BRITISH CHEMICAL ABSTRACTS

Foreword.

The "A" section of the abstracts, dealing with pure chemistry, will be issued to Fellows of the Chemical Society and other subscribers at the end of each month, whilst the "B" section, covering applied chemistry, will appear each week, and will be circulated along with the *Journal of the Society of Chemical Industry* to members of that Society and to special subscribers.

The price of the "A" and the "B" sections is £3 13s. 6d. each per annum, post free (including joint Index), but Fellows of the Chemical Society may obtain the "B" abstracts for £1 10s. 0d., whilst Members of the Society of Chemical Industry may obtain the "A" abstracts for £2 0s. 0d. [The yearly membership subscriptions are £3 0s. 0d. in the case of the Chemical Society and £2 10s. 0d. in the case of the Society of Chemical Industry.] Copies of "A" or "B" abstracts printed on one side of the paper, and suitable for filing purposes, may be obtained at reasonable charges.

The general basis of classification adopted in the two sections is printed below. For the guidance of readers of "A" abstracts, it should be pointed out that abstracts of analytical papers may be found not only at the end of each section as tabulated below, but sometimes also, when the analytical method described has a very specialised object, in the body of the section, according to the material with which the analytical method deals. In such cases there will be a reference in the "analytical" portion to other abstracts of analytical interest appearing in the same section.

A.—PURE CHEMISTRY.

General, Physical, and Inorganic Chemistry.

Sub-atomics.

(*a*) Atomic spectra. Infra-red, visible, ultra-violet, *X*-ray emission and absorption spectra, Zeeman and Stark effects, Compton effect.
(*b*) Electrical properties: Ionisation potentials of atoms, photo-electric and thermionic effects.
(*c*) Properties of electrons and gaseous ions. Magnetic properties.
(*d*) Isotopes—atomic weights.
(*e*) Radioactive processes.
(*f*) Other sub-atomic processes.
(*g*) Theories of atomic structure and sub-atomic mechanism.
(*h*) Atomic dimensions (except in solid state).

Molecular Structure.

(*a*) Molecular spectra: Emission and absorption spectra of organic and inorganic substances. Fluorescence, luminescence, and phosphorescence. Raman effect.
(*b*) Ionisation potentials. Photo-electric effect with compounds.
(*c*) Conductivity. Dielectric constants. Dipole moment.
(*d*) Molecular volumes.
(*e*) Optical properties: Molecular refraction, dispersion, rotatory dispersion, optical activity, magnetic rotation.
(*f*) Theories of molecular structure. Valency, secondary valency, including co-ordination, electronic and magnetic theories, constitutional formulæ of inorganic substances.
(*g*) Molecular sizes and forces. Surface tension.

Crystal Structure.

(*a*) *X*-Ray examination.
(*b*) Crystal models.
(*c*) Magnetic and electrical properties of crystals: Piezo-electricity; magnetostriction.
(*d*) Optical properties. Rotatory dispersion.
(*e*) Compressibility. Tensile strength.
(*f*) Mesomorphic state.

Physical Properties of Pure Substances (not included above).

(*a*) Molecular weights.
(*b*) Electrical constants: Conductance, thermoelectric power, light sensitivity, etc. Magnetic susceptibility.
(*c*) Optical constants.
(*d*) Thermal constants: Specific heats, heat of change of state, boiling points, freezing points, transition points.
(*e*) Chemical constants.
(*f*) Pressures and volumes: Density, vapour pressure, coefficient of expansion, equations of state, theory of corresponding states.
(*g*) Compressibility.
(*h*) Viscosity; fluidity; plasticity.
(*i*) Diffusion.

Solutions and Mixtures.

(*a*) Gaseous mixtures, liquid mixtures (excluding dilute solutions), solid solutions (including alloys), property–composition curves.
(*b*) Miscibility of liquids and of solids. Solubility of gases and solids in liquids.
(*c*) Distribution phenomena: Partition, absorption, adsorption, surface films, surface energy, membrane effects.
(*d*) Dilute solutions: (i) Non-electrolytic solutions; (ii) Solutions of electrolytes. Colligative properties; non-colligative properties.
(*e*) Disperse systems. Preparation and properties of suspensions, emulsions, smokes, foams, sols, gels, jellies. Coagulation, peptisation, ageing, cataphoresis, imbibition, etc.

Kinetic Theory. Thermodynamics.

- (*a*) Equilibrium in homogeneous systems; equilibrium, dissociation, ionisation constants, activity coefficients, etc.
- (*b*) Equilibrium in heterogeneous systems; uni- and multi-component systems, phase rule.
- (*c*) Thermochemistry.

Electrochemistry.

- (*a*) Electrical conductance.
- (*b*) Transport phenomena.
- (*c*) Electrode and diffusion potentials; *E.M.F.*, concentration cells, etc.
- (*d*) Polarisation, overvoltage, passivity, etc.
- (*e*) Application of electrochemical methods.

Reactions.

- (*a*) Velocity studies in (i) Homogeneous systems; (ii) Heterogeneous systems.
- (*b*) Catalysed reactions: (i) and (ii) as above.
- (*c*) Electrode reactions.
- (*d*) Photochemical reactions.
- (*e*) Irradiated reactions.

New Methods of Preparing Substances arranged according to periodic table), etc.
Improved Methods of Preparing Substances, etc.
Analysis.
Apparatus.
Lecture Experiments.
Historical.

Geochemistry.

Organic Chemistry.

Aliphatic.

- Hydrocarbons.
  - Halogen, nitro-, and nitroso-derivatives.
- Alcohols.
  - Ethers.
  - Alkyl salts.
  - Sulphur compounds, including sulphonic acids.
- Acids.
  - Thio- and sulpho-acids.
- Aldehydes.
  - Aldoximes.
- Ketones and diketones.
  - Ketoximes.
- Sugars, glucosides, and carbohydrates.
- Amines.
  - Amino-alcohols.
  - Amino-acids.
  - Cyano-acids, thiocyano-acids.
  - Amino-aldehydes and -ketones.
- Amides (including cyanic, cyanuric, and thiocyanic acids).
- Nitriles, carbylamines, metallic cyanides.
- Amidoximes, imino-ethers.
- Diazo-compounds.
- Phosphorus compounds.
- Arsenic, antimony, boron, silicon, etc. compounds.
- Aliphatic organo-metallic compounds.

Homocyclic.

- Hydrocarbons C_nH_{2n} to C_nH_{2n-6}.
  - Halogen, nitroso-, and nitro-derivatives.
  - Sulphonic acids.
- Hydrocarbons C_nH_{2n-8} to C_nH_{2n-4}. Derivatives under each.
- Amines. Includes anilides, carbamides, thiocarbamides, and sulphonic acids.
- Azoxy-compounds.
- Azo- ,,
- Hydrazo- ,,
- Diazo- ,,
- Diazoamino- ,,
- Phenols. Aminophenols, thiophenols, sulphides, sulphonic acids.
- Alcohols.
- Phenol-alcohols.
- Acids. Sulphonic acids and hydrazines under each member.
- Aldehydes. Derivatives under each.
- Ketones. ,, ,, ,,
  - Diketones and oxyketones.
- Quinones.
- Camphor group.
- Terpenes.
- Ethereal oils.
- Resins and balsams.
- Bitter principles and indifferent substances.
- Colouring matters (unclassified natural and artificial).
- Tannins.

Heterocyclic, etc.

- Furan group.
- Thiophen group (Se).
- Bases: N_1, N_2, N_3, etc.
- Alkaloids.
- Phosphorus compounds.
- As, Sb, Bi, B, Si compounds.
- Organo-metallic compounds.
- Proteins.

Analysis.

Biochemistry.

Respiration.
Blood: Gases; constituents; reactions (hæmolysis, anti-body formation, etc.).
Organs and their Proximate Constituents: Analytical data of constituents of organs: pure substances isolated from organs.
Secretions: Milk; lymph, etc.
Excretions: Urine; fæces; other excretions.
Diseases: Natural and experimental (in alphabetical order).
Metabolism: General; special; intermediary; fate of substances in the animal body.
Physiological Action: Variation of physiological conditions; action of drugs; toxicology.
Enzymes: General; specific.
Micro-organisms: yeasts, moulds, protozoa, bacteria.
Hormones.
Vitamins.
Vegetable Physiology: General; reproduction and fertilisation; respiration; growth; proximate principles; diseases; poisons.
Analysis.

B.—APPLIED CHEMISTRY.

I. General; Plant; Machinery.
II. Fuel; Gas; Tar; Mineral Oils.
III. Organic Intermediates.
IV. Dyestuffs.
V. Fibres; Textiles; Cellulose; Paper.
VI. Bleaching; Dyeing; Printing; Finishing.
VII. Acids; Alkalis; Salts; Non-Metallic Elements.
VIII. Glass; Ceramics.
IX. Building Materials.
X. Metals; Metallurgy, including Electrometallurgy.
XI. Electrotechnics.
XII. Fats; Oils; Waxes.
XIII. Paints; Pigments; Varnishes; Resins.
XIV. Indiarubber.
XV. Leather and Glue.
XVI. Agriculture.
XVII. Sugars; Starches; Gums.
XVIII. Fermentation Industries.
XIX. Foods.
XX. Medicinal Substances; Essential Oils.
XXI. Photographic Materials and Processes.
XXII. Explosives.
XXIII. Sanitation; Water Purification.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1931.

General, Physical, and Inorganic Chemistry.

Absolute intensity of the aurora line in the night sky, and the number of atomic transitions required to maintain it. (Lord) Rayleigh (Proc. Roy. Soc., 1930, A, 129, 458—467).—The brightness of the green auroral line of the night sky, λ 5577, is found to be $3{\cdot}2\times10^{-5}$ candles per sq. m. The energy of emission is 6·4 ergs per sec. per sq. m., requiring for its maintenance $1{\cdot}81\times10^{12}$ atomic transitions per sec. per sq. m. L. L. Bircumshaw.

Transverse Zeeman effect of the green auroral line; experimental proof of the existence of quadrupole radiation. R. Frerichs and J. S. Campbell (Physical Rev., 1930, [ii], 36, 1460—1467; cf. Rubinowicz, A., 1930, 513, 653).—Since the existence of quadrupole radiation can be demonstrated from measurements of the transverse but not of the longitudinal Zeeman effect, the former for the green auroral line excited in a helium–oxygen mixture was photographed. Results are in complete agreement with the theoretical predictions. N. M. Bligh.

Spectra of several long-period variable stars. P. W. Merrill and C. G. Burwell (Astrophys. J., 1930, 71, 285—335).—Hydrogen, Fe I, Fe II, Mg I, Si I, Mn I, Sr II (?), and In I (?) have been identified in the spectra of long-period variable stars of type Me and Se. L. S. Theobald.

Flashing afterglow in a discharge tube. H. J. J. Braddick (Nature, 1930, 126, 725).—After passing a discharge from an induction coil a strong afterglow persisting several seconds has been observed in a tube of pyrex glass with nickel electrodes. The afterglow is probably due to the dissipation of charges on the walls of the tube. L. S. Theobald.

Multiple interference spectroscope. E. Gehrcke and E. Lau (Physikal. Z., 1930, 31, 973—974).—A multiple interference spectroscope of high resolving power is described in detail. The spectroscope has revealed the fine structure of the mercury line at 5461 Å., and helium λ 5876 Å. is shown to consist of two lines separated by 0·33 Å. The resolving power of the instrument is approximately 2×10^{6} and the instrument can be used for measuring the Doppler effect in spectral lines. W. R. Angus.

Correlation of atomic *J* values and molecular quantum numbers, with applications to halogen, alkaline-earth hydride, and alkali molecules. R. S. Mulliken (Physical Rev., 1930, [ii], 36, 1440—1450; cf. Wigner and Witmer, A., 1929, 117).—Theoretical. Rules are deduced for determining certain quantum relations for the molecular states resulting from the union of two atoms with specified *J* values, for cases of strong *L*,*S* coupling. Examples are considered, and the difficulties of extending the method to cases of weak coupling are discussed. Electron configurations and dissociation products are examined for the halogen molecules, and the analogies and differences of spectra for the halogens, alkali and alkaline-earth metals are interpreted in terms of electron configurations. N. M. Bligh.

Oscillating arc in spectrochemical analysis. E. Z. Stowell and W. S. Huxford (Physical Rev., 1930, [ii], 36, 1348—1351; cf. A., 1929, 1359).—It is shown that the alkaline-earth metals but not the alkali metals will allow radio-frequency oscillations to be generated across an arc in hydrogen. Spectra were photographed of the two groups of elements when burned in the hydrogen arc, and the intensification and reduction of the lines of various elements are described. The effect of minute additions of magnesium in large amounts of rubidium and sodium is described, and from the oscillations produced a method for determining the content of magnesium is indicated (cf. Crew, A., 1929, 366; Duffendack, A., 1930, 2). N. M. Bligh.

General electric type *S*-1 lamp as a spectroscopic source. D. Dooley (Physical Rev., 1930, [ii], 36, 1476—1479).—The lamp is a 300-watt alternating-current tungsten–mercury arc in argon. Spectrograms were obtained of radiation from the lamp and also when hydrogen, helium, neon, or carbon dioxide was substituted for argon, with and without a small amount of mercury. In nitrogen alone the second positive bands were greatly modified; hydrogen with mercury showed the mercury hydride bands, and carbon dioxide showed the third positive bands. N. M. Bligh.

Conditions for initiation of electrodeless discharges in gases. N. T. Gordon and S. Dushman (Physical Rev., 1929, [ii], 33, 632).—The minimum current through a copper coil which is sufficient to start a glow in a bulb placed inside the coil when this is supplied with high-frequency current from a vacuum tube oscillator has been determined at various gas pressures (0·1—40 mm.) and frequencies for neon, helium, and oxygen. For each frequency there exists a critical pressure at which the current required to initiate the glow is a minimum. A parallelism with positive column discharges exists. L. S. Theobald.

Formation of MH molecules; effects of H atom on M atom. R. S. Mulliken (Physical Rev., 1929, [ii], 33, 285—286).—Observed electronic states of diatomic hydride molecules (CH, NH, OH, MgH, etc.) can be derived from unexcited H and familiar low-energy states of M atoms. The observed states and $\Delta\nu$ intervals in ^2P or ^3P states of such MH molecules indicate that the effects of the H on the M atom are confined to the following effects: (i) the couplings between l_τ vectors of M atom outer electrons to give a resultant l are broken down by the field of the H nucleus, (ii) the uncoupled vectors l_τ are separately space-quantised with reference to the electric axis, (iii) the electron of the H atom takes its place with the M electrons, and (iv) the original couplings of s_τ vectors are often broken down.

L. S. Theobald.

Influence of slit width on the intensity distribution in spectral lines. P. H. van Cittert (Z. Physik, 1930, 65, 547—563).—The expression for the intensity at any point in the focal plane of the telescope for an infinitely narrow collimator slit is integrated across the width of the slit to determine the intensity distribution in an actual spectral line. Three cases are distinguished, viz., when radiation falls on the collimator slit from (i) an incoherent unfocussed source, (ii) a coherent unfocussed source, and (iii) a coherent focussed source. In (i) a maximum brightness of the centre of the spectral line occurs when the product of the slit width, in wave-lengths, and the angular aperture of the collimator equals unity; the slit width should, in practice, be less than this. In (ii), the spectral line becomes double when the above product equal two, and the incident beam just fills the collimator lens. The spectroscope is most efficient when the slit width and the angular width of the incident beam have approximately three quarters these limiting values. In (iii) an indefinite condenser focus complicates the calculation, but the results of (ii) apply approximately.

A. B. D. Cassie.

Theory of complex spectra. E. U. Condon (Physical Rev., 1930, [ii], 36, 1121—1133).—Mainly mathematical. The work of Slater is extended (cf. A., 1930, 126) and it is shown that the assignment of definite electron configurations to spectral terms is an approximation, having meaning only when the multiplet systems of the several configurations are widely separated. The effect of including spin terms is outlined. Non-diagonal matrix elements for the N-electron problem are reduced to corresponding elements for the two-electron problem, and the results are applied to the theory of two-electron jumps.

N. M. Bligh.

Principle of identity and the exclusion of quantum states. G. N. Lewis (Physical Rev., 1930, [ii], 36, 1144—1153).—Theoretical. Considerations are presented to show that all exclusion rules of quantum states, of which rules Pauli's was the prototype, are direct mathematical consequences of quantum mechanics when full consideration is given to the identity of certain elementary particles. The assumption that a system of two bodies, both having the same mechanical and electrical properties, would show the same behaviour gave rise to the Gibbs-Einstein paradox of the change of entropy on mixing two gases continuously approaching complete identity, and must be abandoned in favour of a distinction of identical and quasi-identical particles. The new mathematical condition of complete identity, operating with the wave equation and its boundary conditions, gives rise to the empirically obtained exclusion laws. The method is applied to the rotational states of monatomic and diatomic gases. The influence of spin is discussed.

N. M. Bligh.

Passage of an electric discharge through gases. J. B. Seth and B. Mokand (Nature, 1930, 126, 808).—The effect previously observed with air (A., 1928, 107) has been extended to hydrogen, oxygen, nitrogen, carbon dioxide, and chlorine with nearly similar results. For a fixed *P.D.* the amount of shift of the interference fringes varies with pressure to a maximum which is different for different gases and voltages. The effect is greatest in carbon dioxide and least in hydrogen. The shift and pressure change can be observed at the ordinary pressure with no visible glow when long electrodes reaching the end of the light beam are used. That the effect is due to the pushing away of gas from the discharge can be demonstrated by means of lycopodium powder.

L. S. Theobald.

Energy levels of atoms in an electric field. J. S. Foster (Nature, 1930, 126, 845).—The conclusions of Ishida (A., 1930, 1327) are discussed.

L. S. Theobald.

Intensities and summation rules for quadrupole multiplets. A. Rubinowicz (Z. Physik, 1930, 65, 662—676).—Theoretical. Radiation transitions can occur only between dipoles possessing "proper" functions of opposite symmetry, whereas quadrupoles must have "proper" functions of like symmetry. Thus, lines due to transitions between dipoles and between quadrupoles must be distinct. Relative transition probabilities for quadrupole multiplets are determined, and from them a summation rule is shown to exist. Examples are the O II multiplets, $^2D-^2P$, and $^6D-^6S$, and the Fe II multiplets, $^4F-^4G$, found in stellar spectra. A. B. D. Cassie.

Evidence for quadripole radiation. E. Segrè (Nature, 1930, 126, 882).—The transverse Zeeman effect of the 4642·17—4641·58 potassium doublet, which is a $S\longrightarrow D$ combination, has been observed. The Zeeman pattern agrees with the predictions of Rubinowicz for quadripole and not dipole radiation.

L. S. Theobald.

Spectra in condensed discharges. J. W. Beams (Physical Rev., 1929, [ii], 33, 1086).—The light emitted by an electric spark between metallic electrodes in air together with that emerging from condensed discharges at low pressures has been investigated by the rotating-mirror method. Photographs of single discharges have been obtained. The velocities of propagation of the luminosity of metallic vapours in the spark have been measured. The air lines appeared first, followed successively by the spark and the arc lines of the metal. The spark probably appears first as a narrow thread and then expands rapidly during its initial stage.

L. S. Theobald.

Existence of a "resonance time" or a time-lag in light emission. H. T. Wolff (Z. Physik, 1930, 65, 730—733).—It is shown that where it is necessary to assume the presence of a fading-out period ("Abklingzeit"), a time-lag ("Verweilzeit") need not also be required. An experiment which definitely shows the existence of a fading-out time is given.

A. J. Mee.

Refraction of X-rays for the determination of the specific charge of the electron. H. E. Stauss (Physical Rev., 1930, [ii], 36, 1101—1108).—With the view of correcting discrepancies in existing values of e/m, a method depending on the refraction of X-rays by a prism is described. For crystalline quartz of density 2·6480 g./cm.^{3} the value of $1-\mu$ was determined for the $K\alpha_1$ and $K\beta$ radiation of molybdenum as $1{\cdot}804\pm0{\cdot}001\times10^{-6}$ and $1{\cdot}436\pm0{\cdot}001\times10^{-6}$, respectively. Using the absolute X-ray wave-lengths of Bearden (cf. A., 1929, 984) and of Cork (cf. A., 1930, 1079), the calculated values of e/m were found to lie between those given by spectroscopic and deflexion methods. N. M. Bligh.

X-Ray scattering coefficient as a function of wave-length and atomic number. E. N. Coade (Physical Rev., 1930, [ii], 36, 1109—1115).—With an improved form of the apparatus of Mertz (cf. A., 1927, 83) the mass scattering coefficients for gold, tin, silver, iron, and carbon were compared with those of aluminium for the wave-length range 0·48—1·09 Å., by collecting the scattered radiation in an ionisation chamber surrounding the scatterer on one side. The primary beam consisted of characteristic fluorescence radiation excited in radiators of tin, silver, molybdenum, and selenium by a water-cooled tungsten tube. Results obtained are tabulated, and are transformed into absolute scattering coefficients, which are plotted against wave-lengths.

N. M. Bligh.

Atomic scattering powers of nickel, copper, and iron for various wave-lengths. R. W. G. Wyckoff (Physical Rev., 1930, [ii], 36, 1116—1120; cf. A., 1930, 655; Armstrong, A., 1929, 1354).—Using the methods previously described, the atomic scattering powers were measured for the atoms in nickel, copper, and iron reflecting the $K\alpha$ lines of molybdenum, copper, nickel, and iron, and show that the scattering power of an atom passes through a minimum at its K absorption limit to a maximum at or near its resonance wave-length. The atomic F curves of the nickel atom in the metal and its oxide are practically identical. N. M. Bligh.

X-Ray anomalous dispersion in the region of the L series of platinum. E. Dershem (Physical Rev., 1929, [ii], 33, 120; cf. A., 1929, 747).—The indices of refraction of platinum in the neighbourhood of its L absorption limits have been measured by the total reflexion method. One depression in the curve obtained by plotting $1-\mu=\delta$ against λ shows lowered values of δ at a wave-length corresponding with the mean of the wave-lengths of the L_{I} and L_{II} limits and another at the L_{III} limit. Different surfaces of the same material may have indices of refraction which are markedly different. L. S. Theobald.

Position and structure of the modified line of the spectrum of scattered X-rays. F. L. Nutting (Physical Rev., 1930, [ii], 36, 1267—1272).—Measurements were made of the shift in wave-length of scattered X-rays by a photographic method for molybdenum X-radiations scattered by a paraffin block, and by a single-crystal ionisation method for scattering by graphite. Photomicrographic analysis for the shift of the centre of gravity of the lines and of the peaks gave h/mc 0·02305 and 0·02374 Å., respectively. Some error may be due to the $K\gamma$ line. The average value from the ionisation curves was $0{\cdot}0240\pm0{\cdot}00024$ Å., in good agreement with the theoretical value, 0·02422 Å. The value and the fine structure of the modified line reported by Davis and Purks (cf. A., 1929, 986) are not supported. N. M. Bligh.

Relative intensities of X-ray lines in the tantalum L spectrum. V. Hicks (Physical Rev., 1930, [ii], 36, 1273—1284).—Special precautions are described for an investigation of the relative intensities of 17 lines in the L spectrum of tantalum, using the ionising spectrometer. The results for lines of small wave-length separation agree well with those of Allison and Armstrong (cf. A., 1925, ii, 1015) on tungsten, and their qualitative estimates for lines of longer wave-length. The assumption that the ionisation currents produced are proportional to the relative intensities is supported by Compton (cf. A., 1930, 138). If the ν^4 correction, indicated by quantum mechanics, is made to the intensities at high voltage the summation rules are approximately valid except for lines having the initial state L_1.

N. M. Bligh.

Relation between continuous and line spectra of X-rays from thin targets. D. L. Webster and W. W. Hansen (Physical Rev., 1929, [ii], 33, 635—636).—K-Electron ionisation by cathode-ray impact has a continuous-spectrum counterpart in the emission of a quantum of any frequency above the K limit. For thick targets of silver, the ratio of the probability of the former to the latter process appears to be constant, whilst for thin targets the same constancy probably holds, but is subject to wider limits of error. The calculated probability of the continuous-spectrum process is approximately proportional to the $K\alpha$-line intensities between 25 and 85 kilovolts, furnishing additional evidence that the ratio is constant for thin targets. L. S. Theobald.

Intensities of general X-radiation proceeding from an atom in different directions. W. Duane and J. C. Hudson (Physical Rev., 1929, [ii], 33, 635).—The radiation projected forward at an angle of 45° from the direction of motion of a homogeneous stream of electrons impinging on the atoms of mercury vapour is approximately twice as intense as that projected backward at an angle of 135° from the same direction. L. S. Theobald.

Fine structure of scattered X-rays. D. Mitchell and B. Davis (Physical Rev., 1929, [ii], 33, 292).—Four lines attributed to Mo-$K\alpha$ have been found in the scattering of Mo-$K\alpha$ rays from aluminium. Two of these are shifted lines corresponding with approximately 2·3 and 5·6 X from Mo-$K\alpha_1$. Two of the aluminium absorption limits are given as 57±6 and 136±6 equivalent volts. L. S. Theobald.

X-Ray spectroscopic measurements of the L absorption of elements between 74, tungsten, and 92, uranium. A. Sandström (Z. Physik, 1930, **65**, 632—655).—The three L levels for the elements from tungsten to bismuth and from thorium to uranium were determined with a Siegbahn tube spectrometer. Absorption edges are most clearly defined when the intensity difference between wave-lengths at equal but opposite distances from the edge is greatest. This, with the Jönsson's absorption law (Diss., Uppsala, 1928), determines the thickness of the most efficient absorbing layer for each element. These layers were prepared in three ways: (i) by pouring an emulsion of the element and cellulose lacquer on to a glass plate, (ii) by distillation and subsequent deposition on an aluminium foil 6 μ thick, and (iii) by sputtering. The edges were examined photometrically, and some absorption lines were detected. The results are discussed, and compared with those of other workers. Their deviation from Moseley's linear law, due to the presence of outer electron shells, is noted. A. B. D. Cassie.

Structure of K-radiation in the ultra-soft X-ray region. M. Söderman (Z. Physik, 1930, **65**, 656—661).—Recent measurements on X-ray lines in the region 49—115 Å., where optical measurements have been made, are described. The photographic plate was examined with a microphotometer, using a slit width corresponding with 0·08—0·2 Å. The $K\alpha$ X-ray lines obtained with carbon, boron, and beryllium are broad compared with the optical lines obtained from a condensed spark. This broadening is not due to satellites, but may be due to the use of solids in obtaining the X-ray photographs, as compared with the gaseous atoms or ions which are effective in producing the quenched spark.
A. B. D. Cassie.

X-Ray spectra of gases. K Series of krypton and of xenon. A. Dauvillier (Compt. rend., 1930, **191**, 937—939).—The gaseous anticathode method was used, the pressure being regulated by an oil–mercury manometer adjusted so that the volume of the anticathode was of the order of 10 c.c., *i.e.*, about 15 cm. of mercury for krypton at 45 kilovolts and xenon at 60 kilovolts. The values $\alpha_1\alpha_2$ 978 and 417, and β 875 and 360 found for 36 Kr and 54 X, respectively, are in accord with theoretical predictions. Owing to the feeble dispersion, the βγ and $\alpha_1\alpha_2$ doublets cannot easily be distinguished, and the continuous spectrum is too feeble to enable the limits of energy distribution to be defined. J. Grant.

New bands in the secondary spectrum of hydrogen. G. S. Monk and A. E. Elo (Physical Rev., 1929, [ii], **33**, 114).—Using the electronic and vibrational levels associated with the Balmer lines, the wave-numbers of the remaining lines of the band groups have been computed and compared with lines already measured. Only Q branches are present. Bands attributable to the H_3 molecule have been found in some new measurements and are discussed.
L. S. Theobald.

Displacement of hydrogen terms in intense electric fields. C. Lanczos (Z. Physik, 1930, **65**, 431—455).—Theoretical. The method of direct asymptotic investigation of the wave functions for the Stark effect in intense fields is applied in improved form to a determination of proper values. A closed formula is deduced for these proper values in place of the older successive approximations, which become divergent with increasing field intensity.
A. B. D. Cassie.

Molecular states of hydrogen with two excited electrons. W. Weizel (Z. Physik, 1930, **65**, 456—463).—The two hydrogen molecular terms X and 3^1K cannot, on account of the angular momenta which show coupling, be associated with a molecule containing a $1s\sigma$ electron. These terms may coincide with $(2p)\sigma^2\,{}^1\Sigma$ and $2p\sigma 3p\sigma\,{}^1\Sigma$, respectively.
A. B. D. Cassie.

Continuous spectrum of hydrogen. J. Kaplan (Physical Rev., 1929, [ii], **33**, 638—639).—A discussion. L. S. Theobald.

Relativity separation of spectral lines of hydrogen-like atoms in parallel and crossed electric and magnetic fields. D. P. R. Chaudhuri (Z. Physik, 1930, **65**, 824—829; cf. Sen, A., 1929, 1115).—The calculation of Sen is extended, taking into account the small relativity effect for very weak fields. The separation of the H_α lines in weak parallel fields is calculated. Owing to the complexity of the calculation, only the Lyman lines can be considered for crossed fields. For these lines the intensity of the split lines is easily obtained. For H_α lines in parallel fields of strength 10^4 volts and 10^4 gauss, the relativistic separation of some lines is of the order of 0·008 Å., whilst for the first Lyman line in crossed fields the relativity effect results only in a displacement of the line, which is approximately fifty times as great as this. A. J. Mee.

Numerical calculation of the $2S$ terms of ortho- and par-helium. E. A. Hylleraas and B. Undheim (Z. Physik, 1930, **65**, 759—772).—An accurate calculation of the ground term of ortho-helium and the $2S$ terms of par-helium is carried out. The calculated figure shows almost complete agreement with the experimental value (cf. A., 1930, 1487). The effective quantum number is 1·689. For par-helium, the difference between the observed and the calculated values amounts to 0·7% of the energy associated with the " light electron," or 0·05% of the total energy. Expressed otherwise, the effective quantum number is calculated to be 1·858, as against 1·851 for the experimental value. A. J. Mee.

Life-period of excited helium atoms and a direct method of determining the diffusion coefficient of excited atoms. E. Ebbinghaus (Ann. Physik, 1930, [v], **7**, 267—292; cf. Meissner and Graffunder, A., 1928, 212).—Experiments are described from which, by determining the absorption of light by helium atoms in the 2^3S_1 state at known intervals of time after their excitation, the rate of decay of the excited atoms and their rate of diffusion can be calculated. The diffusion coefficient at the ordinary temperature and 1 mm. pressure is 400 cm.^{2} per sec., which gives $4{\cdot}5\times10^{-8}$ cm. as the effective diameter of the excited atom, assuming that of the normal atom to be $2{\cdot}5\times10^{-8}$ cm. The degradation of the excited atoms occurs only by collisions of the second kind, and in the conditions of these experiments only collisions with the walls of the tube are effective. F. L. Usher.

Band spectrum of He_2 in stellar spectra. O. Struve and A. Christy (Astrophys. J., 1930, 71, 277—282).—An examination of the spectrum of 88 γ Pegasi shows that whilst several coincidences are present, the band spectrum of the helium molecule is not sufficiently strong to appear in this star. L. S. Theobald.

