\alpha]_D^{25} +434.78^\circ$  in chloroform (methiodide, m. p. 209°,  $[\alpha]_D^{25} +373.36^\circ$  in water). The methiodide of I with sodium hydrogen carbonate in methyl alcohol gives the methiodide of II, whilst both of these



methiodides yield that of III in cold 10% sodium hydroxide. In several cases sinomeninol (and disino-

meninol) were obtained by heating the above substances with alkali. The prefixes to the new names refer to the colours produced by the substances and their derivatives with concentrated mineral acids. The constitutions I, II, and III are suggested.

A. A. LRVI.

**Oxonitin.** T. A. HENRY and T. M. SHARP (J.C.S., 1931, 581—582).—In the oxidation of aconitine,  $C_{34}H_{47}O_{11}N$ , to oxonitin, acetaldehyde is produced and the methyl group attached to nitrogen is lost; oxonitin cannot therefore contain more than 31 carbon atoms. The present work indicates  $C_{31}H_{41}O_{12}N$  as the probable formula rather than  $C_{32}H_{43}O_{12}N$  (cf. Späth and Galinovsky, this vol., 243).

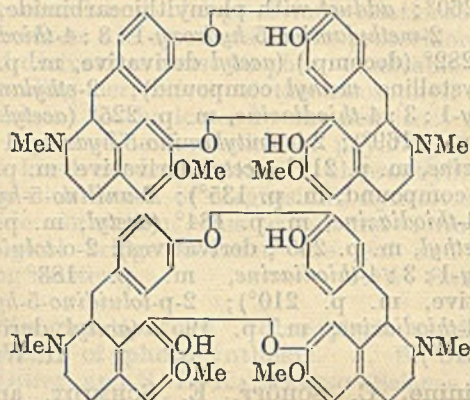
F. R. SHAW.

**Aconitine from *Aconitum chasmanthum*, Kashmir.** K. H. BAUER and T. C. RADJHAN (Pharm. Zentr., 1931, 72, 145—152).—*Aconitine-chasmanthum*,  $C_{21}H_{27}O_3N(OAc)(OBz)(OMe)_4$ , m. p. 197.5°,  $[\alpha]_D^{20} +20.0^\circ$  (hydrobromide,  $[\alpha]_D^{20} -18.1^\circ$ ; hydrochloride,  $[\alpha]_D^{20} -15.3^\circ$ ; chloroaurate, m. p. 135°), from the ether extract of the root, differs from indaconitine, isolated from the same species (Dunstan, J.C.S., 1905, 87, 1620), in failing to give crystalline salts. It is oxidised by nitric acid at 100° to a substance,  $C_{16}H_{14}O_2N_2(OBz)(OMe)_2CO_2H$ , m. p. 251° (cf. Brady, J.C.S., 1913, 103, 1827). *Aconine-chasmanthum*,  $C_{21}H_{27}O_3N(OH)_2(OMe)_4$  (also +EtOH), m. p. 95°,  $[\alpha]_D^{20} +4.0^\circ$  [amorphous hydrochloride, m. p. 168—179° (decomp.); tetra-acetyl derivative, m. p. 213—214°, and its hydrochloride, m. p. 142—144°], is distinguished from indaconine by its solubility in ether. It is oxidised by nitric acid to oxalic acid and a substance,  $C_4H_7O_8N$  (also +H<sub>2</sub>O), m. p. 132°.

H. E. F. NOTTON.

**Constitution of oxyacanthine.** II. F. VON BRUCHHAUSEN and P. H. GERICKE (Arch. Pharm., 1931, 269, 115—125).—The structure proposed by Kondo and Tomita (this vol., 242, 243) for dauricine is shown to be incorrect. The authors' previous views on the structure of oxyacanthine are confirmed by a new degradation of the methine base,  $C_{40}H_{46}O_6N_2$  (A., 1930, 98, formula III). This is ozonised almost quantitatively in aqueous solution slightly acidified with sulphuric acid to the base (I) (1 mol.) and 2'-methoxydiphenyl ether-4 : 5'-dialdehyde (1 mol.), m. p. 72° [disemicarbazone, m. p. 228° (decomp.); di-phenylhydrazone, m. p. 218°; oily oxime], identified by oxidation to 2'-methoxydiphenyl ether-4 : 5'-dicarboxylic acid. The dialdehyde affords with malonic acid in pyridine in presence of piperidine 2'-methoxydiphenyl ether-4 : 5'-diacrylic acid, m. p. 283°, reduced by sodium amalgam and water to 2'-methoxydiphenyl ether-4 : 5'-( $\beta$ )-dipropionic acid, m. p. 144°. The base, I, m. p. 76°, which may be 2 : 3 : 2'-trimethoxy-5 : 4'-bis-( $\beta$ -dimethylaminoethyl)-diphenyl ether-6 : 5'-dialdehyde, the position of the methoxyl groups and the ether linking being uncertain, yields a dimethiodide, m. p. 259° (decomp.). The corresponding ammonium base when gently heated in a vacuum gives trimethylamine and trimethoxydivinyldiphenyl ether-dialdehyde, m. p. 140° (disemicarbazone, decomp. 250°), hydrogenated (palladised barium sulphate) to trimethoxydiethyldiphenyl ether-dialdehyde, m. p. 88—89° [disemicarbazone, m. p.

248° (decomp.); monoazlactone, m. p. 252°]. On the assumption that oxyacanthine is formed by the



condensation of two molecules of *N*-methylcoclaurine, it must have one of the above structures, the other being assigned to berbamine (cf. Kondo and Tomita, *loc. cit.*).

H. E. F. NOTTON.

**Derivatives of *p*-arsanilic acid. I. *p*-Arsinosuccinanilic acid and related compounds.** G. T. MORGAN and E. WALTON (J.C.S., 1931, 615—619).—Monosodium *p*-arsanilate (atoxyl) with excess of succinic anhydride gives *p*-arsinosuccinanilic acid (I), whereas with succinic acid in smaller proportions, succinanilido-*pp'*-diarsinic acid (disodium salt) is formed (also obtained by heating I with atoxyl in equimolecular proportion). I gives products of type II,  $AsO_3H_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot [CH_2]_x \cdot CO \cdot NR_1R_2$  on warming with (a) aniline, succinilide- (II,  $x=2$ ,  $R_1=H$ ,  $R_2=Ph$ ); (b) methylamine, succinanilomethylamide- (II,  $x=2$ ,  $R_1=H$ ,  $R_2=Me$ ) (monosodium salt, 2H<sub>2</sub>O); (c) ethylamine, succinanilethylamide-*p*-arsinic acid (II,  $x=2$ ,  $R_1=H$ ,  $R_2=Et$ ) (monosodium salt). On reduction with sulphur dioxide, I yields *p*-dichloroarsinosuccinanilic acid (crystallising in needles and prisms, both varieties m. p. 210—211°), which could not be converted into the acid chloride. When heated at 240°, I affords succinanil-*p*-arsinic acid, which regenerates I on addition of water. The crude anil, heated in a sealed tube, is converted by (a) anhydrous alcoholic ammonia into succinanilamide- (II,  $x=2$ ,  $R_1=R_2=H$ ) (monoammonium salt, 1H<sub>2</sub>O, monosodium salt, 1H<sub>2</sub>O); (b) alcoholic dimethylamine, into succinanildimethylamide- (II,  $x=2$ ,  $R_1=R_2=Me$ ) (monosodium salt; 1H<sub>2</sub>O); (c) piperidine, into succinanilopiperidide-*p*-arsinic acid (II,  $x=2$ ,  $R_1R_2=C_4H_{10}N$ ).

The monosodium salts of compounds of type II, in comparison with tryparsamide, show very low toxicities combined with therapeutic activity.

F. R. SHAW.

**Azo-dyes derived from arsanilic acids.** V. DEULOFEU and F. R. MARÍN (Anal. Fis. Quím., 1931, 29, 65—73).—The following compounds have been prepared by diazotisation of the aminophenylarsinic acids and coupling with phenols in alkaline solution. From *p*-aminophenylarsinic acid : 2 : 4-dihydroxyazobenzene-4'-arsinic acid [mono- and di-sodium (+5.5H<sub>2</sub>O) salts], 2 : 4 : 6-trihydroxyazobenzene-4'-arsinic acid [disodium salt (+4H<sub>2</sub>O)], 2-methyl-4 : 6-dihydroxyazobenzene-4'-arsinic acid [disodium salt (+4H<sub>2</sub>O)];

from 4-amino-3-methylarsinic acid : 2:4-dihydroxy-2'-methylazobenzene-4'-arsinic acid; from o-amino-phenylarsinic acid : 4-hydroxyazobenzene-2'-arsinic acid, 2:4-dihydroxyazobenzene-2'-arsinic acid, and 2:4:6-trihydroxyazobenzene-2'-arsinic acid. The compounds are yellow to deep reddish-brown; the depth of colour increases with mol. wt. in each series in accordance with Nietzki's rule. R. K. CALLOW.

**Arsinic acids of the fluorene series.** G. T. MORGAN and (Miss) J. STEWART (J.C.S., 1931, 620—623).—2-Nitrofluorenone is reduced by a modified catalytic method (cf. Bennett and Noyes, A., 1930, 1291) successively to 2-amino-fluorenone, -fluorenol, and -fluorene. 2-Aminofluorene on diazotisation and conversion by the Bart reaction gives fluorene-2-arsinic acid (monosodium salt,  $1H_2O$ ). Fluorenone-2-arsinic acid (monosodium salt, disodium salt,  $6H_2O$ , and semicarbazone), similarly prepared, on nitration in sulphuric acid, yields the 7-nitro-compound (monosodium salt,  $1H_2O$ ). The nitro-derivative is reduced with ferrous hydroxide to 7-aminofluorenone-2-arsinic acid (monosodium salt,  $3H_2O$ ); on acetylation this affords 7-acetamido- (monosodium salt, I) and, on boiling with chloroacetic acid in alkaline solution, 7-glycine- (somewhat unstable, monosodium salt), or with chloroacetamide, 7-glycinamido-2-arsinic acid (monosodium salt). 2-Dichloroarsino-fluorene, m. p.  $109^\circ$ , and -fluorenone, m. p.  $142^\circ$ , are also described. Of the foregoing I has proved to have the greatest trypanocidal activity. F. R. SHAW.

**Oxidation of heterocyclic arsenious derivatives by iodine.** G. A. RAZUBAIEV and V. S. MALINOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 2173—2186).—A volumetric method for the determination of trivalent arsenic by oxidation with iodine in alcoholic solution is described. The use of sodium hydrogen carbonate to neutralise the hydriodic acid formed is recommended. The method is applicable to phenoxarsine oxide, triphenylarsine, and compounds of the type 10-R-9:10-dihydrophenarsazine. The product of oxidation of the latter is the corresponding dihydroxide if sodium hydroxide is used to neutralise the hydriodic acid formed, and the oxide if silver oxide is used. The following of these were prepared: R=Me, dihydroxide, m. p.  $201—215^\circ$ , oxide, decomp.  $256—257^\circ$ ; R=Et, dihydroxide, m. p.  $141—143^\circ$ , oxide, m. p.  $239^\circ$ ; R=Pr, m. p.  $81—82^\circ$ , dihydroxide, m. p.  $93^\circ$ , oxide, m. p.  $111—112^\circ$ ; R=isoamyl, m. p.  $76—78^\circ$ , dihydroxide, m. p.  $95—96^\circ$ , oxide, m. p.  $101—102^\circ$ ; R=Ph, oxide, m. p.  $280—300^\circ$  (decomp.).

E. B. UVAROV.

**New water-soluble organomercury compounds.** J. H. WALDO (J. Amer. Chem. Soc., 1931, 53, 992—996).—By the interaction of various organomercury halides (prepared by the usual Grignard method) with thio-acids in dilute alcoholic sodium hydroxide are obtained various new organomercury compounds which, with sodium hydrogen carbonate, form water-soluble salts with germicidal properties:  $RHgX + SH \cdot R' \cdot CO_2H$  (or  $SO_3H$ ) =  $RHgS \cdot R' \cdot CO_2H + HX$ . The values of their therapeutic indices (product of the toxicity and germicidal value relative to that of sodium ethylmercurithiosalicylate as unity) for *B. typhosus* and *Staph. aureus*, respectively, are given

in parentheses. Thus are prepared: methyl-, m. p.  $174^\circ$  (0.533; 0.80); ethyl-, m. p.  $111^\circ$  (1; 1); isoamyl-, m. p.  $78^\circ$  (0.80; 0.90); phenyl-, m. p.  $228.5^\circ$  (decomp.) (0.10; 0.075); and benzyl-, m. p.  $144.5^\circ$  (decomp.), -mercurithiosalicylic acid: p-ethylmercurithiolbenzoic acid, not melting up to  $250^\circ$  (0.667; 0.50);  $\alpha$ -ethylmercurithiobutyric, m. p.  $76^\circ$  (0.533; 0.40); p-ethylmercurithiol-phenylacetic, m. p.  $116.7^\circ$  (0.667; 1.0), and -benzenesulphonic, m. p. above  $300^\circ$  (0.167; 0.125), acid. Thus the alkylmercuri-derivatives are less toxic than the aryl, and the salts of carboxylic acids less so than those of the sulphonic acids. The alkyl compounds are less stable than the alkaryl derivatives. All m. p. are corrected. J. W. BAKER.

**Tertiary arylalkyl phosphines. II.** I. K. JACKSON and W. J. JONES (J.C.S., 1931, 575—578).—The action of p-xylyldichlorophosphine on the required Grignard reagent results in: p-xylyl-dimethylphosphine, b. p.  $106^\circ/12$  mm.,  $d_4^{25}$  0.9541 [oxide, m. p.  $94—95^\circ$ , mercurichloride, m. p.  $225^\circ$ ; methiodide, m. p.  $204^\circ$  (mercuri-iodide, m. p.  $152^\circ$ ; chloroplatinate, m. p.  $236^\circ$ ; tri-iodide, m. p.  $91^\circ$ )]; -diethylphosphine, b. p.  $157^\circ/52$  mm.,  $d_4^{25}$  0.9392 [mercurichloride, m. p.  $184^\circ$ ; methiodide, m. p.  $137^\circ$  (chloroplatinate, m. p.  $217^\circ$ ; mercuri-iodide, m. p.  $105^\circ$ ; tri-iodide, m. p.  $85^\circ$ )]; -di-n-propylphosphine, b. p.  $161^\circ/25$  mm.,  $d_4^{25}$  0.9281 [mercurichloride, m. p.  $188^\circ$ ; methiodide, m. p.  $105^\circ$  (chloroplatinate, m. p.  $141^\circ$ ; mercuri-iodide, m. p.  $90^\circ$ , tri-iodide, m. p.  $76^\circ$ )]; -di-n-butylphosphine, b. p.  $171^\circ/16$  mm.,  $d_4^{25}$  0.9124 [mercurichloride, m. p.  $179^\circ$ ; methiodide, m. p.  $93^\circ$  (chloroplatinate, m. p.  $215^\circ$ ; tri-iodide, m. p.  $70^\circ$ )]; -diisobutylphosphine, b. p.  $184^\circ/20$  mm. (mercurichloride, m. p.  $227^\circ$ ; methiodide, m. p.  $120^\circ$ ); -di-n-amylphosphine, b. p.  $214^\circ/23$  mm. (mercurichloride, m. p.  $117^\circ$ ; methylchloroplatinate, m. p.  $151^\circ$ ). All p-xylylphosphines give a coloration with carbon disulphide but, with the exception of the inner anhydride of p-xylyldimethylhydroxyphosphino-carbithionic acid, m. p.  $76^\circ$ , no solid compound can be isolated. F. R. SHAW.

**Distibyls. I. Tetraphenyldistibine. Attempts to obtain tetraphenyldibismuthine.** F. F. BLICKE, U. O. OAKDALE, and F. D. SMITH (J. Amer. Chem. Soc., 1931, 53, 1025—1029).—Tetraphenyldistibyl oxide, prepared by slight modification of Schmidt's method (A., 1920, i, 900), is converted by acetic acid into the acetate, m. p.  $133—135^\circ$  (lit. m. p.  $132^\circ$ ), converted by the appropriate hydrogen halide in acetic acid into the corresponding chloride, and bromide, m. p.  $86^\circ$ , the iodide, m. p.  $68—70^\circ$ , being obtained by the action of sodium iodide on the chloride in acetone solution. Experiments on the conversion of the iodide into the distibyl by shaking with bromobenzene and copper-bronze are described, but it is best converted into tetraphenyldistibine, m. p.  $121—122^\circ$  (in sealed tube, nitrogen-filled), by the action of sodium hypophosphite in aqueous alcohol in the absence of oxygen. Like the corresponding diarsine (A., 1929, 1090) it rapidly absorbs oxygen to form the peroxide  $(SbPh_2 \cdot O)_2$  and reacts with iodine. Conditions for a greatly improved yield (84%) of triphenylbismuthine from magnesium phenyl bromide and bismuth trichloride are given, but similar attempts to convert diphenylbismuthyl iodide (Challenger and

Allpress, J.C.S., 1915, 107, 19) into tetraphenyl-dibismuthine were unsuccessful. J. W. BAKER.

**Aromatic compounds of tin with halogen in the benzene nucleus.** K. A. KOZESCHKOV and A. N. NESMEJANOV (Ber., 1931, 64, [B], 628—636; cf. A., 1930, 1603).—Mercury di-*p*-chlorophenyl is transformed by stannous chloride in boiling alcohol into mercury and tin di-*p*-chlorophenyl dichloride, m. p. 86.5°. Tin di-*p*-chlorophenyl dibromide, m. p. 73°, is analogously prepared, whereas the corresponding di-iodide, m. p. 46—47°, is derived from the dichloride and sodium iodide in boiling alcohol. The dichloride is transformed by aqueous potassium hydroxide into tin di-*p*-chlorophenyl oxide and by alcoholic potassium hydrogen sulphide into tin di-*p*-chlorophenyl sulphide, m. p. 179°; with stannic chloride at 150° the dichloride affords tin *p*-chlorophenyl trichloride, m. p. 39°, converted into *p*-chlorophenylstannonic acid and the sulphide (C<sub>6</sub>H<sub>4</sub>Cl·Sn)<sub>2</sub>S<sub>3</sub>, which darkens at 295° after softening at 240°. The following tin di-*p*-bromophenyl compounds are prepared by analogous methods: dichloride, m. p. 103°; dibromide, m. p. 82°; di-iodide, m. p. 79—80°; oxide; sulphide, m. p. 228—229°. Tin *p*-bromophenyl trichloride, m. p. 64.5—65°, is converted into the corresponding stannonic acid and the sulphide (C<sub>6</sub>H<sub>4</sub>Br·Sn)<sub>2</sub>S<sub>3</sub>. Tin di-*p*-iodophenyl dichloride, m. p. 147°, the corresponding dibromide, m. p. 102°, and di-iodide, m. p. 88.5°, are described. When treated with chlorine in cold chloroform the dichloride gives the iodochloride (Cl<sub>2</sub>·IC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>, m. p. 82—82.5°. Tin di-*p*-iodophenyl oxide and sulphide, m. p. 248°, are described. Tin *p*-iodophenyl trichloride, m. p. 55—56°, yields the iodochloride Cl<sub>2</sub>·IC<sub>6</sub>H<sub>4</sub>·SnCl<sub>2</sub>, gradual decomp. 50—70°. Tin *p*-iodophenyl tribromide, m. p. 80—80.5°, *p*-iodophenylstannonic acid, and the sulphide (C<sub>6</sub>H<sub>4</sub>I·Sn)<sub>2</sub>S<sub>3</sub> are described. H. WREN.

**Protein structure and denaturation.** C. RIMINGTON (Nature, 1931, 127, 440—441).—A discussion. L. S. THEOBALD.

**Alkaline decomposition of serine.** F. S. DAFT and R. D. COGHILL (J. Biol. Chem., 1931, 90, 341—350).—Serine in hot alkaline solution gives ammonia, glycine, alanine, and oxalic and lactic acids. Pyruvic acid is an intermediate product. In the determination of arginine by the method of Van Slyke the decomposition of serine does not falsify the result, as the serine is effectively separated from arginine by the phosphotungstic acid precipitation, but errors may be introduced when the method suggested by Plimmer and Rosedale (A., 1926, 313) is followed.

W. O. KERMAK.

**Tube for micro-determination of carbon and hydrogen according to Pregl.** A. VERDINO (Mikrochem., 1931, 9, 123—125).—The apparatus described consists essentially of a tube 65 mm. long, having an external diameter of 30 mm. and an internal diameter of 11 mm. so that the combustion tube passes axially through it. The tube is filled with about 30 c.c. of decalin, which is kept steadily boiling. The advantage thus obtained is a constancy of temperature of the lead peroxide layer superior to that obtained by direct gas or electric heating.

E. S. HEDGES.

**Ter Meulen-Heslinga method for determination of nitrogen, carbon, and hydrogen in organic material.** E. P. GRIFFING and C. L. ALSBERG (J. Amer. Chem. Soc., 1931, 53, 1037—1039).—Several improvements in the technique of this method of analysis which allow accurate results to be obtained with 20—40 mg. of material are described.

J. W. BAKER.

**Determination of nitrogen by a micro-Kjeldahl method.** A. C. ANDERSEN and B. N. JENSEN (Z. anal. Chem., 1931, 83, 114—120).—The method previously described for macro-determinations (A., 1926, 375) has been adapted to micro-analysis.

A. R. POWELL.

**Detection of carbon disulphide.** F. FEIGL and K. WEISSELBERG (Z. anal. Chem., 1931, 83, 93—104).—The sensitivity of various methods which have been proposed for the detection of carbon disulphide has been determined and two new very sensitive reactions are described. Of the known methods the xanthate-copper salt test detects 1 part of carbon disulphide in 90,000 parts of solution and the sodium azide-iodine test 1 part in 500,000 parts after waiting 10 min. Just as sensitive as the latter test is the instantaneous development of a characteristic brown to black colloidal suspension of lead sulphide when a drop of the carbon disulphide solution is treated with an alkaline solution of sodium plumbite and formaldehyde. An even more sensitive reaction comprises heating in a water-bath a closed test-tube containing the solution to be tested together with a few crystals of nickel acetate and of Hector's base; in the presence of carbon disulphide a rose colour or red precipitate is produced due to the formation of a complex nickel salt of the empirical formula C<sub>30</sub>H<sub>22</sub>N<sub>8</sub>S<sub>6</sub>Ni (sensitivity 1 part of CS<sub>2</sub> in 2 × 10<sup>6</sup>).

A. R. POWELL.

**Determination of benzene in alcoholic solutions.** G. GRÓH and E. FALTIN (Magyar Chem. Fol., 1930, 36, 156—159; Chem. Zentr., 1931, i, 490).—The extinction coefficients of alcoholic solutions of benzene were determined; the Beer-Lambert law is valid. The limiting concentration of benzene for sufficiently accurate determination is about 0.01 g. per litre.

A. A. ELDRIDGE.

**Colour reaction of aromatic amines.** I. DE PAOLINI (Atti R. Accad. Sci. Torino, 1930, 65, 201—204; Chem. Zentr., 1931, i, 490—491).—The aromatic amine is added to a cold alcoholic suspension of benzoyl peroxide; a reddish-brown or violet colour is developed, the reaction being accelerated by heat. With benzylamine the reaction is: 3C<sub>7</sub>H<sub>7</sub>·NH<sub>2</sub> + Bz<sub>2</sub>O<sub>2</sub> → C<sub>7</sub>H<sub>7</sub>·NHBz + CHPh·NH + OBz·NH<sub>2</sub>·C<sub>7</sub>H<sub>7</sub> + H<sub>2</sub>O.

A. A. ELDRIDGE.

**Titrimetric determination of acetylsalicylic acid.** A. EDWARDS (Svensk farm. Tidskr., 1929, 33, 557—560; Chem. Zentr., 1930, ii, 1106—1107).—The procedure given in the Swedish pharmacopoeia for the titrimetric determination of acetylsalicylic acid is confirmed. The detection of salicylic acid in this acid is also investigated. The colour reaction with ferric chloride is unsuitable, but Hoffmann's fluorescence test will detect the presence of 0.1% of salicylic acid in spite of a weak fluorescence of acetylsalicylic acid.

L. S. THEOBALD.

**Rapid volumetric determination of nicotine with silicotungstic acid.** B. KASANSKY (Z. anal. Chem., 1931, 83, 107—114).—The material (*e.g.*, 10 g. of tobacco) is made into a paste with 150 c.c. of water and 50 g. of sodium chloride, and after addition of 5 g. of magnesia or sodium hydroxide the nicotine is removed by steam distillation or extraction with a mixture of ether and light petroleum. An aliquot part of the distillate or extract is treated with 2 g. of ammonium chloride and titrated with a 2.5% solution of silicotungstic acid with vigorous shaking until no further turbidity is produced, when another drop of the acid is added. The reagent is standardised against a solution containing a known amount of nicotine, as the reaction does not appear to be stoichiometric, more acid being required than corresponds with the formation of  $2C_{10}H_{14}N_2 \cdot 2H_2O \cdot 12WO_3 \cdot SiO_2 \cdot 5H_2O$ .

A. R. POWELL.

**Determination of pyrimidone by cyanogenometry.** R. MACHTOU (J. Pharm. Chim., 1931, [viii], 13, 329—333).—Pyrimidone is quantitatively precipitated by an excess of aqueous mercuric chloride as a complex containing 2Hg per mol. of pyrimidone. Mercury is determined in the original solution and in an aliquot part of the filtrate by addition of ammonia and potassium cyanide and titration with silver nitrate. Mercuric chloride does not precipitate "dioxypyrimidone." It precipitates antipyrine, but not quantitatively.

H. E. F. NOTTON.

**Sensitiveness of the thalleioquinine reaction.** J. EISENBRAND (Arch. Pharm., 1931, 269, 65—67).—The limit of sensitiveness given by Salomon (*A.*, 1919, ii, 87; cf. Hart, J.S.C.I., 1921, 40, 72) applies only when ammonia is added immediately after the

bromine. When 0.0005% quinine sulphate solution (10 c.c.) is treated with one-tenth saturated bromine water and, after 10—15 sec., with excess of ammonia, a faint positive reaction is observed. The substance responsible for the reaction is formed by the action of hypobromous acid and is itself easily oxidised. Accordingly its formation is retarded by a decrease in  $p_H$ , whilst both changes are accelerated by an increase in  $p_H$  or in bromine-ion concentration, until at  $p_H$  7 the intermediate compound can no longer be detected.

H. E. F. NOTTON.

**Microchemical detection of alkaloids in plants.** XV. **Echinopsine.** G. KLEIN and F. SCHUSTA (Oesterr. Bot. Z., 79, 231—248; Chem. Zentr., 1930, ii, 3821).—Sensitive and characteristic micro-reactions with various iodo-salts were employed for the determination of echinopsine in various species of *Echinops*.

A. A. ELDRIDGE.

**Microchemical detection of alkaloids in plants.** G. KLEIN (Oesterr. Bot. Z., 78, 67—70; Chem. Zentr., 1930, ii, 3821).—Polemical (*cf.* Mothes, *Planta*, 1928, 5, 563).

A. A. ELDRIDGE.

**Microchemical detection of alkaloids in plants.** II. **Nicotine.** G. KEIN and E. HERNDLHOFER (Oesterr. Bot. Z., 76, 222—228; Chem. Zentr., 1930, ii, 3821).—The gold chloride-sodium bromide reaction is suitable for the histochemical detection of nicotine; the sensitivity is 1 in  $4 \times 10^5$ . For determination the alkaloid is liberated by micro-distillation. Nicotine is present in all organs of *Nicotiana* plants in all stages of growth, and in fresh, dried, and fermented tobacco.

A. A. ELDRIDGE.

**Determination of methylglyoxal, pyruvic acid, acetaldehyde, and lactic acid.** E. SIMON and C. NEUBERG.—See this vol., 662.

## Biochemistry.

**Respiratory quotient of fish as a function of temperature.** L. BAUDIN (Compt. rend., 1931, 192, 637—639).—The oxygen intake and carbon dioxide output increase with rise of temperature. A minimum *R.Q.* is observed for *Carassius auratus* at 15°. Similar results are observed in *Cottus bubalis*.

C. C. N. VASS.

**Resistance of *Eurytemora hirundoides*, Nordquist, to oxygen depletion.** H. O. BULL (Nature, 1931, 127, 406—407).—*E. hirundoides* can survive in brackish water, highly polluted, when the oxygen concentration is only 4 g. per  $10^8$  g., but total deprivation of oxygen can be suffered only for short periods.

L. S. THEOBALD.

**Lack of inhibition of respiration of cells by hydrogen cyanide.** O. WARBURG (Biochem. Z., 1931, 231, 493—497).—The conclusions of Dixon and Elliott (*A.*, 1929, 1197) concerning the supposed incompleteness of the inhibition of respiration by hydrogen cyanide are rejected on the ground that these authors worked with damaged cells. The views of other workers are also criticised.

W. McCARTNEY.

**Determination of blood-volume. Behaviour of colloidal substances in blood.** B. MINZ (Z.

klin. Med., 1930, 114, 623—641; Chem. Zentr., 1931, i, 323).—No existing methods are sufficiently exact. Experiments designed to explore the use of colloidal silver for the determination show that the metal is detectable in blood after 24 hrs.; the concentration remains constant for 4—10 min., but the silver is quickly absorbed by organs. Silver-protein gave similar results. When a silver salt is added to blood *in vitro* it is found only in the plasma. Part of the colloidal silver in circulating blood passes into the erythrocytes; after 3 min. a large part of the colloidal silver is converted into a silver salt; this is more rapidly removed, as silver-protein, by organs.

A. A. ELDRIDGE.

**Combination of the stroma-substance of red blood-corpuses with thymol.** LUTOWSKI (Schmerz, Narkose, Anaesth., 1930, 3, 233—247; Chem. Zentr., 1930, ii, 3800).—Unchanged and defatted stromata differ markedly in their thymol-combining power. The curve supports the lipid theory of narcosis, and not Warburg's adsorption process.

A. A. ELDRIDGE.

**Colloid-osmotic pressure. XIII. Arterial and venous blood.** E. KYLIN (Arch. exp. Path. Pharm.,

1931, 159, 401—407).—The colloid-osmotic pressure of arterial blood 2—3 hrs. after a meal is higher and the protein content lower than the corresponding values for venous blood. In cardiac inefficiency and anæmia from loss of blood the pressure is lower for arterial blood.

F. O. HOWITT.

**Osmotic changes in some marine animals.** R. MARGARIA (Proc. Roy. Soc., 1931, B, 107, 606—624).—When living in diluted sea-water the osmotic pressure of the blood of crabs and dogfish falls in general to the level of that of the medium within the limits of dilution of one third to one half, whilst the blood of the conger and one species of crab is maintained at an osmotic pressure higher than that of the surrounding medium. The mechanism of the osmotic regulation is discussed.

B. LEVIN.

**Specific viscosity of native fibrinogen.** W. STARLINGER and E. WINANDS (Z. ges. exp. Med., 1930, 71, 389—394; Chem. Zentr., 1930 ii, 3722).—The viscosity of 1 g.-% fibrinogen in unchanged human blood-plasma, determined by measurement of the viscosity of the plasma before and after precipitation of fibrin, is 0.400—0.904 (average 0.568).

A. A. ELDRIDGE.

**Chemical constitution of serum-proteins. IV.** A. FISCHER and A. BLANKENSTEIN (Biochem. Z., 1931, 231, 404—411; cf. this vol., 247).—The proteins of two pathological sera have been separated by the authors' methods into their various fractions. In these sera the amount of the euglobulin which can be precipitated by sodium chloride is greater than the corresponding amount in normal sera. It has been found that the method used for determining the tryptophan content of the fractions does not give absolute values, but that satisfactory relative values can be obtained provided that the reaction of the solution used is kept constant.

W. MCCARTNEY.

**Dialysis in the determination of serum-proteins.** A. A. SCHMIDT and K. TULJTSCHINSKAJA (Biochem. Z., 1931, 232, 323—334).—By precipitation with ammonium sulphate and subsequent dialysis the proteins in 1 c.c. of serum can be sharply separated into euglobulin, pseudoglobulin, and albumin fractions, and the amounts of these fractions can be deduced from nitrogen determinations. Very little denaturation of the proteins occurs during the process.

W. MCCARTNEY.

**Globulin and albumin fractions of serum. III. Elementary composition of the various fractions of ox-serum and distribution of amide-, humin-, diamino-, monoamino-, and non-amino-nitrogen and of tryptophan and carbohydrate in them.** B. LUSTIG and P. HAAS (Biochem. Z., 1931, 231, 472—492; cf. this vol., 505).—The fractions were prepared as previously described, but were further purified by precipitation with acetone or alcohol and freed from lipins by extraction with ether. Great differences in the chemical composition of the fractions were revealed. Of the globulin fractions the euglobulins which are soluble in water and sodium chloride solutions have the lowest, the pseudoglobulins which are soluble in the same liquids the highest, carbon and hydrogen contents. The sulphur contents of the albumin fractions are approximately the same, but

those of the globulins vary from 1.28 to 1.71%. The globulins soluble in sodium chloride solution have high methylimino-contents. The water-soluble pseudoglobulin has a high methoxyl content. As regards their contents of nitrogen in its various forms of combination and of tryptophan the albumin fractions do not differ much from each other, but the globulin fractions exhibit great differences. The albumin fractions have low carbohydrate contents. The globulin fractions which are soluble in sodium carbonate and hydroxide solutions contain from two to six times as much carbohydrate as do the other globulin fractions. Since all the fractions are hygroscopic, account must be taken of their water content when analytical determinations are made.

W. MCCARTNEY.

**Influence of lipins on the separation of proteins by neutral salts.** A. BOUTROUX (Compt. rend., 1931, 192, 854—857).—Precipitation by sodium sulphate (cf. A., 1922, ii, 172) affords larger yields of protein from pneumonia serum than does acetone. After removal of the lipins, the yield of serum-albumin is approximately 3% less, whilst the intermediate concentrations of the globulin show similar divergences. A comparative photometric study of the opalescence produced in 0.075% serum-protein solutions shows that in whole serum the globulins commence to flocculate at 33% saturated ammonium sulphate solution and in lipin-free protein solution at 25% saturation; further, that the myxoproteins I and II and the globulin fractions obtained by treatment of serum with acetone have closely-related flocculation characteristics although in distinct groups.

C. C. N. VASS.

**Inter-relationship of cholesterol and protein fractions.** W. N. NEKLUDOV (Biochem. Z., 1931, 232, 50—57).—A portion of the cholesterol of normal horse and dog plasma is united with the globulin fraction and with a fraction of fibrinogen. A similar but less firm union is obtained with certain fractions of egg-albumin, and with the fraction precipitated from horse-serum by phosphotungstic acid after preliminary removal of albumin and globulin fractions.

P. W. CLUTTERBUCK.

**Determination of phosphatides in blood and tissues.** A. CRUTO (Biochim. Terap. sperim., 1930, 17, 242—248; Chem. Zentr., 1931, i, 118).—Blood or plasma (1 c.c.) is well mixed with 95% alcohol (10 c.c.); after a few min., benzene (20 c.c.) is added, well mixed, and 15—20 c.c. are then distilled off. To the cold residue is added anhydrous ether (10 c.c.), the mixture being kept for several hours with frequent shaking; the filtered solution and washings (anhydrous ether) are evaporated to dryness and the residue is heated for a few min. with sulphuric (1 c.c.) and nitric (2 c.c.) acids, with final evaporation to fuming after addition of 0.5 c.c. of nitric acid. The residue is dissolved in water, treated with magnesia mixture, and centrifuged; the determination is completed colorimetrically by Bell and Doisy's method.

A. A. ELDRIDGE.

**Blood-glycolysis.** C. REID and B. NARAYANA (Biochem. J., 1931, 25, 337—341).—Starvation decreases and the administration of food increases the rate of glycolysis in the blood of the dog. The factors

responsible for glycolysis in blood are present both in erythrocytes and serum. S. S. ZILVA.

**Blood-sugar.** K. P. JACOBSON (Biochem. Z., 1931, 231, 498—499).—The view of Rona and Fabisch (this vol., 110) that the author's results confirm theirs is incorrect, and this is supported by the findings of other workers. W. McCARTNEY.

**Variations in blood-urea and -chlorine during venesection.** A. DAUMAS and G. PAGÈS (Compt. rend. Soc. Biol., 1930, 103, 1030—1031; Chem. Zentr., 1930, ii, 3590).—Variations during venesection (300—500 c.c. of blood) were not observed. A. A. ELDRIDGE.

**Diurnal variations in blood-urea and -chlorine.** A. DAUMAS and G. PAGÈS (Compt. rend. Soc. Biol., 1930, 103, 1031—1034; Chem. Zentr., 1930, ii, 3590).—Constant values are observed so long as food is not taken; a marked increase is observed after meals (cf. preceding abstract). A. A. ELDRIDGE.

**Micro-determination of chloride in blood.** J. A. F. KOK (Arch. Néerl. Physiol., 1931, 16, 132—135).—The method of Kolthoff and Bak (cf. A., 1922, ii, 159) for the determination of chloride has been applied to blood. The proteins in blood hæmolysed by dilution with an equal volume of distilled water are precipitated with sulphosalicylic acid and to 8 c.c. of the filtrate 3 drops of a solution of sodium nitroprusside are added as indicator. The chloride is then titrated with a standard solution of mercuric nitrate until a turbidity just appears. W. O. KERMAK.

**Micro-determination of calcium in blood-serum.** L. VELLUZ and R. DESCHASEAUX (Compt. rend. Soc. Biol., 1930, 104, 977—978; Chem. Zentr., 1931, i, 324).—A procedure for the precipitation of calcium as oxalate is described; the precipitate is washed with a mixture of 95% alcohol (18 c.c.), ether (18 c.c.), and water (15 c.c.), then with equal parts of alcohol and ether, and finally with ether. Sulphuric acid and *N*/150-potassium permanganate are added with agitation; after 5 min. potassium iodide is added, and the iodine liberated is titrated with 0.005*N*-thiosulphate. The permanganate solution must be similarly titrated. The error is with serum 5%, with pure salt 3%. A. A. ELDRIDGE.

**Determination of sodium in blood-serum.** A. GRIGAUT and A. BOUTROUX (Compt. rend. Soc. Biol., 1930, 104, 872—874; Chem. Zentr., 1931, i, 118).—The serum (1 c.c.) is deproteinised with 9 c.c. of a solution containing uranyl acetate (6 g.) and acetic acid (2 c.c.) in water (to 100 c.c.); 5 c.c. of the filtrate are treated with 15 c.c. of Kahane's reagent (uranyl acetate 32 g., magnesium acetate 100 g., acetic acid 20 c.c., 90% alcohol 500 c.c., water to 1000 c.c.), the precipitate being collected, washed with 90% alcohol, and dried at 100° for 30 min. The weight  $\times 30$  is that of sodium in 1000 c.c. of serum. The titrimetric determination depends on the reduction of hexa- to quadri-valent uranium by means of copper and titration with permanganate. A. A. ELDRIDGE.

**Use of Folin's method for determination of amino-nitrogen in 0.2 c.c. of blood.** S. A.

POVORINSKAJA (Biochem. Z., 1931, 232, 69—71).—A method is described. P. W. CLUTTERBUCK.

**Amount of ammonia and of its precursors in blood and muscle.** E. FREUND and B. LUSTIG (Biochem. Z., 1931, 232, 442—448).—Normal fresh blood, after being deproteinised in the cold, gives no ammonia reaction with Nessler's reagent, but by means of this reagent it can be shown that the precursors of the ammonia which is produced in blood and in muscle extracts are compounds containing carbamic acid and adenine nucleotide. These precursors give a green precipitate with the reagent, but if they are previously warmed with alkali they yield ammonia and hence give the usual brown precipitate. Although carbamates are decomposed by water they are stable, even in hot acid solutions, if deproteinised blood or muscle extracts are present. W. McCARTNEY.

**Effect of physical factors on blood-catalase. II. Effect of some physico-therapeutic procedures.** A. I. ALEXEEV and K. G. RUSSINOVA (Biochem. Z., 1931, 231, 460—471).—Variations, caused by physical and physiological factors, in the activity of the blood-catalase of healthy and diseased men have been measured. Where the physical factors remain constant, the activity of the catalase likewise remains constant, other things being equal. Since the activity is considerably influenced by the temperature of the surrounding medium, this must be taken into account when determinations are made. In men who have taken electric, hot water, or warm water baths (the latter at 2.5 atm. pressure) the activity of the catalase is decreased. Baths in cold water, in mineral waters, or in air have no effect on the activity. Consumption of food and light muscular exercise likewise have no effect. W. McCARTNEY.

**Presence of proteolytic enzymes in serum.** K. YOKOTA (Biochem. Z., 1931, 232, 58—68).—Human serum is able to decompose animal fibrin to a small extent, but cannot attack human fibrin. Serum of carcinomatous and luetic patients is unable to attack normal human fibrin and shows no greater action on animal fibrin than does normal serum. Ligaturing the pancreatic duct in dogs often, but not always, leads to a small increase of serum-protease. P. W. CLUTTERBUCK.

**Oxidation of ethyl alcohol by blood.** W. FLEISCHMANN and E. TREVANI (Biochem. Z., 1931, 232, 123—127).—Ethyl alcohol is oxidised *in vitro* both by the red and the white corpuscles of the horse, but not by the serum, the oxidation being inhibited by 0.005*M*-hydrogen cyanide. The oxidation may be demonstrated using Warburg's charcoal model in presence of some aldehyde-fixing agent (calcium sulphite). P. W. CLUTTERBUCK.

**Hydrogen-ion concentration of the alimentary tracts of the fowl, the cat, and the rabbit.** A. R. McLAUGHLIN (Science, 1931, 73, 191—192).—The  $p_H$  values, determined by means of the quinhydrone electrode, are recorded. L. S. THEOBALD.