Series relationships in Be I. R. F. Paton and R. E. Nusbaum (Physical Rev., 1929, [ii], **33**, 1093; cf. A., 1929, 226).—With higher resolution and a low-pressure arc the beryllium line at 4553·07 Å. has been resolved from the barium line at 4554 ± 1 Å. in the furnace spectrum of beryllium. L. S. Theobald.

Arc spectrum of carbon C I. F. Paschen and G. Kruger (Ann. Physik, 1930, [v], 7, 1—8).—C I spectral lines and series have been measured. The fundamental $(2p)^2\,{}^3P_{2,1,0}$ term is the limit of three series of strong lines: from the terms $2pns^3P_{2,1,0}$ there result a series of PP' groups of which the first three only are fully resolved; the terms $2pnd^3P_{3,2,1}$ yield narrow groups of strong lines of which the first three are resolved, the remainder being characterised by diffuse lines; the terms $2pnd^3P_{2.1,0}$ yield with the fundamental term partly resolved groups, each value of n corresponding always with three adjacent groups of lines in the sequence 1, 2, 3, from the longer wavelengths. Most members of series 2 have been observed, and the value of $(2p)^2\,{}^3P_2$ is $90{,}836\pm10$ (11,212 volts). The fundamental term $(2p)^2\,{}^1D_2$ is the limit of at least four series, viz., $2pnd^1F_3$, $2pnd^1P_1$, $2pnd^1D_1$, and $2pns^1P_1$; a term nX, in which $n=5$, is probably the continuation of the first of these, and gives very strong lines which for a given value of n lie close together in the sequence 1, 5, 2, 3, 4 from the longer wave-length region. The third of these four series yields the strongest lines, and gives for $(2p)^2\,{}^1D_2$ the value $80{,}686\pm3$ (99,588 volts). The fundamental term $(2p)^2\,{}^1S_0$ is the limit of a series having the terms $2pns^1P_1$, from which the value of $(2p)^2\,{}^1S_0=69{,}231\pm3$ (85,449 volts). Of the series derived from the term $2pnd^1P_1$, only the first line, $n=3$, has been observed. Fowler and Selwyn's values (A., 1928, 450) of -139 and -626 for the triplet and single terms are corrected. H. F. Gillbe.

Metastable states of atomic nitrogen. K. T. Compton and J. C. Boyce (Physical Rev., 1929, [ii], **33**, 115).—The analysis of near-visible lines made by Kiess has been extended to give almost the entire spectral structure predicted by the Hund theory. The "ground" state $2p^4S$ has a term value of about 117,345; the next lowest states, which are metastable, are $2p^2D_{2,3}$ and $2p^2P_{1,2}$ about 98,143 and 88,537, respectively. The energies of the active nitrogen states are 2·37 and 3·56 volts, which are the energies of the entities in active nitrogen found necessary by Kaplan and Cario to account for the production of the afterglow by excitation of the ^3S metastable molecules, and for excitation of other spectra in active nitrogen. L. S. Theobald.

Active nitrogen. J. Kaplan (Physical Rev., 1929, [ii], **33**, 638).—The fact that the bands arising on the B_{11} level are the most intense in the nitrogen afterglow can be accounted for by the recombination between two normal atoms to form a metastable molecule possessing 9·1 volts and then the subsequent excitation of this molecule by an atom in the ^2D state. L. S. Theobald.

Decay of the spectrum of the afterglow of nitrogen mixed with argon. A. G. Worthing and H. E. Way (Physical Rev., 1929, [ii], **33**, 1086).—Three spectrograms of the afterglow in succeeding stages have been obtained with periodic discharges in a mixture of 99% of argon and 1% of nitrogen at about 2 cm. pressure. The early stage shows a maximum in the orange sequence for the $8\longrightarrow4$ vibrational transition and in the red sequence for the $8\longrightarrow5$ and the $4\longrightarrow1$ transitions; the third stage shows maxima for the $11\longrightarrow7$, $9\longrightarrow5$, and $9\longrightarrow6$ transitions, whilst the second stage shows an intermediate shift. With time the afterglow spectrum appears to approach that in pure nitrogen. L. S. Theobald.

O and N spectra in the extreme ultra-violet. D. C. Sheldon (Physical Rev., 1929, [ii], **33**, 267).—Using the method of grazing incidence with a concave speculum metal grating, spectra for O and N have been observed down to 225 Å. L. S. Theobald.

Red coronal line in oxygen. J. J. Hopfield (Nature, 1930, **126**, 846).—The nebular lines 6300 and 6364 Å., as well as the strong line 6374·29 Å., have been identified in the spectrum of oxygen. The last line appears to be identical with the red coronal line 6374·2. This is supported by the fact that the line occurs in an isolated position in the oxygen spectrum only when lines of O I are present. Strong evidence of the presence of oxygen in the sun's corona is thus afforded. L. S. Theobald.

Band spectrum of fluorine. H. G. Gale and G. S. Monk (Physical Rev., 1929, [ii], **33**, 114—115).—The bands consist of P, Q, and R branches with alternate weak and strong lines in each branch; the Q branch is about twice as strong as the other two. The bands at $v=16{,}378{\cdot}8$, 17,439·5, 15,337·6, 17,075·0, and 18,550·0 have been analysed either partly or completely. There are strong perturbations in all bands in both frequency and intensity. The bands are probably of the $^1S\longrightarrow{}^1P$ type. The ratio of intensity of weak to strong lines is about 1 : 3, indicating that the fluorine atom possesses a nuclear spin of one half. L. S. Theobald.

Excitation functions in the neon spectrum. W. Hanle (Z. Physik, 1930, **65**, 512—516).—The excitation functions of some red and yellow neon lines were measured. The large variation of intensity distribution with pressure is discussed. A. B. D. Cassie.

Discharges in neon. P. Johnson (Phil. Mag., 1930, [vii], **10**, 921—931).—The relationship between *E.M.F.* and current in high-frequency discharges through neon has been determined by Townsend and

Nethercot's method (A., 1929, 482). As in the case of nitrogen, the mean force in the luminous column of a high-frequency discharge in neon is independent of the current in the tube for 1—10 milliamp. and of the wave-length of the oscillator from 30 to 120 m. The force in the uniform column of a direct-current discharge has substantially the same value as the above. The mean force X in the high-frequency discharge increases linearly with the pressure p above values of the latter of 10 mm., but at a little below this value the ratio X/p increases with fall of pressure. Addition of 1% of helium increases by 6 or 7% the electric force required to maintain the current. Neon can be satisfactorily tested for impurities by observing the spectrum of a high-frequency discharge in a wide tube containing the gas at high pressure.

M. S. Burr.

Extreme ultra-violet spectra of neon and argon excited by electrodeless ring discharge. K. T. Compton, J. C. Boyce, and J. L. Nickerson (Physical Rev., 1929, [ii], **33**, 1085; cf. A., 1929, 1359).—The electrodeless discharge brings out higher stages of excitation than do the controlled electron impacts. The ionisation potential found for Ne III is 511,700 ν and the higher limits occur at 545,350 and 566,517, approximately. Metastable singlet states are about 22,300 and 52,250 above the low triplet state. Two triplet series of three members each and one singlet series of two are found together with the low quintuplet state and the low states associated with the higher limits. All predicted $a-b$ lines are found. The ionisation limit of A III is 329,476 ν. The $a-b$ lines of Ne IV and A IV are strong, whilst those of Ne V or A V are too weak to be identified.

L. S. Theobald.

New terms in the spectrum of Al I. R. F. Paton and W. D. Lansing (Physical Rev., 1929, [ii], **33**, 1099; cf. A., 1929, 1206).—The vacuum furnace spectrum of aluminium gives lines of the sharp and diffuse series in both absorption and emission; in addition, the well-known lines 3057·15 and 3050·07 appeared in emission at the same temperature as the first lines of the diffuse series. These lines, together with a weaker one at 3060·20, are assigned to the transition $3^2P-3p^1\,{}^2D$, where the latter term arises from the configuration $3s3p^2$. A pair observed by Sawyer and Paschen at 1910·91 and 1906·57 are assigned to the transition $3^2p-3p^1\,{}^2S$. The term values, based on the ${}^1S_0$ state of the Al II core, are $3p'\,{}^2D_3=15{,}468$, $3p'\,{}^2D_2=15{,}504$, and $3p'\,{}^2S_1=-4166$.

L. S. Theobald.

New resonance series of sulphur vapour. J. Genard (Bull. Acad. roy. Belg., 1930, [v], **16**, 923—930).—The fluorescence spectrum of sulphur vapour, emitted at 600° and 2 mm. pressure, when excited by a copper arc, has been studied. The series excited by the lines 3248, 3274, and 3287 Å. consist of 21, 17, and 17 lines, respectively, of ranges 3032—5086, 3060—4567, and 3069—4602 Å. The lines of the second series appear to be triplets.

C. W. Gibby.

Relative intensities of lines in a generalised multiplet of Ti II. H. Engwicht (Physical Rev., 1929, [ii], **34**, 541).—Measurements have been made on the multiplets $a^4P'-a^4D'[(3d)^2]3d-4p$ of Ti II and $a^2P'-a^2D'$ together with their inter-system combination lines, many of which are strong. The quadruplet, doublet, and their inter-system lines form a generalised multiplet. When an excitation correction corresponding with 3500° Abs. is applied the total intensities of quadruplet to doublet have the theoretical ratio 2 : 1.

L. S. Theobald.

Spectra of trebly-ionised vanadium, V IV, and quadruply-ionised chromium, Cr V. H. E. White (Physical Rev., 1929, [ii], **33**, 286).—The neutral atoms of vanadium and chromium contain five valency electrons, $3d^34s^2$, and six valency electrons, $3d^54s$, respectively. The removal of three electrons $3d4s^2$ from vanadium and four electrons $3d^34s$ from chromium gives two isoelectronic systems V IV and Cr V, the lowest energy levels of which are represented by the two remaining electrons $3d^2$. The spectra from these two systems should resemble those of neutral calcium, Sc II, and Ti III, and extrapolations have led to the identification of 30 energy levels in both V IV and Cr V. The strongest lines arise from combinations between ${}^3P$, ${}^3D'$, ${}^3F$, ${}^1P$, ${}^1D'$, ${}^1F(3d4p)$ and $3D$, ${}^1D(3d4s)$, and ${}^1S$, ${}^3P'$, ${}^1D$, ${}^3F'$, ${}^1G(3d)^2$. The voltages necessary to remove one $3d$ electron from the normal state ${}^3F_2(3d)^2$ of V IV and Cr V to the normal state ${}^2D_2(3d)$ of the atoms again ionised are approximately 48·2 and 72·4 volts, respectively.

L. S. Theobald.

Probe and radiation measurements in the normal copper arc. W. B. Nottingham (Physical Rev., 1929, [ii], **33**, 280).—With an increase in arc current from 2·5 to 6·0 amp., the electron temperature fell from 19,000° Abs. to 15,500° Abs. The average velocity is probably controlled by the electron transition in the copper atom from the metastable D level to the 2^2P level, involving energies of 2·14 and 2·4 volts.

L. S. Theobald.

Multiplets in the spectrum of doubly-ionised copper, Cu III. R. C. Gibbs and A. M. Vieweg (Physical Rev., 1929, [ii], **33**, 1092).—The lowest terms in the spectrum of Cu III arise from the configuration $3d^9$, and successively higher terms from the configurations $3d^84s$ and $3d^84p$. Quadruplets and doublets, as well as intercombinations, arising from the transition $3d^84p$ to $3d^9({}^2D_{23})$ have been classified in the region of 800 Å.

L. S. Theobald.

Zeeman effect in the ZnH and CdH bands. W. W. Watson (Physical Rev., 1930, [ii], 36, 1134—1143).—The Zeeman effect in the ${}^2\Pi\longrightarrow{}^2\Sigma$ bands of ZnH at λ 4326 and CdH at λ 4509 with large ρ type doubling was investigated in detail for field strengths up to 30,400 gauss. Intensity relations among the twelve branches of each band are discussed. The ρ type doubling in the ${}^2\Sigma$ states is measured by the separation of the satellite and main lines having the same K values and is proportional to $K+\frac{1}{2}$ rather than to K. The positions and widths of the blocks of components for all the lines are computed from the quantum formulæ of Hill (cf. A., 1930, 265). Results are in good agreement with experimental data on a number of details unique to these bands, and are fully tabulated for a field of 16,400 gauss.

N. M. Bligh.

Fine structure of zinc lines in the visible and ultra-violet regions. W. Mohammed and P. N. Sharma (Phil. Mag., 1930, [vii], **10**, 916—921).—Eighteen zinc spectral lines have been carefully examined and the following found to possess one satellite: λ 4722·26, 3345·13, 3303·03, 3075·99, 3035·93, and 2770·94. The line λ 4298·54 has two satellites, one strong and the other very faint and diffuse. M. S. Burr.

Spectrum of γ Geminorum. S. Albrecht (Astrophys. J., 1930, **72**, 65—97).—H_γ is the strongest line, followed by Mg^+ 4481; 276 lines are due in nearly equal proportions to ionised and neutral atoms, the former including Fe^+, Ti^+, Cr^+, Sc^+, Ce^+, Zr^+, Sm^+, Rb^+, V^+, Mo^+, Mn^+, Mg^+, and Pr^+ and the latter Fe, Ti, Cr, Mn, Ca, V, and Ni. Other elements have also been identified. There appear to be no appreciable relative displacements between lines due to neutral and those due to ionised atoms. L. S. Theobald.

Second spark spectrum of krypton. D. P. Acharya (Indian J. Physics, 1930, **5**, 385—405).—The spark spectrum of krypton has been explored in the region 2500—1900 Å. Previously-measured lines of the Kr^{++} spectrum are classified and together with the newly-measured lines are given in tabular form. The ionisation potential of Kr^{++} is calculated to be 31·4 volts. J. W. Smith.

Structure of the spectra of doubly- and trebly-ionised zirconium. C. C. Kiess and R. J. Lang (Bur. Stand. J. Res., 1930, **5**, 305—324).—The spectral lines of Zr III and Zr IV have been photographed and analysed, and the terms found accord fully with the quantum theory; the spectra resemble closely the corresponding Ti III and Ti IV spectra. The Zr IV spectrum is a doublet spectrum resulting from the migration of a single 4_3 electron. The value of the fundamental $4^2D_{3,2}$ term, derived from a series of S terms, is 274,067 cm.$^{-1}$, corresponding with an ionisation potential of 33·83 volts. The Zr III spectrum is derived from the interaction of two 4_3 electrons, and exhibits singlet and triplet systems; sequences of ^1D and ^3D terms, resulting from one electron in an n_1 orbit and one in a 4_3 orbit, yield for the fundamental term $^3F_2$ 194,441 cm.$^{-1}$, corresponding with an ionisation potential of 24·00 volts. The transition $4f \longrightarrow 4d$ is represented by multiplets which, like those derived from inter-system combinations, exhibit anomalous intensities.

H. F. Gillbe.

Polarisation of cadmium resonance radiation $1^1S_0-2^3P_1$, 3261 Å. A. Ellett (Physical Rev., 1929, [ii], **33**, 124).—This line is completely polarised in the absence of a magnetic field and also in a field parallel to the electric vector of the exciting, plane polarised light. The mean life of the 2^3P state of cadmium is $2·30\times10^{-6}$ sec. L. S. Theobald.

Magnetic extinction of iodine fluorescence and its relation to predissociation phenomena. L. A. Turner (Z. Physik, 1930, **65**, 464—479).—The extinction of iodine fluorescence by a magnetic field and its dependence on the exciting wave-length were investigated. Both monochromatic light and light from a carbon arc passed through a spectrometer were used. Passing from long to shorter wave-lengths, extinction begins suddenly and then gradually diminishes; it appears almost as predissociation in the vibrational degree of freedom. This phenomenon is fully discussed on Bonhoeffer's theory of predissociation, and appears to fit in with this scheme. The conception of predissociation in the vibrational degrees of freedom also explains Norrish's results (A., 1929, 893) on the fluorescence and photochemical decomposition of nitrogen peroxide. A. B. D. Cassie.

Excitation of iodine fluorescence with monochromatic light. L. A. Turner (Z. Physik, 1930, **65**, 480—488).—The determination of the quantum numbers (vibrational and rotational) defining the excited state due to absorption of a given monochromatic radiation is fully discussed. The examples of the two yellow mercury lines at 5771·2 and 5792·3 Å., the neon line at 5852·5 Å., and the cadmium line at 5085·9 Å. are worked out. A. B. D. Cassie.

Interference measurements in the first spectra of krypton and xenon. C. J. Humphreys (Bur. Stand. J. Res., 1930, **5**, 1041—1055; cf. A., 1929, 1118).—New determinations of the stronger arc lines of the krypton and xenon spectra in the region 4000—9000 Å. have been made with the Fabry–Perot interferometer. Accurate relative values of all the $1s$, $2p$, and $3p$ terms of the krypton spectrum have been established, the average deviation of the calculated term combinations from the observed wave-numbers being 1 in 20×10^6. In the xenon spectrum all the $1s$, $2p$ (except $2p_{10}$), and $3p$ terms, and four of the $4p$ terms have been redetermined. Nearly 75% of the combinations permitted by the selection principle have been observed. Since the infra-red combinations which are photographically inaccessible can now be predicted accurately, it is suggested that their wave-lengths should be employed as standards in the infra-red region. Fine structure has not been observed with any of the krypton lines, and the intensities of any satellites which may exist are too small to influence the wave-lengths; five of the xenon lines show satellites. The "pressure effect" of McLennan and Quinlan (Trans. Roy. Soc. Canada, 1929, **24**, III, 1), which causes a change of wave-length of the xenon lines as the emission tube ages, appears to be due to experimental error; under conditions required to excite the spark spectrum a change of wave-length of the arc lines of both elements has been observed, and is ascribed to the Stark effect.

H. F. Gillbe.

Characteristics of the electric furnace spectra of europium, gadolinium, terbium, dysprosium, and holmium, 3900—4700 Å. A. S. King (Physical Rev., 1929, [ii], **33**, 540).—The separation of lines arising from neutral and ionised atoms, respectively, and the temperature classification of both groups have been accomplished. Groups of strong low-temperature lines were noted, especially for europium, dysprosium, and holmium, and the furnace emitted strongly many lines which are faint in the arc and were unidentified hitherto. Hyperfine structure was distinguished for many lines, usually ionised, in the spectra of europium, terbium, and holmium; in the

graduated spacing of components these often resemble the lines of ionised praseodymium.
L. S. Theobald.

Spectral terms of platinum, and classification. P. J. Ovrebo (Physical Rev., 1929, [ii], **33**, 1098; cf. A., 1929, 1352).—Forty-nine new terms have been found for platinum; of these 17 are low, 12 intermediate, and 19 upper levels. Combinations with previously-known levels give 250 lines, of which 150 are newly described. Combinations between low and high levels have been found. The term 29,600·8 combines with high, intermediate, and low terms; 31,900·5 combines with low as well as other intermediate terms, whilst 44,760·9 acts as both intermediate and high levels. New levels have been classified.
L. S. Theobald.

Origin of the bands in the spectrum of mercury vapour. S. Mrozowski (Physical Rev., 1930, [ii], **36**, 1168—1171).—A reply to the arguments of Rollefson (cf. A., 1930, 970). New observations are reported of shaded absorption bands at 2267 and 2247 Å.
N. M. Bligh.

Electro-optical modification of light waves. L. H. Stauffer (Physical Rev., 1930, [ii], **36**, 1352—1361).—Broadening of the satellites of the mercury green line λ 5461 was observed when the light passed between the plates of a Kerr cell containing nitrobenzene, on which was impressed a varying *E.M.F.* The broadening was in agreement with the classical and quantum theories of dispersion, and increased rapidly with the oscillator voltage.
N. M. Bligh.

Optical constants of solid mercury. R. S. Baldwin (Physical Rev., 1929, [ii], **33**, 1072).—The refractive index for the solid state is at least 10% greater than that for the liquid for the wave-lengths used (5790—5769, 5460, and 4358 Å.). The absorption coefficient is practically unchanged.
L. S. Theobald.

Continuous spectrum of mercury. W. N. Thornton and W. H. Crew (Physical Rev., 1929, [ii], **33**, 1072; cf. A., 1929, 1).—Photographs with a small quartz spectrograph of the continuous spectrum of mercury support the view that it is due to the recombination of electrons with molecules or with atoms held in molecular linking. A low current and voltage, high-frequency, condensed discharge in the vapour between two liquid mercury surfaces gave two strong bands with maximum intensities at approximately 4500 and 3300 Å. and four weak lines 5461, 4358, 4047, and 2536 Å.
L. S. Theobald.

Mercury spectrum by high-voltage electrodeless discharge. O. Stuhlman, jun., and M. W. Trawick (Physical Rev., 1929, [ii], **33**, 287—288).—Spectra of the electrodeless discharge through a capillary and of the ring discharge in a 12-cm. spherical bulb have been compared with that from a quartz mercury vapour lamp. The spectra of the discharge through the capillary and of the ring are identical, with spark and arc lines about equal in number. No continuous spectra were observed. The frequencies of $1s-mp_1$ up to $m=17$ have been classified.
L. S. Theobald.

Polarisation phenomena in the gradual excitation of the fluorescence of mercury. E. F. Richter (Ann. Physik, 1930, [v], **7**, 293—328; cf. A., 1929, 741).—The colour effects obtained in the gradual excitation of fluorescence in mercury vapour by polarised light from a quartz mercury arc have been examined spectroscopically in relation to the direction of an applied magnetic field. The results are discussed theoretically. Measurements of the degree of polarisation confirm theoretical expectations qualitatively. Under conditions where the line 4047 Å. should be completely polarised the maximum polarisation observed was 80%, the discrepancy being attributed to fine structure. Ultra-violet lines showed similar behaviour. The life-period of the excited atoms, determined by two independent methods, varied from about 10^{-9} to 10^{-7} sec., that of λ 5461 Å. being four times as great as that of the other triplet lines. In all the experiments nitrogen was present in the mercury vapour.
F. L. Usher.

Spectrum of doubly-ionised thallium. P. Pattabhiramayya and A. S. Rao (Indian J. Physics, 1930, **5**, 407—416).—The spark spectrum of thallium in air and in hydrogen at different pressures and under varying conditions of excitation has been re-examined. The results have been combined with those of previous investigators in a systematic classification of the Tl^{++} spectrum. In accordance with the theory of Hund, the spectrum consists of two parts, an ordinary doublet spectrum and a quadruplet–doublet spectrum the deepest term of which is a metastable ^2D term which is inverted and very low. The two types of ion on which these two spectra are built are (d^{10}) and (d^9s), which are spectroscopically terms of the type ^1S and ^3D and ^1D.
J. W. Smith.

Spark spectra of bismuth, Bi II and Bi III. Evidence of hyperfine structure. J. C. McLennan, A. B. McLay, and M. F. Crawford (Proc. Roy. Soc., 1930, **A**, **129**, 579—588).—Progress has been made in the identification of the multiplet term structure of Bi II and Bi III from a study of the frequencies of the wave-lengths in (*a*) the spectrum of a condensed discharge in heated bismuth vapour (λ 7050—2000 Å.), (*b*) that of a condensed spark between metallic terminals in hydrogen (λ 2000—1340 Å.), and (*c*) that of a hot spark between metallic terminals in a vacuum (for wave-lengths below 1340 Å.). Evidence of hyperfine structure was apparent in the spectra, the effect in a few cases being of large magnitude.
L. L. Bircumshaw.

Occurrence of addition and subtraction potentials of 1·4 volts in the mercury atom. R. G. Loyarte (Physikal. Z., 1930, **31**, 929—939; cf. this vol., 18).—The origin of certain optical lines of the mercury spectrum can be explained by adding to or subtracting from the value of the potential energy of a line of known origin 1·4 volts or low multiples of this value. The physical significance of the procedure is discussed. The good agreement between observed and calculated values is shown by a number of tables.
W. R. Angus.

Dependence of photo-electric properties of cæsium on its adsorption on salt layers. J. H. de Boer and M. C. Teves (Z. Physik, 1930, **65**, 489—505).—Experiments on the adsorption of sublimed alkali metals by thin sublimed salt layers are described. The surface ions of the thin salt layer induce dipoles in the metal molecules or atoms, and so form a firmly-adsorbed layer. This process recurs, and metal layers of one, two, or more atoms thick are obtained. The polarisation greatly affects light absorption; thus iodine on calcium fluoride is brown, whilst cæsium is blue. Increasing thicknesses of cæsium displace the absorption towards the violet. Cæsium layers adsorbed on calcium or barium fluoride show a photo-electric sensitivity (to white light) which increases to a maximum with increasing thickness, then falls to a constant value. The maximum of the wave-length–photo-electric sensitivity curves, and the long wave-length limit are displaced towards the violet with increasing thickness of the metal layer. Pure cæsium shows a photo-electric sensitivity of 0·17 μ amp. per lumen for white light, whilst cæsium adsorbed on barium or calcium fluoride may show 1·6 μ amp. per lumen. In similar experiments with cæsium oxide replacing barium fluoride the limiting wave-length is displaced towards the red to 1·15 μ. A. B. D. CASSIE.

Influence of gases on photo-ionisation of cæsium by line absorption. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1930, **5**, 399—410).—The influence of nitrogen, hydrogen, helium, and argon on the photo-ionisation of cæsium vapour by line absorption has been studied by space-charge measurements. Nitrogen reduces the ionisation at all wave-lengths greater than 3200 Å., and at constant cæsium vapour pressure $E_0/\Delta E$, where E_0 is the probability of ionisation in absence of a foreign gas and ΔE is the change of the probability produced by the gas at pressure p, appears to be a linear function of $1/p$; the same obtains for helium, except at pressures above about 2 mm. The ionisations of the states from $4P$ to $8P$ are reduced by nitrogen to about the same extent, whereas helium increases the ionisation of the $4P$ state and decreases that of other lines. The influence of nitrogen increases with fall of the cæsium pressure on account of the change of the life of the excited state. The theoretical significance of the results is discussed with especial reference to the types of transition which occur. H. F. GILLBE.

Effect of systematic surface treatment on the photo-electric emission from metals. R. F. HANSTOCK (Phil. Mag., 1930, [vii], **10**, 937—944).—An investigation has been made of the photo-electric emission from metal surfaces in a vacuum at intervals during the process of polishing, beginning with the surface in an annealed state. The polishing was carried out by rubbing with a metal harder than the one under consideration. The curves obtained by plotting degree of polish against photo-electric current indicate that the current is increased when the metal surface is rubbed, and that the increase is approximately a linear function of the number of rubs until just before a constant maximum value is reached. The ratio of the current after polishing to the current from the annealed surface shows no regular dependence on the pressure of gas in the tube. The effect is obtained with radiation of a restricted wave-length as well as for the full spectrum. The increased activity due to rubbing does not disappear, even after several days, but by heating to above 150° the metal can be reduced to its less active state. The results are reproducible by successive heating and polishing, and seem to be best explained as due to the modified layer of thickness 50—500 μ known to be produced at the surface of a metal by rubbing, and restored to its original state by heat. M. S. BURR.

Origin of the photo-electrons in the copper–cuprous oxide photo-cell. W. SCHOTTKY (Physikal. Z., 1930, **31**, 913—925).—The photo-decay of the cell, copper plate–cuprous oxide layer–auxiliary electrode, with increasing distance between electrodes follows an exponential law. The decay distance is a few mm., and can be calculated from resistance measurements. The photo-effect is due to a unidirectional layer at the surface of the copper plate, the photo-electrons being liberated at the copper–cuprous oxide boundary after the light has penetrated the oxide layer. J. E. MILLS.

New kind of photo-cell. B. LANGE (Physikal. Z., 1930, **31**, 964—969; cf. A., 1930, 391).—The behaviour of the new photo-cells is compared with that of the crystal detector. Such comparison is made possible by the fact that in each there are two materials in the crystal detector, the crystal and the needle, whilst in the new photo-cell there is a metal plate and a unidirectional layer of a unipolar half-conductor through which liberated photo-electrons are made to pass. New copper–cuprous oxide photo-cells are described and discussed. The spectral sensitivity of these cells is selective and the spectral range for which a cell is sensitive depends on the thickness of the unidirectional layer of cuprous oxide. The industrial application of such photo-cells is considered. In conjunction with a microphotometer these cells can be used for measuring the absorption of substances within the limits of the spectral range of their sensitivity. A differential photo-cell has been devised on the same principles. W. R. ANGUS.

Variation with temperature of the unidirectional layer photo-electric effect in a copper–copper oxide cell. H. TEICHMANN (Z. Physik, 1930, **65**, 709—713).—The copper–copper oxide cell is fully described. Measurements of the photo-electric emission at different temperatures show that the cell has a negative temperature coefficient. A. B. D. CASSIE.

Preparation of photo-electric cells with thin films of lithium as the photo-active material. H. E. IVES (Physical Rev., 1929, [ii], **33**, 1081—1082).—A method for preparing thin films of lithium on a plate of tungsten, avoiding the usual difficulties of handling lithium in a vacuum, is described. The film at one stage in its formation is sensitive to red light at 6708 Å. L. S. THEOBALD.

Photo-*E.M.F.* in single crystals of selenium. R. M. HOLMES and N. L. WALBRIDGE (Physical Rev., 1929, [ii], **33**, 281).—With thin lamellar single crystals of selenium the photo-*E.M.F.* is greater than that found for acicular crystals (A., 1929, 1371). When the radiation from a tungsten lamp passes through one of two platinum films sputtered on each of the two parallel faces of the crystal, electrons flow from selenium to platinum at the illuminated contact. The photo-current increases with an increase in illumination, reaching the value 5·5 microamp. for 4 lumens per cm.^{2} L. S. Theobald.

Photo-electric effect of liquid tin and two of its allotropic modifications. A. Goetz (Physical Rev., 1929, [ii], **33**, 265).—The photo-electric emission of tin has been measured from the ordinary temperature up to 550°. The red limit of emission is different for the liquid and the crystalline phases. The photo-electric threshold changes at the transition tetragonal ⟶ hexagonal tin. The photo-electric thresholds are liquid tin (232—550°), 2925±10 Å.; hexagonal tin (203—232°), 2820±10 Å.; and tetragonal tin (70—150°), 2740±10 Å. The change tetragonal ⟶ hexagonal tin is slow and occurs between 203° and 100°. L. S. Theobald.

Infra-red sensitivity of cæsium oxide photo-electric cells. J. W. Ballard (J. Opt. Soc. Amer., 1930, **20**, 618—623).—The maximum sensitivity of cæsium oxide photo-electric cells lies between 7500 and 8000 Å., and the minimum at 5500 Å. The sensitivity extends into the infra-red almost to 12,000 Å. C. W. Gibby.

Departure from Einstein's photo-electric equation with certain alkali metal films. W. B. Nottingham (Physical Rev., 1929, [ii], **33**, 1081).—The long wave-length limit is probably greater than 8400 Å. for sodium and 9600 Å. for potassium, and departures from Einstein's photo-electric equation have been found for thin films of both metals near their long wave-length limits. L. S. Theobald.