**Buffering power of central nervous tissue.** M. MITOLO (Atti R. Accad. Lincei, 1930, [vi], 12, 246—251).—The central nervous tissue of *Bufo*

*vulgaris* exhibits a marked buffering power. This power is probably due to acid-salt systems equilibrated near to the neutral point and of low dissociation constant, and not to proteins. T. H. POPE.

**Occurrence of ergosterol in the human brain.** I. H. PAGE and W. MENSCHICK (Biochem. Z., 1931, 231, 446—459).—Spectroscopic and chemical examinations of material extracted from the brains indicate that the organ contains both cholesterol and ergosterol. The absolute amounts and the percentages of these substances vary according to the age of the brain. At the age of a little less than one year the absolute amount of ergosterol reaches its maximum and thereafter decreases and possibly even disappears.

W. McCARTNEY.

**Volumetric determination of fats and lipins by Bang's chromic acid oxidation method.** H. STAUB (Biochem. Z., 1931, 232, 128—145).—The reduction quotients of a series of fats, sterols, and lipins are obtained by Bang's method and compared with those of other authors, the effect of the various factors which change the reduction quotient, e.g., the amount of the excess of dichromate, the rise in temperature on addition of sulphuric acid, etc., being examined. A convenient apparatus for carrying out determinations by Bang's method is described, the method extended to determinations on larger amounts of fat (0.5—10 mg.), and curves are given from which the amounts of fat and lipin corresponding with a known utilisation of dichromate may be read. Examples are given of the determination of fat and lipins in human, dog, and rabbit blood and in cat's liver. P. W. CLUTTERBUCK.

**Fatty substance in the interstitial cells of the cock's testicle.** J. BENOIT and A. WENSLAW (Compt. rend. Soc. Biol., 1929, 102, 45—47; Chem. Zentr., 1931, i, 302).—The fatty deposit consists of cholesteryl esters covered with a thin film of phosphatides. A. A. ELDRIDGE.

**Biology of the meal-worm (*Tenebrio molitor*).** II. Tenebrioglycol, a wax-like material. F. N. SCHULZ and M. BECKER (Biochem. Z., 1931, 232, 189—195).—The wax-like substance of the envelope of the meal-worm (this vol., 115) is shown to be a glycol,  $C_{30}H_{62}O_2$ , m. p. 116°, which cannot be acetylated or benzoylated but readily gives an anhydride,  $C_{30}H_{60}O$ , m. p. 85—86°, reconverted quantitatively into the glycol on hydrolysis with alcoholic alkali. P. W. CLUTTERBUCK.

**Determination of glycogen in liver-tissue.** A. CARRUTHERS (Chinese J. Physiol., 1931, 5, 85—92).—The tissue is extracted with boiling water, the proteins are precipitated from the extract by trichloroacetic acid, and the glycogen present in the filtrate is precipitated by the addition of sufficient alcohol to make the concentration of the latter 70%. The precipitated glycogen is washed by centrifuging with alcohol and ether and hydrolysed with 2% hydrochloric acid. The reducing sugars are then determined. Evidence is presented that liver-tissue contains a carbohydrate insoluble in 70% alcohol, but destroyed by aqueous potassium hydroxide solution at 100°. This carbohydrate is not present if less than

1 min. elapses between the time of death and treatment of the liver with boiling water.

W. O. KERMACK.

**Determination of total sugar in liver-tissue.** A. CARRUTHERS (Chinese J. Physiol., 1931, 5, 93—102).—The liver-tissue is extracted with boiling water and the protein in the filtrate precipitated by trichloroacetic acid. The carbohydrates present are hydrolysed by boiling with 2% hydrochloric acid for 3 hrs. and the non-sugar reducing substances in the solution after neutralisation are precipitated by means of the mercuric sulphate reagent employed by West, Scharles, and Peterson (A., 1929, 714). After elimination of the mercury the reducing sugar is determined. W. O. KERMACK.

**Animal sinistrin.** F. MAY (Z. Biol., 1931, 91, 215—220).—A method is described for separating sinistrin from glycogen in the carbohydrate from *Helix pomatia* by repeated precipitation with alcohol after enzymic hydrolysis of the glycogen. The product has  $[\alpha]_D -13.55^\circ$ , and inversion experiments show that it contains a polysaccharide of galactose (90.12%) and an unknown substance. A. COHEN.

**Synthesis of glutathione in the adrenals.** L. BINET, A. BLANCHETIÈRE, and A. ARNAUDET (Compt. rend. Soc. Biol., 1930, 104, 56—57; Chem. Zentr., 1931, i, 303).—The glutathione content of the adrenal vein increases on perfusion with citrated blood only after addition of cystine and glutamic acid.

A. A. ELDRIDGE.

**Constituents of the epidermis with a thiol function.** A. GIROUD and H. BULLIARD (Bull. Soc. Chim. biol., 1931, 13, 138—140).—Extracts of the mucous cells of the "chestnut" of the horse give with the nitroprusside or the starch reaction 100—118 mg. per 100 g. glutathione in fresh tissues, whilst the hoof of the ox gives with the nitroprusside reaction 145 mg. and with the starch reaction 200 mg. per 100 g. Histological examination of these cells and determination of their fatty acid content suggest that prior to keratinisation there is an accumulation of sulphur in the tissues. Although the sulphur content of the mucous cells of the hoof of the ox is twice as large as that in the chestnut of the horse the S:P ratios are identical. C. C. N. VASS.

**Tissue substances with a thiol function.** A. GIROUD (Bull. Soc. Chim. biol., 1931, 13, 141—142).—Micro-injection of tissues with sodium nitroprusside solution indicates the existence of a soluble (glutathione) and a fixed thiol linking in the cells. C. C. N. VASS.

**Protein sulphuric acid ester from the spleen.** A. EBEL (Biochem. Z., 1931, 231, 306—308; cf. Mathis, this vol., 379).—A protein sulphuric acid ester has been isolated in purified form from the spleen of the ox. It is very soluble in water, but can be salted out from aqueous solution with ammonium sulphate. It contains neither tyrosine nor phenylalanine, but traces of tryptophan are present. All the sulphur (about 1.7%) in the ester is present in sulphuric acid radicals. W. McCARTNEY.

**Coagulin of muscle.** I. F. KRAUS and H. J. FUCHS (Z. ges. exp. Med., 1929, 64, 583—593; Chem. Zentr., 1931, i, 308).—Muscle contains thermolabile



prothrombin, which coagulates plasma-fibrinogen similarly to, and has the same complement action on sensitised blood-corpuscles as, plasma-prothrombin.

A. A. ELDRIDGE.

**Determination of lipins in thyroid gland powder.** E. LABORDE and ENVER (Bull. Soc. Chim. biol., 1931, 13, 148—149).—Powdered sheep's thyroid contains 1.4% of unsaponifiable matter, 5.66% of fatty acids, and 0.48% of cholesterol.

C. C. N. VASS.

**Iodine content of the thyroid glands of the horse.** H. COURTH (Biochem. Z., 1931, 232, 310—322).—In horses, donkeys, and mules large variations are found in the weight and total and percentage of iodine of the thyroid glands. No relation exists between the weight of the glands and the amount of iodine which they contain, but the absolute amount of iodine usually increases with increase in the weight of the gland. Although the percentage of iodine in the glands is greatest soon after birth, the weight of the glands increases until the sixth year of age. As regards the percentage iodine contents of their thyroid glands horses of different breeds exhibit no differences. In geldings the absolute iodine content of the glands is greater than in stallions or mares.

W. MCCARTNEY.

**Tin in the animal organism.** G. BERTRAND and V. CIUREA (Compt. rend., 1931, 192, 780—782).—Tin may be determined in animal organs as follows. The dried material is heated for several days with a nitric acid-sulphuric acid mixture in a quartz vessel, the excess of acid removed by evaporation in a platinum dish, and the residue treated with hydrochloric acid. The solution is filtered from silica, and treated with hydrogen sulphide. The tin sulphide is then converted into, and weighed as, stannic acid. The organs of the cow, horse, and sheep contain 0.0005—0.004 g. per kg., with the exception of the skin (0.00948 g., 0.00853 g., and 0.00620 g. per kg., for the cow, horse, and sheep, respectively), and the tongue (0.01865 g., 0.02611 g. per kg., for the cow and sheep).

B. LEVIN.

**Preparation and analysis of representative samples from the bovine skeletal structure.** W. M. NEAL and L. S. PALMER (J. Agric. Res., 1931, 42, 107—113).—Longitudinal sections of bone are cut with a double-bladed hacksaw. Analytical data representative of the skeletal structure may be obtained by taking sections of the femur, humerus, and the sixth and eleventh ribs. A. G. POLLARD.

**Staining of calcium.** G. R. CAMERON (J. Path. Bact., 1930, 33, 929—955).—Alizarin reacts readily with recently deposited calcium phosphate or carbonate, but may fail to stain older deposits. Hæmatxylin does not stain calcium salts, although it may identify areas favourable to their deposition.

CHEMICAL ABSTRACTS.

**Action of formaldehyde in histological fixation.** K. ZEIGER (Z. wiss. Mikros., 1930, 47, 273—293; Chem. Zentr., 1931, i, 322—323).—Sections of organs were stained with methylene-blue or crystal-ponceau after fixation with alcohol or formaldehyde. The protein colloids fixed by the latter become more acid than those fixed by alcohol. A. A. ELDRIDGE.

**Determination of the alkali metals in sea-water and in the tissue fluids of some marine invertebrates.** A. LEULIER and A. BERNARD (Bull. Soc. Chim. biol., 1931, 13, 133—137).—The dry residue, ash, sodium content as determined by the uranium acetate method (cf. A., 1923, ii, 579), and the potassium content as determined by the cobalt-nitrite method (the nitrite is oxidised by an excess of potassium permanganate) of Mediterranean sea-water and the body-fluids of *Holothuria tubulosa*, *Aplysia fasciata*, *Phallusia mamillata*, and *Pinna nobilis*, which give only traces of or no precipitates with trichloroacetic acid, are practically identical. In *Maia squinado*, *Carcinus mænas*, *Octopus vulgaris*, and *Sepia officinalis*, the body-fluids of which contain varying amounts of protein, the sodium content is identical with that of the sea-water, but the potassium content is generally increased. C. C. N. VASS.

**Intestinal secretion in insects. IV. Comparison of the  $p_H$  optima of the digestive enzymes from different groups of insects.** O. SHINODA (Chikashige Anniv. Vol., 1930, 9—24).—The  $p_H$  of the intestinal secretions of various orders of insects are parallel with their systematic position. The  $p_H$  optima of proteases from the same orders of insects are in general parallel with the  $p_H$  of the intestinal juice, but the carbohydrates depend to a greater extent on the food habits of the insect. B. LEVIN.

**Effect of ultra-violet irradiation of the skin on the secretion of gastric juice.** F. DIEHL (Arch. exp. Path. Pharm., 1931, 159, 367—371).—When human subjects were irradiated with ultra-violet light sufficiently intensely to cause the rapid development of an erythema there was a histamine-like effect on the secretion of gastric juice, but with less intense irradiation no noticeable stimulation of the gastric secretion ensued. This result supports the view that a histamine-like substance produced in the skin by irradiation is the cause of the erythema.

W. O. KERMAK.

**Significance of the thiocyanogen content of gastric juice.** G. LOCKEMANN and W. ULRICH (Deut. med. Woch., 1930, 56, 1900—1902; Chem. Zentr., 1931, i, 478).—The thiocyanogen in presence of hydrogen ions has a bactericidal action.

A. A. ELDRIDGE.

**Change of some physico-chemical properties of aqueous colloidal sericin solution of the cocoon during storing.** H. KANEKO and M. MIYASAKA (Bull. Sericult. Japan, 1930, 3, 4—5).—Slow denaturation of the sericin of the cocoon takes place during storage in a sealed vessel. The solubility, relative viscosity, refractive index, degree of turbidity, surface tension, and adsorptive capacity for dyes decrease, whilst the coagulation value towards platinic chloride and the rate of diffusion through 0.1% agar gel increase. These changes occur more quickly in the open atmosphere. Carbon dioxide and especially ammonia preserve the sericin. The solubility of sericin is increased by ammonia and decreased by carbon dioxide. E. S. HEDGES.

**Occurrence of citric acid in the amniotic fluid.** S. GENELL (Biochem. Z., 1931, 232, 335—337).—Citric acid to the extent of, on the average, 0.005%

is a normal constituent of the amniotic fluid. Blood from the placenta probably contains less citric acid than does the fluid, and the acid is absent from the urine of new-born children. The citric acid of the fluid is probably secreted by the amniotic epithelium.

W. McCARTNEY.

**Colouring matter of milk.** M. LUNDBORG (Biochem. Z., 1931, 231, 274—289).—The yellow colouring matter of butter-fat is carotene. Methods of extracting the fat from milk and of determining the carotene content of the unsaponified and saponified fat are described and discussed. The most rapid and satisfactory method for the determination of carotene in milk is the author's modification, here described, of the method of Röse and Gottlieb.

W. McCARTNEY.

**Significance of liver-glycogen in liver function.** I, II. T. IKUSHIMA (Japan. J. Gastroenterol., 1930, 2, 213—219, 220—225).—A study of the rate of excretion of azorubin-S in the bile after injection into the blood; the pigment excretion function falls or rises when the liver-glycogen diminishes or increases, respectively.

CHEMICAL ABSTRACTS.

**Excretion of halogen from the liver.** I. Chlorine. Y. MARUNO (Japan. J. Gastroenterol., 1930, 2, 231—238).—After intravenous injection of sodium chloride (10%; 5 c.c. per kg.) into rabbits the blood-chlorine increases, becoming normal in 2—3 hrs.; the bile-chlorine is maximal in 15—30 min. and is high after 23 hrs. Injury to the liver disturbs the excretion of chlorine.

CHEMICAL ABSTRACTS.

**Formation of bilirubin.** I. M. ASCOLI and A. FIORETTI. II. M. ASCOLI and G. B. MALAGO (Bull. Atti Acad. Med. Roma, 1930, 54, 6 pp., 6 pp.; Chem. Zentr., 1930, ii, 3596).—In nephrectomised dogs plasma-hæmoglobin is converted in the liver into bilirubin. Determinations of the quantity of bilirubin in various arteries and veins have been made. The liver is the chief source of bilirubin, although other places of formation exist.

A. A. ELDRIDGE.

**Fate of bilirubin introduced into the blood-vessels.** I. S. SAIKI (Japan. J. Gastroenterol., 1930, 2, 203—212).—When injected into the circulating blood of rabbits or dogs, bilirubin rapidly disappears from the plasma. It readily passes into the bile and urine.

CHEMICAL ABSTRACTS.

**Absorption spectrum of bilirubin in chloroform, alcohol, and alkalis.** L. HEILMEYER (Biochem. Z., 1931, 232, 229—239).—Bilirubin in chloroform and alcohol possesses a well-defined absorption with a maximum at 450 m $\mu$ , the absorption falling away continuously to the ultra-violet. The absorption ratio at the maximum is  $1.054 \times 10^{-5}$ . On keeping in light, the absorption decreases in the short-wave range and increases in the long-wave range. In alkaline solution, bilirubin shows a continuous absorption in the visible range, but the solution is too unstable to obtain a curve. The difference between the alkaline and neutral spectrum is not due to oxidative changes, but to the alkaline medium (salt formation?).

P. W. CLUTTERBUCK.

**Cholesterol of protoplasm.** VII. Ox-bile. G. PFEIFFER (Biochem. Z., 1931, 232, 255—259);

cf. this vol., 507).—The bile of young cattle contains oxysterol, the ratio of the amount of this to that of total cholesterol compounds present not differing much from the ratio found in liver. The ratio of oxysterol to precipitable cholesterol, however, is about 25% lower in the case of the bile than in that of the liver, possibly because the liver oxidises oxysterol to bile acids. The liver contains a larger percentage of cholesterol esters than does the bile.

W. McCARTNEY.

**Urinary composition and acid-base equilibrium.** I. S. M. NEUSCHLOSZ. II. S. M. NEUSCHLOSZ and J. PLANAS (Biochem. Z., 1931, 232, 82—97, 98—105).—I. A method is given for determining the ratio of weak bases (ammonia, creatinine) to weak acids (organic acids, acid phosphate ion) in urine; in 100 normal human urines this base-acid quotient is a linear function of the  $p_H$  of the urine, and equals unity at  $p_H$  5.7. The quotient also stands in direct relationship with the "buffer constant" calculated from the hydrogen-ion concentration of the urine and its concentration in primary and secondary phosphates.

II. The effect of slow intravenous injection of various acids (hydrochloric, sulphuric, phosphoric, lactic, and acetic), bases (ammonia and sodium hydroxide), and salts (ammonium and calcium chlorides, sodium hydrogen carbonate), 10 c.c. of 0.1N solution per kg. body-weight being used in hydrogen carbonate-free Ringer's solution at a rate of a 100 c.c. per hr., on the alkali reserve and the urinary composition in dogs is investigated. Hydrochloric and sulphuric acids cause a decrease of alkali reserve, which persists over 24 hrs., whilst the urinary acidity may increase, decrease, or remain unchanged. The base-acid quotient decreases in every case. With lactic and phosphoric acids, and also with ammonium and calcium chlorides, a decrease in alkali reserve is obtained, but this persists only a short time. The urine becomes more acid and the base-acid quotient increases considerably. Acetic acid causes a long-persisting decrease of alkali reserve, alkalisation of the urine, and a decrease of base-acid quotient. Sodium hydroxide and hydrogen carbonate cause a prolonged increase of alkali reserve, an alkaline urine, and a decrease of base-acid quotient. The action of ammonia depends on the initial alkali reserve. With low initial reserve, an increase of reserve occurs with ammonia, the urine becomes more acid, and the base-acid quotient increases. With high initial reserve, ammonia produces but little effect, the urine becomes more alkaline, and the base-acid quotient decreases.

P. W. CLUTTERBUCK.

**C:N-quotient. Determination of carbon.** W. BIEHLER (Knoll's Mitt. für Ärzte, 1929, 3 pp.; Chem. Zentr., 1930, ii, 3611).—Urine (3—5 c.c.) is diluted with water (to 50 c.c.), and heated for 15 min. at 70° with potassium persulphate (10 g.) and mercuric nitrate (1 crystal); air free from carbon dioxide is passed through the combustion vessel, then through potassium antimonyl tartrate solution, and into a known quantity of barium hydroxide solution.

A. A. ELDRIDGE.

**Detection of lactose in urine.** E. FREUND and B. LUSTIG (Biochem. Z., 1931, 232, 449—451).—The

method of Bauer (A., 1907, ii, 310) for the determination of mucic acid (derived from lactose) in urine gives satisfactory results as far as lactose orally administered is concerned. Certain constituents of urine, however (urea, ammonium salts), prevent the conversion of the small amounts of lactose present in urine by nitric acid into mucic acid. A method is described by which these constituents may be removed and this lactose also determined.

W. McCARTNEY.

**Solubility of urinary uric acid.** R. ASCOLI (Biochim. Terap. sperim., 1929, 16, 33—46; Chem. Zentr., 1931, i, 492—493).—Synthetic uric acid is soluble in alkaline or neutral urine, but at  $p_{H}$  6.5—7 it is practically insoluble. When urine at  $p_{H}$  5.5—6.5 is shaken with synthetic uric acid, natural uric acid separates. The solubility of synthetic uric acid in alkaline urine is closely related to the natural uric acid content.

A. A. ELDRIDGE.

**Clinical colorimetry. IX. Urochrome. Analysis of urinary residual colouring matter.** L. HELMEYER and W. OTTO (Z. ges. exp. Med., 1930, 74, 490—513; Chem. Zentr., 1931, i, 324).—“Urochrome” is separated by saturation of urine with ammonium sulphate into two substances with different absorption spectra: A, 26—42%, sensitive towards oxygen, B, 50—74%. Lead acetate cannot be used for the separation of the colouring matters of normal urine.

A. A. ELDRIDGE.

**Allergy and the acid-base equilibrium.** F. DIEHL and E. G. SCHENCK (Arch. exp. Path. Pharm., 1931, 159, 372—382).—Modification of the acid-base equilibrium, e.g., by administration of ammonium chloride, does not significantly affect the allergic skin reactions of human patients.

W. O. KERMAK.

**Dialysability of proteins.** A. F. COCA (J. Immunol., 1930, 19, 405—410).—The dialysability of the excitants of atopic hypersensitiveness in egg-white is confirmed.

CHEMICAL ABSTRACTS.

**Goats' milk anæmia. Experiments with growing pigs.** C. KRONACHER, J. KLIESCH, and W. SCHÄPER (Z. Tierzücht., 1930, 14, 231—294; Chem. Zentr., 1930, ii, 1093—1094).—Goats' milk anæmia is not due to avitaminosis, in particular, -C.

A. A. ELDRIDGE.

**Gastric acidity in diabetes mellitus.** I. M. RABINOWITCH, A. F. FOWLER, and B. A. WATSON (Arch. Int. Med., 1931, 47, 384—390).—Of 100 cases of diabetes in which there were no digestive disorders, more than fifty had gastric juices in which the total acidity and free hydrochloric acid were below normal, and free hydrochloric acid was absent in 39 cases. Since the incidence of achlorhydria in non-diabetics is 20%, diabetes *per se* may be responsible for low gastric acidity.

A. COHEN.

**Biological diagnosis of gout.** P. ESCUDERO and A. ESCUDERO (Semana Méd., 1930, II, 1945—1954).—The method is based on measurement of the retention of purine substances.

CHEMICAL ABSTRACTS.

**Congestive heart failure. VI. Effect of overwork and other factors on the potassium content of the cardiac muscle.** J. A. CALHOUN, G. E.

CULLEN, G. CLARKE, and T. R. HARRISON. VII. **Skeletal muscle.** J. A. CALHOUN, G. E. CULLEN, and T. R. HARRISON (J. Clin. Invest., 1930, 9, 393—403, 405—408).—VI. The potassium content of the right ventricle is diminished owing to overwork in pneumonia and massive collapse and in myocardial insufficiency.

VII. Overwork of the muscles of one leg of a dog led to loss of potassium. CHEMICAL ABSTRACTS.

**High carbonuria in severe hepatic injury after administration of menthol.** K. VOIT and H. WENDT (Z. klin. Med., 1930, 114, 432—438; Chem. Zentr., 1931, i, 307).—On administration of menthol normal urine contains an amount of carbon approximately corresponding with the anticipated quantity of mentholglycuronic acid; in hepatic disease much larger quantities are excreted.

A. A. ELDRIDGE.

**Glyoxaline derivatives in the urine in liver disease.** F. KAUFFMANN and R. ENGEL (Z. klin. Med., 1930, 114, 405—431; Chem. Zentr., 1931, i, 304).—Glyoxaline derivatives are normal constituents of urine. The “glyoxaline value” increases on a protein diet; it is related to the dietary histidine. It increases in water diuresis or on administration of histidine hydrochloride or glyoxalinelactic acid, and decreases slightly in hunger acidosis. High values are observed in hepatic disease; the cause is discussed.

A. A. ELDRIDGE.

**Intermediary protein and carbohydrate metabolism. I—III.** J. BLÖCH (Z. ges. exp. Med., 1930, 74, 439—448, 449—453, 454—457; Chem. Zentr., 1931, i, 307—308).—Galactosuria following administration of galactose in degenerative hepatic disease is markedly diminished by administration of glycine, alanine, or aspartic acid. In glycogen impoverishment the alanine or aspartic acid is partly employed in the production of sugar.

A. A. ELDRIDGE.

**Distribution of bile-pigments in the organism.** F. K. GASSMANN (Z. klin. Med., 1930, 114, 477—480; Chem. Zentr., 1931, i, 474).—In hepatic disease with icterus and in dogs with experimental icterus the pancreas and spleen are almost free from bile-pigments; the liver, skin, kidneys, adrenals, and lungs contained bilirubin.

A. A. ELDRIDGE.

**Biochemical investigation of blood in cases of experimental disturbance of liver function. I. Liver function and carbohydrate metabolism.** T. SAWADA (Japan. J. Gastroenterol., 1930, 2, 191—202).—Rabbits' blood-sugar at first increases and then becomes subnormal after liver injury by chloroform, carbon tetrachloride, or yellow phosphorus. X-Ray injury produced a rise in blood-sugar for 3 days; partial hepatectomy decreased it. Ligation of the common bile duct increased and then decreased the blood-sugar.

CHEMICAL ABSTRACTS.

**Blood-phosphorus in parathyroid- and thyro-parathyroid-ectomised animals.** C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1930, 104, 228—229; Chem. Zentr., 1931, i, 304).—The total, inorganic, and total organic phosphorus increase, whilst the ester-phosphorus falls.

A. A. ELDRIDGE.

**Causative agent of a chicken tumour.** J. B. MURPHY, O. M. HELMER, A. CLAUDE, and E. STURM

(Science, 1931, 73, 266—268).—Adsorption of the active agent by aluminium hydroxide leaves an extract more active than the original in spite of the removal of a large proportion of the agent by the hydroxide. Evidence of an inhibiting principle in the chicken tumour has been obtained, and the increased activity resulting after adsorption by aluminium hydroxide is explained by preferential adsorption of this principle. L. S. THEOBALD.

**Western duck sickness produced experimentally.** E. R. KALMBACH (Science, 1930, 72, 658—660).—Duck sickness has been produced by the administration of a toxic material resulting from incubation of the tissues of ducks which have succumbed to the disease. L. S. THEOBALD.

**Changes of serum-proteins in under-nutrition.** S. M. LING (Chinese J. Physiol., 1931, 5, 1—10).—In 24 human subjects on a diet poor in protein and showing marked oedema, the serum-albumin was below normal, the serum-globulin in most cases was within the normal limits, the basal metabolism was low, and there was a negative nitrogen balance. On an adequate diet, the oedema soon disappeared, the serum-albumin returned more slowly to the normal limits, the basal metabolism rose, and the nitrogen balance was positive. The low colloid osmotic pressure is probably the cause of the oedema which occurs on a diet poor in protein.

W. O. KERMACK.

**Metabolism as related to chromosome structure and the duration of life.** J. W. GOWEN (J. Gen. Physiol., 1931, 14, 463—472).—The rates of production of carbon dioxide by *Drosophila* flies possessing different types of chromosome constitution have been measured. The types possessing balanced chromosomes, namely males and triploid females, have smaller rates than do those types possessing unbalanced chromosomes, namely males and sex-intergrades. The smaller rates of the former two types appear to be correlated with their longer average life. W. O. KERMACK.

**Metabolism of tissue cultures. I. Measurement of respiration. II. Determination of weight of tissue cultures. Relation of increase of weight to increase of surface.** R. MEIER (Biochem. Z., 1931, 231, 247—252, 253—259).—I. A method of measuring the respiration of tissue cultures is described, a modified form of Carrel flask being used. The carbon dioxide produced is measured after respiration has ceased.

II. Since the measurement of the area of tissue cultures involves many errors, a method of determining their weight is used and the amounts of lactic acid produced by unit weight of various cultures have been determined. W. MCCARTNEY.

**Standard metabolism of Australian aborigines.** C. S. HICKS, R. F. MATTERS, and M. L. MITCHELL (Austral. J. Exp. Biol., 1931, 8, 69—82).

**Metabolism of nerves on electric stimulation.** H. WINTERSTEIN (Biochem. Z., 1931, 232, 196—201).—A reply to Meyerhof and Schulze (this vol., 254) and to Gerard (Science, 1930, 72, 196).

P. W. CLUTTERBUCK.

**Increase in the  $p_H$  of the white and yolk of hens' eggs.** P. F. SHARP and C. K. POWELL (Ind. Eng. Chem., 1931, 23, 196—199).—The  $p_H$  of the white rises from 7.6 to 9.3 during the first few days after laying, due largely to loss of carbon dioxide; this change takes place more rapidly at higher temperatures. Fertile eggs then fall to about 8.0, but infertile ones show no change unless kept at high temperatures. Hydrolysis of the protein takes place more rapidly the further is the  $p_H$  from its isoelectric point, and the loss of carbon dioxide may be prevented by increasing its amount in the air in which the eggs are stored, or by dipping the eggs in oil. The yolk shows a slower and smaller change than the white. T. MCLACHLAN.

**Sugar, the fuel of life.** F. FISCHLER (Arch. Pharm., 1931, 269, 9—22).—A lecture.

H. E. F. NOTTON.

**Influence of amino-acids on the glycogen mobilisation in the toad's liver through adrenaline.** Y. TANIUCHI (Folia Pharm. Japon., 1930, 10, No. 1, 64—99).—When perfused with adrenaline, glycine and tryptophan ( $1$  in  $2-4 \times 10^4$ ) have a weak, but histidine and cystine no, sugar-producing action. The sugar mobilisation of the adrenaline is strengthened, especially by histidine and cystine. The combined effect of two amino-acids is weaker than their separate action. The sugar mobilisation is not parallel to the concentration of the amino-acid or the combination with adrenaline. CHEMICAL ABSTRACTS.

**Carbohydrate tolerance at high altitudes.** G. FERRALORO (Arch. Sci. biol., 1929, 13, 109—126; Chem. Zentr., 1930, ii, 3803).—In rarefied air and intense sunlight, hyperadrenalinæmia is accompanied by a rise in blood-sugar and an increase in dextrose tolerance. A. A. ELDRIDGE.

**Tolerance of normal subjects to lævulose. Factors influencing the variations in rise in blood-sugar.** N. JOLLIFFE (J. Clin. Invest., 1930, 9, 363—380).—Oral ingestion of 30—50 g. of lævulose normally causes a rise in blood-sugar to 115 mg. per 100 c.c. (max.). A value above 95—110 appears to stimulate a sugar-storage mechanism, which rapidly lowers the blood-sugar. The rapidity of disappearance of the blood-sugar probably depends on the glycogen-forming ability of the sugar used.

CHEMICAL ABSTRACTS.

**Metabolism of galactose. I. Use of galactose in tests of the function of the liver.** H. SHAY, E. M. SCHLOSS, and M. A. BELL (Arch. Int. Med., 1931, 47, 391—402).—Galactose is regarded as a suitable sugar for testing liver function, since (a) it is readily absorbed from the intestine, (b) its conversion into glycogen by the liver is relatively difficult, (c) it is not appreciably utilised by tissues other than the liver, and (d) its excretion is not influenced by endocrine activity. A. COHEN.

**Effect of yeast on the chemical processes in the liver and muscle of exercising animals. I. C. PI-SUÑER BAYO, G. LISS, and T. OSUKA. II. C. PI-SUÑER BAYO and G. LISS (Anal. Fis. Quím., 1931, 29, 193—199, 200—205).—I. Administration of 0.2 g. of dried yeast daily to well-exercised rats caused**

an increase of the liver-glycogen and a smaller increase of the muscle-glycogen; the lactic and phosphoric acid content of both the liver and muscle also increased slightly.

II. The daily administration of 2 g. per kg. of dried yeast to dogs maintained in regular training for 48 days caused the liver-fat to increase to 6—8 times its normal value without influencing the liver-glycogen. In the case of dogs which, after resting for several days, were exercised for only 1 hr., the liver- and muscle-glycogen increased very greatly. It appears that the glycogen deposit, which attains a maximum after a few hours, is gradually converted into fat.

H. F. GILLBE.

**Inhibition of glycolysis and accumulation of methylglyoxal.** H. K. BARRENSCHEEN, K. BRAUN, and M. DREGUSS (Biochem. Z., 1931, 232, 165—180).—Addition of iodoacetic and bromoacetic acids to fresh muscle, liver, or kidney pulp containing hexosediphosphate causes accumulation of methylglyoxal. Addition of pancreatic extract to muscle or yeast pulp treated with iodoacetic acid causes the formation of methylglyoxal from glycogen. Methylglyoxal may be detected in the musculature of animals poisoned with iodoacetic or bromoacetic acid. The organ pulp of animals so poisoned added to hexosediphosphate formed methylglyoxal, and in two of these experiments pyruvic acid also accumulated. Organ pulp of animals poisoned with insulin also formed methylglyoxal from added hexosediphosphate.

P. W. CLUTTERBUCK.

**Pyruvic acid as a food for *Drosophila melanogaster*.** L. NÉMETH (Biochem. Z., 1931, 231, 385—392).—An agar medium containing pyruvic acid and yeast but free from sugars is a sufficient food for *Drosophila melanogaster*, since the fly thrives on this material and lays fertile eggs. If pyruvic acid is absent or is replaced by acetic, tartaric, formic, lactic, or succinic acid, the insects cannot live on the medium.

W. McCARTNEY.

**Passage of chemical substances from the mother to the foetus at the end of gestation.** E. BRANDSTRUP (Bull. Soc. Chim. biol., 1931, 13, 172—185).—In the rabbit during the last quarter of gestation dextrose, glycine, alanine, aspartic acid, glutamic acid, and urea diffuse slowly across the placenta, xylose and arabinose diffuse more rapidly, whilst there is no diffusion of sucrose or lactose. The chloride ion diffuses rapidly across the placenta.

In woman at the commencement of labour there is a slow diffusion of urea across the placenta, equilibrium being attained after some hours. C. C. N. VASS.

**Ammonia content of, and production of ammonia in, muscle. Relation of these to change in function and condition. IX. Stage at which ammonia is produced during the chemical processes occurring in active muscle.** W. MOZOŁOWSKI, T. MANN, and C. LUTWAK (Biochem. Z., 1931, 231, 290—305).—The greater part of the ammonia produced in active frog muscle which has been poisoned with iodoacetic acid is formed when a state of fatigue has been reached, the creatinephosphoric acid being exhausted and rigor about to appear.

W. McCARTNEY.

**Pyrimidine base metabolism.** A. BOIVIN (Compt. rend. Soc. Biol., 1930, 104, 99—100; Chem. Zentr., 1931, i, 308).—Pyrimidine bases are absent from animal and from normal or pathological human urine. An analytical method is described.

A. A. ELDRIDGE.

**Biochemistry of sulphur. VIII. Rate of absorption of cystine from the gastrointestinal tract of the white rat.** M. X. SULLIVAN and W. C. HESS (U.S. Publ. Health Rep. Suppl., 1931, No. 89, 1—16).—The rate of absorption of cystine administered as the sodium salt is approximately 50 mg. per 100 g. body-weight per hr. as determined by the Sullivan and Okuda iodometric methods, and 30 mg. per 100 g. body-weight per hr. by the Folin-Marenzi method (cf. A., 1929, 1093). Hydrolysates of amino-acids containing no cystine react positively as cystine in the Folin-Marenzi method, but are negative in the other two. The Okuda method shows that there is an accumulation of S-S compounds, calculated as glutathione, in the liver of rats fed with cystine compared with those of fasting rats or those fed with glycine and alanine.

C. C. N. VASS.

**Origin of creatine and creatinine in the animal organism. I—III.** E. ABDERHALDEN and S. BUADZE (Z. ges. exp. Med., 1929, 65, 1—26; 66, 635—652; 1930, 69, 561—576; Chem. Zentr., 1930, ii, 3803).—II. Kidney, brain, thyroid, thymus, pancreas, testicle, lung and spleen tissue can form creatine (creatinine) from nucleic acid or from guanine and adenine. In the liver, formation is masked by decomposition. The minced tissue loses its activity when boiled. Urea is not formed from allantoin; allantoin, in presence or absence of choline, gives no creatine. Negative results were obtained with carbonyldicarbamide and methylglyoxaline. In gout the urinary and blood-total creatinine is diminished.

III. Allantoin, uric acid, uracil, methylglyoxaline, and caffeine do not increase the excretion by the adult dog of total creatinine; increase results from ingestion of placenta powder or subcutaneous administration of menoformone. Administration of globin or hæmoglobin considerably increases the excretion of total creatine, with simultaneous increase in urinary uric acid and allantoin. Purine, creatine, and creatinine metabolisms thus appear closely related. Hydrolysed globin from which arginine and histidine were removed was ineffective; addition of histidine, but not of arginine, partly restored the activity.

A. A. ELDRIDGE.

**Do allantoin and purines of the urine of mammals arise partly from the degradation of proteins?** E. F. TERROINE and G. MOURROT (Bull. Soc. Chim. biol., 1931, 13, 94—109).—When the mineral salts are decreased in the diet of pigs well supplied with proteins (caseinogen) a sharp increase occurs in the total nitrogen excretion and also in the excretion of allantoin and purines. These substances therefore arise in part from the degradation of proteins.

W. O. KERMAK.

**Do protein reserves exist in frog's liver prior to hibernation?** C. GAUTIER (Bull. Soc. Chim. biol., 1931, 13, 142—147).—Average determinations show that whilst the total weight of frog's liver is

increased twofold prior to hibernation the protein content increases by almost a third.

C. C. N. VASS.

**Specific dynamic action of protein.** H. BORSOOK and H. M. WINEGARDEN (*Proc. Nat. Acad. Sci.*, 1931, 17, 75—91).—The specific dynamic action of protein is parallel to nitrogen excretion and in the well-nourished animal is the result of at least two processes, one of which is the work imposed on the kidney and the other is due to the metabolism other than excretion of nitrogen and of carbon. The increase in metabolism following the ingestion of protein or amino-acid shows a close correlation between the specific dynamic action of proteins and the increase, over the basal level of excretion, in the urinary nitrogen. Neither the experimental evidence nor consideration of energy relations supports the view that the specific dynamic action of protein is due to the conversion of deaminised fractions into dextrose.

E. S. HEDGES.

**Partition of urinary nitrogen in endogenous nitrogen metabolism during growth.** E. F. TERROINE, G. BOY, M. CHAMPAGNE, and G. MOUROT (*Compt. rend.*, 1931, 192, 634—636).—The total expenditure of nitrogen per kg. of body-weight diminishes considerably with growth. Whilst the urea, ammonia, amino-nitrogen, and allantoin decrease correspondingly, the amount of creatinine remains constant or increases slightly. In the pig, the urinary amino-nitrogen forms 15—20% of the nitrogen excreted as ammonia, urea, and amino-nitrogen.

C. C. N. VASS.

[Biological formation of] ketonic substances.

O. STEPPUHN and A. TIMOFEEVA (*Z. ges. exp. Med.*, 1930, 74, 467—481; *Chem. Zentr.*, 1931, i, 307).—When the liver is impoverished in glycogen peripheral fat migrates to the liver; ketonic substances are formed and the degradation of protein is increased. The protein-carbohydrate metamorphosis is stimulated by the ketonic acids only under certain conditions.

A. A. ELDRIDGE.

**Resorption of fat by desaturation of fatty acids.** H. TANGL and N. BEREND (*Biochem. Z.*, 1931, 232, 181—188).—The desaturation of fatty acids is brought about by the action of bile, an action which is augmented by pancreatic juice, although the latter alone is inactive. The action is inhibited by heating and is therefore probably an enzymic process.

P. W. CLUTTERBUCK.

**Effect of diet on the composition of adipose tissue.** K. MOSSE and C. BRAHM (*Jahrb. Kinderheilk.*, 1928, 122, 151—167; *Chem. Zentr.*, 1930, ii, 1093).—Experiments on piglings are described. Data relating the weight and the quantity of fat to the diet are recorded; the chemical characteristics of the fat remained practically constant. With a protein-rich diet, the protein, water, and ash of the adipose tissue were high; with a carbohydrate-rich diet the phosphorus content was high. A. A. ELDRIDGE.

**Growth studies with swine.** J. H. LONGWELL, H. O. HENDERSON, and W. M. INSKO, jun. (*W. Virginia Agric. Exp. Sta. Bull.*, 1930, No. 230, 24 pp.).—Butter and oleomargarine were equally effective as

sources of vitamin-D for pigs. Lard and vegetable-oil margarine gave less satisfactory results.

A. G. POLLARD.

**Influence of the consumption of fats and oils, meat, and bread on the growth of rats.** W. A. LEIBOVITSCHE-LIVSCHINA (*Biochem. Z.*, 1931, 231, 260—273).—The consumption of small amounts of cod-liver oil considerably stimulates the growth of rats, but large amounts have a toxic effect, causing loss of weight and early death. Correspondingly large amounts of olive oil have a similar, but not so pronounced, effect. Administration of small or medium amounts of olive, hemp-seed, and linseed oils to growing rats does not stimulate growth. Medium amounts of meat or of meat with bread produce the greatest increases in weight, especially in fasting rats which have previously received large amounts of cod-liver or olive oil. The effect of the consumption of meat lasts longer in fasting rats than in those which have not fasted.

W. MCCARTNEY.

**Bread. II. Physiological action of whole-meal bread.** I. ABELIN (*Biochem. Z.*, 1931, 232, 278—294; cf. A., 1930, 108).—Young rats fed exclusively on whole-meal bread which has been so baked as to avoid damage to certain valuable constituents grow and develop practically normally. If calcium lactate is added to such bread in order to compensate for the excess of phosphoric acid which it contains, the result is even more satisfactory. White and other breads, although alone insufficient and unsatisfactory as foods, are also improved, although to a smaller extent, by such addition of calcium salt.

W. MCCARTNEY.

**Inadequacy of white wheat flour and fish meal for prolonged growth of pigs and its amelioration with yeast or stout.** A. H. BLISSETT and J. GOLDING (*Biochem. J.*, 1931, 25, 349—357).—Daily additions of dried brewer's yeast to the inadequate diet of white wheat flour and fish meal made the ration satisfactory. Stout had a similar effect.

S. S. ZILVA.

**Lipin metabolism. I. Metabolism in experimental fever of rabbits.** H. HAMANO (*Proc. Imp. Acad. Tokyo*, 1931, 7, 80—81).—In rabbits after piqure, the amount of fatty acids in the blood and blood-plasma decreases, reaching a minimum in 24 hrs., thereafter returning to normal. Cholesterol and lecithin in the whole blood and plasma increase at first, and then decrease to normal. The leucocytes increase during fever. The serum-protein and -lipase both decrease during the initial stage. The author concludes that there is a relation between the amount of blood-lipin and the body temperature.

B. LEVIN.

**Cholesterol balance in chicks in the first two weeks after hatching.** H. DAM (*Biochem. Z.*, 1931, 232, 269—273; cf. A., 1930, 951).—In chicks, during the first two weeks after hatching, both the total amount of cholesterol and the ratio of cholesteryl ester to total cholesterol decrease.