Ionisation of helium, neon, and argon by electron impact. P. T. Smith (Physical Rev., 1930, [ii], **36**, 1293—1302).—In view of the divergencies of existing data on the efficiency of ionisation by electron impact in gases, the total number of positive charges produced per electron path at constant pressure was determined as a function of the energy of the impacting electrons up to 4500 volts in helium, neon, and argon, the respective maximum efficiencies being found as 1·256 at 110, 3·008 at 170, and 13·01 at 88 volts. An empirical relation is given for the efficiency of ionisation of helium for energies greater than 60 volts. Results are not in agreement with those of other investigators (cf. Compton and Van Voorhis, A., 1926, 769; Hippel, A., 1929, 228; Bleakney, cf. following abstract). N. M. Bligh.

Ionisation potentials and probabilities for the formation of multiply-charged ions in helium, neon, and argon. W. Bleakney (Physical Rev., 1930, [ii], **36**, 1303—1309).—Using the mass-spectrograph method previously described (cf. A., 1929, 970; 1930, 969) the multiply-charged ions in helium, neon, and argon were investigated. The He^+ ion was strong, but only faint evidence was found for the formation of He^{++}. Neon gave Ne^+, Ne^{2+}, and Ne^{3+} as the result of single-electron impacts at minimum electron energies of 21·5, 63, and 125 volts, respectively. Curves are given for the efficiency of ionisation as a function of the electron velocity and show maxima for Ne^+ and Ne^{2+} at 2·75 and 0·16 for 150 and 250 volts, respectively. In argon, the ions A^+, A^{2+}, A^{3+}, A^{4+} and A^{5+}, were observed, with ionisation potentials for the first four of 15·7, 44, 88, and 258 volts, respectively, for single impact, and efficiency maxima of 11·4, 1·1, and 0·04 at 50, 115, and 250 volts for A^+, A^{2+}, and A^{3+}, respectively (cf. preceding abstract). There were indications of critical potentials above the ionisation potentials for Ne^{3+} and A^{4+}. N. M. Bligh.

Ionisation of cæsium vapour by light of frequency greater than the series limit. E. O. Lawrence and N. Edlefsen (Physical Rev., 1929, [ii], **33**, 265; cf. A., 1929, 1121).—The ionisation of cæsium vapour by light of wave-length from the series limit to 2200 Å. has been studied. The ionisation efficiency of the light falls rapidly from the limit to shorter wave-lengths except for wave-lengths near 2536 Å., where it is of the same order of magnitude as that of the series limit. The anomalous ionisation by light of wave-length 2536 Å. is probably due to a trace of mercury vapour. L. S. Theobald.

Optical excitation function of helium. W. C. Michels (Physical Rev., 1930, [ii], **36**, 1362—1374; cf. Hanle, A., 1929, 1116; Elenbaas, A., 1930, 387).—The excitation function of helium for electrons with energies between the excitation potentials and 100 volts was investigated, using a special discharge tube, and a method designed to eliminate collisions of the second kind, ionisations, and recombinations, to give a linear dependence of intensity on current or pressure, and to allow a determination of the electron velocity distribution curve. Intensity–voltage curves are given for the singlet and triplet system of helium, correcting existing data, and allowing the true optical excitation function values to be obtained; these are plotted against electron energies, and show that each line has maximum excitation probability at or near the excitation potential, the probability falling above this value, but more rapidly for the triplet than for the singlet system. N. M. Bligh.

Electro-osmose theory of the electrolytic rectifier. A. Dobiaš (Z. Physik, 1930, **65**, 859; cf. A., 1930, 999).—Polemical against Müller, who claims priority (A., 1929, 770; 1930, 165). A. J. Mee.

Thermionic emission of oxide-coated cathodes containing a Ni–Ba alloy core. N. C. Beese (Physical Rev., 1930, [ii], **36**, 1309—1313; cf. Reimann, A., 1930, 657; Lowry, *ibid.*, 973).—Comparisons were made of the electron emission of an alloy containing 0·15% Ba, and of pure nickel, and of the alloy after removal of the barium content. Curves of electron emission plotted against time show the marked influence of the added barium on increased emission. N. M. Bligh.

Diffusion of ions of salts into aluminium. Cichocki (Compt. rend., 1930, **191**, 841—842; cf. A., 1929, 482).—A tube of aluminium, 2 mm. internal and 4 mm. external diameter, filled with nickel chloride was drawn out until its external diameter was 0·83 mm., and placed in the centre of a copper tube 20 mm. in diameter, the whole being enclosed in a vacuous glass tube. A *P.D.* of 80 volts was maintained between the copper and aluminium tubes, and the latter heated electrically to 600°. No negative thermionic current passed, but the positive emission increased with time for 60 min., and then rapidly decreased. This is attributed to absorption of the salt by the metal followed by emission of ions into the vacuous space around the tube.

C. A. SILBERRAD.

Shot effect of the emission from oxide cathodes. H. N. KOZANOWSKI and N. H. WILLIAMS (Physical Rev., 1930, [ii], **36**, 1314—1329; cf. A., 1929, 736).—An apparatus for the investigation of the fluctuations associated with the emission from barium–strontium oxide cathodes, especially in the space-charge region, is described. The presence was verified of positive ions, which, moving in an electron space charge, cause abnormally high shot fluctuations in an aperiodic circuit at high amplifier frequencies. The characteristic fluctuations associated with the emission from oxide cathodes have been reproduced in a special vacuum tube in which positive ions from an independent Kunsman potassium ion emitter interact with the electron space charge about a metal emitter, indicating a similar process in the emission from barium–strontium oxide cathodes. Some results are given of the shot effect of films evaporating from a tungsten wire. N. M. BLIGH.

Abnormal shot effect of ions of tungstous and tungstic oxide. J. S. DONAL, jun. (Physical Rev., 1930, [ii], **36**, 1172—1189).—The formation of positive ions when oxygen attacks a hot tungsten filament is discussed. The ions consist of a mixture of tungstous and tungstic oxides. The abnormal shot effect when these positive ions are accelerated through the dense electron space-charge region surrounding the filament and drawn to a collecting electrode in series with a tuned shot circuit was investigated, using the apparatus of Williams and Vincent (cf. A., 1927, 85). Assuming that the shot voltage arises from fluctuations in the inter-electrode capacitance of the tube, caused by variations of thickness of the electron sheath with penetration by the ions, an expression for the resulting mean square-shot voltage is deduced, in good agreement with experiment. When positive ions were trapped in the minimum of potential surrounding a hot cathode, an abnormal shot voltage resulted, varying inversely with the square of the resonance frequency of the tuned-shot circuit; an expression is obtained for the mean square-shot voltage, from which are deduced values of the average plate current increase, the number of electrons released by each positive ion, average time of trapping of the ions, and electron space-charge density in the minimum of potential, in good agreement with available data.

N. M. BLIGH.

Secondary radiation of solid elements in relation to the nature of the element and the hardness of the primary *X*-rays. E. VETTE (Ann. Physik, 1930, [v], **5**, 929—990; cf. Espe, A., 1929, 1122).—The emission of secondary electrons and characteristic radiation by elements from aluminium to bismuth was investigated, using strongly filtered impulse radiation from a tungsten anticathode. The results showed the increase in the velocity of the secondary electrons with increase in the hardness of the exciting radiation, and the decrease in velocity with increase in the atomic number of the element irradiated. For the characteristic radiation it was found that only that portion of the spectrum of the primary radiation that is shorter in wave-length than the characteristic radiation was effective, so that, with constant voltage, as the atomic number of the irradiated element increased the emission increased first to a maximum, and then decreased as the *K* absorption edge of the element passed through the spectrum of the exciting radiation, and finally increased again with increasing proximity to the *L* absorption edge. H. A. JAHN.

Distinction between contact-potential effects and true reflexion coefficients for low-velocity electrons. H. E. FARNSWORTH and V. H. GOERKE (Physical Rev., 1930, [ii], **36**, 1190—1194; cf. A., 1929, 1212).—A method is described for determining the apparent electron reflexion coefficient in two ways, with distinction between a contact potential and a true reflexion coefficient for very low-velocity electrons. Results indicate that for a carefully degassed copper target the true electron reflexion coefficient approaches zero with the primary voltage, and that the apparent increase in reflexion coefficient below about 1 volt is due to a change in the contact potential between the target and the surrounding electrodes, the increase for the copper specimen tested being about 1·2 volts. N. M. BLIGH.

Velocity distribution of secondary electrons from molybdenum. T. SOLLER (Physical Rev., 1930, [ii], **36**, 1212—1220).—Using the magnetic deflexion method with improved vacuum conditions, the velocity distribution curves of secondary electrons from a molybdenum target were investigated for primary electron velocities of 7·5—100 volts, and were similar to those for other metals, showing a broad low-velocity maximum of secondary electrons, and a sharp "reflected" peak, with measured velocity 2 volts less than the corresponding accelerating voltage, in agreement with contact potential considerations. Degassing at 850° produced only slight changes in the curves, whilst for 1250° a marked decrease in the low-velocity maximum and an increase in the height of the "reflected" peaks were found, both changes being ascribed to the degassing. The curves height of reflected peak–primary electron velocity show several maxima, the voltages corresponding with the critical potentials of molybdenum.

N. M. BLIGH.

Scattering of light by electrons. G. GLOCKLER (Physical Rev., 1929, [ii], 33, 116).—The scattering of light by fast electrons can be predicted from the principle of microscopic reversibility. The equation showing the change of wave-length for head-on collision between a quantum and a free fast electron is given. The interaction of visible light with fast electrons should modify the quantum. The mercury line 5461 Å. should show a change of 685 Å. when interacting with a 1000-volt electron in a head-on collision. L. S. THEOBALD.

Scattering of electrons by atomic fields. E. C. BULLARD and H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1930, **26**, 556—563).—Mathematical. The variation of the intensity of elastic scattering with velocity and angle of scattering is obtained by applying the Thomas–Fermi electron distribution to Born's approximate scattering formula (cf. Mott, A., 1930, 974). For heavy atoms the scattered intensity is shown to be a function of the electron mass, scattering angle, and atomic number of the scattering medium. This function is tabulated, and the range of validity of such values is discussed. Born's formula is inaccurate for electrons of less than 400 volts velocity, except for atoms of low atomic number. For high-velocity electrons an approximate expression is obtained for the angular distribution, allowance being made for screening by the extra-nuclear electrons.

N. M. Bligh.

Scattering of electrons by crystals and adsorbed gas films. H. J. Verweel and J. M. Bijvoet (Chem. Weekblad, 1930, **27**, 626—629).—A survey. H. F. Gillbe.

Optical determination of the sphere of action of atoms for electrons. L. S. Ornstein and A. M. van Dommelen (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 683—689; cf. Ornstein and Elenbaas, A., 1930, 392).—By using a mixture of helium and mercury, it is possible to extend the measurements of the effective diameters of atoms to electronic energies below the excitation potential. At 48·35° and 0·012 mm. pressure (mercury) the values of the active diameters of the helium and mercury atoms for 30-volt electrons are 8·2 and 63 cm.^{2}/cm.^{3}, respectively, in fair agreement with the values of Ramsauer and of Brode. O. J. Walker.

Attachment of free electrons to neutral molecules in air and oxygen. A. M. Cravath (Physical Rev., 1929, [ii], **33**, 266—267).—The fraction, *h*, of the collisions between electrons and neutral electrons which result in the formation of a negative ion has been measured over a wide range of field strength and pressure in air and in oxygen. In oxygen, *h* has a minimum at 0·9 volt average electronic energy, whilst at constant energy, pressure has little effect. In air, *h* rapidly increases as the electronic energy falls below 0·9 volt, and varies rapidly with pressure. Proof of the permanence of the negative ions in weak fields, and evidence of the detachment of electrons from negative ions in high fields, were also obtained.

L. S. Theobald.

"Anomalous dispersion" of electron waves by nickel. C. J. Davisson and L. H. Germer (Physical Rev., 1929, [ii], **33**, 292—293).—The dispersion curve for nickel has a discontinuity near 1·3 Å, which suggests optical anomalous dispersions.

L. S. Theobald.

Polarisation of electrons. G. P. Thomson (Nature, 1930, **126**, 842).—The difference in the intensity of a beam of electrons twice reflected from gold surfaces observed by Rupp (A., 1930, 392) could not be confirmed. L. S. Theobald.

Behaviour of methane molecules and argon atoms in collisions with very slow electrons. H. L. Brose and J. E. Keyston (Nature, 1930, **126**, 806—807).—Using Townsend's diffusion method, the absolute value of the effective cross-section, *Q*, of methane molecules is found to be low, like that of argon. The curves obtained by plotting *Q* against voltage$^{1/2}$ closely resemble each other in both cases, and for methane the minimum value of *Q* is 4·3 cm.^{2}/cm.^{3} at a velocity $0{\cdot}52V^{1/2}$, but the similarity does not mean that the molecule of methane behaves in collisions with slow electrons like the atom of argon. The use of Townsend's method for investigating the collisions of gases is defended. L. S. Theobald.

Search for radiation accompanying the scattering of comparatively slow electrons at the surface of incandescent solids. E. Rudberg (Proc. Roy. Soc., 1930, **A**, **129**, 652—656).—Experiment shows that there is no appreciable radiation emitted in the visible region and the ultra-violet above 2300 Å., under the conditions for which the characteristic energy losses suffered by electrons scattered from incandescent solids have been found to occur.

L. L. Bircumshaw.

Energy losses of electrons in nitrogen. E. Rudberg (Proc. Roy. Soc., 1930, **A**, **129**, 628—651).—Measurements have been made, with a greater accuracy than those of previous investigators, of the energy given up by electrons at inelastic impacts in nitrogen under such conditions that no appreciable amount of multiple collisions occurs. Only collisions for which the resulting deflexion of the colliding electron from the original line of flight is very small can be studied with the apparatus used. The method of velocity analysis adopted is similar to that of Harnwell (A., 1929, 619). Seven maxima have been measured in the distribution curves in the region corresponding with individual energies 0—30 volts less than the primary voltage. The smallest energy loss observed is attributed to collisions with the electrodes. The strongest maximum observed indicates a loss of 12·78 volts, and, together with a further prominent maximum, is interpreted as being due to excitation of the first singlet levels of the nitrogen molecule. Two further maxima are probably related to similar unknown levels. From the fact that a sensitive test for a characteristic energy loss connected with the ionisation of the nitrogen *K* level gave negative results, it is concluded that the probability for the colliding electron to produce the emission of a *K* electron is small compared with that of displacing an outer electron, for the range of primary velocities studied (up to 600 volts).

L. L. Bircumshaw.

Elastic scattering of electrons in molecular hydrogen. H. S. W. Massey (Proc. Roy. Soc., 1930, **A**, **129**, 616—627).—Mathematical. Using Born's collision formula, the scattering cross-sections presented by hydrogen molecules to electron beams are calculated. Diffraction effects are found to occur, and the intensities of these are determined. The effects would be very difficult to detect experimentally, owing to the smallness of the peaks relative to the "atomic" background. L. L. Bircumshaw.

Low-voltage electron impacts in hydrogen. F. G. Slack (Physical Rev., 1929, [ii], **33**, 1085).—The effect of electron impacts with hydrogen streaming at 0·05—0·50 mm. pressure in a three-electrode tube with a unipotential, oxide-coated, hot filament has been investigated. The breaks in the curves of

Richardson and Tanaka (A., 1925, ii, 13) below 10·2 volts are missing, confirming the view that they were due to mercury vapour. No Balmer lines could be detected. L. S. Theobald.

Experiments on electron diffraction. F. Kirchner (Physikal. Z., 1930, **31**, 1025—1028).—Electron diffraction patterns give a sharper atom factor curve than *X*-ray patterns, because the nucleus governs the scattering of electrons, and the electron cloud the scattering of *X*-rays. In electron diffraction patterns, then, the second order spectra due to the (111) planes of sodium fluoride are not entirely extinguished, since the nuclear charges of Na^+ and F^- are unequal. Debye–Scherrer diagrams due to electrons diffracted by comparatively large crystals sometimes show interference points at the ends of a diameter of one or more of the rings. This can be ascribed to a mosaic-like structure of the crystal. Sublimation, under vacuum, of mercuric chloride from a heated platinum strip to a celluloid surface gives a cubic instead of a rhombic crystal. Diffraction by gaseous nitrogen, oxygen, or carbon dioxide gave patterns in accord with Debye's *X*-ray patterns.
A. B. D. Cassie.

Electron diffraction and molecular structure. R. Wierl (Physikal. Z., 1930, **31**, 1028).—Electron diffraction by gases can be used to determine the distance between atomic nuclei in an molecule. The distance S—S in carbon disulphide is 3·20 Å., O—O in carbon dioxide is 2·26 Å., N—N in nitrous oxide is 2·38 Å. The distance S—O in sulphur dioxide is doubtful, because of the triangular structure of the oxide, but it may be 1·37 Å. A. B. D. Cassie.

Heats of condensation of electrons on metals in ionised gases. C. C. Van Voorhis and K. T. Compton (Physical Rev., 1930, [ii], **36**, 1435—1439; cf. A., 1927, 926, 1001).—Heats of condensation of electrons on electrodes of molybdenum, platinum, and tungsten coated with potassium were measured in ionised argon, neon, helium, nitrogen, and hydrogen by measuring the heat developed in Langmuir collectors of these metals when a known number of electrons of known energy was received by the collector. Results varied from 5·21 volts for platinum in nitrogen to 0·93 volt for potassium-coated tungsten in helium, and depended on the metal and the ionised gas, the effect of the latter being indicated as due to its ions rather than its neutral atoms.
N. M. Bligh.

Direct determination of the volume of the electron. V. Posejpal (Compt. rend., 1930, **191**, 1000—1002).—The volume is deduced from the formula $\sigma_s/\rho=\pi r^2/m_H$, where σ_s/ρ is the specific coefficient of true scattering of very hard γ-rays in hydrogen, r the radius of the electron, m_H ($=1{\cdot}662\times 10^{-24}$) the mass of the hydrogen atom. Using the values of σ_s/ρ for γ-rays from radium-$B+C$ filtered through 2·6 cm. of lead, for water (0·0383) and glycerol (0·0406) the values $1{\cdot}42\times10^{-13}$ and $1{\cdot}47\times10^{-13}$ cm., respectively, are obtained for r, which agree with its electromagnetic value, $1{\cdot}9\times10^{-13}$ cm. The same formula is deduced from the author's corpuscular theory of an ether consisting of neutrons of diameter approximately equal to that of an electron, a neutron being defined as resulting from the emission by a normal hydrogen atom of energy equal to m_Hc^2.
C. A. Silberrad.

Affinity of the hydrogen atom for the electron. P. Starodubrovski (Z. Physik, 1930, **65**, 806—813).—Mathematical. The affinity of the hydrogen atom for the electron is calculated to the fourth approximation, and the result is claimed to be better than that of Hylleraas (A., 1930, 518, 1231). The value obtained is 16·40 kg.-cal. per mol.
A. J. Mee.

Evidence of gas degeneration and applicability of Pauli's exclusion to metallic conduction electrons. J. Du Mond (Physical Rev., 1929, [ii], **33**, 123).—The distribution of velocities of the scattering electrons can be inferred from the breadth and structure of the Compton shifted line. The structure of this line has been studied experimentally and the results support the assumption that conduction electrons are subject to the Pauli exclusion principle and have the velocity distribution predicted by Sommerfeld. L. S. Theobald.

Geiger–Müller tube as a quantitative ion counter. J. A. Van den Akker (Rev. Sci. Instr., 1930, **1**, 672—683).—The conditions for the use of the new type Geiger–Müller tube as a quantitative detector of individual ions were investigated (cf. Geiger and Müller, A., 1929, 114). The rate of counting at various voltages was measured, using very weak sources of radium-*D* and mesothorium. The count–voltage curves are analysed and discussed. The tube is found to be quantitative when the rate of counting is moderate, the accuracy increasing when the rate of counting is very low. Spurious discharges seem inseparable from this form of tube.
N. M. Bligh.

Absorption of slow hydrogen positive rays in hydrogen. R. E. Holzer (Physical Rev., 1930, [ii], **36**, 1204—1211).—The absorption coefficients of H^+, H_2^+, and H_3^+ in hydrogen were measured for the range 60—850 volts, using an ionisation tube and a Dempster mass spectrograph for analysing the rays. The values obtained were, for H^+, nearly constant at 8 cm.²/cm.³; for H_2^+, 40 decreasing to 20 cm.²/cm.³ from 60 to 850 volts, and for H_3^+, 17 decreasing to 12 cm.²/cm.³ from 60 to 500 volts; no minimum of absorption was found. Qualitative experiments indicate that the absorption of H_2^+ is due to neutralisation, and that scattering is the main factor in the absorption of H^+ and H_3^+ ions. N. M. Bligh.

Collisions by canal rays. C. Gerthsen (Physikal. Z., 1930, **31**, 948—953).—By allowing canal rays to pass from the observation chamber into a gas-filled chamber considerable ionisation results, the number of ion pairs produced being proportional to the initial energy of the ionising particles. The reflective power of metals for high-velocity canal rays is approximately proportional to the square of their at. wt. Methods of measuring the scattering of canal rays by thin films and the velocity of secondary electrons from these films are discussed. Consideration is given to the distribution of secondary electrons from metal films; the discharge of doubly-charged helium atoms by means of He^+ canal rays; the velocity and energy decrements of canal rays by passage through celluloid films of various thicknesses, and the ionising power and range of canal rays in air as a function of their velocity. W. R. Angus.

Velocities of H^+ ions formed in hydrogen by dissociation following electron impact. W. W. Lozier (Physical Rev., 1930, [ii], 36, 1285—1292; cf. Bleakney, A., 1930, 969).—An apparatus is described for the study of the velocity distribution of ions formed by single electron impact, the velocity distribution being determined from the positive ion current collected expressed as a function of the retarding voltage. If, as shown by theory, the H_2 molecule, on ionisation by electron impact, dissociates into $H^+ + H$, the H^+ ions should occur at minimum electron velocities of about 27—40 volts, and possess 5—11 volts velocity, and if into $H^+ + H^+$ with removal of two electrons, the corresponding values should be 46—56 volts and 7·5—12·5 volts velocity. In agreement with theory, the velocities of the ions resulting from dissociation, and the ionisation potentials were found to satisfy linear relationships. The results are considered to confirm the essential correctness of the quantum mechanical theory of the hydrogen molecule. N. M. Bligh.

Diffraction phenomena in molecular rays. O. Stern (Physikal. Z., 1930, 31, 953—955).—A *résumé* of work in this field with special reference to reflexion of molecular rays from polished surfaces and crystal cleavage faces and diffraction from the "Kreuzgitter" of crystal cleavage faces.

W. R. Angus.

Experiments with high-velocity positive ions. J. D. Cockcroft and E. T. S. Walton (Proc. Roy. Soc., 1930, A, 129, 477—489).—The advantages of experiments with positive ions accelerated by high potentials over α-particle experiments in dealing with problems of the atomic nucleus are discussed. The main difficulty lies in the production and application of the very high potentials required to accelerate the particles if velocities approaching that of the α-particle are to be obtained. It is decided that 300 kilovolts is the minimum acceleration voltage at which useful work can be carried out in this field. Full details are given of the experimental arrangements. The canal-ray tube is used as a source of protons, which are accelerated by means of a steady potential produced by rectifying the current from a low-frequency transformer. From preliminary experiments carried out at voltages up to 280 kilovolts with a mixed stream of protons and molecules, targets of lead, and a beryllium salt, definite indications were obtained that the impact of protons on matter produces a radiation of a non-homogeneous type. The intensity of the radiation was of the order of 0·0001 of that produced by an equal electron source, and increased very rapidly between 250 and 280 kilovolts.

L. L. Bircumshaw.

Electrodeless ring discharge and the production of atomic rays of hydrogen. J. Kunz amd J. T. Tykociner (Physical Rev., 1929, [ii], 33, 117).—Atomic rays are produced by inducing high-frequency discharges in an electrodeless quartz bulb supplied with hydrogen. L. S. Theobald.

Ionisation of nitrogen and air by positive-ion bombardment. R. M. Sutton and J. C. Mouzon (Physical Rev., 1929, [ii], 34, 547—548; cf. A., 1929, 483).—Nitrogen and air both show ionisation for accelerating potentials greater than 100 volts at pressures between 0·1 and 0·7 mm. The abnormally high pressures indicate the presence of long mean free paths for the positive ions. The calculated ionisation at 750 volts expressed as the number of ions formed per initial positive ion per cm. path at 1 mm. pressure is: argon 0·288, neon 0·112, nitrogen 0·124, air 0·098, and hydrogen none detectable. L. S. Theobald.

Hydrogen molecular ion as a wave-mechanical perturbation of the helium ion. P. M. Morse and E. C. G. Stueckelberg (Physical Rev., 1929, [ii], 33, 290).—The molecular electronic levels have been obtained from the perturbation caused by splitting the nucleus of a simple atom. The hydrogen molecular ion has been obtained from the helium ion. The electronic energy as a function of nuclear separation gives a curve in agreement with that calculated by Barrau for the ground state. The curves for the excited states show the "promotion of the electron" predicted by Hund and Millikan.

L. S. Theobald.

Reflexion of atoms from crystals. A. Ellett and H. A. Zahl (Physical Rev., 1929, [ii], 33, 124; cf. A., 1929, 1125).—Cadmium and arsenic are diffusely reflected from crystals of fluorite and orthoclase. Cadmium incident upon potassium chloride gives a specular beam, whilst arsenic upon sodium chloride gives a weak specular beam with considerable diffuse scattering. Thick layers of arsenic deposited at the temperature of liquid air are black; these change abruptly to deep red, then to bright yellow, and finally to the usual grey modification on warming to the ordinary temperature. L. S. Theobald.

Repeated reflexion of atoms from crystals. A. Ellett and H. A. Zahl (Physical Rev., 1929, [ii], 33, 635; cf. A., 1929, 1125).—The beam of cadmium atoms specularly reflected from a crystal of halite and impinging upon a second crystal is specularly reflected only when the angle of incidence on the second crystal is equal to or nearly equal to the angle of reflexion from the first. A change of 10° in the angle of incidence causes marked loss of intensity in the reflected beam which disappears when the angles differ by 25—30°. The specular reflexion probably depends in a critical manner on the velocity of the incident atoms. L. S. Theobald.

Velocity of cadmium atoms specularly reflected from rock-salt crystals. A. Ellett and H. F. Olson (Physical Rev., 1929, [ii], 33, 118—119).—The beam of cadmium atoms specularly reflected from a crystal of rock salt consists of atoms all having nearly the same velocity, which varies with the angle of incidence but not with temperature of the crystal. An equation which represents the results and can be interpreted in terms of de Broglie's wave equations is given. L. S. Theobald.

Polarisability of the helium atom and the lithium ion. H. R. Hassé (Proc. Camb. Phil. Soc., 1930, 26, 542—555).—Mathematical. The method of Eisenschitz and London (cf. A., 1930, 525) for calculating the approximate force between two atomic systems at large distances apart from the disturbance produced by a small external electric field is used to confirm the work of these authors for hydrogen, and is extended to the polarisability of helium and the lithium ion. N. M. BLIGH.

Mobility of aged ions in air. O. LUHR and N. E. BRADBURY (Physical Rev., 1930, [ii], 36, 1394—1397; cf. A., 1930, 974, 1231).—The mobility of air ions produced by *X*-rays was measured by the Rutherford alternating-current method using a slightly modified form of the apparatus previously described. No change in mobility with age was detected for ions aged to one second. The average mobilities of positive and negative ions in dry air was 1·64±0·05 and 2·25±0·05, falling in moist air to 1·4 and 1·8 cm./sec. per volt/cm., respectively. No satisfactory explanation was found for the continual decrease in the coefficient of recombination with age while the mobility remains unchanged. N. M. BLIGH.

Molecular rays of hydrogen chloride in an electric field. M. J. COPLEY and W. H. RODEBUSH (Physical Rev., 1929, [ii], 33, 1083—1084).—Deflexion of a large fraction of molecules is indicated by passing a beam of hydrogen chloride molecules initially at −80° through an electrostatic field between a wire and a cylinder with a *P.D.* of 10,000 volts and condensation on a target cooled in liquid air and bearing a layer of condensed ammonia.

L. S. THEOBALD.

Positive-ray analysis of hydrogen sulphide. J. H. BARTLETT, jun. (Physical Rev., 1929, [ii], 33, 117; cf. A., 1929, 379).—The ions $(S)^+$, $(HS)^+$, $(H_2S)^+$ are all formed by the initial process of the electrons colliding with the gas molecules. Hydrogen ions, $(S_2)^+$ ions, or negative ions could not be observed in studying hydrogen sulphide by Dempster's method of positive-ray analysis. L. S. THEOBALD.

Basis of the chemical at. wts. A. VON GROSSE (Z. physikal. Chem., 1930, B, 10, 395—396).—Owing to the complications arising from the fact that oxygen is composed of isotopes, it is proposed that helium (=4·0000) should be employed as the basis of the at. wt. system. The importance of the helium nucleus in atomic structure, and the fact that the difference between the at. wt. of atoms containing an integral number of α-particles and the next integer represents the energy of formation of the atom from α-particles and electrons, are adduced in favour of the proposal. H. F. GILLBE.

New graphical arrangement of the periodic table. A. E. CASWELL (Physical Rev., 1929, [ii], 34, 543).—The elements are represented by a spiral plotted on polar co-ordinate paper.

L. S. THEOBALD.

Determination of the abundance ratios of isotopes from band spectra. A. ELLIOTT (Nature, 1930, 126, 845—846; cf. A., 1930, 1232).—The determination of the correction to be made in order to obtain the relative abundance from the intensity ratio of isotopic bands of boron is described. For Chilean boron the mean isotope ratio is 3·63±0·02, giving an at. wt. 10·794 corrected for O^{17} and O^{18}.

L. S. THEOBALD.

Evidence from band spectra of the existence of a carbon isotope of mass 13. A. S. KING and R. T. BIRGE (Astrophys. J., 1930, 72, 19—40).—The evidence bearing on the existence and appearance of C^{13} is reviewed and discussed. Faint band structures appearing in different regions of the spectrum can be accounted for by a carbon atom of mass 13 and the relative abundance of C^{13} and C^{12} appears to be of the order 1 : 400. Furnace and low excitation sources, especially N-type stars, are effective emitters of the C^{13} spectrum; in the arc, the only evidence of C^{13} is a group of lines in the cyanogen band at 3883 Å.

L. S. THEOBALD.

Constitution of tungsten. F. W. ASTON (Nature, 1930, 126, 913).—The mass spectrum has been obtained using the carbonyl $W(CO)_6$. Tungsten has four isotopes of which the two strongest give lines of practically equal intensity. The mass numbers and relative abundances (provisional) are 182 and 22·6, 183 and 17·2, 184 and 30·1, and 186 and 30·0, respectively. The at. wt. deduced is 183·96.

L. S. THEOBALD.

Half-life period of uranium II. Ratio of weights of the isotopes uranium I and uranium II in the mixed element uranium. E. WALLING (Z. physikal. Chem., 1930, B, 10, 467—475).—The half-life period of uranium II has been calculated from measurements of the activity of uranium-*X* and the uranium II formed from it, taken in conjunction with the known period of the former, to be $3·4\times10^5$ years, with a maximum uncertainty of ±15%. From this value it is deduced that ordinary uranium contains 13,200 atoms of uranium I for each atom of uranium II. R. CUTHILL.

Behaviour of radioactive coatings on heating. W. SEITH and A. H. W. ATEN (Z. physikal. Chem., 1930, B, 10, 296—298).—By heating to 600—700° a material on the surface of which a radioactive substance has been uniformly deposited the latter breaks up into discrete agglomerates; the effect is less marked with a glass surface than with platinum. By application of this phenomenon it has been shown that an exchange of lead ions can take place between a film of thorium-*B* chloride and a lead oxide surface on which it is deposited. H. F. GILLBE.

Unsuccessful attempt to influence the normal decay of a weak source of polonium. N. FEATHER (Proc. Camb. Phil. Soc., 1930, 26, 538—541; cf. A., 1930, 659).—An apparatus is described by which the effect of γ-rays from mesothorium on the rate of decay of a weak source of polonium was investigated. From counts of particles taken over long periods during normal decay and during irradiation no anomaly was detected. N. M. BLIGH.

Experiments on influencing radioactive disintegration. (FRL.) S. MARACINEANU (Physikal. Z., 1930, 31, 1032—1036, 1038—1039).—A reply to criticisms by Běhounek (A., 1930, 516; also following abstract) of work by the author (A., 1926, 879; 1927, 710, 807; 1928, 455). It is suggested that the different experimental arrangements used by the two authors account for many of the discrepancies in their results. W. R. Angus.

[Experiments on influencing radioactive disintegration.] F. Běhounek (Physikal. Z., 1930, **31**, 1036—1038).—A reply to Maracineau (cf. preceding abstract). W. R. Angus.

[Experiments towards] decomposition of the lead atom. III. A. Smits and (Frl.) H. S. Vening Meinesz (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 737—748).—In confirmation of the work of Maracineanu (A., 1928, 455), it is found that lead sheets exposed to sunlight become radioactive and emit α-particles. Further work has been done on the irradiation of lead by *X*-rays (cf. Smits and Frederikse, *ibid.*, 933), and the production of active lead by this means confirmed both by electrometer measurements and by counting of scintillations. The activation increases at first with the period of irradiation, but on further exposure to the *X*-rays the lead loses its activity. This indicates that the activation is not produced by radioactive dust. Similar results of Pokrowski (A., 1930, 1086) are discussed. O. J. Walker.

Directional distribution of H-particles expelled from aluminium by polonium α-rays. H. Pose (Physikal. Z., 1930, **31**, 943—945; cf. Bothe, A., 1930, 1339).—Disintegration experiments on aluminium have shown that three energetically different groups of H-particles are expelled (*ibid.*, 7) and that the number and energy of the H-particles depend on the primary energy (*ibid.*, 1232). The directional distribution of H-particles was measured for a primary range of 3·72 cm. with different angles (between 0° and 135°) between the primary and secondary rays. As the angle is increased the range of H-particles in each group diminishes, but the yields of the different groups do not change appreciably. Assuming that the α-particles are captured by collision with atomic nuclei, the change in the velocity of H-particles with the angle between the primary and secondary rays can be calculated from the energy and impulse states. The end-points of the velocity vectors lie on a circle, the centre of which is at a distance, *d*, from the origin of the α-rays. The value of *d* is obtained from the formula $d=m_\alpha v_\alpha/(M+m_H)$, where m_α and v_α are, respectively, the mass and velocity of the α-particle, M is the mass of the nuclear residue, and m_H the mass of the H-particle. The values of *d* for the three groups are 0·23, 0·18, and $0{\cdot}22\times10^9$ cm./sec., in good agreement with values obtained theoretically. The results are in good agreement with conceptions which have been made on the basis of the new quantum theory. W. R. Angus.

Theoretical treatment of atomic disintegration processes. G. Beck (Physikal. Z., 1930, **31**, 945—946).—In collisions between α-particles and atomic nuclei five types of quantum processes are encountered: (*a*) elastic collisions, (*b*) inelastic collisions during the emission of the radiation, (*c*) inelastic collisions during the excitation of the nucleus, (*d*) disintegration processes, (*e*) disintegration with subsequent emission of radiation. The characteristics and probabilities of these processes are discussed. Assuming that each nuclear particle behaves as if it were under the influence of a central field, three quantum numbers can be assigned to each H- or α-particle. These determine the total rotational momentum and the rotational momentum round a certain axis in the particular state. W. R. Angus.

Range of the α-particles from thorium. G. H. Henderson and J. L. Nickerson (Physical Rev., 1930, [ii], **36**, 1344—1347).—With the view of correcting divergent existing data, the range of α-particles from thorium was determined photographically, using a modified Wilson expansion chamber (cf. Laurence, A., 1928, 684) as 2·59±0·05 cm., in fair agreement with, and extending the applicability of, the Geiger–Nuttall relation. N. M. Bligh.

New magnetic spectrograph for α-rays. S. Rosenblum (Compt. rend., 1930, **191**, 1004—1006).—The apparatus described is capable of giving a field of 18 kilogauss, and utilising merely the resources of an ordinary laboratory, *e.g.*, a current of 1·9 amp. and 110 volts. With it the fine structure of the thorium-*C* α- and α′-rays (cf. A., 1930, 837) was confirmed. C. A. Silberrad.

Scattering of γ-rays. J. C. Jacobsen (Naturwiss., 1930, **18**, 951—952).—The scattering of radium γ-rays on passing through solutions of various substances was followed by means of a gold-leaf electrometer. A graph of the ionisation current against the number of electrons per c.c. gives a smooth curve, showing that the weakening of the radiation is determined by the number of electrons encountered. F. O. Howitt.

Wave-length measurements of γ-rays from radium and its products. L. T. Steadman (Physical Rev., 1929, [ii], **33**, 1069).—A method which gives the background of the spectrum directly is described; the relative intensities of the lines can then be obtained in a simple manner. The twelve lines of the shortest wave-length are 8·72, 7·45, 6·78, 5·55, 4·97, 4·12, 3·38, 2·86, 2·38, 1·59, 0·95, and 0·42 X. L. S. Theobald.

Directional distribution of recoil radiation produced by scattered γ-rays. D. Skobelzyn (Z. Physik, 1930, **65**, 773—798).—The directional distribution of the recoil electrons produced in the Compton effect is investigated by the cloud chamber method. The results of a great number of experiments are given. The mean statistical distribution is in good agreement with the conclusions of the quantum theory. It is shown that ordinary theories lead to the same result for the distribution formulæ as far as the larger recoil angles (*i.e.*, smaller scattering angles) are concerned. Within this range (60—90°) there is also satisfactory agreement between experimental results and the theoretical curve. The forward displacement of the emission direction for a diminution of wave-length, predicted by all the theories, is clearly shown. There is some disagreement with the Dirac–Gordon solution, the results of the experimental investigation agreeing better with the older Compton method. Many conclusions from the experiments support the recent theory of Klein and Nishina (A., 1929, 373). The distribution shows a heaping at an angle of 10°, predicted by this theory but not by others, and there are other quantitative coincidences. The dependence on frequency is also correctly predicted by this theory alone. The statistical results require the existence of certain favoured directions in the distribution, *i.e.*, secondary, sharp maxima and minima impressed on the distribution curve, which were not expected. A. J. Mee.

Influence of nitrogen peroxide on the glowing of phosphorus. F. Schacherl (Coll. Czech. Chem. Comm., 1930, **2**, 665—679).—The oxygen pressure p_x at which white phosphorus begins to glow in a mixture of nitrogen peroxide and oxygen has been determined as a function of the nitrogen peroxide concentration at 15·1°, 20·0°, and 25·1°, the phosphorus vapour pressure being maintained at the saturation point. The results are in accordance with Tausz and Görlacher's equation (A., 1930, 876) $p_x=k/(a+x)$, where $x=[NO_2]/[O_2]$ and k and a are constants; this equation has been deduced theoretically. The values of p in absence of nitrogen peroxide are in good agreement with those of earlier observers, although the variations with temperature are not, as proposed by Kowalski (A., 1929, 1242), directly related to the vapour pressure of phosphorus. The influence of nitrogen peroxide increases with rise of temperature, and is greater in oxygen mixtures than in air. The poisoning action of nitrogen peroxide, as given by the slope of the p_x–x curve at $x=0$, is of the same magnitude as that of allyl iodide or *cyclo*hexane, and is due to its reaction with oxygen atoms produced by thermal dissociation, and consequent disturbance of the chain reactions responsible for the glowing. Determination of the quantity of gas or vapour admixed with air or oxygen by measurement of the lowering of p produced is unsatisfactory, as the sensitivity of the method falls rapidly with increasing concentration and the measurements of p are rather untrustworthy. H. F. Gillbe.

Quantum defects for non-penetrating orbits. L. Pauling (Physical Rev., 1929, [ii], **33**, 270).—The contribution of polarisation of the atomic core to the quantum defect for "non-penetrating" orbits of alkali-like atoms and ions has been calculated. These values are smaller than the observed quantum defects. Values calculated by taking into account both penetration and polarisation of the atom core agree well with those observed. L. S. Theobald.

New theory of the rectifying action of the aluminium cell. W. B. Pietenpol and A. P. Friesen (Physical Rev., 1929, [ii], **33**, 277—278).—The oxide layer–gas film theory is modified. The behaviour of the cell is attributed to a double layer of aluminium oxide and aluminium hydroxide, the latter acting as a semipermeable membrane to certain ions. The accumulation of negative ions in the double layer when aluminium is the anode accounts for the high resistance and for the contra-*E.M.F.* observed. The layer also accounts for the capacity of the cell. L. S. Theobald.

Helium ratios of the basic rocks of the Gwalior series. V. S. Dubey (Nature, 1930, **126**, 807; cf. A., 1929, 622).—The thorium, uranium, and helium contents of four rocks from the Morar group of the Gwalior series are recorded. Geologically, these rocks are of the same age. Helium is retained better by fine- than by coarse-grained basaltic rocks. The ages now given for Tertiary, late Carboniferous, and late Pre-Cambrian rocks as exemplified by Cleveland Dyke, Whin Sill, and Gwalior basalt are 26, 182, and 468×10^6 years, respectively. L. S. Theobald.

Optical treatment of Fourier analysis. B. Germanski (Ann. Physik, 1930, [v], **7**, 453—469).—The application of Fourier analysis to the determination of wave form and of lattice structure is discussed. The mathematical theory and practical details of a new and widely applicable technique are given. H. F. Gillbe.

Interaction of inert gases. M. Delbrück (Proc. Roy. Soc., 1930, **A**, **129**, 686—698).—Mathematical. The inertness of the inert gases is studied from a quantum-mechanical point of view, and it is shown that the attractive field of the higher rare gas atoms is probably due to the first-order perturbation rather than to polarisation. The electrostatic as well as the exchange energy of two rare gases can be written as a sum, of which the terms correspond with the interaction of pairs of completed shells. The electrostatic energy is always negative for great distances, whilst the exchange energy tends to negative values for increasing azimuthal quantum numbers. L. L. Bircumshaw.

Perturbation problems in quantum mechanics. J. E. Lennard-Jones (Proc. Roy. Soc., 1930, **A**, **129**, 598—615).—A modified form of the Schrödinger perturbation theory is given, and applied to calculating the van der Waals field of two hydrogen atoms at large distances. A more general perturbation theory is also developed, which is not limited to small perturbations. The advantages of this method are illustrated by a consideration of the perturbation of rotating polar molecules under the influence of an external electric field. L. L. Bircumshaw.

Dependence of emissivity on temperature for black-body radiation. A. Press (Z. Physik, 1930, **65**, 734—738).—Theoretical. The Stefan–Boltzmann fourth-power law is extended to more complex cases, in which it does not hold strictly. A. J. Mee.

Recombination of atoms. E. L. Kinsey and J. Kaplan (Physical Rev., 1929, [ii], **33**, 545).—The collision of two atoms can result in the formation of a homopolar molecule only when the minimum energy in an excited state of the molecule is equal to or less than the heat of dissociation of the normal molecule. L. S. Theobald.

Transition effect of cosmic radiation shown by varying the absorbing medium. E. Steinke (Physikal. Z., 1930, **31**, 1019—1022).—A new differential method of detecting cosmic radiation is described. Measurements of the absorption coefficient for this radiation traversing lead, iron, aluminium, water, and paraffin show that iron and the heavier elements appear to absorb anomalously; the absorption coefficient diminishes with increasing thickness, probably because of a secondary radiation excited by the cosmic radiation in the heavier atoms. An unsuccessful attempt was made to detect scattered electrons by means of a magnetic field. A. B. D. Cassie.

Distribution of electrons in the atom. L. Goldstein (Compt. rend., 1930, **191**, 766—768).—A mathematical extension of the Fock–Dirac relation between orbital moment and atomic potential (A., 1930, 271), in which Poisson's equation is used to calculate the latter quantity. An expression is thence obtained, the terms of which represent, under limiting conditions, the Fermi–Thomas equation for the interaction of electrons between themselves and with the nucleus, and the effect on distribution of electronic exchange. It is suggested that by appropriate generalisation the Fock–Dirac equation could be applied to the statistical theory of homopolar linkings in molecular fields. J. Grant.

Electronic orbits within atoms. V. Karapetoff (J. Franklin Inst., 1930, **210**, 609—624).—Information regarding the probable number and characteristics of electronic orbits in atoms has been summarised in the form of a graphical chart for all known chemical elements. An empirical rule is described which governs the appearance of different kinds of orbits when the elements are arranged in order of atomic number. W. Good.

Potential and potential energy of space lattices. C. N. Wall (Physical Rev., 1930, [ii], **36**, 1243—1250).—Mathematical. The electrostatic potential of a general space lattice is developed, and an expression for the lattice energy is obtained which can be connected with the structure factors of the lattice. The theory is applied to sodium chloride and sodium and lithium fluorides. The lattice energy is calculated for different grating spaces, and is shown to be a minimum in the neighbourhood of the accepted grating space of the crystal. N. M. Bligh.

Atomic electric charges in the electromagnetic quantum theory. C. L. Sagui (Physical Rev., 1929, [ii], **33**, 123).—Theoretical. The magnetic fields which a proton and an electron would possess under certain conditions are described.

L. S. Theobald.

Quantised rotation of atoms. E. Loedel-Palumbo (Physikal. Z., 1930, **31**, 926—929; cf. A., 1926, 1073; 1927, 602; 1928, 100; 1929, 366).—A criticism of the work of Loyarte. The "addition potential" postulated by Loyarte has no physical significance. A table is given for the mercury spectrum showing that values other than 1·4 volts for this "addition potential" can be used to give the same results as Loyarte obtained. This can be done for any spectrum which contains a large number of lines. W. R. Angus.

Photographic method of determining atomic structure factors. D. K. Froman (Physical Rev., 1930, [ii], **36**, 1330—1338).—The intensities of X-rays reflected from powdered crystals of magnesium oxide and potassium chloride were measured photographically, higher orders of reflexion being measurable than by the ionisation method. Relative intensities and corresponding structure factors are tabulated for each substance. The radial electron distribution for each of the atoms was determined and results indicate that both compounds form polar crystals.

N. M. Bligh.

Extrapolation of atomic structure factor curves. D. K. Froman (Physical Rev., 1930, [ii], **36**, 1339—1343).—Mathematical. An approximate extrapolation formula for atomic structure factors of high order is deduced from the form of the electron distributions indicated by the wave equation, and gives results in satisfactory agreement with the factors found by Hartree (cf. Proc. Camb. Phil. Soc., 1928, **24**, 189) from the electron distribution for Na^+. An analogous treatment is shown to apply to the curves obtained from the scattering of X-rays by gases (cf. Compton, A., 1930, 834). N. M. Bligh.

Electron theory of metals. R. H. Fowler (J. Inst. Elect. Eng., 1930, **68**, 1469—1475).—A lecture.

Physical methods in the chemical laboratory. XV. Investigation of internal structure of crystallised inorganic compounds. W. Jander (Z. angew. Chem., 1930, **43**, 1057—1060).—The application of infra-red spectroscopy and of X-ray analysis to the study of atomic arrangement in crystals is briefly surveyed. A detailed description is given of the employment of comparative physical data, such as mol. vol., m. p., conductivity, and of diffusion and reactivity in the solid state, to the investigation of the internal forces operative within crystalline substances. H. F. Gillbe.

Spectrography using a non-inclined plate. A. Couder (Compt. rend., 1930, **191**, 772—774).—Since spectra inclined to the axis of the objective are obtained with non-achromatic spectrographs, an almost achromatic quartz spectrograph involving the use of a catadioptic lens is described. The objective is a simple crown-glass convergent lens, whilst the plane mirror of the ordinary Duboscq autocollimated spectrograph is substituted by a flint-glass divergent-meniscus lens, the convex posterior face of which is metallised. Calculations are given to determine the curvature of the lenses from a consideration of the aberrations of the system. An advantage is the suppression of extraneous light from the slit.

J. Grant.

Excitation of band spectra. J. Kaplan and E. L. Kinsey (Physical Rev., 1929, [ii], **33**, 114).—The β bands of nitric oxide are weakly excited in electric discharges and strongly excited in active nitrogen; the first excitation is due to electron impact, the second to collisions of the second kind. This difference can be explained by means of the Franck–Condon curves for the two levels involved in the transition. The most probable transition for electron impact is one in which the vibrational motion in the upper level is determined by the instantaneous values of the separation of the atoms and their relative momentum. L. S. Theobald.

Double refracting structure of "Corex" glass. (Lord) Rayleigh (Nature, 1930, **126**, 845).—The ultra-violet-transmitting "Corex" glass shows a doubly refracting structure. L. S. Theobald.

Validity of the Hill and Van Vleck intensity formula for the NO γ bands. R. Schmid, T. von Neugebauer, D. von Farkas, and C. Barabás (Z. Physik, 1930, **65**, 541—546).—The distribution of intensity in the branches of the NO γ bands is given correctly by the Hill and Van Vleck intensity formula for a $^2\Sigma_{(b)} \longrightarrow {}^2\Pi_{(x)}$ transition. A. B. D. Cassie.

Band spectrum of antimony oxide. B. C. Mukherji (Nature, 1930, **126**, 725).—The spectrum of the flame surrounding the antimony arc in air has at least three systems with origins at approximately 29,619, 26,480, and 24,203 cm.$^{-1}$ The bands show a doublet structure consistent with an emitter of the neutral antimony oxide molecule.

L. S. Theobald.

New band system probably due to singly-ionised hydrogen chloride. B. A. Brice and F. A. Jenkins (Physical Rev., 1929, [ii], **33**, 1090—1091; cf. A., 1929, 864).—The bands form a doublet system with $\Delta\nu=663$ cm.$^{-1}$ The heads are given by $\nu=28{,}446$ (and 27,783)$+1561p-36{\cdot}3p^2-2569n$, where (p,n) are (−1,0), (0,0), (1,0), (2,0), (3,0), (4,0), (5,0), (0,1), and (3,1). A $^2S \longrightarrow {}^2P$ system is indicated.

L. S. Theobald.

Ultra-violet absorption of aqueous solutions of hydrochloric acid. R. Tréhin (Compt. rend., 1930, **191**, 774—776).—Aqueous solutions (0·5—13M) of hydrogen chloride, purified by drying over phosphorus pentoxide and solidification in liquid air, were examined at λ 2816—1990 Å. in thicknesses of 10 and 20 mm. For a given concentration and thickness absorption increases continuously with decrease in λ. The absorption increase is a constant function of increase in concentration above 2320 Å., but below this value a maximum absorption is obtained for a particular concentration. Beer's law, therefore, is not satisfied, and absorption is due to the Cl^- ion in dilute solution only. J. Grant.

Analysis of hydrogen chloride bands in the ultra-violet. M. Kulp (Physikal. Z., 1930, **31**, 959—960).—The bands of hydrogen chloride have been examined between 3000 and 4000 Å. and it is found that each band consists of six branches, P, Q, R, and P', Q', R'. The separation between the lines of the R and Q branches is the same as between the lines of the Q' and P' branches; also the lines of the P and Q branches and of the P' and R' branches are separated by an equal amount. Such a doublet system is attributed to HCl^+. The transition $^2\Sigma \longrightarrow {}^2\Pi$ is considered the only possible. For the $^2\Sigma$ term the component of the total rotational momentum of electronic orbits (Λ) is zero. By taking into account the spin about the axis of rotation all rotational levels of the $^2\Sigma$ state are split into two except the lowest level, which remains simple. In the case of the $^2\Pi$ term Λ is unity. The alternating effect between Λ and the spin is strong and for parallel and anti-parallel disposition of spin corresponding with the doublet character two terms, $^2\Pi_{+\frac{1}{2}}$ and $^2\Pi_{-\frac{1}{2}}$, are obtained. Each rotational level in the $^2\Pi$ state is divided into two levels. The transitions from $^2\Sigma \longrightarrow {}^2\Pi_{+\frac{1}{2}}$ and from $^2\Sigma \longrightarrow {}^2\Pi_{-\frac{1}{2}}$ are discussed and the bands allocated according to selection rules.

W. R. Angus.

Spectrum of hydrogen bromide. W. Weizel, H. W. Wolff, and H. E. Binkele (Z. physikal. Chem., 1930, **B**, **10**, 459—466).—The emission spectrum of hydrogen bromide excited by discharge in a Geissler tube consists of a continuous spectrum of varying intensity which starts in the green, dies away below about 2500 Å., and exhibits several flat maxima in the near ultra-violet. This is interpreted as the dissociation spectrum of either HBr or HBr^+.

R. Cuthill.

Action of the electric field on the radiations of the ions of the rare earths in chemical compounds. R. Brunetti and Z. Ollano (Nuovo Cim., 1929, **6**, 345—355; Chem. Zentr., 1930, i, 2056—2057; cf. A., 1929, 1126).—The absorption spectra of the ions of the rare earths vary in compounds and a distinction is drawn between the changes which appear in the same crystal structure and those which are observed in compounds definitely of different structure. To the first type belong the changes which are brought about by lowering of temperature. The spectral displacement of the Pr^{III} radiation thus produced can be traced to changes in intensity of the intramolecular electrical field and in the different praseodymium halides is dependent on the difference in intramolecular distances. The displacements in crystals of different structure are, for the main part, to be assigned to the varying conditions for the probability of quantum transitions. Attempts were made to produce an artificial displacement of the lines of a didymium glass, but the results were of the same order of magnitude as that of the experimental error and were not greater than the displacements which are produced by strong cooling of a crystal. The order of magnitude of the intramolecular field is calculated to be 10^7 to 10^8 volts per cm. Such a field, however, has the character of a weak field. L. S. Theobald.

Absorption and explosion spectra of cyanogen. K. Tawada (J. Soc. Chem. Ind. Japan, 1930, **33**, 417B).—The absorption and emission spectra of cyanogen have been measured with the view of determining the radiation from the cyanogen–oxygen flame; the results for the absorption spectrum confirm those of Baumeister. It is suggested that the spectrum resembles that of the explosion of carbon monoxide–oxygen mixtures. H. F. Gillbe.

Ultra-violet absorption of tartaric acid solutions. Influence of concentration. G. Bruhat and J. Terrien (J. Phys. Radium, 1930, [vii], **1**, 351—364).—A more detailed account of work already noted (A., 1930, 1090).

Effect of adding a colloid on the absorption spectrum of the solution of a colouring matter. A. Boutaric and M. Doladilhe (Compt. rend., 1930, **191**, 1008—1011).—A method of determining whether a colouring matter is colloidal or not is based on the effect on the absorption spectrum of adding a small quantity of a hydrosol to a solution thereof. If the colouring matter is in molecular solution the addition has no effect, but if it is in colloidal solution addition of a sol of a lyophile colloid causes uniform decrease in the opacity of the coloured solution, marked if the two are of different sign, very slight if of the same sign. If the added colloid is lyophile, opacity is similarly reduced to an extent dependent on the p_H of the added sol. These results are exemplified by the effects of adding sols of ferric hydroxide and arsenious sulphide to diamine-blue 4R. C. A. Silberrad.

New band in the absorption spectrum of methane. D. M. Dennison and S. B. Ingram (Physical Rev., 1930, [ii], **36**, 1451—1459; cf. Cooley, A., 1926, 659).—With the object of finding overtones of the fundamental vibrations at 3·3 and 7·7 μ, the absorption spectrum of methane was photographed in the infra-red region 6500—9500 Å., using a tungsten filament as a source of continuous radiation. A band, identified as the third overtone ($n=0 \longrightarrow 4$) of the fundamental at 3·3 μ, was observed at 8900 Å., and showed complex irregular fine structure. Wave-lengths and determined intensities of 100 lines are tabulated. The theory of the overtones of a methane type molecule is examined, and a quantum analysis of the observed complexity is deduced.

N. M. Bligh.

Infra-red measurements on rock-salt as a verification of dispersion theory. M. Czerny (Z. Physik, 1930, **65**, 600—631).—Former experiments on the dispersion coefficients of rock-salt were confined to regions where absorption is small. An attempt has been made to complete these data by measurements of the reflecting and absorbing power of thin parallel plates. Apparatus used in both the grating spectrometer and residual ray methods, including apparatus for obtaining plane parallel plates as thin as 8 μ, is described. General formulæ for the reflecting and transmitting powers of thin, absorbing, plane parallel plates are given. Observations of the reflecting power at normal incidence and of the intensity of transmitted radiation then determine the refractive index and absorption coefficient for the plate. Near the known reflexion maximum at 52 μ, a second smaller maximum at 39 μ was found. Sylvine showed a similar maximum at 46 μ, near the known maximum at 62 μ. The simple dispersion formula, using one characteristic infra-red frequency, does not fit experimental observations between 40 and 60 μ. Closest agreement is obtained by the use of two damped infra-red characteristic frequencies. The refractive index–wave-length curve shows no systematic deviations, but the extinction coefficient–wave-length curve shows systematic deviations on the short-wave side of the characteristic frequencies. A convenient logarithmic method of applying the dispersion formula is given. A. B. D. Cassie.

Infra-red absorption spectrum of chlorophyll and xanthophyll. R. Stair and W. W. Coblentz (Physical Rev., 1929, [ii], **33**, 1092).—In xanthophyll absorption bands have been located at 1·3, 3·05, 3·45, 4·3. 6·0, 6·9, 7·3, 8·05, 8·45, 8·80, 9·05, 9·60, 9·75, 9·9, 10·4, 10·9, 11·3, 11·6, 11·9, 12·1, 12·5, 12·9, 13·2, 13·4, 13·8, and 14·2 μ, whilst films of chlorophyll on plates of fluorite and rock-salt showed bands at 1·3, 3·05, 3·5. 3·8, 4·7, 6·0, 6·2, 6·5, 6·9, 7·3, 7·8, 8·2, 8·6, 9·1, 9·6, 10·1, 10·4, 10·8, 11·1, 11·9, 12·6, 12·9, 13·4, and 13·7 μ. None of these bands is as deep as are those found in molecules of simpler structure.

L. S. Theobald.

Infra-red absorption spectrum of carbon tetrachloride as related to the Raman spectrum of scattered radiation. W. W. Coblentz and R. Stair (Physical Rev., 1929, [ii], **33**, 1092).—The latest observed values for the infra-red absorption spectrum are in good agreement with the values calculated by Langer (A., 1929, 379). The band at 12—14 μ is very complex, and other bands occur at 14—15 μ. L. S. Theobald.

Raman effect apparatus, using standard tubular lamps. L. J. Buttolph (Rev. Sci. Instr., 1930, **1**, 650—653).—An apparatus previously described (cf. Reynolds and Benford, A., 1930, 1151) is modified for use with standard tubular lamps. The reflector is of chromium-plated brass to withstand higher temperatures, and the tube can be surrounded by glass filter-jackets or jackets containing liquid filters circulated for cooling. Spectrograms of the transmission of the mercury and neon arc through special filters are reproduced. N. M. Bligh.

Improved technique for the Raman effect. R. W. Wood (Physical Rev., 1930, [ii], **36**, 1421—1430).—The unsuitability of light from a mercury arc for the analysis of Raman spectra is illustrated in the case of benzene. The object of a filter is to limit the exciting light to a single wave-length, and to suppress the continuous spectrum in the Raman spectral region. Raman spectra of benzene excited by various mercury arc lines and by the hot-cathode helium arc were investigated and photographed through various filters. N. M. Bligh.

Temperature variations of the Raman effect in quartz. F. G. Brickwedde and M. F. Peters (Physical Rev., 1929, [ii], **33**, 116).—The Raman effect in crystalline quartz over the range 2400—5000 Å. and between −180° and 550° has been photographed. The variations of the Stokes lines and the anti-Stokes lines with temperature agree qualitatively with the assumption that the intensities of Raman lines vary as the populations of the initial states giving rise to them, which, in turn, vary with temperature in accordance with Boltzmann's law. The intensity of the Raman scattering increases markedly in passing from longer to shorter wave-lengths of incident light. L. S. Theobald.

Raman effect for liquid hydrogen chloride. E. O. Salant (Physical Rev., 1929, [ii], **33**, 1096).—The liquid at −100° shows the Raman effect when illuminated by a mercury arc. An absorption band at 3·6 μ is indicated. L. S. Theobald.

Combination scattering in liquids. R. M. Langer and W. F. Meggers (Physical Rev., 1929, [ii], **33**, 115; cf. A., 1929, 379).—The scattered light of modified wave-length predicted from quantum considerations differs from the incident light by a frequency equal to an absorption frequency of the scattering substance. This frequency produces a shift of wave-length which increases with the wave-length of the scattering line. Using the high dispersion of a 21-foot concave grating, modified lines have been observed to vary in character; those in benzene corresponding with a shift of 992 cm.$^{-1}$ are comparable in sharpness with the exciting mercury lines. L. S. Theobald.

Raman spectra of benzene and diphenyl. R. W. Wood (Physical Rev., 1930, [ii], **36**, 1431—1434).—Using suitable filters with mercury arc and helium arc excitation, a number of new Raman lines for benzene has been recorded. The complete spectrum given in frequency differences is, $\Delta\nu=606$, 849, 992, 1178, 1584, 1603, 2460, 2542, 2597, 2617, 2784, 2928, 2947, 3046, 3060, 3164. Anti-Stokes lines corresponding with $\Delta\nu$ values 606, 849, and 992 were verified. The Raman spectra of diphenyl with mercury arc excitation and a quinine sulphate filter consisted of 5 faint diffuse and 7 strong lines. The $\Delta\nu$ values are: 416, 606, 731, 766, 810 and 990, 1023, 1280, 1544, 1584, 1603, 3055, 3170. Six of these coincide with benzene lines. N. M. Bligh.

Raman effect in water. E. L. Kinsey (Physical Rev., 1929, [ii], **34**, 541).—The light of a glass mercury arc scattered by distilled water at the ordinary temperature yields three bands at 4150, 4680, and 5157 Å.; the first is a doublet excited by the 3650 mercury line, whilst the second is a triplet excited by the mercury pair 4046 and 4077. These two bands can be accounted for by the infra-red wave-lengths 2·92 μ and 3·13 μ. L. S. Theobald.