W. MCCARTNEY.

**Mineral feeding [of animals]. Iodine, lime, and salt-licks.** B. W. SIMPSON (*New Zealand J. Agric.*, 1931, 42, 18—23).—Plants from seed soaked

in potassium iodate solution and grown in soil treated with potassium iodate contained more iodine than control plants and, when fed to rabbits, improved their growth rates. Addition of lime to rations, either direct or in the form of salt-licks, did not cause enlargement of the thyroid in rabbits. Lime alone did not appreciably affect the gland size or rates of growth, but the salt-lick increased the rate of growth and reduced the size of the glands. Large glands of low iodine content were produced by feeding healthy rabbits with food grown in goitrous areas.

A. G. POLLARD.

**Effect of age and nutrition on the calcium phosphate : calcium carbonate ratio in the bones of cattle.** W. M. NEAL, L. S. PALMER, C. H. ECKLES, and T. W. GULLICKSON (*J. Agric. Res.*, 1931, 42, 115—121).—The ratio of residual calcium to residual phosphate (excluding calcium present as carbonate and phosphate as trimagnesium phosphate) of cattle bones approximates to the ratio in tricalcium phosphate, and is not affected by deficiency of calcium or phosphorus in the ration. The ratio of calcium phosphate to calcium carbonate in the bones of dairy cattle decreases with age and is affected by nutrition, decreasing if the ration is deficient in phosphorus and returning to normal with the subsequent use of phosphate supplements. High values may occur if the ration has a high phosphorus content. Calcium deficiency is probably without effect on the proportion of phosphorus in the whole skeleton. High-calcium rations do not influence the calcium : phosphorus ratio.

A. G. POLLARD.

**Physico-chemical theory of the action of substances on living matter.** P. LASAREV (*J. Chim. phys.*, 1931, 28, 42—48).—On the assumptions that the effect of a substance on the function of a living cell is dependent on its concentration ( $C$ ), and that the function of the cell ( $E$ ) may be expressed in measurable quantities (*e.g.*, amount of liquid secreted etc.), formulæ are derived mathematically giving  $E$  in terms of  $C$  and the period of time ( $t$  in sec.) during which the effect of the substance is felt. In the case of the depressing effect of ether on chlorophyll assimilation (Bose), the difference between the normal oxygen content and the oxygen liberated in the presence of ether is given with great precision, compared with experimental values, by the expressions  $108(1 - e^{-0.114t})$  and  $121[1 - 1/(1 + 0.017t)]$ . The theory is also applied to the action on the nervous centres of substances introduced into the blood and, in the general case, into the stomach.

J. GRANT.

**Vital staining and permeability. II.** E. GELLHORN (*Protoplasma*, 1931, 12, 66—78).—The permeability of the surface layer of sea-urochin eggs to dyes is decreased by the presence of calcium salts and increased by sodium and magnesium salts, the effect of the latter being greater than that of salts of any univalent cation. The increased permeability caused by sodium or magnesium chlorides is diminished or entirely suppressed by the addition of calcium chloride. The antagonistic effect of barium or strontium chlorides is very slight in comparison with that of the calcium salt. Changes in permeability

due to salt treatment do not prevent fertilisation or development of the eggs.

A. G. POLLARD.

**Effect of intravenous injection of dyes on blood-cholesterol.** A. LESZLER (*Z. ges. exp. Med.*, 1930, 71, 477—479; *Chem. Zentr.*, 1930, ii, 1092).—Intravenous injection of tetraiodophenolphthalein, trypanflavine, and indigo-carmin to patients suffering from different diseases resulted in a diminution in blood-cholesterol.

L. S. THEOBALD.

**Alcohol content of blood under various conditions.** P. I. TUOVINEN (*Skand. Arch. Physiol.*, 1930, 60, 1—134; *Chem. Zentr.*, 1931, i, 310).—The relation depends on the amount and nature of the stomach contents as well as on the concentration of the alcohol ingested. The sensation is proportional to the blood-alcohol value, and is perceived at 0.006—0.01%.

A. A. ELDRIDGE.

**Exhalation of alcohol in breath.** G. LILJESTRAND and P. LINDE (*Skand. Arch. Physiol.*, 1930, 60, 273—298; *Chem. Zentr.*, 1931, i, 310).—After ingestion of alcohol the alcohol contents of arterial and venous blood are practically identical. The alcohol content of expired air is a measure of that of the body-fluids. Variations and their physiological causes are considered.

A. A. ELDRIDGE.

**Action of chloroform and ether on the oxidoreductive properties of tissues.** N. GAVRILESCO (*Bull. Soc. Chim. biol.*, 1931, 13, 47—60).—The reduced glutathione in the minced muscle of fish of several species diminishes very slowly on exposure to air. When the tissue is exposed to ether or chloroform vapour the rate of disappearance of reduced glutathione is even less rapid. Anæsthetisation of the fish before extraction of the muscle does not affect the quantity of reduced glutathione in the latter. Experiments on the rate of reduction of methylene-blue at  $p_H$  7.4 by aqueous extracts of brain or by solutions of pure glutathione in presence or in absence of tissue residues show that the action of chloroform and ether is exercised on the tissue residues.

W. O. KERMACK.

**Reversible coagulation in living tissue. I.** W. D. BANCROFT and J. E. RUTZLER, jun. (*Proc. Nat. Acad. Sci.*, 1931, 17, 105—111).—The physiological effect of ether, amytal, morphine, and histamine is to coagulate certain nerve-colloids, apparently the proteins. Anaphylactic shock is due to the coagulation of certain nerve-proteins, chiefly those of the sympathetic nerves. Sodium thiocyanate peptises proteins and should therefore alleviate or counteract disturbances due to coagulation of the nerve-proteins. Intravenous injections of solutions of sodium thiocyanate bring rabbits out of the unconsciousness due to ether, amytal, or morphine more rapidly than is normal. The treatment can also prevent death from strychnine or histamine and can prevent anaphylactic shock in rabbits previously sensitised by subcutaneous injection of an egg-white sol.

E. S. HEDGES.

**Influence of  $p_H$  on the activity of certain local anaesthetics as measured by the rabbit's cornea method.** T. D. GERLOUGH (*J. Pharm. Exp. Ther.*, 1931, 41, 307—316).—The durations of the local

anæsthetic actions of solutions of procaine hydrochloride, procaine borate, and of butyn as measured by the rabbit's cornea method increase with increase of the  $p_H$  of the solution, whilst that of butesin picrate is apparently independent of  $p_H$ . The duration of anæsthesia produced by procaine hydrochloride or butyn was greater when the anæsthetic was dissolved in buffer solutions or at concentrations greater than 0.01M. The anæsthetic activity of buffered butyn solutions was not influenced by *N*/8-sodium chloride, *N*/8-potassium chloride, *N*/7-sodium sulphate, and *N*/5-magnesium sulphate.

W. O. KERMACK.

**Effect of certain drugs on blood-sugar concentration.** I. BURDI (Z. ges. exp. Med., 1930, 71, 480—488; Chem. Zentr., 1930, ii, 1091—1092).—Administration of chloral hydrate, hedonal, and paraldehyde leads to an increase in blood-sugar which in the case of the first is counteracted by insulin. Sulphonal leads to hypoglycæmia and alcohol also lowers the blood-sugar. Veronal and trional produce no regular changes, and dionin is without significant effect. In dogs, morphine and heroin hydrochlorides increase the blood-sugar.

L. S. THEOBALD.

**Avertin detoxication by glycuronic acid.** W. STARK (Schmerz, Narkose, Anæsth., 1930, 3, 247—261; Chem. Zentr., 1930, ii, 3808).—Detoxication is conditioned by pairing with glycuronic acid. Moderate doses of thyroxine favour detoxication, whilst large doses increase the toxic action.

A. A. ELDRIDGE.

**Irritative properties of various halogenated and unhalogenated oils and their compounds.** L. A. CRANDALL, P. H. HOLINGER, and E. L. WALSH (J. Pharm. Exp. Ther., 1931, 41, 347—354).—Forty-eight different halogenated and unhalogenated oils have been injected intrapleurally and intrapericardially into dogs. Of the natural oils suitable as bases for halogenation, olive oil and lard oil are the least irritating. Halogenation increases the irritative properties of an oil. Increased irritation is also caused by the presence of small quantities of free fatty acid.

W. O. KERMACK.

**Tolerance to benzene.** N. V. LAZAREV, L. P. BRÛLLOVA, S. N. KREMNEVA, L. T. LARIONOV, M. P. LÛBIMOVA, and D. J. STALSKAJA (Arch. exp. Path. Pharm., 1931, 159, 345—358).—The effect of benzene on white mice is less marked in a fasting condition than after feeding only in as far as it brings about epileptoid convulsions. When the animals are repeatedly exposed to the effects of benzene a deterioration in their condition occurs followed by development of tolerance to the poison which exhibits itself in an increase in weight, and in the erythrocyte count as well as in the disappearance of abnormal forms of red blood-cells. In the first stage a lowering of resistance to infection is observed, but normal resistance returns during the acquirement of tolerance.

W. O. KERMACK.

**Pharmacological action of certain phenol esters with special reference to the etiology of so-called ginger paralysis.** M. I. SMITH, E. ELVOVE, and W. H. FRAZIER (U.S. Publ. Health Rep. Reprint No. 1419, 1930, 1—16).—*o*-Tolyl

phosphate is much more toxic to the rabbit than phenol or the *p*-ester, or *o*-, *m*-, or *p*-cresol. Whereas the systemic action of phenol and the cresols is prompt, that of the *o*-ester is delayed. In the monkey, the toxicity of phenol and the cresols is of the same order as in the rabbit; the *p*-ester has the same pharmacological action as *p*-cresol, but the *o*-ester can produce a partial motor paralysis after 6—8 days. In the chicken the symptoms of the disease produced in man after taking adulterated fluid extract of Jamaica ginger are reproducible with remarkable uniformity; such symptoms were obtained only on administration of *o*-tolyl phosphate. It is probable that the lethal dose for man is about 1 g. of the *o*-ester per kg. body-weight, whilst 2 g. would cause a moderate motor paralysis. The difference in species susceptibility to the *o*-ester is attributed to differences of absorption from the alimentary canal. The fraction behaving pharmacologically like *o*-tolyl phosphate was obtained from the adulterated extract after removal of the alcohol, on distillation at 246—275°/50 mm.; it contained no free phenols and gave Melzer's benzaldehyde test. C. C. N. VASS.

**Chemical constitution and biological action.**

II. T. SASAKI and H. UEDA (Biochem. Z., 1931, 232, 260—268; cf. J. Biochem. Japan, 1930, 12, 429).—3-Aminocarbostyryl is an amyostatic poison, but the 3 : 6-diamino-derivative has scarcely any such effect, whilst the 1- and 7-amino-derivatives as well as the ethyl ester of *p*-aminophenylalanine have none. Of five ethyl diaminobenzoates the 2 : 4-compound has the most powerful amyostatic action on mice, the 2 : 5-compound is half as powerful, and the 2 : 3-, 3 : 4-, and 3 : 5-compounds (equal) are again half as powerful as the 2 : 5-compound. In guinea-pigs, however, the 3 : 4- and 3 : 5-compounds are most powerful, the 2 : 4- and 2 : 5-compounds are much less active, and the 2 : 3-compound is least so. *o*-Nitrobenzylidenehydantoin, m. p. 300° (decomp.), from *o*-nitrobenzaldehyde and acetylhydantoin, gives 3-aminohydrocarbostyryl (acetyl derivative, m. p. 241—242°) when boiled with hydriodic acid and phosphorus. 6-Nitro-3-acetamidohydrocarbostyryl, m. p. 289—290°, is reduced to the hydrochloride, m. p. above 300°, of the corresponding diamino-compound. The ethyl ester of *dl*-*p*-aminophenylalanine has m. p. 243—244°. The hydrochloride, m. p. 219—220°, of ethyl 2 : 3-diaminobenzoate is obtained by reduction of 2-nitro-3-acetamidobenzoic acid. The hydrochloride of ethyl 2 : 4-diaminobenzoate has m. p. 203—204°. The hydrochloride of ethyl 2 : 5-diaminobenzoate was also prepared by reduction of 5-nitroacetanthranilic acid.

W. MCCARTNEY.

**Influence of  $\beta$ -1-piperidylethyl acetyltropate ("navigan") on the blood-sugar mobilisation in the liver.** K. TODA, Y. TANIUCHI, and M. NAKANO (Folia Pharm. Japon., 1930, 11, No. 2, 15).—In perfusion experiments with toad livers navigan slightly increased the sugar content; when injected with adrenaline it depresses the sugar mobilisation of the latter. CHEMICAL ABSTRACTS.

**Physostigmine-like action of certain synthetic urethanes.** A. C. WHITE and E. STEDMAN (J. Pharm. Exp. Ther., 1931, 41, 259—288).—The action



of miotine (methylurethane of  $\alpha$ -*m*-hydroxyphenylethyldimethylamine) on the eye, intestine, uterus, bladder, bronchioles, heart, vessels, vagus, and response to acetylcholine, salivary glands, suprarenals, and voluntary muscle is similar to that of physostigmine. The methylurethanes of *o*-hydroxybenzyltrimethylammonium iodide, *m*-hydroxybenzyl-dimethylamine, and of *p*-hydroxybenzyl-dimethylamine behaved similarly. The toxicities of miotine and physostigmine are not significantly different, and the symptoms produced are identical, but the toxicities of the other three urethanes are considerably smaller. It is concluded that the actions of physostigmine and of miotine are exerted in large measure through the same mechanism, probably by inhibiting the action of the esterase responsible for hydrolysis of acetylcholine and thus preventing the destruction and thereby producing an accumulation of the latter in the tissues. W. O. KERMAK.

**Chemotherapy of quinoline compounds. II. Action of certain quinoline compounds on *Paramecia*.** U. BRAHMACHARI, T. BHATTACHARYYA, P. BRAHMACHARI, R. BANERJEA, and B. B. MAITY (J. Pharm. Exp. Ther., 1931, 41, 255—257).—Besides the quinoline derivatives previously reported (A., 1930, 1316), 8-amino-4-phenylquinoline hydrochloride has a toxic action on *Paramecia*. 6-Amino-4-phenylquinoline hydrochloride as well as certain styryl- and anil-quinoline derivatives (cf. A., 1930, 1445) were not toxic to *Paramecia* at concentrations of 1:2000 or below. W. O. KERMAK.

**Hyperthermia and hyperglycemia with tetrahydro- $\beta$ -naphthylamine.** J. F. HEYMANS (Ar. Int. Pharm. Ther., 1929, 35, 153—168; Chem. Zentr., 1931, i, 303).—Insulin diminishes tetrahydro- $\beta$ -naphthylamine hyperglycemia, and may even cause hypoglycemia, without affecting the hyperthermia. The hyperthermia and hyperglycemia are therefore independent; the former is observed in dogs after adrenal- and parathyroid-ectomy, and the latter is attributed to liberation of adrenaline.

A. A. ELDRIDGE.

**Effect of certain diuretics on the concentration of blood-chlorides in dogs.** H. L. HANSEN, L. S. FOSDICK, and C. A. DRAGSTEDT (J. Pharm. Exp. Ther., 1931, 41, 325—331).—Neither in intact nor in nephrectomised dogs is there any significant change in the blood-chloride content prior to, during, or following the diuresis produced by diuretics such as ephyllin (theophylline-ethylenediamine) or by mercurials such as novasurol or salyrgan. The fall that occurs in the blood-chloride concentration of nephrectomised dogs when distilled water is injected into the peritoneal cavity was slightly but definitely less when either type of diuretic was simultaneously administered. W. O. KERMAK.

**Accumulation of guanidine in the blood following acute liver injury by carbon tetrachloride, chloroform, arsenic, or phosphorus.** J. T. CUTLER (J. Pharm. Exp. Ther., 1931, 41, 337—345).—During the poisoning there is an increase in blood-guanidine and a fall in blood-sugar. There may be no general retention of nitrogenous substances, so

that the increase in blood-creatinine is presumably due to liver and not to kidney damage. The increase in amino-acid nitrogen which occurs is also probably to be referred to the same cause. W. O. KERMAK.

**Chronic morphine poisoning. I. Blood picture of morphinism. II. Sedimentation of the blood-corpuses in the morphine addict and the addicted dog.** M. SUO (Folia Pharm. Japon., 1930, 11, No. 2, 127—143, 143—152).

CHEMICAL ABSTRACTS.

**Relationship between vomiting, blood-sugar, and uric acid regulation centre. I. Influence of emetics on vomiting and blood-sugar.** M. MUN (Folia Pharm. Japon., 1930, 11, No. 1, 75—83).—The following emetics, injected intravenously into dogs, are in order of reduction of blood-sugar: emetine hydrochloride, antimonial wine, copper sulphate, erycon, apomorphine hydrochloride.

CHEMICAL ABSTRACTS.

**Responses of sheep to *Zygodenus gramineus*.** A. R. McLAUGHLIN (Science, 1931, 73, 135—136).—Intravenous injection of an extract of *Z. gramineus* is followed by respiratory inhibition. Caffeine dissolved in sodium benzoate and sodium chloride solution stimulates respiration affected by this extract.

L. S. THEOBALD.

**Chinese antidiabetics. III. Effect on the blood-sugar of rabbits.** P. MIN (Folia Pharm. Japon., 1930, 11, No. 2, 181—187; cf. this vol., 510).—Alcoholic extracts of *Bupleurum falcatum*, *Lycium chinense*, *Fritillaria verticillata*, and *Anemarrhena asphodeloides* rapidly increase the blood-sugar; those of *Cannabis sativa*, *Pachyma coccus*, *Astragalus membranaceus*, *Morus bombycis*, *Actractylis ovata*, *Phellodendron amurense*, *Pueraria hirsuta*, and *Rehmannia lutea* first increase and then decrease it.

CHEMICAL ABSTRACTS.

***Leonurus sibericus*, L. II. Pharmacological study of leonurine.** S. KUBOTA and S. NAKASHIMA (Folia Pharm. Japon., 1930, 11, No. 2, 159—167).

CHEMICAL ABSTRACTS.

**Active principles of digitalis leaves.** Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1931, 7, 76—79).—Various fractions obtained from the alcoholic extract of the leaves of digitalis by fractional precipitation with water, saturated sodium chloride, and ammonium sulphate solutions, ether, chloroform, and benzene showed a digitalis-like action. The glucoside which was most soluble in water had the least effect on the heart. B. LEVIN.

**Effect of ions. IV. Influence of various ions on the toad's heart-beat. V. Influence of various ions on the excitability of strips of frog's heart muscle.** S. HOMMA (Japan J. Med. Sci., III, 1930, 1, 109—146, 147—156).—IV. Perfusion with Ringer solutions containing bromine and iodine ions increases the rate of beat of the isolated heart of the Japanese toad, whilst the lithium ion markedly decreases it. The sulphate ion has only a small effect, whilst the nitrate and thiocyanate ions are negatively chronotropic in concentrated solutions, positively chronotropic in dilute solutions. The use of rubber tubing must be avoided, since it is positively chronotropic. The potassium ion exerts

an antagonistic action on the lithium ion, 1 part of potassium ion to 18 parts of lithium ion neutralising the effect of the latter.

V. Bromine, iodine, and thiocyanate ions increase the excitability of strips of the ventricle in dilute solution, whilst they decrease it in more concentrated solutions. The sulphate ion increases it in nearly all concentrations used, whilst the nitrate ion acts in the opposite manner.

B. LEVIN.

Toxicity of fresh and preserved mineral waters. J. GODONNÈCHE (Bull. Soc. Chim. biol., 1931, 13, 41—46).—The toxicity of various natural waters has been examined by intraperitoneal injection into guinea-pigs. In general the toxicity is greater when the water is injected fresh from the spring, otherwise it has approximately the same effect as an artificial solution of the same composition.

W. O. KERMACK.

Vascular action of iodide ion. M. KOCHMANN (Arch. exp. Path. Pharm., 1931, 159, 516—519).—Sodium iodide solutions of concentrations from 1 : 60 to 1 : 1000 have a vasodilator action on the frog.

F. O. HOWITT.

Influence of arsenic and antimony compounds on enzymic functions of the organism. VII. Buffering power of arsenates and arsenites. A. N. ADOVA and J. A. SMORODINCEV (Biochem. Z., 1931, 232, 459—468).—The buffering power of 1% disodium arsenite solution is four times as great as that of 1% disodium arsenate solution. When sodium arsenate solution is diluted (1 : 1) the  $p_H$  is decreased. Moderate dilution of sodium arsenite solution increases the  $p_H$ , but great dilution (50-fold) decreases it. The buffering power of 1% sodium arsenite solution is equal to that of phosphate buffer and 6 times as great as that of citrate buffer. At a dilution of 0.033*N* the hydrogen-ion concentrations of solutions of sodium arsenate and sodium arsenite are equal, and when this is so the buffering power of the arsenite towards alkali is two thirds, and towards acid one third, of that of the arsenate. The buffering power of arsenic acid towards alkali is twice that of phosphate buffer and 12 times that of citrate buffer. Towards acid the buffering power of sodium arsenate solution is half that of phosphate buffer and one quarter of that of the latter towards alkali. Phosphate mixture has 6 times the buffering power towards alkali and 1.5 times that towards acid of citrate mixture. The detrimental effect produced by the sodium arsenate solutions used medically for injection is due to the disturbance in acid-base equilibrium. Such solutions should have the same  $p_H$  as have the blood and the fluids of the tissues.