Incoherent scattering in Rochelle salt. R. M. Langer (Physical Rev., 1929, [ii], **33**, 1100).—The spectrum scattered by crystalline Rochelle salt differs from that of calcite and quartz in that the modified lines are all very diffuse. Further, there are two broad continuous bands which coincide with those obtained in water and in aqueous solutions. These are due to water of crystallisation and correspond with two found in infra-red absorption. Combinations among the scattered lines appear to account for most of the frequency shifts (about 10) which range from 500 to 3000 cm.$^{-1}$ L. S. Theobald.

[Intensity and polarisation of coherent and incoherent light scattered by diatomic molecules.] C. Manneback (Z. Physik, 1930, **65**, 574; cf. A., 1930, 840).—An error in two formulæ is corrected. A. B. D. Cassie.

Classical theory of the Raman effect. E. H. Kennard (Physical Rev., 1929, [ii], **33**, 289—290).—A simple example of the Raman effect is described in classical theory. L. S. Theobald.

Raman effect. VIII. Calculation of simple molecule models. M. Radaković (Monatsh., 1930, **56**, 447—460).—Mathematical. Raman spectra will give information concerning the direction of forces within the molecule, and from this the actual structure of the molecule can be calculated. Previously only a few systems have been examined in this way, and then only under the assumption of certain symmetry relationships with regard to the arrangement of the mass points. It is necessary to solve the problem more generally. Here the problem of three mass points is dealt with, it being pointed out that the extension of the theory to more complex molecules presents no great difficulty. A. J. Mee.

Raman effect. IX. Raman spectra of organic substances. A. Dadieu and K. W. F. Kohlrausch (Monatsh., 1930, **56**, 461—476; cf. A., 1929, 976, 1127; 1930, 14, 522, 664, 1091).—The Raman spectra of the following substances have been investigated: propionitrile, phenylacetonitrile, methylene bromide, methylene iodide, and dimethylamine. The results of the whole investigation involving some 100 organic compounds are discussed. The mode of oscillation of four types of molecule is considered, the types being CH_3X, CH_2X_2, CHX_3, and CX_4. The calculation in some cases leads to quantitative results on the space structure of the molecule (the angles between the valency directions), in good agreement with structures arrived at by other physico-chemical methods. In other cases the agreement is not so good, although the Raman spectra themselves are in qualitative agreement with theory. A. J. Mee.

Dependence of Raman radiation on frequency [of incident radiation]. L. S. Ornstein and J. Rekveld (Z. Physik, 1930, **65**, 719—722).—Sirkar (A., 1930, 1344) has investigated the dependence of the intensity of Raman radiation on the frequency of the incident radiation, using carbon tetrachloride, and finds that Rayleigh's fourth-power law does not hold. This is at variance with previous results of the authors (*ibid.*, 840). It is denied that the deviations are due to the fact that Ornstein and Rekveld have neglected the effect of absorption (as suggested by Sirkar), it being pointed out that the error would be within the experimental error. A. J. Mee.

Scattering of light in protein solutions. I. Gelatin solutions and gels. K. Krishnamurti (Proc. Roy. Soc., 1930, **A**, **129**, 490—508).—Experiments have been made on the effects of temperature on the intensity and depolarisation of the light scattered by gelatin sols and gels. These sols are considered to be polydisperse systems, part of the gelatin being molecularly dispersed and the remainder multimolecular micelles. Supersaturation is produced if the sol is cooled below 25°, with the production of fresh and larger particles. An ultracentrifugal and ultramicroscopic examination of the sols at p_H 4·8 indicates considerable aggregation of gelatin molecules. The variation of the intensity of the scattered light with the concentration of gelatin sols and gels has been investigated. The Tyndall number increases with concentration up to 4% of gelatin at 40°, and remains constant above this concentration. An explanation is suggested for the fact that, on cooling to 12°, the dilute gels are more turbid than the more concentrated. When gelatin sols of various concentrations are cooled to 10°, the depolarisation of the scattered light first decreases and then increases, this effect being most pronounced in dilute sols. The phenomenon is of importance in indicating changes in the size and shape of the micelles. The parallelism between the Tyndall intensity and the sedimentation constant in sols at different p_H values indicates that the turbidity near the isoelectric point is produced by the aggregation of gelatin molecules. The molecular state of gelatin in its sols is discussed, with special reference to the use of the term "molecules" for protein particles. L. L. Bircumshaw.

Nature and size of the luminescent centre. J. Ewles (Proc. Roy. Soc., 1930, **A**, **129**, 509—519).—Assuming that a luminescent centre, responsible for a given band in emission, consists of a definite number *n* of solvent molecules associated with one atom or molecule of the activator, and that if there is more than one band, each band arises from a different centre (cf. Lenard, "Handbuch der Physik," 23), the following expression is deduced for the relation between brightness of luminescence and concentration c of the activator: $F=Ace^{-nc}$ (A is a constant). This is tested by experiments with luminescent solid solutions formed by the intimate mixture and subsequent heating of antimony, bismuth, and lead oxides, respectively, in calcium oxide. On plotting log F/c against c for the antimony and lead solutions, each of which shows only one band, the linear relation to be expected from the theory is found to be fairly well followed. In the case of the bismuth solutions, for which two bands are shown in the direct-vision spectroscope, the calculated values of F are found to be in good agreement with the observed values. Similar experiments, carried out with luminescent solutions of uranine in water, rhodamine-6G in water, and fluorescein in ethyl alcohol, lead to the conclusion that the luminescence of liquid solutions of this type can be quantitatively accounted for by the existence of absorbing and re-emitting centres consisting of one molecule of the solute associated with a definite number of solvent molecules. L. L. Bircumshaw.

Phosphorescence phenomena in fused silica discharge tubes. R. Zouckermann (Compt. rend., 1930, **191**, 776—777).—Brilliant phosphorescence phenomena are observed after a 300-volt discharge in tubes containing nitrogen at the ordinary temperature, or metal vapours (at 0·6 mm. Hg pressure) heated at several hundred degrees. The fluorescence is probably due to ionic and electronic bombardments, and may be divided into (*a*) ultra-violet phosphorescence produced after the discharge (bluish-green) and stable only for a few minutes, but reproducible after a subsequent discharge; (*b*) a more intense bluish-green thermophosphorescence obtained several months after a discharge at above 200°, and decreasing in duration with successive or more prolonged heatings, or with rise in temperature. At high temperatures the usual violet-brown colorations are also obtained. J. Grant.

Ultra-violet fluorescence of iodine bromide and iodine. F. W. Loomis and A. J. Allen (Physical Rev., 1929, [ii], 33, 639).—A fluorescence spectrum in the ultra-violet has been detected for iodine bromide at low pressures. A series of close groups of lines is excited by 1849 Å. and the strongest line in each can be represented by the formula $\nu=54{,}048-276{\cdot}2p+1{\cdot}28p^2$, where p is an integer. The odd terms can be identified as strong, single lines as far as $p=43$. Near 2500 Å. the line structure changes to diffuse, headless bands extending to 3700 Å. The fluorescence series of I_2 excited by 1849 and 1942 Å. show rotational structure. No fluorescence could be obtained with bromine, or with iodine and bromine monochlorides. L. S. Theobald.

Effect of impurities on the phosphorescence of calcium sulphide. D. N. Goyle and N. Singh (J. Chim. phys., 1930, 27, 443—451).—For each impurity examined there was an optimum concentration corresponding with a maximum of the luminescence intensity of the sulphide, a higher concentration decreasing the luminescence. Fluorescent substances produced a far greater effect than metallic salts. The intensity diminishes as the mixture ages and darkens in colour, with the formation of concentric rings round the sample. The decrease in intensity is shown to be due to the hydrolysis of the sulphide and the consequent increase in the concentration of the impurity. Full results for different concentrations are tabulated.
N. M. Bligh.

Polarised fluorescence of solutions of rhodamine-*B* and uranine. E. Merritt and D. R. Morey (Physical Rev., 1930, [ii], **36**, 1386—1393; cf. Vavilov, A., 1926, 335; Pringsheim, *ibid.*, 885).—With a view of obtaining information on the symmetry of a molecule as exhibited in absorption and emission of radiation and on the duration of these processes, measurements were made of the extent of polarisation in the fluorescence of solutions in glycerol of uranine and rhodamine-B. Results indicate polarisation to the same extent throughout any one fluorescence band. For uranine, under certain conditions of concentration, two bands exist, the polarisation being constant for each band. Theoretical explanations of the processes involved are discussed (cf. A., 1926, 1193). N. M. Bligh.

Tribothermoluminescence. R. E. Nyswander and B. E. Cohn (Physical Rev., 1930, [ii], **36**, 1257—1260).—The intensity of the light emitted by glass, rendered thermoluminescent by grinding, was measured by a polarisation photometer for glass particles of various sizes. Results show that the quantity of emitted light depends on the nature of the substance and the size of the particles, and diminishes slowly with the time after grinding. Glass tubing crushed to various size grains emitted a maximum of light for particles of average linear dimensions 0·015—0·025 cm. N. M. Bligh.

Effect of water on triboelectric luminescence with mercury in glass. T. S. Logan and R. K. Taylor (Science, 1930, 72, 89—90).—Unsaturated water vapour does not destroy the faint flashing observed with mercury moving over a surface of a pyrex glass vessel containing gas at a low pressure.
L. S. Theobald.

Spectral distribution of the inner photoelectric effect in plastically deformed rocksalt crystals. M. N. Podaschevski (Z. Physik, 1930, 65, 799—805; cf. A., 1929, 969).—The effect of plastic deformation on the spectral distribution of the primary photo-current for rock-salt crystals coloured by X-rays was investigated. Both natural and tempered crystals were used, the method being analogous to that previously described. The thickness of the crystals was 1—1·5 mm., and the wavelength range was 410—690 mμ. With ordinary natural crystals the deformation causes a general diminution of the sensitivity and a displacement of the maximum towards the longer waves. Increase in charge causes a further decrease in sensitivity, and a displacement of the maximum of the curve. The displacement can be as much as 30 mμ. In some cases there was a regression in the size and position of the maximum with the time. When tempered crystals were used analogous results were obtained, but there was greater sensitivity towards deformation. A. J. Mee.

Demonstration of electric lines of force, and a new method of measuring the electric moment of tourmaline. (Miss) M. E. Maurice (Proc. Camb. Phil. Soc., 1930, 26, 491—495).—An electrostatic charge on a substance is demonstrated by the formation of ice filaments, which follow the lines of electric force, when the substance is removed from liquid air. The same effect was shown by particles of ammonium chloride smoke and magnesium oxide smoke. The experiments were conducted with the pyroelectric crystals tourmaline and boracite. The deformation of liquid surfaces by an electric field was used to indicate the order of magnitude of the charge developed on tourmaline on cooling through about 140°. A new method of measuring the electric moment of tourmaline by observing the rotation of a charged crystal suspended near a dipole is described. N. M. Bligh.

Application of the ultra-short wave method to the measurement of small capacities and dielectric constants. D. V. Gogate and D. S. Kothari (Indian J. Physics, 1930, 5, 417—428).—Using the same methods as in previous work (*ibid.*, 4, 349) the harmonics always present along with ultra-short waves have been located and measured. The conditions necessary for maximum oscillations have been studied. The general theory of the coupling of two non-resonant circuits to the same valve is developed and applied to the measurement of the inter-electrode grid-plate capacity of a valve. This leads to results in fairly good agreement with those given by the resonance method. The ultra-short wave method is also applied to the determination of the dielectric constants of kerosene oil and of petrol. J. W. Smith.

Properties of dielectrics in electric fields. G. L. Addenbrooke (Nature, 1930, 126, 808—809).—Concerning nomenclature. L. S. Theobald.

Modern theory of dielectrics. L. G. Carpenter (World Power, 1930, 14, 391—396).—A review.

Oscillation method for the determination of dielectric constants of conducting liquids. W. Graffunder and R. Weber (Z. Physik, 1930, 65, 723—725).—A new method of finding dielectric constants of liquids which can be applied to conducting liquids is described. The conduction is compensated for by the use of parallel valves. The method has been used to determine the dielectric constants of electrolytes and other aqueous solutions. A. J. Mee.

Dielectric constant of helium. J. V. Atanasoff (Physical Rev., 1930, [ii], 36, 1232—1242; cf. Hylleraas, A., 1928, 698; 1929, 616).—Mathematical. The Ritz method of investigating unperturbed helium in its normal state is extended to perturbation problems. The value of the dielectric constant, which depends on the effect of a perturbing electric field on the normal levels, is calculated as a minimum of 1·0000665, which is 5% below the accepted value. N. M. Bligh.

Electric moments of CH_3 and Br radicals in certain organic molecules. C. R. Daily (Physical Rev., 1929, [ii], 34, 548).—The electric moments obtained for various combinations of substituent methyl and bromine are: toluene $0\cdot50\times10^{-18}$, bromobenzene $1\cdot70\times10^{-18}$, *p*-bromotoluene $2\cdot15\times10^{-18}$, *n*-propyl bromide $2\cdot00\times10^{-18}$, *iso*propyl bromide $2\cdot20\times10^{-18}$, and ethyl bromide $2\cdot12\times10^{-18}$ e.s.u. L. S. Theobald.

Dipole moment of naphthalene and its monohalogen derivatives. A. Parts (Z. physikal. Chem., 1930, B, 10, 264—272).—The dielectric constants at 20° of benzene solutions of naphthalene and of certain of its derivatives have been measured, and the dipole moments of the solutes have been calculated. For all the halogen derivatives studied the density and dielectric constant of the solutions bear a linear relationship to the fractional molar concentration. The dipole moment of naphthalene is zero, in accordance with its symmetrical structure. Substitution of a halogen in the 1-position in the naphthalene nucleus results in a molecule having the same moment as the corresponding benzene derivative. The moments of the 2-monohalogen substitution products are slightly greater than those of the corresponding 1-derivatives; the properties of the β-carbon atoms of naphthalene lie between those of aliphatic and purely aromatic carbon atoms. The chloro- and bromo-, and the fluoro- and iodo-derivatives have approximately the same moments. The following constants have been determined: 1-fluoronaphthalene, $d_4^{19\cdot6}$ 1·1345, $n_{H\beta}^{19\cdot6}$ 1·61474, $n_D^{19\cdot6}$ 1·59388, $n_{H\alpha}^{19\cdot6}$ 1·58611; 1-iodonaphthalene, $d_4^{19\cdot5}$ 1·7409, $n_{H\beta}^{19\cdot5}$ 1·72995, $n_D^{19\cdot5}$ 1·70256, $n_{H\alpha}^{19\cdot5}$ 1·60244. H. F. Gillbe.

Dielectric polarisation of liquid mixtures. L. M. Das and S. C. Roy (Indian J. Physics, 1930, 5, 441—462).—The dielectric constants of solutions of chlorobenzene and bromobenzene in carbon tetrachloride have been measured by the heterodyne method due to Zahn (A., 1924, ii, 809) and their densities determined by use of a modified form of specific gravity bottle. From the results the molecular polarisations have been calculated. The zero concentration intercepts on the curves relating the partial polarisation and the concentration of the polar liquids give values which satisfy the Debye formula $P=A+B/T$. The dipole moments of the chlorobenzene and bromobenzene are calculated as 1·59 and $1\cdot52\times10^{-18}$, respectively. The molecular association increases with both concentration and rise of temperature. J. W. Smith.

Dipole moments of organic sulphur compounds and related substances. III. Significance of measurements of dipole moment in the stereochemistry of carbon. E. Bergmann, L. Engel, and S. Sándor (Z. physikal. Chem., 1930, B, 10, 397—413; cf. A., 1930, 1501).—The dipole moments of benzene derivatives containing sulphur and the halogens have been measured and used to calculate the characteristic angle, ϕ, of various substituents (cf. *ibid.*, 979). The value of 71° for ϕ has been derived for the PhS group, leading to the value of 142° for the angle between the two valencies of the sulphur atom. With such compounds as the aromatic ethers and thio-ethers the dipole moment depends on the polarisability of the central atom as well as on its valency angle. The values of ϕ for the thiocyano- and cyano-groups are 127° and 154°, respectively, but the carbimido-group seems to be straight. The dipole moments of diphenyl sulphoxide, dibenzyl sulphoxide, and nitrobenzene give no evidence of the presence of semi-polar double linkings in these compounds, and it is suggested that a more probable explanation of the occurrence of optical isomerism among the sulphoxides is that the oxygen atom does not lie in the same plane as the sulphur atom and the two hydrocarbon radicals. R. CUTHILL.

Structure of some organic molecules. O. HASSEL and E. NÆSHAGEN (Tids. Kjemi Berg., 1930, **10**, 126—127).—Measurements of the dipole moments of the methyl esters of the *meso*-, racemic, and active forms of dichlorosuccinic acid at 18° give values of $2{\cdot}47\times10^{-18}$, $2{\cdot}93\times10^{-18}$, and $2{\cdot}96\times10^{-18}$, respectively. Corresponding measurements for β- (*trans*-) and α-hexachloro*cyclo*hexane (*cis*-) give 0 and $2{\cdot}20\times10^{-18}$, respectively. The bearing of these results on the question of the structure of the molecules is discussed (cf. A., 1930, 1347). M. S. BURR.

Variation of the rotatory power of camphorsulphonates in the presence of neutral salts. E. DARMOIS and J. P. PÉREZ (Compt. rend., 1930, **191**, 780—782).—Addition of inactive neutral salts (*e.g.*, thorium nitrate or chlorides of barium, sodium, or lanthanum) to aqueous solutions of camphorsulphonic acid and of its sodium and barium salts at 20° decreases $[\alpha]_{5461}$ to an extent which increases with increase in concentration of the added salt and with increase in valency of the cations. The curves $[\alpha]=f\sqrt{\mu}$ $(\mu=\Sigma\frac{1}{2}mz^2)$, where m is the molality of the ion and z its valency, are similar for the various salts used, the influence of valency being represented (to a first approximation) by $\sqrt{\mu}$. The failure to produce an increase in $[\alpha]$ (cf. Darmois, A., 1928, 1320) is attributed to absence of dehydration of the ions. J. GRANT.

Effect of X-rays on the rotatory power of some substances. A. A. BLESS (Physical Rev., 1929, [ii], **33**, 121—122).—No effect of X-rays on the rotation of the plane of polarisation of light passing through quartz crystals could be detected, neither could the positive results claimed by Allison (A., 1929, 1220) be substantiated for water, sugar solutions, or xylene. L. S. THEOBALD.

Magneto-optical dispersion of organic liquids. I. Magneto-optical dispersion of *n*-butyl alcohol, *iso*butyl alcohol, and propionic acid. E. STEPHENS and E. J. EVANS (Phil. Mag., 1930, [vii], **10**, 759—785).—The magneto-optical rotations and refractive indices were determined for various wave-lengths, both visible and ultra-violet. Equations are given representing the magneto-rotatory and natural dispersions of the different compounds. The controlling absorption band in the case of the two alcohols has a wave-length of approximately 0·1150 μ, and in the case of the acid 0·1051 μ. The following values of e/m have been determined in e.m.u. : *n*-butyl alcohol, $1{\cdot}07\times10^7$; *iso*butyl alcohol, $1{\cdot}11\times10^7$; propionic acid, $1{\cdot}00\times10^7$. M. S. BURR.

Thermal variation of the magnetic birefringence of *p*-azoxyanisole. (MLLE.) J. ZADOC-KAHN (Compt. rend., 1930, **191**, 1002—1004; cf. A., 1930, 524).—Determinations of the magnetic birefringence of *p*-azoxyanisole have been repeated and extended by improved methods in a field of 33,900 gauss at temperatures up to 180°. The maximum rotation of the analyser β occurs at the point of transformation (133°), and (that of nitrobenzene at 22·5° being β=1°) at 134·5° is β 77·65°, falling hyperbolically to β 4·25° at 172·6°. Previous views are confirmed. C. A. SILBERRAD.

Density and refractivity of crystallised ammonium halides. P. WULFF and H. K. CAMERON (Z. physikal. Chem., 1930, **B**, **10**, 347—367).—The following values of d^{25} and n_D^{25} have been determined: ammonium fluoride, 1·0092±0·0004, 1·3147 (ordinary) 1·3160 (extraordinary) ±0·005; ammonium chloride, 1·5274±0·0003, 1·63851±0·00003; ammonium bromide, 2·4295±0·0009, 1·71239±0·00003; ammonium iodide, 2·5142±0·0005, 1·70070±0·0001. The differences between the observed molecular refractivities of the crystalline salts and the values calculated from the sum of those of the anion and cation follow essentially the same law as applies to the alkali halides. There is no evidence from the optical measurements that the ammonium protons in the chloride, bromide, and iodide are displaced towards the halogen ion, but in the case of the fluoride there is some evidence of such displacement. As with cæsium salts, the ammonium halides show clearly the increase of the total refraction effect resulting from transition of the lattice type to a higher co-ordination number. H. F. GILLBE.

Molecular and atomic volumes. XXIV. Technique of volumetric measurements of densities at low temperatures. E. WÜNNENBERG, W. FISCHER, and A. SAPPER. **XXV. Space occupied by crystalline organic substances at low temperatures.** W. BILTZ, W. FISCHER, and E. WÜNNENBERG. **XXVI. Molecular volumes of silver and potassium salts of monobasic fatty acids.** W. FISCHER and A. LEMKE. **XXVII. Space occupied by some cellulose preparations and capacity of cellulose acetate for absorbing gases.** E. WÜNNENBERG, W. FISCHER, and W. BILTZ. **XXVIII. Molecular volumes of substituted benzoic acids.** L. KLEMM and W. KLEMM (Z. physikal. Chem., 1930, **151**, 1—12, 13—55, 56—64, 65—70, 71—79; cf. A., 1930, 399).—XXIV. Procedure in measuring the volume of solids at temperatures down to −195° is described, and the corrections necessitated by the compressibility of the gas used for filling and its absorption by the solid are discussed.

XXV. The densities of crystallised normal aliphatic monocarboxylic acids, alcohols, and a number of other aliphatic and aromatic substances have been determined at low temperatures with the object of securing a more accurate extrapolation to zero volume. The results confirm the "principle of additivity," the curves connecting mol. vol. with number of carbon atoms in a given homologous series being rectilinear, whilst those relating to series of different derivatives (hydrocarbons, alcohols, mono- and di-carboxylic acids) are parallel. The following mean values are deduced for the zero volume of atoms and radicals: oxygen (hydroxyl), 4·1; methylene, 13·7; C_4H_2 (from ethylene and benzene series), 33·3; carboxyl ($\cdot CO_2 \cdot$), 17·5. The alternating effect observed in a homologous series is a property characteristic of the crystals, and has not been established for amorphous substances. Examples are given to show that the zero volumes of both aliphatic and aromatic compounds can be expressed approximately as the sum of the volumes of the constituent elements, using the volume of diamond in aliphatic, and that of graphite in aromatic, compounds.

XXVI. The densities of nine silver and three potassium salts of normal fatty acids have been determined at the ordinary temperature and at —78°. The results are discussed from the point of view of at. vols. The following values of d_4^{25} are given: silver salts: acetate, 3·279; propionate, 2·687; *n*-butyrate, 2·428; *n*-valerate, 2·167; *n*-nonoate, 1·733; *n*-decoate, 1·686; laurate, 1·585; palmitate, 1·432; stearate, 1·391; potassium salts: acetate, 1·568; palmitate, 1·104; stearate, 1·095.

XXVII. Densities of cellulose, cellobiose, and cellulose acetate at temperatures down to —195° (—79° for the acetate) have been determined. Coefficients of expansion were determined for cellulose and cellulose acetate. Zero volumes of the three substances are calculated. Acetylation gives rise to a considerable expansion of the cellulose molecule. Both air and hydrogen are absorbed in appreciable quantity at the ordinary temperature by the acetate, but not by cellulose. Figures relating to the absorption are given.

XXVIII. Densities of methyl-, hydroxy-, amino-, nitro-, chloro-, and bromo-benzoic acids have been determined. The results are discussed theoretically. The following values (previously unrecorded) of d_4^{25} are given: *o*-, 1·256, *m*-, 1·232, *p*-methyl-, 1·275; *p*-nitro-, 1·597; *m*-, 1·518, *p*-chloro-, 1·534; *o*-, 1·924, *m*-, 1·823, *p*-bromo-, 1·892; *o*-amino-, 1·353.

F. L. Usher.

Structure and b. p. III. Unipolar organic open-chain compounds. B. B. Nekrassov (J. Russ. Phys. Chem. Soc., 1930, 62, 1499—1508).—The b. p. of an organic compound is given by the formula $T=KM^{3/2}/\Sigma$, where T is the b. p. Abs., K is a constant characteristic of each class of compounds and varying from 11·6 to 13·6, M is the mol. wt., and Σ is derived from the refractive index. Of 1508 compounds, belonging to 22 different classes, the b. p. is given by the above formula with an error of 5° by 80%, of 6—10° by 11·7%, and of more than 10° by 8·3%.

R. Truszkowski.

Arrangement of electrons in the commoner organic compounds. M. Dunkel (Z. physikal. Chem., 1930, B, 10, 434—458).—An attempt is made to apply the principles governing the arrangement of electrons in diatomic molecules to more complex organic molecules. Electronic configurations for the principal organic radicals and linkings are suggested, and the theory is also extended to a consideration of the effect of one organic linking on another, as in semipolar linkings, and conjugated and cumulated double linkings.

R. Cuthill.

Relation between the paramagnetic property of the molecule and its chemical constitution. D. M. Bose (Z. Physik, 1930, 65, 677—699).—The constitution of a large number of compounds is discussed. A variation is found in the magnetic behaviour of a series of halogen compounds of suitable elements of the different transition groups. In the series nickel, palladous, and platinous chloride, the first is paramagnetic and the others are diamagnetic. Nickel chloride is assumed to have heteropolar linking, either of the 4*s* electrons of nickel being transferred to a chlorine atom; in palladous and platinous chlorides both the chlorine atoms are coupled by homopolar linking with both odd electrons in the 4*d* or 5*d* shell of palladium and platinum. Nickel cyanide heptahydrate is paramagnetic, whilst the dehydrated salt is diamagnetic; during dehydration there is a change from hetero- to homo-polar linking. Compounds with complex linking, consisting mainly of four or six groups of atoms so bound to a paramagnetic atom that it has a positive or negative electrovalency, are divided into three groups by their magnetic behaviour. (1) In the hydrated salts of elements of the first transition group the magnetic moments of the cations are very nearly equal to those of the dehydrated salts. To this group belong the hexammino-complexes of manganese, iron, cobalt, and nickel. It is assumed that ammonium and water form dipole molecules which are bound to the central atom by electrostatic forces. (2) In a number of tetrammino-complexes of nickel and copper and analogous hydrazine complexes of manganese, iron, cobalt, and nickel there is a small diminution of the moments of the cations compared with corresponding simple salts. (3) Complex compounds of paramagnetic elements, which are diamagnetic or show a great reduction in the magnetic moment of the central atom, belong to the class of stable co-ordinated compounds. To this class belong double salts and cyanogen compounds of paramagnetic elements. The formation of co-ordinated compounds is as follows. Each co-ordinated group, NH_3, CO, CN^-, Cl^-, contains a pair of coupled electrons, so that both 2*s* electrons of N in NH_3, both 3*s* electrons in CO and CN^-, and the 2*p* electrons in Cl^- effect the co-ordinated linking. If the co-ordinated group is bound to the *d* shell of the central atom then one of the electron pairs of the co-ordinated group reacts in the *d* shell and the other in the *p* shell of the central atom. The magnetic moments of these compounds depend on the number of empty positions in the *d* shell.

J. Farquharson.

Molecular and atomic volumes. XXIX. Three volume laws for solids. W. Biltz. **XXX. Low-temperature volumes of crystallised nitrogen oxides.** W. Biltz, W. Fischer, and E. Wünnenberg (Z. anorg. Chem., 1930, 193, 321—350, 351—366).—XXIX. The volume relationships of compounds are classified into three groups. (1) The principle of additive volumes is exemplified by many intermetallic compounds, double salts, silicates and aluminates, ammoniates and hydrates, organic compounds, and chlorides. (2) Variations from the additive law caused by constitutive factors are demonstrated by polymorphous substances such as arsenic, by the influence of oxygen in organic compounds and in metallic oxides, by that of ammonia in complex ammines, and particularly by the apparent reduction of the at. vol. of the alkali and alkaline-earth metals in certain compounds. (3) The principle of equivalent volumes is exemplified by the formation of higher from lower oxides without appreciable change of mol. vol., by the equivalence of the mol. vol. of many oxides with the mol. vol. of the oxygen atoms contained therein, and by the absence of a change of mol. vol. of certain ammines when the valency of the central atom increases and an additional negative atom enters the molecule. The significance of polymerisation for space chemistry, and of at. vol. for atomic structure, is discussed.

XXX. The mol. vols. of nitrous oxide, nitric oxide, nitrogen trioxide, and nitrogen peroxide, measured pyknometrically under hydrogen at −195°, are 27·4, 19·3, 42·7, 46·5, respectively, and that of nitrogen peroxide at −79° is 48·45; nitrogen pentoxide, for which an oxygen-filled pyknometer must be used, has a mol. vol. of 49·6 at −195°. The zero volumes have been determined in each case by combining these results with other determinations made at 20·42° Abs. The zero volumes of nitrogen and nitrous oxide are almost identical, whilst the differences between the mol. vol. of nitrous oxide and nitric oxide (2 mols.) and between those of nitric oxide (2 mols.) and nitrogen pentoxide are equal to the volume of 1 g.-atom of oxygen; the mol. vol. of nitrogen trioxide is the mean of those of nitric oxide (2 mols.) and nitrogen peroxide. H. F. Gillbe.

Parachor and chemical constitution. XV. Constitution of sulphonium and ammonium mercuri-iodides. H. J. Cavell and S. Sugden (J.C.S., 1930, 2572—2579).—*Dibenzyl*-n-*propylsulphonium mercuritri-iodide*, prepared according to the method of Hilditch and Smiles, has m. p. 78°, d_4^t 2·446−0·00174t, [P] 952·0; *dibenzyl*-n-*butylsulphonium mercuritri-iodide* has m. p. 81°, d_4 2·335−0·00147t, [P] 1000; *phenyltrimethylammonium mercuritri-iodide*, prepared by warming together in acetone solution equimolecular quantities of methyl iodide, dimethylaniline, and mercuric iodide, has m. p. 137—138°, d_4^t 2·923−0·00145T, [P] 719·1. The parachors of dibenzylethylsulphonium mercuritri-iodide, phenyldimethylethylammonium mercuritri-iodide, phenylmethyldiethylammonium mercuritri-iodide, and phenyltriethylammonium dimercuripentaiodide are 915·2, 754·0, 789·5, and 1060, respectively. The conductivities of these compounds in acetone solution indicate that they are binary electrolytes, and the results accord well with Onsager's equation, especially in the case of the sulphonium compounds. The anion appears to be HgI_3', but it is not possible to decide which of the two structures suggested, viz., $I^6{=}Hg(-I^7)_2$ and $I^6{=}Hg({=}I^6)_2$, represents the structure of the anion; the parachor of the dimercuripentaiodide is in agreement with the structure $I^6{=}[Hg({=}I^6)_2]_2$. H. F. Gillbe.

Reality of "Neumann's triangle." N. Fuchs (Z. Physik, 1930, **65**, 714—718).—"Neumann's triangle," used in calculations on capillarity, has real physical significance, which is shown by experiments described, and is not merely a mathematical fiction. A. B. D. Cassie.

Critical angle of reflexion and index of refraction of X-rays. H. E. Stauss (J. Opt. Soc. Amer., 1930, **20**, 616—617).—The total reflexion of X-rays is characteristic of the body of the reflector, and is not appreciably influenced by the surface conditions of good reflectors, even for X-rays of short wave-length. C. W. Gibby.

New method of producing and controlling the emission of X-rays. F. G. Cotterell, C. H. Kunsman, and R. A. Nelson (Rev. Sci. Instr., 1930, **1**, 654—661).—An apparatus is described for the investigation of the emission of K^+ ions from an emitting surface after electrolysis from a hot anode through a layer of glass. For electrolysis through glass the migrating ion is the one which is emitted thermionically. This suggested the possibility of controlling the emission by altering the alkali metal concentration on the surface. Curves are given and discussed for the voltage saturation with various types of anode, and for the variation of positive thermionic current with electrolysis potential. The positive ion emission was found to obey Richardson's equation; the advantages of this source of ions are surveyed. N. M. Bligh.

[Determination of intensity of X-rays by the ionisation method.] W. Roché (Ann. Physik, 1930, [v], **7**, 375—380).—A criticism of the conclusions reached by Schechtmann (A., 1930, 843). F. L. Usher.

Representation of crystal structure by Fourier series. W. L. Bragg and J. West (Phil. Mag., 1930, [vii], **10**, 823—841).—The extent to which the representation of a crystal structure on a given plane by a Fourier series (cf. A., 1929, 748) may be regarded as a faithful image of the actual structure is discussed. The diffraction of an ideal crystal of sodium chloride composed of Hartree atom models has been calculated as if observations were being made experimentally for a limited range of crystal planes. These results are expressed in the form of a double Fourier series and the projection is compared with the original model. It is shown that a truer image of the structure is obtained by making the final coefficients of the Fourier series converge by means of a temperature coefficient. M. S. Burr.

X-Ray histology. I. Determination of the texture of individual ramie fibres by an X-ray micro-method. K. Eckling and O. Kratky (Z. physikal. Chem., 1930, B, **10**, 368—370).—The structure of single ramie fibres has been investigated by photographing them under illumination by a pencil of X-rays perpendicular to the axis and of smaller diameter than the thread. As different portions of the cross-section of the fibre give the same diagram, which is identical also with the usual cellulose fibre diagrams, the structure must be either completely homogeneous or extremely complex (radial or concentric). H. F. Gillbe.

Interferometric measurements with molecules. P. Debye, L. Bewilogua, and F. Ehrhardt (Ber. Sächs. Ges. Wiss., math.-physikal. Kl., 1929, 81, 29—

37; Chem. Zentr., 1930, i, 3400—3401).—Measurements of *X*-ray scattering for carbon tetrachloride, chloroform, and dichloromethane are described.
A. A. ELDRIDGE.

Crystal structure of solid mercury. K. LARK-HOROVITZ (Physical Rev., 1929, [ii], **33**, 121).—The crystal structure of thin deposits of solid mercury formed in a vacuum has been determined at different temperatures. At the temperature of liquid air sharp lines were obtained with the copper and iron *K* radiations, confirming McKeehan's result; at the temperature of a carbon dioxide–alcohol mixture the structure was identical, showing that no different form of mercury exists at −80°. The lines are sharper at the higher temperature and their relative intensity is sometimes changed. L. S. THEOBALD.

Crystal structure of inert gases. I. Xenon. G. NATTA and A. NASINI (Atti R. Accad. Lincei, 1930, [vi], **11**, 1009—1011).—A more detailed account of work already noted (A., 1930, 528).

Orientation of rolled aluminium. J. THEWLIS (Phil. Mag., 1930, [vii], **10**, 953—961).—The orientation of a flat-rolled aluminium sheet has been determined by an *X*-ray method. No definite direction in the crystal can be identified with the rolling direction or the normal direction. Four sets of crystals occur, the plane of the rolling and normal directions and the plane of the cross and the normal directions behaving like mirror planes. This result confirms that of Göler and Sachs (A., 1927, 504). A square-rolled rod of aluminium, if rolled from a rod possessing random orientation, has the same orientation as a cold-drawn aluminium wire. The result of square-rolling a piece previously flat-rolled has also been investigated. M. S. BURR.

Space-group and crystal structure of potassium sulphate. F. P. GOEDER (Physical Rev., 1929, [ii], **33**, 120—121; cf. A., 1929, 16).—An analysis of a series of Laue photographs places potassium sulphate in space-group $2Di$-13 (V_h^{13}). The potassium sulphate molecule is clearly defined, and consists of a tetrahedral arrangement of the oxygen atoms with sulphur at the centre and the potassium atoms on a straight line and equidistant from the sulphur. The potassium ions have the general positions of the space-group, but the sulphur atoms fit no special cases of the general arrangement. L. S. THEOBALD.

Potassium dichromate crystals. P. L. STEDEHOUDER and P. TERPSTRA (Physica, 1930, **10**, 113—124; Chem. Zentr., 1930, i, 3400).—In addition to the triclinic forms there is a monoclinic form having $a:b:c=1{\cdot}0123:1:1{\cdot}7675$, β 88° 4·5′; n_D^α 1·725, n_D^β 1·762, n_D^γ 1·891. A. A. ELDRIDGE.

Structure of some complex cyanides. C. GOTTFRIED and J. G. NAGELSCHMIDT (Z. Krist., 1930, **73**, 357—364; Chem. Zentr., 1930, i, 3528).—The unit cells of potassium ferri- (space-group C_{2h}^5), chromi-, mangani-, and iridi-cyanides contain 4 mols.; that of cæsium ferricyanide contains 2 mols.
A. A. ELDRIDGE.

Structure of the *cyclo*hexane molecule. O. HASSEL and H. KRINGSTAD (Tids. Kjemi Berg., 1930, **10**, 128—130).—To determine which of the two possible structures for *cyclo*hexane, assuming a ring free from strain, is the true one, *X*-ray measurements have been made and the results are in agreement with a ditrigonal scalenohedral symmetry.
M. S. BURR.

Structure of some fundamental organic substances. J. HENGSTENBERG and H. MARK (Z. Krist., 1929, **70**, 283—296; Chem. Zentr., 1930, i, 3668—3669).—Diphenyl has $a:b:c=1{\cdot}445:1:1{\cdot}670$; β 94·8°, with 2 mols. in the unit cell. Phenanthrene has $a:b:c=1{\cdot}4093:1:1{\cdot}61$; β 98° 15′, with 4 mols. in the unit cell. The substances are isomorphous; space-group C_{2h}^5. Fluorene has $a:b:c=1:1{\cdot}47:1$; β 101° 53′; space-group C_{2h}^5, the unit cell containing 2 (double) mols. Dibenzyl and stilbene (also C_{2h}^5) have 2 mols. in the unit cell. A. A. ELDRIDGE.

Crystalline form of some alkylarsinic acids and alkali alkylarsinates. G. GILTA (Bull. Acad. roy. Belg., 1930, [v], **16**, 942—956).—The values of β (where given) and of $a:b:c$ for the following monoclinic crystals are: methylarsinic acid 99° 3′, 1·2579 : 1 : 1·5202; potassium (+5H_2O), 93° 12′, 1·3131 : 1 : 1·0554; lithium (+5H_2O), 95° 33′, 3·0522 : 1 : 1·2325; and ammonium methylarsinate (+5H_2O), 93° 23·5′, 1·2707 : 1 : 1·0550; *n*-propylarsinic acid, 105°, 1·1633 : 1 : 1·966; and for the following orthorhombic crystals: sodium methylarsinate (+5H_2O), 0·5673 : 1 : 1·2239; ethylarsinic acid, 1·2452 : 1 : 1·1416; sodium ethylarsinate (+3H_2O), 1·0458 : 1 : 0·9038; sodium *n*-propylarsinate (+3H_2O), 0·8317 : 1 : 1·2872. Rubidium methylarsinate (+5H_2O), sodium ethylarsinate (+2H_2O), sodium *n*-propylarsinate (hydrated), and *n*-butylarsinic acid are also monoclinic; cæsium methylarsinate (hydrated) and rubidium ethylarsinate (hydrated) are orthorhombic. C. W. GIBBY.

***X*-Ray study of the structure of the gelatin micelle.** K. HERRMANN, O. GERNGROSS, and W. ABITZ (Z. physikal. Chem., 1930, **B**, **10**, 371—394).—Two sharp interference rings have been found in the Debye diagram of air-dried gelatin, using copper *K*α radiation, together with the four broad rings. The four innermost rings indicate crystalline interference, whereas the two outer diffuse rings are of the liquid interference type, but are not due to water. The changes of the diffraction spectra after stretching and during swelling of the gelatin in water are described, and from the manner in which the rings contract or expand a theory of the gelatin structure is developed which, with certain modifications, is in accordance with that derived by Meyer and Mark for other substances consisting of complex molecules. The structure suggested is that of a fringed micelle in explanation of the mechanical properties of gelatin sols and gels. H. F. GILLBE.

Constitution of cellulose nitrates and acetates and their passage to colloidal film. J. J. TRILLAT (J. Phys. Radium, 1930, [vii], **1**, 340—350).—The nitrates and acetates of cotton were examined as fibres or as particles dissolved in acetone, by means of *X*-rays, using copper *K* radiation. The nitrates can be grouped, according to their nitrogen content, into classes consisting of a crystalline and amorphous phase, the latter increasing as the nitrogen content decreases; below 6% N the interference rings of cellulose appear. The cellulose nitrate films differed slightly in structure from the nitrated cottons; certain molecular spacings were somewhat larger and the distribution of the molecules was more irregular; in the passage from nitrated cotton to film the crystalline phase persists, in agreement with the results of Hess (cf. A., 1930, 750). Intermolecular space measurements for the films agree with those for the thickness of thin layers (cf. Sheppard, *ibid.*, 287). Similar results were obtained for cellulose acetates as powders or films; the fine structure of the film is, however, the same as that of the acetylated cotton, which has passed to the colloidal state. N. M. Bligh.

Periodates as characteristic crystal forms. L. Rosenthaler (Mikrochem., Emich Festschr., 1930, 254—259).—Certain alkaloids, and notably arecoline, berberine, cinchonine, eucodal, heroine, dionine, pilocarpine, and scopolamine, may be identified by the characteristic crystalline precipitates obtained by treatment with potassium iodate. With the exception of lithium, inorganic cations yield amorphous precipitates. H. F. Gillbe.

Dependence of the susceptibility of diamagnetic metals on the field. W. J. de Haas and P. M. van Alphen (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 680—682).—At the ordinary temperature the diamagnetic susceptibility of a pure bismuth rod remains constant with varying magnetic field. At 20·3° and 13·5° Abs. the susceptibility is dependent on the field, and the curves are analogous to those obtained by Schubnikow and de Haas (A., 1930, 675) for the variation of resistance of bismuth monocrystals with the magnetic field. O. J. Walker.

Magnetic properties of iron crystals. D. Foster (Physical Rev., 1929, [ii], **33**, 1071; cf. A., 1930, 673).—Large crystals 1 mm. in diameter up to 15 cm. in length have been grown by annealing hard-drawn wires of electrolytic iron in a vacuum by a new method. The wire axis always lies at a considerable angle to the nearest (111) direction. The hysteresis loop has very steep sides with sharp corners and high remanence. The initial permeability of 175 increases to a maximum at a field intensity of approximately 0·8 gauss. L. S. Theobald.

Influence of an alternating circular field on the discontinuities in magnetisation of iron [Barkhausen effect]. S. Procopiu (J. Phys. Radium, 1930, [vii], **1**, 306—313).—Iron or steel wire is placed in the axis of an induction coil connected with a galvanometer; an alternating current can be passed along the wire, which is also subjected to a magnetic field (H) produced by the rotation of a bar magnet. By varying the distance of this from the wire, H can be varied between 1 and 20 gauss. Denoting by α' and α the Barkhausen effect (as measured by the galvanometer) in presence and absence respectively of the alternating current, it is shown that when such current is constant the ratio α'/α is large for small values of ΔH, but decreases as ΔH increases, becoming approximately unity when it equals the coercivity of the wire. Curves show this relation and also that between the Barkhausen effect and the alternating current for various values of ΔH. A new effect occurs when the alternating current is passed along the wire in absence of the rotating magnet. So long as the circular field produced by the alternating current is less than the coercivity of the wire, the galvanometer indicates no current, but on reaching that value it shows a sudden jump. These results support the author's view that the Barkhausen effect varies with the magnitude of the variation in magnetisation. Tentative explanations are offered. C. A. Silberrad.

Atomic order in ferromagnetism. L. W. McKeehan and O. E. Buckley (Physical Rev., 1929, [ii], **33**, 636).—The fields surrounding a paramagnetic atom in a ferromagnetic substance cannot possess spherical symmetry. The magnetic field has one distinguishable axis, at least, determined by the resultant magnetic moment of the atom. The mechanical field must also have distinguishable lines or planes which must be definitely oriented with respect to the magnetic axis in order to account for magnetostriction. The degree to which such distinguishable parts of different atoms in a substance have a common orientation may be called its degree of magnetic or of mechanical order. In alloys the two sorts of atomic order may be inconsistent. The effects of mechanical, chemical, and thermal processes can be predicted and specifications for a ferromagnetic material with desired combinations of properties can be given. L. S. Theobald.

Ferromagnetic materials in weak alternating fields. R. Goldschmidt [with Läkmäker] (Physikal. Z., 1930, **31**, 1058—1060).—The magnetic properties of various irons and steels and nickel–iron alloys have been determined with a view of investigating the relationship of the permeability and hysteresis constants at small field amplitudes to the magnetisation. Soft iron, steel, and transformer iron exhibit considerable and different deviations from the theoretical equation, there being a marked increase of permeability at the beginning of the magnetisation curve; further, steel does not again acquire its initial permeability at zero magnetisation after the hysteresis cycle has been completed. The nickel–iron alloys all show the same type of deviation from the theoretical curve: the initial magnetisation curve is in accordance with theory, but on continuation of the cycle deviations become apparent. Similar effects are exhibited by the hysteresis–magnetisation curves. H. F. Gillbe.

Atomic moments in ferromagnetic alloys. R. Forrer (J. Phys. Radium, 1930, [vii], **1**, 325—339).—The individual moments of the atoms of ferromagnetic substances are investigated when forming alloys by the substitution of a small number of atoms of another metal without modification of the main lattice. The variation, ΔM, of the moment by the atomic substitution is the slope of the curve of the atomic moments as a function of the atomic composition. Alloys are investigated, and curves given for nickel with copper and cobalt, and iron with nickel and cobalt. ΔM is found to be, in general, an integral multiple of the Weiss magneton. Certain assumptions are considered for the distribution of the mean moment of the alloy among the atoms present. Some new moments for atoms in alloys are indicated, the value 14 being established for iron. It is concluded that the number of magnetons is not characteristic of each atom, but depends on the crystal lattice and the nature of neighbouring atoms. Theoretical interpretations of the results obtained and the relation of the Bohr to the Weiss magneton are considered. N. M. BLIGH.

Orientation of crystals in magnetic fields. D. E. OLSHEVSKY (Physical Rev., 1929, [ii], **33**, 278).—The statistical orientation of small crystals exposed to strong magnetic fields has been investigated. The orientation of a single crystal suspended in a viscous liquid, and the problem of a growing particle and the probability function of orientation for a crystalline deposit at the bottom of a container, are treated theoretically. Distribution curves of orientation have been obtained experimentally for a basic sulphate of iron and ammonium using field intensities of 13,500 gauss. L. S. THEOBALD.

[Magnetic] susceptibility of potassium chromium alum at low temperatures. W. J. DE HAAS and C. J. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 676—679).—The susceptibility of potassium chromium alum has been measured from 14·33° to 290·0° Abs., and found to be independent of the field. The Curie–Weiss law is obeyed, and using $\theta=0{\cdot}16°$ and $C=36{\cdot}58\times10^{-4}$ the value $p=19{\cdot}02$ Weiss magnetons is obtained. This disagrees with the explanation of Laporte and Sommerfeld (A., 1927, 86) of the magneton number in the iron group. O. J. WALKER.

Hall effect and the magnetic properties of some ferromagnetic materials. E. M. PUGH (Physical Rev., 1930, [ii], **36**, 1503—1511).—Using the method previously described (cf. A., 1929, 126), the Hall effect and magnetic properties were accurately measured simultaneously in K.S. magnet steel and in hardened high-carbon steel in order to determine the part of the effect due to the magnetic field H and that due to the magnetisation intensity I. The Hall effect, both for the curves of the material and for the hysteresis loops, was found to be a single-valued straight-line function of I, but not of H nor of the magnetic induction B. The possibility of a formula separating the effect into two components is discussed (cf. Smith and Sears, A., 1930, 281). N. M. BLIGH.

Change in resistance of pure electrolytic iron in longitudinal magnetic fields. O. STURSTADT (Z. Physik, 1930, **65**, 575—588).—Electrolytic iron in a magnetic field exhibits a larger change in resistance than a technical iron with a high carbon content. The size of the relative change in resistance depends on previous thermal and mechanical treatment of the specimen, and on the crystal structure. It appears probable that the Frank–Sommerfeld formula is applicable to ferromagnetics. J. FARQUHARSON.

Properties of sputtered metal resistors. L. C. VAN ATTA (Rev. Sci. Instr., 1930, **1**, 687—690).—The rate of change of resistance with time was investigated for gold on pyrex and platinum on soft glass rods embedded in paraffin. The latter were the more suitable for measuring small currents with an electrometer by the resistance shunt method, and showed absence of polarisation and a negligible temperature coefficient, and obeyed Ohm's law. The nature of the ageing curves depends on the metal used, the thickness of film, conditions of sputtering, and the medium surrounding the film. N. M. BLIGH.

Resistance of bismuth in alternating magnetic fields. W. W. MACALPINE (Physical Rev., 1929, [ii], **33**, 284).—The change in resistance of a bismuth wire was found to be in phase with the field and equal to that calculated from *D.C.* measurements of resistance against field strength. L. S. THEOBALD.

Piezo-electric investigations, using the principle of Giebe and Scheibe's method. A. HETTICH (Z. Physik, 1930, **65**, 506—511).—By observing the change in the piezo-electric behaviour of crystals with change of temperature it is possible to investigate transitions between allotropic modifications and to differentiate between possible crystal lattices. A simple form of Giebe and Scheibe's circuit suitable for this purpose is described. Pentaerythritol does not lose its piezo-electric properties even when heated nearly to its melting and decomposition point. Potassium iodate is piezo-electric and therefore cannot be monoclinic prismatic in structure. An allotropic change occurs in the region 140—150°. Hexamethylenetetramine shows very pronounced changes in the piezo-electric effect with temperature, but the effect remains even at the lowest temperature attainable with carbon dioxide snow and ether. Carbon tetrachloride is not piezo-electric at −80°. An allotropic change occurs in camphor at low temperatures. J. W. SMITH.

Paramagnetic rotatory power of crystals of xenotime at very low temperatures, and paramagnetic saturation. J. BECQUEREL and W. J. DE HAAS (Compt. rend., 1930, **191**, 782—784).—The curves representing the paramagnetic rotations of xenotime (λ 5615·7 and 5780·1) as a function of magnetic field (H)/absolute temperature (T) obey a law which with rise in temperature ($T=1{\cdot}38$—$14{\cdot}34°$ Abs.) approaches the simple hyperbola-tangent law already established for tysonite and parisite (A., 1929, 633, 1134), the active magnetic moment being (approximately) 7 Bohr magnetons. Contrary to results obtained previously (*loc. cit.*), and with glasses of the rare earths, the fraction of saturation is not represented by a function of the single variable H/T. Saturation is almost total (99·2%) at the temperature of liquid helium and $H=27{,}000$ gauss (cf. following abstract). J. GRANT.

Paramagnetic rotation in uniaxial crystals of the rare earths. H. A. KRAMERS (Compt. rend., 1930, **191**, 784—786).—A mathematical extension of the law deduced by Becquerel and de Haas for the rotation (ρ) of tysonite (A., 1929, 633, 1134) to the case of xenotime at low temperatures (cf. preceding abstract). If K is a constant (1·00 cm.$^{-1}$), μ_B the Bohr magneton, $\rho_\infty(T\lambda)$ the saturation-rotation, k Boltzmann's constant, and n a whole number, then $\rho=\rho_\infty(T\lambda)[n\mu_B H/\sqrt{(n\mu_B H)^2+K^2}]\tanh\sqrt{(n\mu_B H)^2+K^2}/kT$. This law is deduced on the assumption that the lower level of the 4_3 layer is converted by intramolecular forces into two non-magnetic levels forming a doublet of magnitude $2K$. The value $n=7$ indicates that the ions of gadolinium are responsible for the rotation.

J. Grant.

Experimental verification of the law of paramagnetic rotation in xenotime. J. Becquerel, W. J. de Haas, and H. A. Kramers (Compt. rend., 1930, **191**, 839—841).—The validity of the relation given by Kramers (preceding abstract) between the paramagnetic rotation of xenotime when the optic axis is parallel to the incident light and to the magnetic field, and the magnetic field at very low temperatures, has been shown to hold, within the limits of experiment, at temperatures of 4·22° and 1·38° Abs., for values of H/T between 530·8 and 6314, and 478·4 and 19,335, respectively. The values of n (7·0) and K ($1{\cdot}96\times10^{-16}$) were deduced from observations at these temperatures and at 14·34° Abs.

C. A. Silberrad.

Optical constants of manganese distilled in vacuum. J. B. Nathanson (J. Opt. Soc. Amer., 1930, **20**, 593—596).—Manganese distilled in a vacuum is very brittle and difficult to polish; this may be accomplished by using aluminium oxide and then magnesium oxide. The reflecting power of the surface, which contained pits and irregularities, varies from 61·6% to 63·5% for polarised light of wave-lengths 4600—6800 Å. The values found for the reflecting power are greater at the blue end of the spectrum and less at the red end than those obtained by previous workers. C. W. Gibby.

Metallic reflexion. J. Zahradníček (Z. Physik, 1930, **65**, 814—823).—The formulæ of Macků and Drude in connexion with metallic reflexion are reviewed. The results of the determination of the optical constants of silver by Minor, those of lead sulphide, and results for a number of metals by Drude are given and compared with the values calculated from the formulæ of Macků, Drude, and the author. A. J. Mee.

Determination of optical constants of metals in the ultra-violet by the interference method. J. Malsch (Ann. Physik, 1930, [v], **7**, 360—374).—A method of determining the refractive index and coefficient of absorption of metals, based on the formation of a thin wedge of air between a quartz plate and a plane reflecting metal surface, is described, and values of these constants for copper are given for wave-lengths down to 2536 Å. The method possesses the advantage that no polariser or compensator is used, and it is therefore applicable in the fluorspar ultra-violet range. F. L. Usher.

Grain-growth of marble. M. Kuroda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 226—227).—On annealing samples of marble, which had been subjected to compressive stresses, at 450—800°, a slight growth of the original grains was observed, but the chief effect was growth of twins and slipping in the plane of cleavage. F. L. Usher.

Mol. wt. determination in camphor solution. R. J. W. Le Fèvre (Nature, 1930, **126**, 760).—Historical. L. S. Theobald.

Conduction of electricity in liquid dielectrics. D. H. Black and R. H. Nisbet (Phil. Mag., 1930, [vii], **10**, 842—862; cf. B., 1928, 737).—The phenomena associated with the conduction of electricity through oils of the paraffin class have been investigated. The results are shown to be in agreement with the gas theory, since $R=R_0+nI$, where R is the resistance when the steady current I is flowing, R_0 the true resistance, and n a coefficient depending on temperature. This applies for a wide range of field strengths. Measurements have been made at short intervals after the initial application and after the reversal of the voltage. The results can be expressed by various simple relationships, but cannot be explained simply. No direct evidence has been obtained as to the nature of the carriers taking part in conduction through liquid dielectrics, but it is probable that they are produced chiefly by internal causes.

M. S. Burr.

Specific resistance of beryllium. E. J. Lewis (Physical Rev., 1929, [ii], **33**, 284).—The specific resistance of beryllium from the temperature of liquid air to 700° reached a steady state only after prolonged heat treatment. The value obtained is approximately 6·8 microhms per cm. at 20°. L. S. Theobald.

Electrical conductivity in silicon. A. Schulze (Physikal Z., 1930, **31**, 1062—1064).—The specific resistance of specimens of silicon from various sources has been determined at temperatures up to 1300°; in general the resistance falls with rise of temperature from 0° to 200°, rises to a maximum at 550—650°, and thereafter falls steadily, but the curve is continuous throughout. Investigations with a single crystal, which had a small positive temperature coefficient, indicate that the negative coefficient usually observed arises at the interface between the crystals; the resistance–temperature curve of a single crystal is linear and unbroken from 0° to 400°, a further indication that no transition takes place. Measurements of the thermal expansion of silicon at temperatures up to 1000° confirm this view.

H. F. Gillbe.

International Bureau of Physico-chemical Standards. IV. Physical constants of 20 organic compounds. J. Timmermans and (Mme.) Hennaut-Roland (J. Chim. phys., 1930, **27**, 401—442; cf. A., 1928, 942).—The following data for the b. p., m. p., and d^0 have been determined: *m*-xylene, 139·30°, 47·4°, 0·88113; *n*-propylbenzene, 159·45°, 99·2°, 0·87864; tetrachloroethylene, 121·20°, 22·35°, 1·65582; *n*-propyl chloride, 46·60°, —122·8°, 0·91686; *n*-butyl chloride, 78·50°, —123·1°, 0·90838; *o*-chlorotoluene, 159·15°, —36·5°, 1·10180; methyl alcohol, 64·65°, —97·0°, 0·81005; ethylal, 88·0°, —66·5°, 0·85021; *n*-propyl ether, 90·1°, —122·0°, 0·76611; *n*-butyl ether, 142·4°, —98°, 0·78536; acetic anhydride, 140·0°, —73·1°, 1·10526; formic acid, 100·7°, 8·40°, d^{15} 1·22647; acetic acid, 118·2°, 16·55°, d^{20} 1·04926; propionic acid, 141·35°, —20·8°, 1·01503; methyl formate, 31·50°, —99·0°, 1·00317; ethyl acetate, 77·15°, —83·6°, 0·92453; ethyl propionate, 99·10°, —73·9°, 0·91251; ethyl carbonate, 126·8°, —43·0°, 0·99707; ethyl oxalate, 185·4°, —40·6°, 1·10169; acetonitrile, 81·60°, —44·9°, 0·80345. Data are also given for the variation of b. p. with pressure, the density at various temperatures, coefficients of expansion, refractive indices and dispersive powers, mol. refractions, viscosities, capillarity constants, and surface tensions. The results obtained by earlier investigators are also given. N. M. Bligh.

Influence of a magnetic field on the thermal conductivity of a paramagnetic gas. H. Senftleben (Physikal. Z., 1930, **31**, 961—963).—The thermal conductivity of air in a field of about 1000 gauss is 1% lower than without field; of the individual constituents of air, oxygen gives the effect, nitrogen does not. Nitric oxide gives the effect, whereas water vapour, hydrogen, helium, and argon do not, with neon doubtful. A quantitative investigation is made of oxygen and nitric oxide. The effect varies at first with the square of the field strength, then linearly, and finally tends to a saturation value; it also varies with pressure. The measured and computed values agree very well. The effect is explained by showing that $\sqrt{T}/p$ is a function of the mean period of collision (t_s) of the molecules, so giving an explanation of the effect of pressure and temperature on the effect. J. Farquharson.

Relationships between m. p., normal b. p., and critical temperatures. R. Taft and J. Stareck (J. Physical Chem., 1930, **34**, 2307—2317). —The data of the International Critical Tables for the ratios m. p./T_c, m. p./b. p., and b. p./T_c have been examined. The first two ratios are not even approximately constant, but certain relationships appear to exist for restricted groups of compounds. The third ratio is nearer to a constant value than are the other two. The relation that T_c is equal to the sum of the m. p. (Abs.) and b. p. (Abs.) holds for a number of common substances. L. S. Theobald.

Calorimetric determination of the thermal properties of saturated water and steam from 0° to 270°. N. S. Osborne, H. F. Stimson, and E. F. Fiock (Bur. Stand. J. Res., 1930, **5**, 411—480). —Details are given of the methods employed and of the results obtained in the determination of the thermal properties of water and steam from 0° to 270°. Tabulated data are given of the latent heat and of the heat contents and entropies of the liquid and vapour. H. F. Gillbe.

Review of calorimetric measurements on the thermal properties of saturated water and steam. E. F. Fiock (Bur. Stand. J. Res., 1930, **5**, 481—505). —A critical review of earlier work and comparison with the recent determinations of the Bureau of Standards. H. F. Gillbe.

Principle of the inaccessibility of the absolute zero. H. Mache (Phil. Mag., 1930, [vii], **10**, 931—937).—A reply to Kolosovski (A., 1930, 847). The principle of the inaccessibility of the absolute zero, as conceived by Clausius, was based on the assumption that the second law of thermodynamics is valid at the absolute zero of temperature and that the specific heat remains finite or disappears at a slower rate than T. Since, however, on the basis of the experimental work of Nernst, and of Debye's theory of specific heats, it may be assumed that the specific heat disappears more rapidly than T, it must be postulated with Nernst that, in the neighbourhood of the absolute zero, every process takes place without change in entropy, and, consequently, the second law is invalid at absolute zero. The principle of the inaccessibility of the absolute zero has thus been raised to an independent postulate with a wider physical meaning than hitherto. M. S. Burr.

Entropy of hydrogen. D. MacGillavry (Physical Rev., 1930, [ii], **36**, 1398—1404; cf. A., 1930, 697).—Mathematical. The entropy difference, in the solid phase at absolute zero, between ordinary hydrogen and hydrogen in perfect equilibrium is calculated to be $0{\cdot}75R\log 3+R\log 4$, in agreement with Giauque and Johnston (cf. A., 1929, 138). The thermodynamical and statistical aspects are examined. N. M. Bligh.

Kinetic theory of liquids. R. O. Herzog (Z. physikal. Chem., 1930, **B**, **10**, 337—346).—Theoretical. Jäger's equation for the viscosity of an ideal liquid is shown by reference to liquid hydrogen, mercury, and ethyl ether, and to associated organic liquids, to be generally applicable provided that the velocity employed refers to the average mobile particle in the liquid phase, whether the association be of a chemical, physical, or purely statistical nature. Riecke's diffusion equation is probably valid under the same conditions, and by combination of this equation with that of Jäger an expression relating the viscosity with the mean distance between the particles has been derived; by further combination of this expression with that previously derived on hydrodynamic grounds for the viscosity (A., 1929, 1112) a simple equation has been obtained for the distance between the particles. The relationship between Lindemann's assumption, that at the m. p. the amplitude of vibration of the atoms is approximately equal to the mean distance between the atoms, Jäger's equation is demonstrated. H. F. Gillbe.