W. MCCARTNEY.

Radioactive indicator method for determining the solubility of acid lead arsenate in the alimentary tract of the silkworm. F. L. CAMPBELL and C. LUKENS (J. Econ. Entom., 1931, 24, 88—94).—A solution of thorium-*B* in acetic acid mixed with lead arsenate was fed to silkworms and the subsequent distribution of lead examined by radioactive measurement. At least 25% of a lethal dose of acid lead arsenate passes into solution in the alimentary tract during the survival period. Basic lead acetate was less soluble.

A. G. POLLARD.

Interaction of metallic containers and living organisms. II. J. SCHWAIBOLD and F. FISCHLER (Biochem. Z., 1931, 232, 240—253).—The growth of young tadpoles (4—6 days after hatching) in vessels made of various materials, and the corrosion of the vessels, were examined. In glass and porcelain vessels growth was normal, aluminium, iron, and tin had little effect, but zinc inhibited growth considerably and copper proved very toxic in extremely small doses.

P. W. CLUTTERBUCK.

Treatment of mercury poisoning with [injected] sodium thiosulphate. J. C. G. PODESTÁ and R. E. TORVISO (Semana Méd., 1931, I, 19—24).

CHEMICAL ABSTRACTS.

Influence of irradiation on the behaviour of silver in the organism. I. Investigation with young rats. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1931, 232, 202—208).—Litters of young rats maintained at 20—40° were injected 4 hrs. to 2.5 days after birth with 0.2 c.c. of 0.5% silver sulphate solution. Half of each litter was irradiated with an Osram lamp or the mercury-vapour lamp and the other half used as controls. All the animals were then killed and the silver fractions (ionised, united with protein, metallic) were determined. The mean percentage recoveries of silver for the three fractions were for the unirradiated animals 54.08, 28.62, 17.31%, for the animals irradiated with the Osram lamp 27.33, 57.16, 15.51%, and for the animals irradiated with the mercury-vapour lamp 61.21, 25.02, 13.77%.

P. W. CLUTTERBUCK.

Fluctuation of blood-cholesterol, -calcium, and -sugar in blood of rabbits poisoned with thallium. S. KOYANAGI (Folia Pharm. Japon., 1930, 11, No. 2, 202—213).—Repeated subcutaneous administration of thallium causes a rise in blood-cholesterol, -free cholesterol, and particularly -cholesteryl esters. Subcutaneous or intravenous administration of thallium causes a fall in blood-calcium. Intravenous administration causes hyperglycemia, whilst subcutaneous administration causes either a rise, or a fall superseded by a rise, in blood-sugar.

CHEMICAL ABSTRACTS.

Curative action of plants and plant juices in sub-acute uranium poisoning. G. EISNER (Biochem. Z., 1931, 232, 218—228).—Rabbits which on poisoning with small amounts of uranium nitrate die on an oats-water diet, remain alive on addition to the diet of turnip, fresh green food, cauliflower leaves, or the fresh press-juice thereof before or after heating and filtering or treating with alcohol.

P. W. CLUTTERBUCK.

Additive compound theory of enzyme action. B. WOOLF (Biochem. J., 1931, 25, 342—348).—An enzyme is a definite chemical compound capable of forming an additive compound with all its substrates, the actual process of catalysis consisting of a series of tautomeric changes in this enzyme-substrate complex.

S. S. ZILVA.

Manometric determination of catalase. A. FUJITA and T. KODAMA (Biochem. Z., 1931, 232, 20—34).—A new method for the manometric determination of catalase is described. The catalase quotient ( $Q_{cat}$ ) is defined as the amount of oxygen

liberated in 30 min. at 38° by 1 mg. of substance (dry weight) from hydrogen peroxide, the result being regarded as valid only if less than 50% of the total peroxide is decomposed. The  $Q_{cat}$  values for a large number of bacteria and tissues are tabulated.

P. W. CLUTTERBUCK.

**Dextrose-oxidase.** IV. **Dextrose-oxidase from *Aspergillus niger*; its behaviour towards disaccharides, glycuronic acid, ethyl alcohol, methylene-blue, and monoiodoacetic acid.** D. MÜLLER (Biochem. Z., 1931, 232, 423—434; cf. A., 1929, 1489).—Neither lactose nor—if accompanying invertase is destroyed—sucrose is attacked by dextrose-oxidase. Maltose is directly attacked by an enzyme, *maltose-oxidase*, which accompanies dextrose-oxidase and is more thermostable than the latter. The product of air-oxidation is a non-reducing substance. So far as at present known the only compounds of which the oxidation is catalysed by dextrose-oxidase are such as have six carbon atoms and the same configuration as dextrose as far as carbon atoms 1 and 6 are concerned. Hence glycuronic acid and ethyl alcohol are not attacked by dextrose-oxidase. The enzyme is less sensitive to the action of monoiodoacetic acid than is zymase. Of the known dehydrases only that of malic acid is separated along with dextrose-oxidase. The accelerated reduction of methylene-blue caused by material containing the enzyme is restricted or inhibited by dextrose, laevulose, gluconic acid, and certain other substances.

W. McCARTNEY.

**Amylosynthase.** S. NISHIMURA (Biochem. Z., 1931, 232, 156—164).—Higher dextrans are enzymically synthesised from "limit" dextrin (lowest achroodextrin) and shown to be much more readily saccharified than the latter by malt-amylase. The greater is the degree of polymerisation the more closely does the course of saccharification approximate to that of starch (cf. A., 1930, 1218, 1477, 1619).

P. W. CLUTTERBUCK.

**Diastase from wheat.** D. V. KARMARKAR and V. N. PATWARDHAN (J. Indian Inst. Sci., 1930, 13A, 159—164).—The diastase from malted wheat is more active than that from barley malt prepared under the same conditions. The temperature and  $p_H$  optima are 49—58° and 4.6, respectively. The enzyme is inactivated when heated for 1 hr. at 160° in the dry state or in solution by 14 days' dialysis or by treatment with pepsin. Neither trypsin nor papain inactivates the enzyme. Neutral salts or amino-acids are without effect on the activity of the diastase.

F. E. DAY.

**Action of ptyalin on starch.** II. **Effects of electrolytes.** J. R. BROEZE (Biochem. Z., 1931, 231, 365—384).—In the absence of electrolytes the velocity of reaction is very small; minute concentrations of these are sufficient to raise it greatly. The velocity is only slightly augmented when the valency of the cations rises. The increase of the velocity under the influence of univalent cations follows a lyotropic series:  $CNS < NO_3 < Cl.F$ .

H. W. DUDLEY.

**Starch.** II. **Limit of enzymic decomposition, and the amylase complement.** III. **Changes in**

**rotatory power occurring in the enzymic decomposition of starch.** R. WEIDENHAGEN and A. WOLF (Z. Ver. deut. Zucker-Ind., 1930, 80, 866—876, 935—948; cf. A., 1930, 1168).—II. The authors failed to confirm the statements of Pringsheim and others (B., 1923, 858; 1924, 28, 843; A., 1926, 864) that yeast and peptic products of certain proteins contain an amylase complement which enables malt-amylase to saccharify the so-called stable dextrin with ease and thus to effect a complete conversion of starch into maltose. Stable dextrin prepared from starch by conversion with malt-amylase and subsequent fermentation was almost non-reducing, had  $[\alpha]_D +167^\circ$ , and appeared to be substantially a single substance. A product obtained similarly by means of pancreatic amylase had 16% of the reducing power of maltose and  $[\alpha]_D +161^\circ$ . Malt-amylase attacked the stable dextrin so slowly that about 224 times as much enzyme was required as for a starch saccharification at the same rate. Neither the rate of saccharification of the stable dextrin nor the limit of saccharification of starch, by malt-amylase, was affected by addition of yeast extract or peptic products from yeast-, egg-, or serum-albumin or gelatin, prepared as described by Pringsheim. The stable dextrin is not altered by heating with glycerol in accordance with Pringsheim's method of preparing trihexosan. The latter substance appears to be only a somewhat modified form of starch; it undergoes saccharification by amylase almost as readily as starch, to the extent of 40%, but when about 60% of sugar has been formed the residual matter is more resistant to saccharification than the stable dextrin.

III. In the conversion of starch and trihexosan by malt-amylase or pancreatic amylase, the mutarotation observed on addition of alkali at various stages confirmed Kuhn's statement that maltose is liberated in the  $\alpha$ -form by pancreatic amylase and in the  $\beta$ -form by malt-amylase (A., 1925, i, 636). In starch conversions by either enzyme the amounts of maltose found iodometrically, up to 40%, agreed fairly well with those calculated from the change in rotation, corrected for mutarotation, but when 60—70% of sugar had been formed discrepancies were encountered indicating a fall in  $[\alpha]_D$  of the unsaccharified residue to 160—170° or lower. Still more pronounced was the calculated fall in  $[\alpha]_D$  of the residue from trihexosan after 40—50% of maltose had been formed.

J. H. LANE.

**Hydrolysis of sucrose by aqueous extracts of mushrooms.** R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930, 80, 569—571).—The statement of Ivanov and others (A., 1930, 1067) that mushrooms contain maltase but no invertase conflicts with the author's view of the nature of these enzymes (A., 1928, 1157, 1281; 1929, 352, 722) and is not borne out by experiments now described, which showed rapid hydrolysis of sucrose and raffinose, but scarcely any action on maltose, melezitose, or melibiose. The inverting enzyme present was accordingly  $\beta$ -*h*-fructosidase.

J. H. LANE.

**Fission of sucrose by  $\alpha$ -glucosidase from yeast.** R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930,

80, 374—383).—Sucrose is hydrolysed almost twice as rapidly as maltose by  $\alpha$ -glucosidase (maltase). In both cases the unimolecular character of the reaction is masked by the retarding influence of  $\alpha$ -dextrose. The enzyme was obtained from neutral yeast autolysate by adsorption on  $\beta$ -aluminium hydroxide, followed by elution with diammonium hydrogen phosphate solution after a preliminary elution with potassium dihydrogen phosphate solution to remove a small amount of adsorbed  $\beta$ -*h*-fructosidase. The latter enzyme also hydrolyses sucrose, but is most active at  $p_H$  3.5—5, whilst the optimum reaction for  $\alpha$ -glucosidase is  $p_H$  6—7 and the limits of its activity are about  $p_H$  5—8. The hydrolysis of sucrose by yeast is thus due, not to a single enzyme, invertase, but to one or both of the enzymes mentioned above. If  $\alpha$ -glucosidase alone is present there is no inversion at  $p_H$  4, whilst if both are present the activity at  $p_H$  7 is more than 40% of that at  $p_H$  4.5, since at  $p_H$  7  $\beta$ -*h*-fructosidase has 40% of its maximum activity. (Cf. A., 1929, 352.) J. H. LANE.

**Specificity of the  $\alpha$ -glucosidases.** H. KARSTRÖM (Biochem. Z., 1931, 231, 399—403).—The  $\alpha$ -glucosidase of *B. coli* which hydrolyses maltase is unable to hydrolyse either sucrose or melezitose and hence the views of Weidenhagen (A., 1928, 1157; 1930, 499) cannot be accepted. W. McCARTNEY.

**Co-enzyme of lactic acid production in muscle.** K. LOHMANN (Naturwiss., 1931, 19, 180).—The system adenylypyrophosphate + magnesium appears to be the co-enzyme in the process of lactic acid formation in muscle. B. LEVIN.

**Analysis of bioluminescences of short duration, recorded with photo-electric cell and string galvanometer.** E. N. HARVEY and P. A. SNELL (J. Gen. Physiol., 1931, 14, 529—545).—The rates of decay of the luminescence produced by mixing solutions containing luciferin and luciferase (from *Cypridina hilgendorffii*; cf. A., 1928, 814, 1051) in presence of an excess of oxygen have been followed by means of a photo-electric cell, the readings being made after amplification on a string galvanometer. For rapid flashes of luminescence the decay is logarithmic if the ratio of luciferin to luciferase is small; logarithmic plus an initial flash if this ratio is greater than 5, but the logarithmic law does not hold exactly when the ratio is very large. The velocity coefficient of rapid flashes of luminescence is approximately proportional to enzyme concentration, is independent of luciferin concentration, and varies approximately inversely as the square root of the total luciferin (luciferin plus oxy-luciferin) concentration. For large total luciferin concentrations, the velocity coefficient is almost independent of the total luciferin. W. O. KERMACK.

**Phosphatases.** I. Kidney-phosphatase of various animals. II. Liver-phosphatase of these animals. III. Phosphatase content of kidneys and liver in experimental nephritis. IV. Optimal and decomposition temperatures of kidney-phosphatase. V. Glycerophosphatase of leucocytes. VI. Phosphatases in bile and in pancreatic juice. M. UMENO (Biochem. Z., 1931,

231, 317—323, 324—327, 328—333, 334—338, 339—345, 346—351).—I. The phosphatase contents of the kidneys of the following animals decrease in the order: hen, cat, dog, ox, toad, rabbit, guinea-pig. The cortex of the kidneys contains more phosphatase than does the medulla and the medulla contains more than do the papilla.

II. Phosphatase from the liver is, in general, about half as active as that from the kidneys of the same animal and varies in its activity according to the species of animal from which it is obtained. The activity of the liver-phosphatases decreases in the order: hen, rabbit, dog, guinea-pig, toad.

III. In experimental nephritis in rabbits the phosphatase content of the liver is slightly reduced, whilst that of the kidneys is reduced to one half to two thirds of the normal amount.

IV. Phosphatase from the kidneys of cattle and dogs exhibits greatest activity at 42.5°. Below this temperature the activity decreases slowly and above it decreases rapidly, being completely destroyed at 60—65°.

V. Leucocytes from leucæmic (but not from normal) human blood and also those from rabbit's blood contain large amounts of phosphatase, but the enzyme is not present either in human or in rabbit erythrocytes.

VI. Bile contains considerable amounts of a glycerophosphatase. The enzyme is also present in pancreatic juice (which contains about half as much as does bile) and in considerable amounts in the mucous membrane of the stomach, duodenum, and small intestine as well as in the salivary glands. Liver, spleen, and pancreatic glands also contain glycerophosphatase. The amount of enzyme in the different organs is independent of that in their secretions. W. McCARTNEY.

**Reversion of protein hydrolysis.** A. SARLUY (Arch. Néerl. Physiol., 1931, 16, 136—144).—The conclusion of Wasteneys and Borsook (cf. A., 1929, 1197) that protein synthesis takes place when a protein hydrolysate is incubated and shaken with benzene, benzaldehyde, toluene, xylene, or benzoic acid is criticised. In the case of benzaldehyde Schiff's bases are probably formed. In the case of benzene, toluene, and xylene only adsorption on the emulsion takes place and no decrease in the number of carboxyl groups can be detected by the titration method of Willstätter and Waldschmidt-Leitz (A., 1922, ii, 169). W. O. KERMACK.

**Action of pancreatin on collagen in the absence of neutral salts and buffers.** I, II. A. KÜNTZEL and O. DIETSCH (Biochem. Z., 1931, 231, 423—434, 435—440).—I. Collagen is decomposed by pancreatin in the absence of neutral salts and buffers to an extent increasing very greatly as the degree of subdivision of the material is increased and, to a smaller extent, as its water content increases. In the early stages of the process the decomposition proceeds more rapidly than in the later stages and its extent likewise increases, although not proportionally, with rise of temperature, at least between 35° and 60°. Within certain limits the extent of decomposition is directly proportional to the amount of pancreatin used.

II. Provided that it is renewed every 12 hrs. pancreatin solution at 40° after 11 days decomposes collagen to the extent of 73% of its weight, and it is probable that the collagen could be completely decomposed and brought into solution if the treatment were sufficiently prolonged. The rate of decomposition increases during about the first 4 days and then gradually decreases. At above 55° the decomposition proceeds very rapidly in a different manner and probably leads eventually to complete decomposition and dissolution. W. McCARTNEY.

**Relation between the swelling and the proteolysis of collagen.** F. NAUEN (Biochem. Z., 1931, 231, 441—445; cf. preceding abstract).—The proteolysis of collagen by pancreatin is greatly stimulated by salts of benzoic, salicylic, and *p*-hydroxybenzoic acids, the extent of the stimulation being proportional to the degree of swelling produced. These salts are much more effective than are the neutral salts used by Stiasny and Ackermann (A., 1923, ii, 301). That the phenomenon is a general one and that the extent of proteolysis depends on that of swelling is proved by the fact that collagen swollen in dilute hydrochloric acid is subsequently decomposed by pancreatin to an extent proportional to the amount of swelling caused.

W. McCARTNEY.

**Proteolytic enzymes. VII. Peptidases of green malt.** M. SATO (Compt. rend. Trav. Lab. Carlsberg, 1931, 19, No. 1, 1—26; cf. A., 1930, 93).—The affinity of the peptidase complex of malt for alanyl- and leucyl-glycine has been determined (cf. A., 1930, 642). The malt extracts used were prepared from fresh and dried malt by extraction with (a) glycerol, (b) water, and the dialysed solution therefrom. The extracts varied in their action on the peptides. At  $p_H$  7.9, the velocity of hydrolysis of alanylglycine is practically independent of the substrate concentration, whilst that of leucylglycine increases rapidly with increasing substrate concentration. At  $p_H$  8.5, the velocity of hydrolysis of leucylglycine first increases with increasing substrate concentration up to 0.1—0.2M, and thereafter decreases. It was found, however, that the addition of leucylglycine strongly inhibits the hydrolysis of alanylglycine. Fresh glycerol extracts of malt have a powerful action on leucylglycylglycyl-, leucylglycyl-, leucyl-, and alanyl-glycine, but attack alanylglycylglycine very little. The experiments support the conclusion that there are two or more distinct peptidases in malt.

B. LEVIN.

**Protein crystals possessing tryptic activity.** J. H. NORTHROP and M. KUNITZ (Science, 1931, 73, 262—263).—A crystalline protein which can digest caseinogen and gelatin in neutral solution has been prepared from commercial preparations of trypsin.

L. S. THEOBALD.

**Beer yeast. Conditions of its action on cystine.** R. FABRE and H. SIMONNET (Compt. rend., 1931, 192, 852—854).—Colloidal silica, kaolin, and fuller's earth cause no diminution of the thiol compounds or the reduction of cystine in an aqueous extract of dried yeast. Ferric ions inhibit the re-

duction and "norit" charcoal removes the thiol derivatives and the reducing power of the solution.

C. C. N. VASS.

**Effect of nickel and cobalt on the development of *Aspergillus niger*.** M. MOKRAGNATZ (Bull. Soc. Chim. biol., 1931, 13, 61—71).—The presence of small quantities of nickel in the culture medium accelerates the growth of cultures of *A. niger*, the maximum effect being observed with concentrations of 1 in 15,000. Cobalt exercises a toxic action at concentrations of 1 in 250,000 or greater. Nickel is taken up from the medium by the mould, the ratio of the amount taken up to the concentration in the medium decreasing as the latter increases.

W. O. KERMAK.

**Biochemical action of boron. I. Influence of boric acid on cultures of *Mycodermes* and its probable rôle in the formation of the bloom of the grape.** I. VOICU and M. NICULESCU (Bull. Soc. Chim. biol., 1931, 13, 150—171).—Boric acid up to 50 mg. per 100 c.c. for *Mycodermes* of wine, and up to 25 mg. per 100 c.c. for *Mycodermes* of medlar juice, promotes growth on Fernbach's medium containing 10—12% of dextrose. The toxicity of the free boric acid is increased and growth inhibited with smaller concentrations of dextrose (1.5%). Cultivation of the organism away from its natural medium diminishes the growth promotion and the toxic action of boric acid.

C. C. N. VASS.

**Reversibility of coupled reactions in biological systems and the second law of thermodynamics.** D. BURK (J. Physical Chem., 1931, 35, 432—455).—The extent to which the applicability of the second law of thermodynamics to life processes has received experimental support is indicated. The law is applicable to autotrophic reduction of carbon dioxide by hydrogen in the case of *Bacillus pycnoticus* (Ruhland, Jahrb. Wiss. Bot., 1924, 63, 321), and the reversibility of this autotrophic reduction is practically complete when account is taken of the extraneous energy consumed in the metabolic processes of the organism. Other biological coupled reactions are described and summarised.

L. S. THEOBALD.

**Primitive form of *Anthomyces Reukaufi* and other inclusions introduced into amber by insects.** J. GRÜSS (Woch. Brau., 1931, 48, 63—68).—A number of micro-organisms associated with insect remains in amber are described and illustrated. The presence of microscopic crystals of pyrites is noted.

F. E. DAY.

**Marine denitrifying organism.** B. LLOYD (J. Bact., 1931, 21, 89—96).—An organism (*B. costatus*) is capable of reducing nitrates under aerobic and anaerobic conditions. No ammonia is produced, reduction proceeding by way of nitrite to free nitrogen.