New law for real gases and vapours. E. J. M. Honigmann (Physikal. Z., 1930, **31**, 1064—1065).— A new thermodynamic relationship, applicable to real gases and saturated vapours, has been developed by integration of the expression $d(PV)=dU.A/(n-1)$ on the assumption that n is constant, which is true for all substances so far examined. A new law of thermodynamics is stated thus: no change in a system can take place spontaneously which results in a diminution of the quantity H, where dH is a complete differential defined by $dH=dQ/A$, A being the capacity of the system for doing work. For a perfect gas H is identified with entropy. The new law is shown to be compatible with the second law of thermodynamics. H. F. Gillbe.

Van der Waals' equation. E. Neusser (Physikal. Z., 1930, **31**, 1041—1051).—The van der Waals constants a and b are expressed as functions of temperature and pressure, and since both vary more rapidly with temperature than with pressure, they should be calculated from isothermal volume determinations made at only slightly different pressures. The gas constant has been recalculated from previous measurements with hydrogen to 0·082051 atm./degree, and the m. p. of ice to 273·20°±0·02° Abs. Existing data for hydrogen and carbon dioxide are critically examined; the constants have been recalculated for a wide range of temperatures and pressures and the results are presented graphically. Although the liquid and gas phases appear, in the van der Waals sense, to be in general continuous, the co-volume and cohesion changing continuously in the interval in which both phases coexist, the van der Waals constants undergo considerable change during the change of state, and there exists a specific temperature effect which vanishes only at relatively high temperatures and pressures. With hydrogen the constants exhibit anomalous variations with pressure in the interval 50—100° Abs. The critical volume and pressure of hydrogen may be calculated from existing data if the critical temperature be assumed, and for carbon dioxide the vapour pressure from 0° to 30° and the critical constants may be calculated approximately. The co-volume and cohesion of carbon dioxide change continuously during the change of phase, but at any given temperature diminish rapidly with increase of pressure in the neighbourhood of the boiling pressure.

H. F. Gillbe.

Viscosity, heat conductivity, and diffusion in gas mixtures. XI. Viscosity of hydrogen, nitrogen, carbon monoxide, ethylene, and oxygen and their binary mixtures. XII. Gas viscosity at high temperatures. M. Trautz (Ann. Physik, 1930, [v], 7, 409—426, 427—452; cf. A., 1930, 1105).—XI. [With A. Melster.] The viscosity coefficients of hydrogen, nitrogen, carbon monoxide, ethylene, and oxygen have been measured by the capillary-flow method previously described from the ordinary temperature up to 276·9°, and the results are in good agreement with the previous determinations. The Sutherland constants are (hydrogen=84·4): nitrogen 103·9, carbon monoxide 101·2, ethylene 241·7, and oxygen 126·7. Determinations have been made also with mixtures of these gases, and the cross-sectional ratios q have been calculated; q is independent of the temperature and of the concentration of the mixture. The viscosity isotherms of carbon monoxide–nitrogen, carbon monoxide–oxygen, and nitrogen–oxygen mixtures are approximately linear, and the cross-sectional ratios are almost unity. The gas triangle and its application in certain cases to the assignment of a correct value to q are described. If the values of q for two mixtures are represented by two sides of a triangle, that for the third mixture is derived from the length of the remaining side. The principle shows the experimental values of q to be mutually concordant, and demonstrates the similarity between nitrogen and carbon monoxide. The mean term $2\eta_{12} \cdot q_{12}^2/q_1 \cdot q_2$ is independent of the concentration, as shown by calculation of the constant F, which may be determined to within 1% from the maxima in the viscosity–molar fraction isotherms (A., 1929, 1227); the values of F lie between 1·0 and 1·5, and assume the higher values for mixtures having a large difference between the mol. wts. of the constituent gases. The characteristic temperature Θ, which has been calculated for a number of gases, falls with increase of the mol. wt. M, whereas $M\Theta$, which varies from 17 to 26, increases in general with M, although for the inert gases the variation is periodic. The ϕ functions ($=q_1M_1\Theta_1/q_2M_2\Theta_2$) of the gas mixtures have been calculated. For those mixtures for which the cross-sectional ratio is high or unity ϕ is approximately equal to q, but for intermediate values of q ϕ increases to about 1·5 q.

XII. [With R. Zink.] Comparative measurements of the viscosity of air between 20° and 830° accord well with a value of 111 for the Sutherland constant. Differential measurements of the viscosities of nitrogen, argon, and carbon dioxide between 20° and 700° made with a simple capillary tube differ only slightly from measurements made with a tube expanded at one end; by this second method results have been obtained for argon, nitrogen, carbon dioxide, oxygen, hydrogen, helium, neon, methane, and sulphur dioxide between 20° and 830°. The Sutherland formula is applicable to nitrogen, argon, and oxygen within the range studied, the constants C being 104·7, 142, and 125, respectively. For hydrogen, helium, and neon the Sutherland formula is totally invalid, but the modified Onnes equation $\eta=kT^n/(1+C/T)$, where n=0·67, 0·67, 0·6, and C=0, 2·5, and 20, respectively, gives values for η which accord well with those determined experimentally. For carbon dioxide and sulphur dioxide the Sutherland constant becomes constant only at temperatures above 300°, the values being 213 and 306; for methane C=162. The variation of the Sutherland constant with temperature has been investigated: for hydrogen, helium, and neon C increases slowly and n diminishes with rise of temperature. For hydrogen n tends to the value 1·5 at very low temperatures; for the other gases examined n converges to the value 0·5, and with falling temperature C passes through a maximum which lies a little above the critical temperature.

H. F. Gillbe.

Kordes' law. K. M. Stachorski (J. Russ. Phys. Chem. Soc., 1930, 62, 1493—1497).—Kordes' law (A., 1926, 798) may be applied in the approximate evaluation of the degree of association of one or both components of a mixture. R. Truszkowski.

Viscosity of mixtures of ethyl acetate with piperidine. N. A. Pushin and T. Pinter (Z. physikal. Chem., 1930, **151**, 135—137; cf. A., 1929, 994).—From the results of measurements of the density and viscosity of mixtures of ethyl acetate and piperidine it is concluded that the associated molecules of the latter substance are partly resolved by ethyl acetate into simpler complexes.

F. L. Usher.

Molecular kinetics of glasses in the softening interval. G. Tammann (Z. anorg. Chem., 1930, **193**, 406—408).—The abrupt changes of specific heat and of the coefficient of expansion of glasses in the softening interval are shown not to be due to polymerisation processes. It is suggested that molecular rotation commences within the glass at the lower temperature limit of the softening interval and is complete at the upper limit. H. F. Gillbe.

Alloys of iron. IX. Constitution of iron–silicon alloys. J. L. Haughton and M. L. Becker (J. Iron Steel Inst., 1930, **121**, 315—335).—Very pure alloys containing up to 73% Si have been studied by means of thermal analysis, dilatometric measurements, magnetic tests, annealing tests, and photomicrographic observations. The liquidus and solidus curves of the α solid solution region lie close together, and fall at 35% Si to 1198°, the eutectic with the ε phase (compound FeSi). The maximum of the liquidus in the ε area is at 1410°, and falls at 51% Si to the eutectic with the ζ phase at 1213°; the ζ phase is probably Fe_2Si_5, which forms a eutectic with silicon at 59% Si and 1208°. Iron is but slightly soluble in silicon, but the solubility of silicon in iron is 18·5% at the eutectic point and falls to 15% at about 800°. Murakami's interpretation of the arrest in the cooling curve at about 1030° as being due to the formation of Fe_3Si_2 has been confirmed, and there appears to be another arrest at about 950°, the cause of which is obscure. Silicon lowers the β–α magnetic transition point rapidly until it meets the η phase boundary at 490° and 14·5% Si, after which the curve is horizontal up to 25% Si. A second magnetic transition exists at 82°, due to a transformation in the η phase.

H. F. Gillbe.

Nature of the β-transition of copper–tin alloys. H. Imai and I. Obinata (Mem. Ryojun Coll. Eng., 1930, 3, 117—135).—Resistance–temperature curves of copper–tin alloys show a sharp fall and subsequent steady rise of resistance at 525°; for alloys containing less tin than the eutectic mixture the curve shows a further break at 590° which is a function of temperature only and not of the time of heating, and is probably due to a change in the β mixed crystal phase. Alloys consisting of the δ+ε phase show a very pronounced fall of resistance at about 590°, and a subsequent rise. Differential heating and cooling curves show that the β transformation takes place in two stages, at 525° and 590°. Alloys quenched from 700° show marked absorption of heat at 525°, and evolution of heat at 200° and 350°; these effects, which increase with the content of the alloy, are attributed to eutectoidal breakdown of the supercooled β mixed crystals. The whole transition of the phase appears to take place in three stages, viz. $\beta\longrightarrow\beta'\longrightarrow\beta''\longrightarrow\alpha+\delta$ and this view is supported also by the resistance–temperature curves of the chilled alloys. The β transition resembles the A2 transformation of steels and the β transformation of copper–zinc alloys in being concerned with a change of atomic energy rather than a simple phase transformation.

H. F. Gillbe.

Compound SnSb. W. M. Jones and E. G. Bowen (Nature, 1930, **126**, 846—847).—The compound SnSb has a crystal structure of the sodium chloride type; *d* 6·94 g./c.c., and a_0 6·092 Å. Reflexions from the 111 planes are absent, but the observed and calculated values of the plane spacings are in good agreement, as are those of intensities of the lines. The structure of the compound SnSb persists over the range 46—60% Sn with some change of lattice constant showing solubility of both constituents in it. Dissolution of up to 4% Sb changes the lattice constant to 6·106 Å. and before annealing dissolution of 10% Sn causes an expansion to 6·124 Å.; after annealing there is no measurable change.

L. S. Theobald.

Crystal structure of the β phase of aluminium-bronze. I. Obinata (Nature, 1930, **126**, 809).—A powder photograph of the binary alloy containing 12·5% Al taken at about 650° shows it to belong to a body-centred cubic super-lattice, of parameter 5·887 Å. Weak spectral lines belonging to the β phase are obtained from the same alloy quenched from 850°, whilst intense lines correspond with a hexagonal lattice of the β′ phase. The lattice constants are: β′ phase, *a* 11·13 Å., *c* 6·342 Å., and *c*/*a* 0·5698, and β phase, *a* 5·835 Å.

L. S. Theobald.

Solubility of naphthalene in some aliphatic alcohols. A. A. Sunier (J. Physical Chem., 1930, **34**, 2582—2597).—The solubility of naphthalene in methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec*.-, and *tert*.-butyl alcohols has been determined between 20° and 70° by the synthetic method. For the normal alcohols the solubility increases from methyl to butyl alcohol; at the lower temperatures *iso*-propyl alcohol dissolves about 30% less naphthalene than does the corresponding normal alcohol. *iso*-Butyl alcohol is a poorer solvent than the normal compound at all temperatures in the range investigated, whilst the secondary compound is the best solvent of all the isomerides at the higher temperatures and the tertiary is the poorest at the lower temperatures. With methyl and ethyl alcohols the presence of about 2% of water reduces the solubility by about 20%. The errors introduced into the determination of solubility by the synthetic method by the presence of undissolved crystals and by too rapid heating are considered. The causes of deviation from Raoult's law are briefly discussed.

L. S. Theobald.

[Solubility of] caseinogen. J. Sladek (Časopis Českoslov. Lék., 1930, **10**, 1—7, 29—38, 61—66; Chem. Zentr., 1930, i, 3314).—The solubility of caseinogen in solutions containing constant amounts of sodium chloride and hydroxide increases with its concentration to a maximum and then diminishes. For equal amounts of caseinogen and equal concentrations of sodium chloride it increases with increasing p_H; when the concentration of sodium hydroxide is constant it increases with increasing concentration of sodium chloride but eventually falls.

A. A. Eldridge.

Nitric acid. VI. Total vapour pressures and densities of solutions of nitrogen peroxide in anhydrous and very concentrated nitric acid. A. Klemenc and J. Rupp (Z. anorg. Chem., 1930, **194**, 51—72; cf. A., 1930, 543).—The densities and total vapour pressures of solutions of nitrogen peroxide in anhydrous nitric acid and in 16*N*- and 19*N*-nitric acid have been determined over a wide range of concentration at 0°, 12·5°, and 25°. As the concentration of the solution in the anhydrous acid is increased, the density rises continuously up to a maximum and then starts to fall again, which is regarded as pointing to compound formation in the mixture. The amount of peroxide dissolved increases with its partial pressure more rapidly than Henry's law would indicate; at 25° and under a total pressure of 0·8 atm., 1 volume of the anhydrous acid dissolves about 590 volumes of peroxide. The depression of the solubility caused by addition of water is probably connected with the existence of the equilibrium

$HNO_3,H_2O+NO_2 \rightleftharpoons HNO_3,NO_2+H_2O$ in the solution. R. Cuthill.

Intensive drying. (Miss) E. J. Greer (J. Amer. Chem. Soc., 1930, 52, 4191—4201).—If in the purification of benzene special care is taken to remove all sulphur compounds, no colour is developed and no additive compounds are formed with phosphorus pentoxide. The vapour pressure of benzene was unchanged after being dried for 3 years with phosphorus pentoxide in a fused pyrex glass apparatus. A few days' contact with activated silica gel gives rise to changes in the vapour pressures of benzene, carbon tetrachloride, and carbon disulphide which are in the same direction as and of similar magnitude to those observed in other investigations on intensive drying. The observed effects are attributed to the additive effect of the partial pressure of minute traces of water in the normal liquid rather than to any catalytic effects. *E.g.*, $2{\cdot}29\times10^{-4}$ g. of water in 1 g. of benzene exerts a partial pressure of 7 mm. at 20°, and thus Raoult's law is not followed. Partial pressures of solutions of water in benzene at 20·89° have been determined. Henry's law is followed rigidly. J. G. A. Griffiths.

Sorption of gases by minerals. II. Laumontite. J. Sameshima (Bull. Chem. Soc. Japan, 1930, 5, 303—310; cf. A., 1929, 757).—Ammonia is absorbed by dehydrated laumontite in amounts which depend on the conditions of dehydration, but not on the temperature between 0° and 25°. Carbon dioxide is not absorbed. C. W. Gibby.

Relation between gas content and adsorption of electrolytes by activated charcoal. V. Poisoning of platinum in platinised charcoal. S. Vassiliev and A. Frumkin (Z. physikal. Chem., 1930, 151, 87—96; cf. A., 1929, 640; 1930, 683, 684).—Mercuric chloride is very strongly adsorbed by platinised charcoal, and is not displaced when the latter is afterwards saturated with hydrogen. The addition of 1 mol. of mercuric chloride per atom of platinum suffices to abolish the capacity of the charcoal to assume a higher oxygen potential, *i.e.*, it adsorbs the same quantity of acid as unplatinised charcoal. In an acid medium, desorption of acid by hydrogen is not affected by the presence of mercuric chloride. If, however, the mercuric chloride is adsorbed from an alkaline solution, or is previously "fixed" by means of hydrogen, the platinum is poisoned and desorption of acid is incomplete. Reduction of adsorbed oxygen by means of hydrogen (development of a hydrogen potential) is also inhibited under similar conditions. Mercuric chloride influences only slightly the development of a hydrogen potential by oxygen-free charcoal. F. L. Usher.

Adsorption time and its measurement by streaming methods. I. P. Clausing (Ann. Physik, 1930, [v], 7, 489—520).—The phenomenon of adsorption of a gas at a solid interface is discussed in the light of the kinetic theory, and a critical survey is given of earlier work on the subject. It is shown that the mean adsorption time τ of a molecule colliding with the surface is equal to the mean interval during which the molecules adsorbed in an element of time dt are retained after collision with the surface, and is related to the probability of re-evaporation, and that the mean adsorption time of the adsorbed molecules in the stationary state is 2τ. If at time $t=0$ a vessel containing gas at a given pressure is put into communication with a second, empty, vessel, by means of a tube, the delay experienced before the first molecules of gas enter the second vessel will be governed by the length of time that each molecule is retained by the walls of the tube after each collision, *i.e.*, by the adsorption time. The theory of the determination of adsorption times by streaming methods based on this principle is developed by regarding the phenomenon purely as one of diffusion, and also by regarding the adsorption times as very great compared with the time of flow of the gas. H. F. Gillbe.

Stabilising effect of adsorption layers of surface-active substances on disperse systems. II. Stability of bubbles and drops at surfaces of separation. P. Rehbinder and E. Wenström (Kolloid-Z., 1930, 53, 145—158).—The factors determining the stability of disperse systems and the methods of measuring it are discussed. The stabilising effect of surface-active substances of sufficient surface rigidity on aqueous suspensions and emulsions is at a maximum when the adsorption layer is completely saturated. Suspensions of barium sulphate, ferric oxide, mercuric oxide, aluminium sulphate, and silica in benzene, toluene, and heptane are stabilised by adsorption layers of polar molecules and excess of the stabilising agent brings about coagulation. In such cases stability is at a maximum at a medium concentration of stabiliser. When a foam is stabilised by a "liquid" adsorption layer such as *iso*amyl alcohol in water, an optimal concentration of the liquid corresponds with maximum stability, but when the stabiliser forms a semi-solid adsorption layer the stability increases with concentration up to saturation of the layer. The stability of foams and emulsions has been measured by determining the time, τ, taken for bubbles or liquid droplets to disappear. In the case of emulsions τ depends on which of the pair of liquids is in the disperse phase. Curves relating the time or stability to concentration of the stabilising agent have led to the recognition of two groups of adsorption layers—liquid and solid. For pure liquids τ is 0, with liquid stabilisers the curve passes through a maximum before saturation is reached and then falls, whilst with solid adsorption layers τ increases with concentration to a limiting value at saturation. Iodine, eosin, crystal-violet, and night-blue form a transition between the two groups. Similar experiments have been extended to more massive systems, such as a broken mercury surface in solutions of stabilising agents.

E. S. Hedges.

Unimolecular films on water and on mercury. I. Surface films on water. E. Fahir (J. Chim. phys., 1930, 27, 471—492).—Three classes of substances which spread on water to form films are recognised: (1) those which spontaneously form stable films (oleic and myristic acids, cetyl alcohol), (2) those giving a film which disappears more or less rapidly through its high solubility (lauric acid) or volatility (camphor), and (3) substances which give a film only when previously dissolved in a suitable volatile liquid, such as benzene or chloroform. Palmitic and stearic acids belong to the third class, but give spontaneous stable films at higher temperatures. The stability of these films on water has been studied by Marcelin's method and curves connecting the area of the film with the pressure have been constructed. The results confirm that oleic, myristic, palmitic, and stearic acids and cetyl alcohol form unimolecular films with one end of the molecule towards the water. The following values for the lengths of the molecules have been determined and are in good agreement with the values calculated from *X*-ray spectrographic data: oleic acid, 23·2; myristic acid, 16·3; cetyl alcohol, 23·5; palmitic acid, 17·8; stearic acid, 19·8 Å.

E. S. Hedges.

Change of the osmotic water attraction of a system of phases. I. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 694—701).—A mathematical consideration of the thermodynamics of general osmotic systems with special reference to the influence of changes of pressure and volume on the osmotic water attraction of the systems.

O. J. Walker.

Osmotic pressure and mol. wt. of cellulose acetate. E. H. Büchner and P. J. P. Samwel (Proc. Akad. Wetensch. Amsterdam, 1930, **33**, 749—754).—A preliminary account of osmotic pressure measurements of cellulose acetate (cellite) in acetone, acetophenone, and benzyl alcohol by the method of van Campen (unpublished) which depends on measuring the velocity with which the solvent diffuses through the semipermeable membrane against an applied pressure and extrapolating for zero velocity. A partly denitrated collodion membrane was found satisfactory. In some cases the osmotic pressure is proportional to the concentration and the temperature, but in other cases deviations are obtained. The mol. wt. in the various solvents is approximately the same, viz., 32·6 to $35{\cdot}8\times10^3$. Different samples of cellite which have different viscosities give the same value for the mol. wt., so that there is no connexion between the latter and the viscosity.

O. J. Walker.

Cryoscopic study of paraldehyde in solutions of sodium and barium chlorides. F. Bourion and E. Rouyer (Compt. rend., 1930, **191**, 1062—1064).—Paraldehyde [taken as $(C_2H_4O)_3$] in $0{\cdot}5M$ solutions of sodium chloride at 0° (mean K_c 23·3) exists as an almost stable molecule, but in $1{\cdot}225M$ solutions is depolymerised to an extent which increases as the concentration decreases, and corresponds with equilibrium between simple and triple molecules only. In $0{\cdot}25M$- and $0{\cdot}6125M$-barium chloride solutions (mean K_c 22·40 and 28·60, respectively) there is no indication of depolymerisation (cf. Bourion and Tuttle, A., 1929, 648, 1236).

J. Grant.

[Cryoscopy and rotatory powers of] solutions of tartrates in molten calcium chloride hexahydrate. E. Darmois and J. Cessac (Compt. rend., 1930, **191**, 1053—1055).—The mean cryoscopic constant obtained from solutions of calcium, methyl, and ethyl tartrates dissolved in molten calcium chloride hexahydrate (m. p. 29·8°) is 40·4, corresponding with the normal mol. wts. of these salts. The solutions of methyl and ethyl tartrates are lævorotatory, and determinations of [α] at 20—80° for the yellow, green, and (mercury) indigo rays indicate an equilibrium between two or more isomeric tartrates, depending on the concentration and temperature. Solutions of calcium tartrate are only feebly lævorotatory, and [α] is only slightly affected by variations in concentration and temperature (cf. A., 1929, 259).

J. Grant.

Osmotic relations of strong electrolytes in solution and hydration of their ions. K. Fajans and G. Karagunis (Z. angew. Chem., 1930, **43**, 1046—1048).—A lecture.

E. S. Hedges.

Generality of the colloid state. P. P. von Weimarn (Kolloid-Z., 1930, **53**, 246—247).—A claim for priority.

E. S. Hedges.

Colloid science, electrotechnics, and heterogeneous catalysis. Wo. Ostwald (Kolloidchem. Beih., 1930, **32**, 1—113).—The fundamental principles of the physics and chemistry of colloids are discussed in terms of the degree of subdivision of matter. It is emphasised that most physico-chemical properties vary with the degree of subdivision and that this variation is greatest in the region of colloidal dimensions, where maxima or minima are often to be observed. Many examples of the change of properties with the degree of dispersion are illustrated by curves. The importance of dimensional characteristics in properties which lie beyond the usual scope of colloid science is indicated, and insulators, electrolytic valves, detectors, photo-cells, and heterogeneous catalysis are discussed from this point of view.

E. S. Hedges.

Evolution of colloidal molecules. General exposition. P. Bary (Rev. gén. Colloid., 1930, **8**, 289—300).—The hypothesis of an "evolution zone" in the dynamic equilibrium of polymerides is advanced, an increase in the number of molecules being regarded as "positive evolution" and a decrease as "negative evolution." The theory of molecular evolution is applied to lyophilic colloids, which are regarded as matter in the evolution zone. Such colloids consist of chain-like polymerides, the ends of the chains being saturated with molecules acquired from the dispersion medium; they are regarded as existing in two states, according to whether their evolution is positive or negative, *i.e.*, whether the number of particles is increasing or decreasing. A marked tendency towards positive evolution is characteristic of a peptisable colloid, the velocity of evolution being modified by temperature, pressure, and the chemical properties of the medium; under certain conditions the direction of evolution may be reversed to negative, leading to coagulation or gelation. The process of positive evolution begins with the swelling of a gel and ends with molecular dispersion. Typically lyophobic colloids, dispersed by mechanical or electrical means, are not regarded as being in the evolution zone; they neither swell nor form jellies. Colloids prepared by chemical methods, such as the

metallic hydroxides and sulphides, are in the zone of evolution, but the direction of evolution is negative.
E. S. Hedges.

Brownian motion. G. E. Uhlenbeck and L. S. Ornstein (Physical Rev., 1930, [ii], 36, 823—841). —Mathematical. The frequency distribution of the velocity and displacement of a particle in Brownian motion, and the Brownian motion of a harmonically bound particle, are investigated. N. M. Bligh.

Cataphoretic and extinctiometric measurements with kaolin suspensions. A. Reifenberg (Kolloid-Z., 1930, 53, 162—170).—Measurements of the velocity of cataphoresis of kaolin particles in dilute electrolyte solutions have been compared with the amount and state of aggregation of the transmigrated portion as determined by nephelometric investigation. The results establish that small concentrations of ammonium, sodium, and calcium hydroxides and disodium hydrogen phosphate raise the charge on the particles and reduce the aggregation simultaneously, the order of effectiveness for both processes being $Ca>Na>NH_4$. Similarly, with falling electrokinetic potential the amount of kaolin transferred is reduced and the degree of aggregation is greater. At somewhat higher concentrations sodium hydroxide has the greatest charging effect, and in more concentrated solutions all the electrolytes have a discharging effect, that of calcium being very pronounced. Coagulation is considered to be due not only to discharge, but also to dehydration of the particles. E. S. Hedges.

Cataphoresis in rotating electric fields. E. M. Pugh and C. A. Swartz (Physical Rev., 1930, [ii], 36, 1495—1502).—A new method of making cataphoresis measurements on colloid particles, using a rotating electric field causing the particles to move in circles, is described. The mobilities of particles smaller than 10^{-4} cm. diameter fluctuate widely; a qualitative explanation is discussed. N. M. Bligh.

Dielectric constant of complex colloidal systems. Adsorption by micelles in solution. Dielectric origin of forces of adsorption. C. Marie and N. Marinesco (J. Chim. phys., 1930, 27, 455—470).—The dielectric constants of suspensions of carbon in water and also in the presence of gelatin, leucine, and glycine have been measured. The results are said to show that the phenomenon of protection of colloids is a simple adsorption due to the dielectric attraction between the dipoles of high moment of the protective agent and the electrically deformable adsorbent particle. Good protective colloids should therefore have high dipole moments and it is shown that this property is a special feature of some of the proteins. E. S. Hedges.

Plasticity and viscosity as criteria of molecular aggregation. S. E. Sheppard (J. Rheology, 1930, 1, 471—483).—A critical discussion of recently published work on the phenomena associated with the viscosity of colloidal solutions and the light thereby thrown on the degree of dispersion of solvated molecules. E. S. Hedges.

Colloidal structure of egg-white as indicated by plasticity measurements. J. L. St. John and E. L. Green (J. Rheology, 1930, 1, 484—504).—Egg-white from fresh eggs consists of two portions (described as thick and thin, respectively), which differ in their physical and colloidal properties. By means of a horizontal capillary-tube plastometer the difference in properties of the two portions has been examined. The mobility of the thick portion appears to increase with the time for which the egg is kept after opening, but this time factor does not affect the behaviour of the thin white, suggesting a colloidal change involving a translation of thick into thin white. The thick portion is not considered to be pseudoplastic, although the thin portion may be. Analyses of the plasticity data and especially of the inconsistencies therein lead to the view that with the thick portion a part of the total work is used to break down the gross structure before the white enters the tube, a part to deform and deflocculate the disperse phase after it enters the tube, and the remainder to cause viscous flow. The effect of the breakdown of the gross structure is probably shown by the difference in the mobility of the thick and thin portions of the white. A mathematical formula for determining the pressure necessary to break down the gross structure has been developed. A method for the accurate calibration of capillary tubes is described.
E. S. Hedges.

Adherence and packing of microscopic particles. A. von Buzágh (Kolloidchem. Beih., 1930, 32, 114—142).—The sedimentation volume of irregular, polyhedral quartz particles of microscopic dimensions has been measured in water, electrolyte solutions, lyophilic colloidal solutions, and some organic liquids and the results have been correlated with the size, form, orientation, and adherence of the particles. In water the sedimentation volume is independent of the particle size, but in the presence of coagulating electrolytes the sedimentation volume is greater the smaller is the particle size. This relation does not hold for particles greater than 100 μ. The sedimentation volume in electrolyte solutions increases with the adherence value of the particles as measured by the angle of tilt method. This apparent contradiction is explained by supposing that when the adherence is small the particles can glide over each other and become packed in a small space, whilst when the adherence is great the particles adhere at edges and corners, thus giving an open structure and larger volume to the sediment. It follows also that the value of the sedimentation volume alone cannot in such cases give a true indication of the size of the lyospheres surrounding the quartz particles. An indication of the size of the lyospheres can be obtained, however, when the size of the particle is small in comparison with the thickness of the solvate sheath or when the particles are in the form of oriented platelets, giving a uniform method of packing. Experiments have been conducted, therefore, with plate-like particles of glass and it has been established that the sedimentation volume and therefore the thickness of the solvate sheath decreases in the presence of a coagulating electrolyte. The mechanical properties of the sediment of coarsely disperse quartz also vary with the size, form, and adherence of the particles, and the thickness of the lyospheres; in water the sediment is dense, but can flow, whilst in electrolyte solutions it is loosely packed, but cannot flow. Aliphatic alcohols in aqueous solution raise the adherence value of the particles, the effect increasing with rising concentration and with the mol. wt. of the alcohol. The sedimentation volumes of quartz particles were also measured in ethyl ether, chloroform, carbon tetrachloride, benzene, and toluene and were found to increase with the adherence values. Carbon tetrachloride is remarkable for the high values obtained. In gelatin solutions of medium concentration the sedimentation volume and adherence value of quartz particles simultaneously vary with time, being at first greater than the values obtained in water and later falling gradually to a low value. This behaviour is due to the slow formation of a gelatin sheath round the particles, a thin layer having a coagulating influence and a thicker layer a stabilising effect. For this reason, very dilute or very concentrated gelatin sols do not show this time effect. E. S. HEDGES.

Polyhydroxy-compound method of synthesis of electronegative sols. III. Formation of ferric hydroxide sol in the presence of citric acid. A. DUMANSKI and T. P. TIASHELOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1313—1334; cf. A., 1930, 992).—Negatively-charged colloidal suspensions of ferric hydroxide are formed from ferric chloride in the presence of alkaline citrate. The first product is a complex of ferric hydroxide with sodium citrate, which reacts with sodium hydroxide to yield the sol. The complex appears, on the basis of measurements of electrical conductivity and of the f. p. lowering, to be identical with Belloni's "ferrisodium citrate," the iron being in the anion. Measurements of the absorption spectrum sharply differentiate solutions of the complex from those of the sol, obtained by adding further alkali. Excess of alkali produces coagulation of the sol. Sols formed in the presence of citric acid are less stable than are those formed in tartaric acid solution. R. TRUSZKOWSKI.

Influence of hydrolysis temperature on some properties of colloidal ferric oxide. II. Stability. G. H. AYRES and C. H. SORUM (J. Physical Chem., 1930, **34**, 2629—2635; cf. A., 1930, 693).—The coagulation values of ferric oxide sols show no regular variation with the temperature of preparation of the sol or with the concentration of ferric chloride hydrolysed. In general, however, the flocculation value towards sodium chloride decreases with a rise in temperature. The sols become opaque and reddish-orange in colour on heating above 160° and show much settling when kept. At the higher temperatures, the sols appear to be less hydrated. The decrease in stability and the increase in turbidity are not due to an increase in particle size.