A. G. POLLARD.

**Cellulose-fermenting organism (*Cl. cellulolvens*, N. Sp.).** P. B. COWLES and L. F. RETTGER (J. Bact., 1931, 21, 167—182).—The organism was isolated from horse faeces. Of numerous carbohydrates examined only cellulose, dextrin, arabinose, and xylose were decomposed by the organism. The products of decomposition of

cellulose were carbon dioxide, hydrogen, and organic acids. A. G. POLLARD.

**Effect of temperature on the production of hydrogen sulphide by *Salmonella pullorum*.** R. P. TITSLER (J. Bact., 1931, 21, 111—117).—Hydrogen sulphide production by *S. pullorum* ceases at temperatures above 37°, the optimum being 30°. Strains producing little or no hydrogen sulphide also produced little or no gas from carbohydrates.

A. G. POLLARD.

***B. coli* in water.** F. DIÉNERT and P. ETRILLARD (Ann. Inst. Pasteur, 1931, 46, 277—290).—A discussion of the various methods of detecting *B. coli* in water. C. C. N. VASS.

**Methylglyoxalylacetic acid. Its dismutation by *B. coli*.** S. VEIBEL (Biochem. Z., 1931, 232, 435—441; cf. Neuberg and Collatz, A., 1930, 1474).—Methylglyoxalylacetic acid can be almost quantitatively converted into almost pure *d*- $\alpha$ -hydroxyglutaric acid by the action of *B. coli*. The former acid yields a *bis*-*p*-nitrophenylhydrazone, m. p. 270—271°, and a *bis*-2:4-dinitrophenylhydrazone which forms a double compound, m. p. 252—253° (decomp.), with an equimolecular amount of pyridine and also a stable double compound, m. p. 245—246° (decomp.), with nitrobenzene. W. MCCARTNEY.

**Acetic fermentation. I. Significance of cytochrome in the physiology of cell respiration.** H. TAMIYA and K. TANAKA (Acta Phytochim., 1930, 5, 167—211).—The formation of acetic acid by the fermentation of alcohol and acetaldehyde by *B. Pasteurianum* is followed. In agreement with the observations of Wieland and Bertho (A., 1929, 219, 1492) benzoquinone is found to be as good a hydrogen acceptor as oxygen; further, the rate of reaction is independent of the oxygen concentration within wide limits. The action of oxygen is strongly inhibited by carbon monoxide. The ratio of the affinities of oxygen and carbon monoxide to the enzyme is about 0.2—0.6/1. With fresh bacterial cultures the inhibiting effect of carbon monoxide is greatly lessened by light. The fermentation with benzoquinone is unaffected by carbon monoxide. The indophenol reaction of the acetic bacteria is inhibited by carbon monoxide and more in the dark than in light. Toluene inhibits the acetic fermentation with oxygen, but not with benzoquinone or methylene-blue; it also inhibits the indophenol reaction of acetic bacteria or yeast but not that of cytochrome-free extract of *Lactarius oxidase*. Shibata and Tamiya (A., 1930, 949) have shown that in presence of less than 0.01*M* concentration of benzoquinone the cytochrome of yeast remains strongly oxygenated. This is attributed to the greater diffusibility of the quinone, enabling it to combine with the activated hydrogen of the donator to the exclusion of the cytochrome-fixed oxygen. Toluene irreversibly denatures cytochrome, and carbon monoxide prevents its combination with oxygen; these two facts are sufficient to explain the results obtained. The experiments support the theory of Shibata and Tamiya that cytochrome acts as a "pressure regulator" for the oxygen and is identical with Warburg's respiration enzyme. F. E. DAY.

**Physiological behaviour of the propionic acid group of bacteria.** S. E. KENDALL and C. H. WERKMAN (Proc. Iowa Acad. Sci., 1929, 36, 111).—Cultures of *Propionibacterium* are catalase-positive; carbohydrates, glucosides, and alcohols are attacked with production of propionic and acetic acids and carbon dioxide. CHEMICAL ABSTRACTS.

**Production of propionic acid from pentoses by *Propionibacterium pentosaceum*.** C. H. WERKMAN, R. M. HIXON, E. I. FULMER, and C. H. RAYBURN (Proc. Iowa Acad. Sci., 1929, 36, 111—112).—In a medium of  $p_H$  7.1 containing potassium monohydrogen phosphate 1 g., dried yeast 10 g., calcium carbonate 5 g., pentose 15 g., and water 750 c.c., xylose or arabinose affords propionic and acetic acids. A small quantity of a substance, probably succinic acid and probably derived from protein, is also formed. Glycerol affords only propionic acid in significant quantity. CHEMICAL ABSTRACTS.

**Concentration of antipneumococcic and anti-meningococcic horse sera.** K. GOODNER (J. Immunol., 1930, 19, 473—484).—During immunisation the amount of a euglobulin, of low solubility, in horse serum is increased. The antibody of the immune serum is associated with this protein.

CHEMICAL ABSTRACTS.

**Advantages and disadvantages of the buffered diluent for diphtheria toxin.** W. E. BUNNEY and B. WHITE (J. Immunol., 1931, 20, 61—70).

CHEMICAL ABSTRACTS.

**New diluent for diphtheria toxin in the Shick test.** W. E. BUNNEY (J. Immunol., 1931, 20, 71—84).

CHEMICAL ABSTRACTS.

**Stability towards heat of diphtheria toxin.** K. ANDO and H. NISHIMURA (J. Immunol., 1930, 19, 465—471).—Thermal stability is greatest in presence of acid. CHEMICAL ABSTRACTS.

**Action of formaldehyde on diphtheria toxin.** W. E. BUNNEY (J. Immunol., 1931, 20, 47—59).—Toxoid formation appears to be due to the action of a compound resulting from interaction between formaldehyde and the amino-group of an amino-acid. A method of preparation consists in concentrating low-grade toxins and diluting in a solution of glutamic acid containing formaldehyde.

CHEMICAL ABSTRACTS.

**Toxic properties of tuberculoproteins and polysaccharides.** F. R. SABIN, F. R. MILLER, C. A. DOAN, and B. K. WISEMAN (J. Exp. Med., 1931, 53, 57—80).—The temperature reaction in tuberculous or normal guinea-pigs and rabbits is elicited by the tuberculoprotein. Both proteins and polysaccharides cause a change in the white blood-cells.

CHEMICAL ABSTRACTS.

**Sorption of bacteriophage by living and dead susceptible bacteria. I. Equilibrium conditions.** A. P. KRUEGER (J. Gen. Physiol., 1931, 14, 493—516).—The distribution of bacteriophage between a broth medium and cells of susceptible *S. aureus* suspended throughout the latter may conform to either of two types. With live resting bacteria, the bacteriophage is distributed in the same manner as is any substance soluble in both phases of a two-

phase system, *i.e.*, it follows the equation  $C_b/C_a=K$ , where  $C_b$  is the extracellular and  $C_a$  the intracellular concentration of the bacteriophage. The equilibrium is perfectly reversible. With heat-killed bacteria the distribution follows the adsorption law  $a=kc^{1/n}$ , where  $a$  is the amount adsorbed per unit weight of bacteria,  $C$  the concentration in the medium at equilibrium,  $1/n=0.80$ , and  $K$  is a constant. The reaction in this case is not reversible. Experiments on the kinetics of the removal of bacteriophage from solution by living and by dead cells failed to reveal any significant difference in the velocities in the two cases.

W. O. KERMAK.

**Cryptotoxic properties of halogenated hydroxybenzoic acids.** H. VINCENT and L. VELLUZ (Compt. rend., 1931, 192, 648—651; cf. A., 1928, 674).—Halogenation of salicylic acid increases its neutralising effect against bacterial toxins, the order being iodine > bromine > chlorine. Sodium 3:5-diiodosalicylate has a cryptotoxic power 100 times as great as that of the sodium salicylate. In the *p*-hydroxybenzoic acid series only the 3:5-dibromo-isomeride shows a marked increase in cryptotoxic power. Halogenation does not increase the cryptotoxic power of *m*-hydroxybenzoic acid.

C. C. N. VASS.

**Germicidal efficiency of sodium hydroxide, sodium carbonate, and trisodium phosphate.** F. W. TILLEY and J. M. SCHAFER (J. Agric. Res., 1931, 42, 93—106).—Sodium hydroxide solutions were relatively highly toxic to a number of pathogenic organisms even in the presence of organic matter. Sodium carbonate or phosphate or slaked lime alone showed no notable germicidal properties, but each increased the efficiency of sodium hydroxide. The activity of such mixed solutions was considerably increased by heat. Additions of sodium carbonate and phosphate increased the germicidal action of soap solutions. Solutions containing 2% of sodium hydroxide and 10% of calcium hydroxide failed to kill *Mycobacterium tuberculosis* after 2 hrs.

A. G. POLLARD.

**Chemistry of disinfection.** W. D. BANCROFT and G. H. RICHTER (J. Physical Chem., 1931, 35, 511—530).—Antisepsis is mainly a state of narcosis which depends on the reversible coagulation of the colloids of the cell. Disinfection results from irreversible coagulation of these colloids. Adsorption of the drug precedes coagulation.

L. S. THEOBALD.

**Influence of adrenaline on the lipins of blood and organs.** I. H. PAGE, L. PASTERNAK, and [in part] M. L. BURT (Biochem. Z., 1931, 232, 295—309; cf. this vol., 528).—Subcutaneous administration to rabbits produces decreases in the phosphatide, cholesterol, fatty acid, and total fat contents of their blood-serum, in the phosphatide, fatty acid, and total fat contents of their kidneys, and in the phosphatide and cholesterol contents of their hearts. In the brains and hearts the degree of unsaturation of the fats is slightly decreased. An increase produced in the cholesterol content of the brains is accompanied by a decrease in the phosphatide content of these organs. The fatty acid, cholesterol, and total fat contents of the livers are increased by adrenaline administration.

In rabbits suffering from lipæmia the effects of adrenaline administration may be masked by those due to the disease. The action of adrenaline on the serum is similar to but less pronounced than that of insulin, although the ways in which the two substances act are different. Except as regards the increase in cholesterol content of the brains and the slight decrease in fatty acid content of the kidneys there is no other similarity between the effects caused by the two hormones.

W. McCARTNEY.

**Influence of the oxytocic and pressor hormones of the posterior pituitary lobe on basal metabolism.** I. I. NITZESCU and I. GAVRILA (Compt. rend. Soc. Biol., 1929, 102, 184—186; Chem. Zentr., 1931, i, 303).—The increase after injection of pitressin, 6.8—14.5%, is greater than after that of pituitrin; oxytocin has practically no effect.

A. A. ELDRIDGE.

**Effect of pitressin and pitocin on human blood-sugar.** I. GAVRILA and G. MIHAILEANU (Compt. rend. Soc. Biol., 1930, 104, 601—602; Chem. Zentr., 1930, ii, 3798—3799).—Subcutaneous injection of pitressin, but not that of pitocin, causes hyperglycæmia.

A. A. ELDRIDGE.

**Effect of pitressin and pitocin on glycæmia and blood-inorganic phosphorus.** I. I. NITZESCU and G. BENETATO (Compt. rend. Soc. Biol., 1930, 103, 1359—1362; Chem. Zentr., 1930, ii, 3798).—Subcutaneous or intravenous injection of pitressin into rabbits causes hyper-glycæmia and -phosphatæmia; intravenous injection of pitocin causes hyperglycæmia, but has no effect on the blood-phosphorus.

A. A. ELDRIDGE.

**Effect of pitocin and pitressin on the blood-calcium and -phosphorus.** C. I. URECHIA, I. GROZE, and RETEZEANU (Compt. rend. Soc. Biol., 1930, 103, 1363—1364; Chem. Zentr., 1930, ii, 3798).—Injection of pitocin increased the blood-phosphorus in half of the cases examined; the blood-calcium was unchanged. Pitressin depressed the blood-calcium, but did not affect the blood-phosphorus.

A. A. ELDRIDGE.

**Action of vagotonin on blood-sugar.** T. BRIEU, G. FUCHS, D. SANTENOISE, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, 104, 768—770; Chem. Zentr., 1931, i, 103).—The hypoglycæmic effect of vagotonin is not due to the presence of insulin; the curves differ. Vagotonin has no hypoglycæmic action on dogs after vagotomy or injection of atropine.

A. A. ELDRIDGE.

**Vagotonin and liver-glycogen.** D. SANTENOISE, H. VERDIER, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, 104, 770—772; Chem. Zentr., 1931, i, 103—104).—A close relation exists between the function of the vagus and the ability of the liver to store glycogen.

A. A. ELDRIDGE.

**Action [on blood] of extracts of salivary glands.** C. I. URECHIA, CIOCANELLI, and RETEZEANU (Compt. rend. Soc. Biol., 1930, 104, 595—598; Chem. Zentr., 1930, ii, 3800).—Extracts of the submaxillary and parotid glands depressed the blood-sugar and -cholesterol, but did not markedly affect the -calcium or -phosphorus.

A. A. ELDRIDGE.

**Standardisation of male sexual hormone on the basis of its anti-feminin action.** L. LENDLE (Arch. exp. Path. Pharm., 1931, 159, 463—487).—The injection of testicular extract into female rats inhibits the normal œstrus cycle. This action depends on an inhibition of ovulation and not on a direct antagonism of ovarian and male sexual hormones. Its application to a method of standardisation of testicular extracts is discussed. Extracts of posterior lobe of pituitary synergise the ovarian hormone, the combined action not being inhibited by simultaneous injection of testicular extract. F. O. HOWITT.

**Determination of potency of male sexual hormone by its effect on the seminal vesicles of rodents.** H. E. VOSS and S. LOEWE (Arch. exp. Path. Pharm., 1931, 159, 532—544).—The seminal vesicles of castrated rats and mice following injection of testicular extracts show macroscopically an increase in the length-breadth index and in weight, and microscopically a formation of secretory cells and increased activity of the epithelial cells. Evidence of the latter precedes the macroscopic changes and the histo-cytological method is preferred for the evaluation of testicular extract potency.

F. O. HOWITT.

**Purification of the male hormone by high-vacuum distillation.** E. DINGEMANSE, J. FREUD, S. KOBER, E. LAQUEUR, and A. P. W. MÜNCH (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1206—1209).—At 0.001 mm. and 80° the male hormone does not distil, but at 90° it is found in the distillate. This is suggested as a possible method for separating the male and female hormones. O. J. WALKER.

**Mol. wt. of insulin.** T. SVEDBERG (Nature, 1931, 127, 438—439).—Sedimentation of insulin in centrifugal fields of  $10^5g$  at 20° between  $p_H$  3.5 and 12.3 shows it to be stable between  $p_H$  3.5 and 7.0. The sedimentation constant is  $3.47 \times 10^{-13}$ . Dissociation into low-molecular products occurs when the stability range is exceeded, but this dissociation is reversible if the material is not too acid or too alkaline. The sedimentation equilibrium at  $p_H$  6.7—6.8 gives a mol. wt. of 35,100. Crystalline insulin is homogeneous with regard to mol. wt. and appears to be a well-defined protein of the egg-albumin class.

L. S. THEOBALD.

**Insulin and liver-glycogen.** D. SANTENOISE, H. VERDIER, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1930, 104, 773—774; Chem. Zentr., 1931, i, 104).—Insulin has only a mobilising action, and vagotonin a fixing action, on liver-glycogen. Earlier contradictory results are due to the use of insulin containing vagotonin. A. A. ELDRIDGE.

**Resistance of insulin to the action of various bacteria.** A. A. SCHMIDT and K. TULJTSCHINSKAJA (Biochem. Z., 1931, 231, 352—364).—The activity of insulin is not destroyed by the action of *B. coli communis*, *Staphylococcus aureus*, *Streptococcus hæmolyticus*, or of some of the anaërobic bacteria of the faces of the dog. Such faces, however, contain putrefactive bacteria which destroy insulin. It seems that only those bacteria which contain proteolytic enzymes can destroy insulin and hence that the latter is a protein-like substance. W. MCCARTNEY.

**Effect of external secretion of the pancreas on insulin secretion.** E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1930, 104, 790—792; Chem. Zentr., 1931, i, 104).—Increase, by means of hydrochloric acid, in the external pancreatic secretion of the dog is accompanied by an increased production of insulin. A. A. ELDRIDGE.

**Initial insulin hyperglycæmia.** D. IONESCO, I. COSMULESCO, and M. TOMESCO (Compt. rend. Soc. Biol., 1929, 102, 167—169, 170—172; Chem. Zentr., 1931, i, 304).—Transitory hyperglycæmia after injection of insulin into the rabbit, dog, or man is observed after 1 min. and is maximal at 5—13 min. Experiments on the injection into dogs of insulin together with adrenaline, ergotamine, pilocarpine, and atropine are described. A. A. ELDRIDGE.

**Existence of a pancreatic hormone which reduces the blood-pressure.** P. GLEY and N. KISTHINIOS (Wien. klin. Woch., 1930, 43, 1530—1536; Chem. Zentr., 1931, i, 476).—The reduction of blood-pressure shown by many insulin preparations is attributed to a substance which is not identical with histamine. The increase in blood-pressure caused by adrenaline is counteracted by such a preparation (angioxyl). A. A. ELDRIDGE.

**Effect of cod-liver oil on the calcium metabolism of young chicks.** A. D. HOLMES and M. G. PIGOTT (Ind. Eng. Chem., 1931, 23, 190—196).—To raise poultry by artificial methods and at the same time to obtain more rapid growth a proper balance of the Ca : P ratio and of vitamins must be maintained. Optimum conditions prevail if the diet has a maximum Ca : P ratio of 1.5 : 1; when this is increased rickets develop, and at a level of 5 : 1 dosage with cod-liver oil causes no alleviation of the symptoms.

T. McLACHLAN.

**Fluorescence of cod-liver oil.** C. A. MOREHOUSE (Proc. Iowa Acad. Sci., 1929, 36, 297).—A bright band extending from 546 to 436 m $\mu$  was observed; the same band was given by solutions of cod-liver oil or cholesterol in alcohol.

CHEMICAL ABSTRACTS.

**Conductivity of cod-liver oil.** L. W. BUTLER (Proc. Iowa Acad. Sci., 1929, 36, 299—300).—The conductivity diminishes as the temperature falls from 50° to -4°; the form of the curves, but not the value, is the same for oils of different origin or under different conditions. Exposure to air causes a slight fall, followed by a considerable rise, in conductivity; decomposition of vitamin-A by air at 90° largely diminishes the conductivity. The oil is not photoelectric on irradiation with ultra-violet light. The specific resistance of the oil varies from  $10^{10}$  to  $10^{13}$  ohms per cm.

CHEMICAL ABSTRACTS.

**Quantitative relationship between vitamin-A in maize and the number of genes for yellow pigmentation.** P. C. MANGELSDORF and G. S. FRAPS (Science, 1931, 73, 241—242).—A white-seeded variety of maize forms vitamin-A in its seeds when the gene for yellow pigmentation is introduced. Each gene for yellow pigmentation induces the formation of approximately 2.5 units of vitamin-A per g. of seed, and is responsible, either directly or indirectly,



for the formation of the vitamin with the intermediate production of carotenoid pigments. A direct chemical reaction between the gene and some substance present in the endosperm of maize is indicated.

L. S. THEOBALD.

**Fat-soluble vitamin requirements of the chick. I. Vitamin-A and -D content of fish meal and meat meal.** W. D. McFARLANE, W. R. GRAHAM, jun., and F. RICHARDSON (Biochem. J., 1931, 25, 358—366).—A sample of white fish meal when fed at a level of 15% in a diet composed of marmite and white rice contained sufficient vitamin-A and -D to promote normal growth of chicks until 8 weeks old. A sample of meat meal contained little or no vitamin-A or -D. More than 1% of cod-liver oil is required to rear chicks in the laboratory to 8 weeks. Some factor other than vitamin-D, calcium, or inorganic phosphorus of the diet of the chick profoundly affects the concentration of inorganic phosphorus in the blood-serum of chicks during the first 8 weeks of growth.

S. S. ZILVA.

**Comparison between irradiation of diet and supplemental irradiation of animals [rats] in vitamin-A and -D deficiency.** F. E. CHIDESTER, A. G. EATON, and N. K. SPEICHER (Science, 1931, 73, 190—191).—The daily addition of 0.01 mg. of irradiated ergosterol to a diet free from vitamin-A and low in vitamin-D stimulated the growth of rats, which had been depleted, for three weeks, after which death soon took place. Daily irradiation with a carbon arc lamp further stimulated growth for a short time but not to the extent previously observed when iron iodide was included in the diet. Relatively short exposures to ultra-violet radiation combined with irradiated ergosterol feeding did not induce marked hypervitaminosis.

L. S. THEOBALD.

**Mode of action of vitamin-D. Hypervitaminosis-D. Influence of the calcium phosphate intake.** L. J. HARRIS and J. R. M. INNES (Biochem. J., 1931, 25, 367—390).—An increase in the calcium phosphate allowance to rats causes an increased severity of hypervitaminosis. By reducing the calcium phosphate sufficiently, a level of vitamin-D excess which is otherwise toxic becomes innocuous. Doses which are just on the border-line of toxicity for a synthetic, salt-rich diet may be partly harmless for bread and milk diets. When, however, slightly larger excesses of vitamin-D are given the difference becomes less noticeable and with still larger excesses the difference vanishes. The addition of calcium and phosphate salts to bread and milk diets renders them indistinguishable from synthetic diets in the production of hypervitaminosis with excess of vitamin-D. A given overdose of irradiated ergosterol, just sufficient to cause rapid loss of weight with diets rich in calcium and deficient in phosphate, becomes less toxic when calcium is balanced by phosphorus and relatively harmless when the calcium is omitted and the phosphorus remains high. Similar results are obtained when the dose is increased or when heavier rats are employed. At least eight times as much irradiated ergosterol is needed to cause loss of weight on a diet high in phosphorus and calcium-free as with a diet with a normal calcium content. The nature of the

hypervitaminosis thus produced differs, however, from the usual condition and resembles the condition produced by the administration of a calcium-free diet without any vitamin excess, but with a more extensive loss of mineral substance from the spongiosa. On a diet deficient in both calcium and phosphorus similar results are obtained. There is a formation of calcium deposits in the soft tissues when there is an abundance of calcium salts in the diet. With insufficient excess of vitamin-D no calcium deposits are formed. With a very large excess the animal usually dies before the deposits are formed. Large doses of vitamin-D with normal diets stimulate osteogenesis and a densely calcified overgrowth appears at the growing end of the bone, in contrast with rickets, whilst in the advanced degrees of hypervitaminosis resorption is extensive and the cortex of the shaft and other "compact" bone becomes spongy. Vitamin-D excess also gives rise to a remarkable overgrowth of cement in the growing animal. In hypervitaminosis produced on diets rich in calcium with moderate overdoses of vitamin-D there is an increased net absorption of calcium and phosphorus from the gut, whilst with calcium-deficient diets and with larger excesses of the vitamin there is a withdrawal of these elements from the bone-shaft.

S. S. ZILVA.

**Calcifying action of irradiated ergosterol on guinea-pigs infected with tuberculosis.** A. POLICARD, PAUFERT-RAVAULT, and P. BARRAL (Compt. rend. Soc. Biol., 1930, 104, 633—635; Chem. Zentr., 1930, ii, 1094).—Infected guinea-pigs were treated with "vigantol" before and after infection. Daily doses of 13 mg. of ergosterol from the 18th day after infection produced calcification in all organs, normal or diseased. Smaller doses had a negligible effect.

L. S. THEOBALD.

**Pharmacological classification of irradiated ergosterol.** H. HANDOVSKY (Arch. exp. Path. Pharm., 1931, 159, 383—386).—The administration of large doses of irradiated ergosterol to animals brings about changes in metabolism similar to those produced by saponin and in particular increases the rate at which oxidation proceeds in the cells of the liver as shown by experiments on tissue sections by the method of Warburg.

W. O. KERMACK.

**Distribution of vitamin-B and its components in the peanut.** F. W. SHERWOOD and J. O. HALVERSON (J. Elisha Mitchell Sci. Soc., 1930, 46, 14).—Whole raw peanuts are fairly rich in vitamin-B<sub>1</sub> but not in -B<sub>2</sub>; the red skins are especially rich.

CHEMICAL ABSTRACTS.

**Differentiation of the so-called antipellagric factor, vitamin-B<sub>2</sub>.** B. SURE, M. E. SMITH, and M. C. KIK (Science, 1931, 73, 242—243).—It is concluded that vitamin-B<sub>2</sub> is composed of two dietary essentials, deficiency of the one producing in the rat symptoms like those of pellagra and of the other, a decline in growth. It is suggested that the former be denoted by the letter *F* and the latter by *G*.

L. S. THEOBALD.

**Content of thiol compounds in striated muscle, liver, and blood of normal and underfed rats, and of those deprived of vitamin-B.** L. RANDOIN and R. FABRE (Compt. rend., 1931, 192, 815—818).—

The striated muscle of normal rats contains on the average, per 100 g. of fresh tissue, 0.020 g. of thiol compounds, the liver 0.172 g., and the blood 0.025 g. With rats which have been deprived of vitamin-B, the muscles contain a smaller amount of substances of the glutathione type (*G*) (average 0.0157 g.), whilst an increase is observed in the amount of other reducing substances (*G'*). The same applies to the liver (average 0.1217 g.). In the blood, the amount of *G* remains approximately the same, but the amount of *G'* is greatly increased. The variations from the average are within fairly wide limits. Malnutrition causes variations in the ratio of *G* to *G'* similar to those caused by deprivation of vitamin-B.

B. LEVIN.

**Accumulation of ternary substances in the blood during avitaminosis-B.** J. ROCHE (Bull. Soc. Chim. biol., 1931, 13, 186—196).—During the initial stages of fasting the C/N ratio in the deproteinised blood of pigeons is normal (approx. 4), but with the onset of hypothermia both this ratio and the dextrose content decrease. On a polished rice diet, the C/N ratio increases with the continuation of the diet, but falls towards the normal value when yeast is added to the diet. A slight degree of hyperglycæmia is induced in avitaminosis-B which disappears on fasting.

C. C. N. VASS.

**Formation of compounds in some cultivated plants.** K. SJÖBERG (Svensk Kem. Tidskr., 1931, 43, 57—69).—Analyses of a number of commonly cultivated plants (principally flax, clover, cress, oats, carrot, and beet) have been made at intervals during the whole period of growth with a view of ascertaining the rate of production of the various components (starch, sugar, pentoses, ash, etc.), together with the total increase in weight.

H. F. HARWOOD.

**Forcing of plants.** A. NIETHAMMER (Biochem. Z., 1931, 232, 146—155).—The effect of freezing and drying elder twigs is examined. The amount of reducing sugar is increased by frost, whilst dryness causes only a transient increase. The sugar content of elder twigs shows considerable variations during the year. The sugar maximum does not, but the plasmolysability of the parenchymatous cells does correspond with the opening of the buds.

P. W. CLUTTERBUCK.

**Photosynthesis in various vine species.** H. SCHANDERL (Pflanzenbau, 1930, 3, 529—560; Chem. Zentr., 1931, i, 298).—Assimilation takes place with *Vitis riparia* in diffused light, but with *V. vinifera* only in direct sunlight. Methods of determination of carbon dioxide assimilation, and the significance of the results in German vine culture, are discussed.

A. A. ELDRIDGE.

**Use of Beijerinck's indigo-white method in quantitative assimilation experiments [with plants].** M. MATSUBARA (Planta [Z. wiss. Biol.], 1931, 12, 670—685).—Oxygen produced during photosynthesis in plants is determined colorimetrically by means of reduced indigo-carmin; 0.001% of oxygen may be detected.

A. G. POLLARD.

**Nitrogen metabolism in higher plants. III.** K. MÖTHES (Planta [Z. wiss. Biol.], 1931, 12, 686—731; cf. A., 1928, 93).—The translocation of nitrogen

in plants under varying conditions is examined. The age of leaves and the water content of the tissues are important factors controlling the translocation of nitrogen within the plant and the extent to which protein synthesis or decomposition occurs in the tissues. Water deficiency is associated with protein decomposition and reduced carbon dioxide production in older leaves, and with protein synthesis and enhanced respiration in younger leaves. Inter-relationships between these functions are discussed. Exhalation of nitrogen in any form was not observed.

A. G. POLLARD.

**Effect of increasing quantities of nitrogen on plant yield.** H. EICHLER (Pflanzenbau, 1930, 3, 494—528; Chem. Zentr., 1931, i, 298).—Curves for yield of root, grain, and straw with increasing quantities of nitrogen are independent; the optima are 0.7—0.9, 1.8—2.0, and 2.4 g. of nitrogen (in pot experiments with sodium or ammonium nitrate or ammonium sulphate) respectively.

A. A. ELDRIDGE.

**Nodule bacteria and leguminous plants. IX. Utilisation of different nitrogenous substances and of the nodule nitrogen by leguminous plants.** A. I. VIRTANEN and S. VON HAUSEN (Biochem. Z., 1931, 232, 1—14).—Growth of red clover in a sterile medium is best with amino-acids (hydrolysed caseinogen) as the source of nitrogen, is much less with ammonium sulphate, and still less with potassium nitrate, whilst growth of white clover is best with ammonium sulphate, poorer with potassium nitrate, and feeblest with amino-acids (cf. A., 1928, 558).

P. W. CLUTTERBUCK.

**Carbohydrate metabolism of *Stipa pulchra*.** A. W. SAMPSON and E. C. McCARTY (Hilgardia, 1930, 5, 61—100).—Analyses of the total carbohydrates, polysaccharides, sucrose, and reducing sugars in the stem bases, roots, and herbage of *S. pulchra* in varying stages of growth are recorded. An accumulation of carbohydrates in the stem bases corresponds with a low or declining rate of growth and is most marked as maturity is approached. Removal of the herbage by cutting or grazing at any time prior to maturity is followed by regenerative growth and a decreased carbohydrate accumulation. Cutting during the early stages of growth does not affect the final yield nor prevent the maximum accumulation of carbohydrate characteristic of maturity. Between the period of flowering and maturity, cutting or grazing prevents the maximum carbohydrate accumulation and tends to prolong the vegetative period. A decreased carbohydrate accumulation at the end of the annual growth cycle may lead to a reduced crop in the subsequent year.

A. G. POLLARD.

**Relation between physiological phenomena in plants and the colouring matters appearing in different organs. II. Relation between activity of assimilation and formation of anthocyanin in *Abutilon avicennæ*.** H. KOSAKA (J. Dept. Agric. Kyushu, 1931, 3, 29—45).—The production of anthocyanin pigments in the stems and leaf stalks of *A. avicennæ* runs parallel with the accumulation of food stores in the cells. It varies with the rate at which the foodstuffs are synthesised as shown

by experiments in which this rate was decreased by plucking off the leaf blades or by covering the latter with black paper. The reduction in the synthetic activity of the plant was associated with a reduction in the rate of formation of the pigments. The rate of formation of the pigments varies inversely with the rate at which the food stores are used up.

W. O. KERMACK.

**Phæophorbide-*b*-iron.** O. WARBURG (Ber., 1931, 64, [B], 682—683).—Iron powder, sodium chloride, and glacial acetic acid are heated in a current of carbon dioxide and phæophorbide *b* is added to the cooled and filtered solution. After being heated on the water-bath the iron salt is filtered and crystallised from propionic acid containing hydrochloric acid. After dehydration, it has the composition  $(Et \cdot CO)C_{35}H_{33}O_6N_4FeCl$ .

H. WREN.

**Protoplasmic substances with a thiol function.** A. GIROUD (Protoplasma, 1931, 12, 23—41).—Plant cells contain two types of thiol substances, an insoluble protein type which is observed by the customary histological reaction, and glutathione. Both forms are present in the reduced condition in living cells and are not produced by secondary reduction processes accompanying intracellular changes. Failure to demonstrate, in certain cases, the thiol grouping in living cells by the nitroprusside test is due to the impermeability of the cell wall to the reagent.

A. G. POLLARD.

**Biochemical studies on the bamboo. VI. Carbohydrates and organic acids of bamboo shoots.** Y. SASAOKA (Chikashige Anniv. Vol., 1930, 175—181).—In addition to the substances mentioned previously (A., 1927, 599), oxalic, tartaric, citric, and lactic acids were isolated from the juice expressed from fresh bamboo shoots.

B. LEVIN.

**Organic acids of wheat plants.** E. K. NELSON and H. HASSELBRING (J. Amer. Chem. Soc., 1931, 53, 1040—1043).—The non-volatile organic acids in green wheat-plants have been determined by extraction with boiling water, precipitation as lead salts with lead acetate, conversion into their esters, fractionation of these, and identification as their hydrazides. The proportions of such acids, calculated on the green plant, are: malonic 0.005, aconitic 0.040, malic 0.06, citric 0.018%, and a trace of oxalic, whilst 0.02% of oxalic acid remains in the residue from the original extraction.

J. W. BAKER.

**Glucosides of the Gramineæ. Importance of the lævulosans.** A. CUGNAC (Bull. Soc. Chim. biol., 1931, 13, 125—132).—Lævulosans are the characteristic glucosides of European Gramineæ and form up to 20% of the fresh tissue. The Gramineæ of warmer countries contain sucrosans. The lævulosans occur in the stems and accumulate in the roots, particularly before flowering. Graminin,  $[\alpha]_D -43^\circ$ , is more soluble than phlerin,  $[\alpha]_D -49^\circ$ ; both, unlike tricitin,  $[\alpha]_D -48.5^\circ$ , are completely hydrolysed by yeast or its autolysate or dilute mineral acids. On the basis of the reaction  $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$  the hydrolysis is incomplete and the specific rotation is less than that of pure lævulose, hence for these lævulosans the equation is only an approximation.

C. C. N. VASS.

**Microchemical detection of glucoside.** A. NIETHAMMER (Mikrochem., 1931, 9, 136—142).—The extraction of æsculin, rhinanthin, syringin, saponarin, digitonin, and salicin from vegetable tissues has been effected by sublimation and the properties of the products are described. The sublimation process and precipitation by means of 20% potassium bromide solution saturated with bromine are useful methods for the microchemical detection of glucosides in plants. E. S. HEDGES.

**Occurrence of methyl mercaptan in the leaves of *Lasianthus lævigatus*, Bl., *L. lucidus*, Bl., *L. purpureus*, Bl., *L. stercorarius*, Bl., and *L. bracteolatus*, Miq.** D. R. KOOLHAAS (Biochem. Z., 1931, 230, 446—450).—The methyl mercaptan is separated by steam-distillation of the freshly plucked leaves and determined by precipitation as the mercuric salt. The amount of mercaptan per 1000 g. of leaves varies from 1.351 g. with *L. purpureus* to none with *L. lævigatus*.

P. W. CLUTTERBUCK.

**Tobacco. IV. Analysis of tobacco smoke.** N. J. GAVRILOV and A. V. KOPERINA (Biochem. Z., 1931, 231, 25—32; cf. A., 1930, 824).—A method and apparatus by means of which all the smoke from a given quantity of smouldering tobacco can be passed into 0.1*N*-sulphuric acid of which the total nitrogen, ammoniacal nitrogen, and nicotine-nitrogen contents can then be determined are described. The deviations in parallel experiments with the same tobacco do not exceed 3—4%. Within certain limits the results obtained are not affected by the rate at which the tobacco is burned nor by its moisture content.

W. MCCARTNEY.

**Distribution of nitrogen in plant extracts that contain a high proportion of nitrate-nitrogen.** A. C. CHIBNALL and E. J. MILLER (J. Biol. Chem., 1931, 90, 189—196).—Analysis is given of an extract from rye-grass (*Lolium perenne*) obtained from a sewage farm. The extract contained abnormally large concentrations of nitrate-nitrogen. It was fractionated according to the method of Vickery and Pucher, but the "other amide-nitrogen" contained in the fractions did not account for the total present in the original extract. It is highly probable that the results are therefore vitiated by the effect of nitrate on amide-nitrogen determinations (see this vol., 537). It also appears from the "apparent amide-nitrogen" content of the various fractions that the easily oxidisable substance detected but not isolated by Vickery and Pucher in tobacco leaf is a nitrogen-containing compound. W. O. KERMACK.

**Amino-acids of glutenin.** M. DAMODARAN (Biochem. J., 1931, 25, 190—199).—The hydrolysis products of glutenin have been fractionated by means of their copper salts. The yields of most of the monoamino-acids are higher than those previously recorded.

S. S. ZILVA.

**Proteins. II. Uniformity of the protein fraction extracted from orange-seed meal by salt solutions.** F. SAUNDERS (J. Amer. Chem. Soc., 1931, 53, 696—700).—Extraction of the oil-free, ground seeds with *N*-solutions of alkali halides gives extracts containing the same amount of nitrogen in

each case. The protein extracted is probably the same in each case. H. BURTON.

**Aluminium content of plants.** G. BERTRAND and G. LEVY (*Compt. rend.*, 1931, 192, 525—529; cf. McCollum and others, and Kahlenberg and Closs, A., 1930, 492).—Data are presented for the aluminium content (determined gravimetrically as phosphate) of several species of edible roots and leaves, showing the variation with age. Leaves contain most aluminium, those of spinach, rhubarb, and radish having 96—104, 166, and 157—280 mg. per kg. dry wt., respectively. A. COHEN.

**Detection and intensity of mitogenetic radiation.** A. GURWITSCH (*Biochem. Z.*, 1931, 230, 505).—A reply to Schreiber and Friedrich (this vol., 125). P. W. CLUTTERBUCK.

**Elongation of roots of Georgia collards as affected by sodium luminal.** T. W. PRATT (*Plant Physiol.*, 1930, 5, 587—597).—The rate of growth of the roots of Georgia collards was retarded by solutions of sodium luminal (0.1—1.0%), the effect being immediate and reaching a maximum within 15 min. of treatment. The extent of the retardation was closely related to the concentration of the sodium luminal solution. Washing with distilled water partly removed the depressive effect. A. G. POLLARD.

**Colloidal zirconium hydroxide as a deproteinising agent.** J. ERDŐS and J. SÜRTÜ (*Biochem. Z.*, 1931, 231, 6—12).—When zirconium tetrachloride is evaporated to dryness several times with anhydrous acetic acid and the product digested for some hours with water the salt is quantitatively converted into the hydroxide  $Zr(OH)_4$ . A colloidal solution of the purified hydroxide is an excellent deproteinising agent, since the substance is non-toxic and harmless to the materials with which it is used. Any excess of the hydroxide is easily removed from deproteinised solutions by heating or by altering the reaction of the medium. W. MCCARTNEY.

**Spectrographic determination of aluminium in biological ash.** D. TOURTELLOTTE and O. S. RASK (*Ind. Eng. Chem. [Anal.]*, 1931, 3, 97—102).—The volatility of the aluminium compound used and the nature of the combined anion or of other salts present simultaneously are without influence on the spectrographic determination of aluminium. The error of the determination at concentrations from 0.5 to 1000 in  $10^6$  is  $\pm 25\%$ . The arc and condensed spark methods are equally satisfactory in most cases, but for certain kinds of biological ash, especially if free carbon is present, the arc method appears to be the more sensitive. H. F. GILLBE.

**Detection of lead in organic tissues.** W. GERLACH and W. GERLACH (*Naturwiss.*, 1931, 19, 111).—The mode of procedure described previously (cf. this vol., 328) has been applied to the detection of lead in the gums. The spectrograms give definite indications of the presence of lead in circumstances in which the histological method is untrustworthy. J. W. SMITH.

**Detection of small amounts of lead and mercury in the organism.** H. BÜLL (*Biochem. Z.*, 1931, 230, 299—303).—Methods are given for blood, urine, and faeces. Lead usually occurs in the faeces when present in the urine, but could not be detected in blood even when present in both urine and faeces. P. W. CLUTTERBUCK.

**Determination of ferric and ferrous ions and of iron in organic combination in biological material.** L. PINCUSSEN and W. ROMAN (*Biochem. Z.*, 1931, 231, 54—58).—To separate the ionised iron from that which is in organic combination a suitable amount of material, after being ground with sand in an ice-cold mortar, is thoroughly mixed and kept for 3 hrs. with frequent stirring with 20% sulphuric acid from which air is excluded by means of a layer of paraffin oil. When the mixture is then centrifuged the organically combined iron remains in the deposit, whilst the ionised iron is in solution. In the solution the ferric iron is determined by titration with titanous chloride solution, using potassium thiocyanate as indicator; the ferrous iron is then oxidised with nitric acid, excess of which is subsequently removed by evaporation to dryness, the residue is dissolved in dilute sulphuric acid and titrated as before with titanous chloride solution. The amount of ferrous iron is then obtained by difference. The organic matter in the deposit is destroyed with nitric acid and hydrogen peroxide and the iron which is present in the residue after the removal of the excess of nitric acid is dissolved in dilute sulphuric acid and titrated with titanous chloride solution. Where required throughout the process suitable measures must be taken to prevent oxidation of dissolved substances. A micro-burette for use with titanous chloride solutions is described. W. MCCARTNEY.

**Spectrophotometric micro-determination of phosphorus [in organic material].** T. TEORELL (*Biochem. Z.*, 1931, 230, 1—9).—The colorimetric method of Fiske and Subbarow (A., 1926, 443) is modified, the blue colour being determined spectrophotometrically. A single phosphorus standard is necessary and 0.01—0.05 mg. of phosphorus may be determined with an error of  $\pm 2\%$ .

F. O. HOWITT.

**Determination of methylglyoxal, pyruvic acid, and acetaldehyde alone or in mixtures. Determination of lactic acid in the presence of these substances and in biological material.** E. SIMON and C. NEUBERG (*Biochem. Z.*, 1931, 232, 479—484).—Methylglyoxal, pyruvic acid, and acetaldehyde (but not lactic acid) in dilute acid solutions (1.0—0.1%) are quantitatively precipitated by excess of acid solution of 2:4-dinitrophenylhydrazine hydrochloride. The hydrazones are separated quantitatively by removing that of pyruvic acid by means of sodium carbonate and dissolving that of acetaldehyde from the residue in 94% alcohol, in which the methylglyoxal compound is insoluble. The process can likewise be applied to the determination of trioses if they are first converted by distillation with 20% sulphuric acid into methylglyoxal. W. MCCARTNEY.