L. S. THEOBALD.

Dye sols. I. Sol formation of Congo acid by washing-out peptisation. R. TANAKA (Kolloid-Z., 1930, **53**, 200—205).—When Congo-red is precipitated by mineral acids and the precipitate washed with water the first washings are colourless, later pink, red, and finally blue, with the formation of sols by peptisation. The electrical conductivity of these sols has been measured and peptisation begins when the liquid has a conductivity of 0·0003 mho. Measurements of filtration velocity and viscosity suggest that immediately before peptisation the precipitate undergoes swelling. Directions are given for the preparation of a concentrated sol of Congo acid, containing 2·46 mg. per c.c. E. S. HEDGES.

Influence of electrolytes on colloidal sulphur. A. BONVARLET (Rev. gén. Colloid., 1930, **8**, 300—309).—When progressively increasing quantities of sodium chloride are added to colloidal sulphur the stability of the sol passes through a maximum, but the concentration of sodium chloride should not exceed 0·54%. Sodium, ammonium, and lithium salts produce a reversible precipitate of sulphur at all concentrations, whilst salts of barium, copper, calcium, potassium, and magnesium give an irreversible precipitate. The precipitation is the more rapid and complete the higher is the at. wt. of the metal concerned. Ultramicroscopical examination of the precipitates has revealed that the reversible precipitates consist of an assemblage of primary particles, which have lost their electric charge, but still preserve their individuality; on the other hand, the particles in the irreversible precipitates have coalesced and cannot redisperse when the conditions of the dispersion medium are changed. The stability of a sol containing 13·4% of sulphur is at a maximum in the presence of 0·93% of sodium chloride, being thus about 7% of the weight of sulphur. Both rise and fall of temperature decrease the stability of the sulphur sols, especially when relatively large quantities of sodium chloride are present. The stability is at a maximum over the range 12—18°. Sulphur is also deposited by the action of light, but deposits formed either by light or temperature changes are redispersed in the sol by shaking. E. S. HEDGES.

Precipitation potential of arsenious sulphide hydrosol in presence of excess of arsenious oxide. S. N. MUKHERJI (Kolloid-Z., 1930, **53**, 159—162).—The cataphoretic migration velocity of the particles of arsenious sulphide sols containing an excess of arsenious oxide decreases with increasing content of the latter and the equicoagulation and precipitation concentrations of electrolytes fall simultaneously. Although dilution of the sol increases its stability towards electrolytes, it has the effect of lowering the velocity of cataphoresis. E. S. HEDGES.

Stabilisation of colloidal systems. III. S. I. DIJATSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 1285—1311; cf. A., 1930, 993).—The stability of a number of sols is diminished by the addition of small quantities of methyl or propyl alcohol, but is augmented by higher concentrations of the alcohol; these effects are ascribed to dehydration of the micelles at low concentrations and to slow augmentation of the dielectric polarisation of the molecules of the lyosphere, involving increase in the dipole moment, in the case of high concentrations. The variation of surface tension of colloidal solutions with temperature attains a maximum value over the interval 30—40°. A colloidal solution can be separated into fractions of different relative dispersion by freezing; the larger micelles remain in the coagulate on thawing, whilst the solution contains particles in a high degree of dispersion. In some cases suspensions containing ultramicrocrystalline particles are obtained on thawing. R. TRUSZKOWSKI.

Reversal and peptisation of metachromic dyes at surfaces. N. VON JANCSÓ (Kolloidchem. Beih., 1930, **32**, 143—155).—When aqueous solutions of metachromic dyes containing electrolytes are shaken with an immiscible organic liquid, the dye undergoes a colour change at the liquid–liquid interface. The colour change in the case of Congo-rubin is a particular colloid-chemical problem, which can be explained in terms of Wo. Ostwald's theory that the colour is a function of the degree of dispersion. When the liquid–liquid surface is increased by shaking, the blue, coarsely disperse substance is peptised at the interface to the red, finely-dispersed form, the phenomenon being most marked when the electrolyte used is a neutral salt having a univalent cation and an anion which falls near the beginning of the lyotropic series. Blue Congo-rubin membranes spread at a large, still surface separating an aqueous electrolyte solution from an immiscible organic liquid, and assume the red form. E. S. HEDGES.

Swelling pressure. J. J. BIKERMAN (Z. physikal. Chem., 1930, **151**, 129—134).—Theoretical. Osmotic pressure and swelling pressure differ in that the forces between solute and solvent in the former effect have their origin in points, and in the latter in surfaces. If l denotes the distance between a molecule of solute and the position of weakest attraction, both types of pressure are represented by the formula $P=3kT/8l^3$. In the case of gels, l is the thickness of the adsorbed layer of solvent, and on introducing this magnitude into the general formula an expression is obtained which agrees with the empirical concentration–pressure relation observed by Posnjak (A., 1912, ii, 912). F. L. USHER.

General regularities of gelatin swelling in electrolyte solutions. K. RUDSIT (Kolloid-Z., 1930, **53**, 205—218).—The results of a large number of measurements on the swelling of gelatin and the influence of the hydrogen-ion concentration of the liquid, the temperature, concentration of salts, and time are presented. The swelling curves of all the kinds of gelatin investigated have two minima at p_H 4·7 and 8·0, respectively, between which lies a "neutral" maximum, the position of which may be on either the acid or the alkaline side and depends on the kind of gelatin. The swelling curve of gelatin in solutions of sodium chloride of different concentrations is essentially similar to those obtained with hydrochloric acid and sodium hydroxide. In mixtures of salt with acid or alkali the presence of sodium chloride reduces the swelling. At higher concentrations of hydrochloric acid or sodium hydroxide this holds only for low concentrations of sodium chloride, for with more of the salt the gelatin dissolves completely. In the region of the minima of the acid–alkali swelling curve small quantities of sodium chloride increase the swelling and larger amounts have the reverse effect. In these systems and also in the presence of lithium, potassium, and calcium chlorides the position of the minimum is displaced in the direction of decreasing hydrogen-ion concentration with rising temperature. E. S. HEDGES.

Titania gel. Comparison with silica gel. S. KLOSKY (J. Physical Chem., 1930, **34**, 2621—2623; A., 1925, ii, 1057).—The preparation and properties of titania gel are discussed. Silica gel is easier to prepare, is more adsorptive, and is a better catalyst support. L. S. THEOBALD.

Morphology of chemical reactions in gels. III. V. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1357—1376; cf. A., 1930, 33).—The phenomena of periodic precipitation in gels are classified. The spreading of a drop of silver nitrate solution over a gelatin surface is not a continuous process, but is made up of a series of spurts; to this phenomena is ascribed the formation of "artificial" Liesegang rings on the surface of an agar gel impregnated with potassium dichromate when drop after drop of silver nitrate solution is placed on the same spot. A number of other physical processes, such as the evaporation of water or milk, the melting of ice, and the flow of mercury, take place similarly in a series of steps. R. TRUSZKOWSKI.

Constitution of soluble proteins as reversible dissociable systems of components. II. S. P. L. SØRENSEN (Kolloid-Z., 1930, **53**, 170—199; cf. A., 1930, 1603).—The dissociation tendencies of egg-albumin, serum-albumin, serum-globulin, casein, and gliadin have been calculated from previously published data. The values are small, especially in the case of egg-albumin, and increase with dilution, particularly when the concentration falls below 1%. Previous work, supplemented in some cases by recent, unpublished data, is described on the solubility of egg-albumin and its dependence on the total protein concentration of the experimental mixture, the fractionation of egg-albumin, the preparation and fractionation of serum-albumin and serum-globulin, their solubility and dependence of solubility on the total amount of protein, the chemical composition of the fractions of serum-albumin, the solubility relations and reversible fractionation of casein and wheat-gliadin. Serum-albumin can be separated into three fractions according to solubility, and, although previous attempts to differentiate between the fractions chemically by acid degradation have failed, it is found that the fractions show differences in the amounts of nitrogen combined as humin, ammonia, cystine, and tryptophan. E. S. HEDGES.

Structure viscosity of caoutchouc solutions. B. DOGADKIN and D. PEWSNER (Kolloid-Z., 1930, **53**, 239—245).—Caoutchouc solutions show the deviations from the Hagen–Poiseuille law characteristic of colloids. The dependence of the relative viscosity on the rate of flow can be expressed by the de Waele–Ostwald formula and the structure viscosity exponent can be taken as a measure of the structural peculiarities of the particular kind of caoutchouc. With rise of temperature the viscosity of the caoutchouc solutions decreases, but the exponent of structure viscosity increases. The state of aggregation of the caoutchouc micelles is reduced by rolling the material and causes

a decrease in the value of the structure viscosity exponent. Ageing produces a similar effect.
E. S. HEDGES.

Effect of plant-lecithin on the swelling and surface tension of flour-glutin and starch. I. Binding materials in cooking. W. ZIEGELNAYER (Kolloid-Z., 1930, 53, 224—231).—The agglutinating effect of egg-yolk in cooking is due to the lecithin and can be increased by adding 1% of soya-lecithin to the flour. This corresponds with the addition of six eggs to 1 kg. of flour. The lecithin has the effect of limiting the amount of swelling through the formation of an adsorption complex. Cytolipoid lecithin produces a starch–glutin–fat adsorption complex, increasing the extensibility, elasticity, and softness of the dough. The syneresis observed in a flour–water mixture is absent when lecithin has been added.
E. S. HEDGES.

Table for kinetic gas theory. T. EDQUIST (Physikal. Z., 1930, 31, 1032).—Of the total number of N gas molecules, the number (dn) for which the kinetic energy possesses values between E and dE can be expressed according to Maxwell's distribution law. This equation has been integrated from 0 to $\sqrt{E/kT}$, and n is expressed as a function of N $(n=N\phi)$. Numerical values of ϕ are tabulated for values of $\sqrt{E/kT}$ from 0·10 to 3·00. W. R. ANGUS.

Thermodynamic treatment of chemical equilibria in systems of real gases. III. Mass-action effects. Optimum hydrogen : nitrogen ratio for ammonia formation in the Haber equilibrium. L. J. GILLESPIE and J. A. BEATTIE (J. Amer. Chem. Soc., 1930, 52, 4239—4246; cf. A., 1930, 1357).—By means of the equations previously developed, optimal initial (r) and equilibrium (r_e) values of the ratio $H_2 : N_2$ have been calculated for total pressures between 100 and 1000 atm. at 500°, with and without the presence of argon. Except at low total pressures the ratios are less than 3; r has a minimum value of 2·90 at 600 atm. and r_e falls to 2·68 at 1000 atm. The corresponding values are 2·91 and 2·72 when atmospheric nitrogen containing 0·012 mol. fraction of argon is used. When yields of ammonia at 500° are calculated for the $H_2 : N_2$ ratios 2 and 4, deviations as great as 1·5% at 1000 atm. are found between values derived from the ordinary and the improved mass-action equations. Argon has a deleterious effect at all total pressures. J. G. A. GRIFFITHS.

Higher stages of dissociation of phosphoric and boric acids. F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1930, 151, 80—86; cf. A., 1930, 560).—The failure to detect a third point of inflexion in the potentiometric titration curve of phosphoric acid is shown by a simple calculation to be due to unfavourable conditions of concentration. By using a saturated solution of disodium hydrogen phosphate and concentrated alkali the third stage of neutralisation becomes apparent. By using the same formula an upper limit for the hitherto undetermined second and third dissociation constants of boric acid may be calculated, the concentrations and the accuracy of the potential measurements which fail to reveal the corresponding points of inflexion being known. The values obtained are: $K_2=1{\cdot}8\times10^{-13}(f_2/f_{OH})$, and $K_3=1{\cdot}6$ to $3\times10^{-14}(f_3/f_{OH})$, where f_2, f_3, f_{OH} are the activity coefficients of the respective acid anions and the hydroxyl ions. F. L. USHER.

Colorimetric investigations of indicators in presence of neutral salts. N. V. SIDGWICK, W. J. WORBOYS, and L. A. WOODWARD (Proc. Roy. Soc., 1930, A, 129, 579—588).—The change of colour exhibited by a definite concentration of an indicator in a solution of given p_H on the addition of a neutral salt is investigated by a colorimetric method. An optical wedge is employed in conjunction with a Lindemann electrometer and a rubidium photoelectric cell, the light absorption being measured by means of the wedge shift. The photo-electric effect enters into the method only as a null-point observation. The Tizard relation $K=[H](c_1-c)/(c-1)$ is used, where K is the apparent dissociation constant of the indicator acid, c the colour of a slightly alkaline solution of methyl-orange at a given concentration, and c_1 the relative colour, which is the ratio of the colour of any other solution to the unit colour. A correction is made for the part of the hydrogen ions combined with the indicator anions to form undissociated indicator acid. Determinations of K are made in the absence of neutral salts with varying concentrations of hydrochloric acid and a method is described for studying the possibilities (1) that the neutral salt may alter the absorption bands of the coloured forms of the indicator, and (2) that it may affect the chemical equilibrium between these forms. The first is studied independently of the second by dealing with solutions in which the indicator is completely in the yellow or the red forms. Measurements are also made of the dissociation constant of methyl-orange in the presence of varying concentrations of several salts (sodium chloride, bromide, chlorate, and nitrate, and potassium chloride and bromide), the concentration of the indicator being $N/40{,}000$. For sodium chloride K rises to a maximum between $N/20$ and $N/10$ and afterwards falls. A series of measurements was also carried out with a constant quantity of acetic acid–ammonia buffer, instead of hydrochloric acid, at an indicator concentration of $N/53{,}000$, and the results were of the same type for all salts; the value of $[\mathrm{H}^{\cdot}_{free}]$ rises with increase of salt concentration, passing through a maximum at about $N/2$. The theoretical significance of these results is discussed. L. L. BIRCUMSHAW.

Ionisation constants of some chloro- and nitro-anilines by the partition method. G. WILLIAMS and F. G. SOPER (J.C.S., 1930, 2469—2474).—The ionisation constants of *o*-, *m*-, and *p*-chloroanilines and of *o*-nitroaniline have been determined and compared with the discordant values given in the literature. A partition method was used, in which attention was directed to the effect of unhydrolysed salt on the distribution equilibrium and to the choice of extracting solvent when dealing with certain very weak bases. The values obtained for the "concentration" basic dissociation constants of the four substances are $K_b\times10^{11}=0{\cdot}371$, 2·88, 8·45, and 0·00353, respectively, and for the "concentration" hydrolysis constants are $K_h\times10^{4}=27{\cdot}1$, 3·49, 1·19, and 2850, respectively. E. S. HEDGES.

Strength of weak bases and pseudo-bases in glacial acetic acid solutions. J. B. Conant and T. H. Werner (J. Amer. Chem. Soc., 1930, **52**, 4436—4450; cf. A., 1928, 129, 1188).—Spectrophotometric observations at wave-lengths between 470 and 680 $\mu\mu$, on glacial acetic acid solutions of crystal-violet buffered with carbamide and sulphuric acid, carbamide and perchloric acid, and acetoxime and sulphuric acid at 25°, and electrometric determinations with these buffers show that the first dissociation constant of crystal-violet (Adams and Rosenstein, A., 1914, i, 1092) and the constants of carbamide and acetoxime increase greatly with increasing ionic strength, and in more concentrated solutions the salts have specific effects. In titrations it is therefore essential to keep the ionic strength constant by the presence of sufficient neutral salt.

Apparent dissociation constants of seven pseudo-bases in glacial acetic acid have been determined. The hydrogen-ion activity of solutions of the stronger pseudo-bases, half neutralised by sulphuric acid, decreases and then increases with increasing concentration of water. Very weak pseudo-bases exhibit the latter effect only. J. G. A. Griffiths.

Electrolytes in mixed solvents. II. Effect of lithium chloride on the activities of water and alcohol in mixed solutions. R. Shaw and J. A. V. Butler (Proc. Roy. Soc., 1930, A, **129**, 519—536).—An air-bubbling method, in which the volume of air required is less than 2 litres, has been devised for the determination of the partial pressures of water and alcohol in mixed solutions (cf. Downes and Perman, A., 1927, 194). Measurements have been made at 25° of the partial vapour pressures of water–alcohol solutions containing 0—100% of alcohol and lithium chloride in 0·5, 1·0, and 4·0*M* concentrations. It is found that, whilst increasing concentration of lithium chloride causes a decrease in the partial pressure of water in all solutions, its effect on the alcohol varies with the composition of the solvent. In solutions containing a large proportion of alcohol, its partial pressure falls steadily as the salt concentration increases, and in solutions containing 6·4 mol.-% of alcohol it rises steadily, whilst in intermediate solutions it first falls and then rises. The fractional lowering of the vapour pressure of water is always greater than that of alcohol. An approximately linear relationship is established between the relative activities of both water and alcohol and the molar fraction of alcohol in the solvent, at constant lithium chloride concentration. It is possible to distinguish approximately the effects of the solvation of ions by alcohol molecules and the salting-out of alcohol by the interaction of the ions and water. L. L. Bircumshaw.

Calculation of activity coefficients from solubility measurements. II. Thallous iodate. III. Unsymmetrical valency type effect. C. W. Davies (J.C.S., 1930, 2410—2421, 2421—2426; cf. A., 1930, 860).—II. From the solubility data for thallous iodate at 25° recorded by La Mer and Goldman (A., 1929, 1387) the activity coefficients have been recalculated, making allowance for the incomplete dissociation of the salts. When so corrected, certain abnormal features disappear; the activity coefficient becomes independent of the nature of the added salt at low concentrations, specific effects not appearing with uni-univalent salts until an ionic strength of 0·1 is reached. The activity coefficient of thallous iodate in the most dilute solutions is expressed by the equation $-\log f = A\sqrt{\mu}$, where $A=0\cdot47$. Since this A value is much greater than those derived from the most accurate data for other uni-univalent electrolytes, it is concluded that A may vary from salt to salt; it appears to be always lower than the Debye–Hückel value 0·50. The solubility data contribute no support, as stated by La Mer and Goldman, for the principle of specific interaction. In dilute solutions containing magnesium iodate allowance must be made for the $MgIO_3^{\cdot}$ ion, the dissociation constant of which is calculated to have the approximate value $K=0\cdot19$. The dissociation constant of magnesium sulphate previously calculated from conductivity and f.-p. data is confirmed by the solubility data.

III. The large deviations from the Debye–Hückel theory of dilute solutions which have been described as "the electric type effect" or "the unsymmetric valency type effect" are considered to be due wholly to the incomplete dissociation of the salts concerned. Calculations based on solubility measurements with two luteocobaltic salts in potassium sulphate solutions support this view, and give closely concordant values for the dissociation constant of the luteocobaltic sulphate cation. The large deviations found with lanthanum iodate in sulphate solutions are interpreted in the same way and lead to a value for the dissociation constant of the lanthanum sulphate cation which agrees with that derived from the conductivity of lanthanum sulphate solutions. E. S. Hedges.

Equilibrium between vapour and solution in the system acetic acid–acetic anhydride. S. I. Tscherbov (J. Russ. Phys. Chem. Soc., 1930, **62**, 1509—1521).—The percentage association of acetic acid is the same in acetic anhydride as in aqueous solution. Vapour-pressure measurements show that Gibbs' law of association is applicable also to the gaseous phase of the above system. R. Truszkowski.

M.-p. curve of sodium chloride dihydrate. Incongruent melting at pressures up to twelve thousand atmospheres. L. H. Adams and R. E. Gibson (J. Amer. Chem. Soc., 1930, 52, 4252—4264).—The m. p. of $NaCl,2H_2O$ has been determined directly and from measurements of the volume changes at pressures between 1 and 12,000 bars. At the ordinary pressure, the m.-p. curve commences at 0·1° with an initial slope of 7·05° per kilobar. Th slope decreases with increasing pressure and finally becomes negative. The maximum of the curve is at 25·8° and 9500 bars. The volume is increased 0·037 c.c. by the melting of 1 g. of $NaCl,2H_2O$ at 0·1°, and hence by means of the Clapeyron–Clausius equation the latent heat of fusion, L_f, is 34·4 g.-cal. per g. L_f has the value 30 when computed from solubility data. $d^{0\cdot1}$ is 1·630 at 1 bar, and the mean compressibility of the dihydrate between 6000 and 12,000 bars at about 22° is $4\cdot8\times10^{-6}$ per bar. When the dihydrate is under conditions close to those corresponding with the maximum of the m. p.–pressure curve, a sudden increase of the applied pressure is followed by a further gradual increase. An interpretation of this abnormal behaviour is offered.

J. G. A. Griffiths.

System cobalt–chromium. F. Wever and U. Haschimoto (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1929, **11**, 293—330; Chem. Zentr., 1930, i, 3482).—The equilibrium diagram has been reconstructed; on account of the small velocity of diffusion of the components complete equilibrium is attained only with difficulty. Chromium has m. p. 1705±10°. Cobalt and chromium are miscible in the fused state in all proportions. The eutectic is at 1408° and 42% Cr. Up to 38% Cr the mixed crystals are face-centred cubic, whilst above 48% Cr they are body-centred. The compounds Co_2Cr_3 and CoCr (tetragonal, with 8 mols. in the unit cell) probably exist. The temperature of polymorphic α–β transformation is maximal for 7·5% Cr, falling with a higher chromium content. The temperature of magnetic transformation falls almost proportionally to the chromium content. The hardness, tensile strength, elastic limit, elongation, and constriction up to 1000° have been determined for alloys containing up to 40% Cr. The resistance to corrosion by acid is considerable, being greatest for nitric and least for hydrochloric acid. The f.-p. curves for cobalt–chromium alloys containing up to 6·5% C or 95% Fe have been determined, and the effects of addition of silicon, manganese, aluminium, copper, nickel, molybdenum, and tungsten are recorded. A. A. Eldridge.

Phase equilibria in the system Cr_2O_3–SiO_2. E. N. Bunting (Bur. Stand. J. Res., 1930, **5**, 325—327).—*X*-Ray study of fused mixtures of chromic oxide and silica indicates that no compounds are formed and that the two substances are practically immiscible in both the liquid and solid state. The m. p. of chromic oxide, determined with the optical pyrometer, is 2140°±25°. H. F. Gillbe.

Equilibrium in the Fe–H_2–O_2 system. Indirect calculation of the water-gas equilibrium constant. P. H. Emmett and J. F. Shultz (J. Amer. Chem. Soc., 1930, **52**, 4268—4285).—By means of a flow method and with synthetic ammonia catalysts as source of iron, the equilibrium constant, $K=P_{H_2O}/P_{H_2}$, of the reaction $FeO+H_2=Fe+H_2O$ at 600°, 700°, 800°, 900°, and 1000° is found to be 0·332, 0·422, 0·499, 0·594, and 0·669, ±0·012, respectively. Similarly, for the reaction $Fe_3O_4+H_2=3FeO+H_2O$, K is approximately 1·18 and 2·37 at 700° and 800°, respectively. These values of K are smaller than those obtained from many static investigations (*e.g.*, Eastman and Evans, A., 1924, ii, 413). The discrepancy is attributed to a "surface effect" in the latter experiments in which the superficial layers of iron oxide consume an abnormal quantity of hydrogen, thus leading to a "false" equilibrium (cf. Emmett and Brunauer, A., 1930, 1131). The "surface effect" is manifest in dynamic experiments by the abnormal ratios between the gaseous products obtained initially (*e.g.*, A., 1930, 861; Pease and Cook, A., 1926, 684). Values of the water-gas equilibrium constant in good agreement with those of Neumann and Köhler (A., 1928, 707) are computed from the above data in conjunction with the best determinations for the reaction $FeO+CO=Fe+CO_2$. J. G. A. Griffiths.

Carburising and graphitising reactions between iron–carbon alloys, carbon monoxide, and carbon dioxide. M. L. Becker (J. Iron and Steel Inst., 1930, **121**, 337—365).—The equilibria between steels of varying carbon content, carbon monoxide, and carbon dioxide have been investigated by maintaining a known carbon dioxide partial pressure by adjustment of the temperature of a dissociating carbonate. The composition of the gas phase in equilibrium with graphite is poorer in carbon monoxide than that in equilibrium with iron carbide and saturated solid solution at the same temperature, and thus the carbon vapour pressure of iron carbide must be greater than that of pure carbon between 650° and 1000°; graphite is therefore stable with respect to iron carbide over this temperature range, in contradiction to the views of Matsubara, and of Johansson and von Seth. Silicon up to 3% does not alter the carbide equilibrium; manganese up to 15·5% does not apparently influence the cementite equilibrium, but it may be the slowness of the reaction which prevents graphitisation. Although the gaseous equilibrium is not altered by nickel, chromium markedly diminishes the carbon vapour pressure of the solid solution. At normal pressures the gas in equilibrium with silicon irons and chromium steels may contain sufficient carbon dioxide to cause the formation of a superficial layer of oxide which protects the metal from further oxidation; such a coating on carbon steels tends to react with the metal at temperatures above 700°, and hence has little protective value. H. F. Gillbe.

Double decomposition in the absence of a solvent. XII. N. M. Waksberg (J. Russ. Phys. Chem. Soc., 1930, **62**, 1259—1283).—The phase diagram for the system $NaI+KCl \longrightarrow KI+NaCl$ has been constructed. The triple eutectic at 504° corresponds with 37% NaCl, 46·5% KI, and 16·5% KCl. R. Truszkowski.

System Na_2SO_4–NaF–NaCl–H_2O. I. Ternary systems with water and two salts. II. Quaternary system at 25° and 35°. H. W. Foote and J. F. Schairer (J. Amer. Chem. Soc., 1930, **52**, 4202—4209, 4210—4217).—I. Solubility isotherms in the system Na_2SO_4–NaF–H_2O have been determined at 35°, 25°, 15°, and 10°. Eutectic and transition points are recorded. Crystallographic data are given for the double salt Na_2SO_4,NaF, which yields NaF and $Na_2SO_4,10H_2O$ below the transition point, 17·5°. Solubility data at 25° and 35°, and significant points for the systems NaCl–NaF–H_2O and Na_2SO_4–NaCl–H_2O are recorded.

II. Solubility data for the quaternary system at 25° and 35° are represented graphically. The double salt, Na_2SO_4,NaF, forms solid solutions in which a small proportion of the fluoride is replaced by chloride. The mineral sulphohalite, $2Na_2SO_4$,NaF,NaCl, was not obtained in these experiments.

J. G. A. Griffiths.

System $NaNO_3$–Na_2SO_4–$MgCl_2$–H_2O in the temperature range 0—100°. II, III, IV. G. Leimbach (Caliche, 1929—1930, **11**, 340—352, 386—

394, 428—436; cf. A., 1929, 1013).—Details are given of the system at 50°, 75°, and 100°.

H. F. GILLBE.

Phase-rule studies on the proteins. V. Quinquevalent nitrogen in organic compounds. VI. W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, **34**, 2433—2471; cf. A., 1930, 1604).—The addition of hydrogen chloride by compounds containing four or more atoms of nitrogen in the molecule is discussed.

L. S. THEOBALD.

Heat of formation of cuprous and cupric chlorides. H. VON WARTENBERG and H. WERTH (Z. physikal. Chem., 1930, **151**, 109—112).—Direct synthesis of the chlorides in aqueous solution in a calorimeter yields 32·1±0·4 and 50·8±0·4 kg.-cal. for the cuprous and cupric salts, respectively. These values differ but slightly from those of Berthelot, and the value for cuprous chloride agrees with that deduced by Noyes from potential measurements.

F. L. USHER.

Heat of formation of fluorine oxide. H. VON WARTENBERG and G. KLINKOTT (Z. anorg. Chem., 1930, **193**, 409—419).—The substance KF,3HF is a definite molecular compound and has a vapour pressure of 28 mm. at 100° and of 130 mm. at 150°. Details are given of the preparation of fluorine from this salt by Lebeau's electrolytic method and of the production of fluorine oxide by passage of fluorine through dilute sodium hydroxide solution (A., 1929, 779). The oxide reacts quantitatively with potassium and sodium hydroxides according to the equation $F_2O+2MOH \longrightarrow 2MF+H_2O+O_2$, and with ammonia solution with liberation of nitrogen which is, however, oxidised to nitric acid. Hydrochloric, hydrobromic, and hydriodic acids are oxidised with liberation of the halogen. Benzene and "benzine" absorb the oxide quantitatively. The heat of formation of fluorine oxide, calculated from the heat effects of the reactions with potassium hydroxide and hydrobromic and hydriodic acids, is −8 to −15 kg.-cal. per mol., the most probable value being −11±2 kg.-cal. The following thermal data have been redetermined: $2(I)+2KI\,aq=2KI_3aq-0{\cdot}73$ kg.-cal.; $(Br)+HBr\,aq=Br\,aq+HBr\,aq+1{\cdot}5$ kg.-cal. Fluorine oxide absorbs light of wave-length below 2150 Å., but is not decomposed even after prolonged irradiation.

H. F. GILLBE.

Heats of dilution of potassium chloride in sucrose and carbamide solutions as solvents below 0·1*M* at 25°. E. LANGE and A. L. ROBINSON (J. Amer. Chem. Soc., 1930, **52**, 4218—4224; cf. Lange and Robinson, A., 1930, 997).—The integral and differential heats of dilution of potassium chloride at concentrations between 0·0001 and 0·1*M* in 15 wt.-% aqueous sucrose and 5% aqueous carbamide have been determined at 25°. At concentrations, *c*, below 0·008*M*, the integral heat of dilution, V_c, is related to *c* by the equation $V_c=A\sqrt{c}$, the constant *A* having the values 386 and 332 for the sugar and carbamide solutions, respectively. The V_c–$\sqrt{c}$ curves are of the same form as those obtained with 1 : 1 type salts in pure water, but the observed deviations are outside experimental error and are possibly due to the different dielectric properties of the solvents rather than to concentration or association effects.

J. G. A. GRIFFITHS.

Heat of combustion of salicylic acid. P. E. VERKADE and Y. COOPS, jun. (J. Physical Chem., 1930, **34**, 2549—2553).—A reply to Keffler (A., 1929, 267), whose suggested value for the heat of combustion of salicylic acid is not accepted.

L. S. THEOBALD.

Heat of hydrogenation of ethylene. H. VON WARTENBERG and G. KRAUSE (Z. physikal. Chem., 1930, **151**, 105—108).—Calorimetric measurements lead to the value 30·0±0·3 kg.-cal. for the reaction $C_2H_4+H_2=C_2H_6$ at constant volume. Hydrogenation was effected with palladium sol by Skita's method.

F. L. USHER.

Heats of association of acetic and heptoic acids in the vapour state. H. DOHSE and M. DUNKEL (J.C.S., 1930, 2409—2410).—The comparison of the heat of dissociation of the double molecule of acetic acid, calculated by Fenton and Garner (A., 1930, 677) from the influence of temperature on the equilibrium, with the heat of vaporisation determined calorimetrically is not permissible. The heat of dissociation should be halved and brought into relation with the heat of vaporisation as determined from the variation of vapour pressure with temperature. The heat of dissociation of acetic acid is then found to be 6900 g.-cal. per mol. The measurements of Beckmann (cf. A., 1891, 389) for the heat of dissociation of benzoic acid in benzene can be treated similarly and lead to the value 5600 g.-cal. per mol. There is no reason for supposing that such associations are concerned with "chemical" combination.

E. S. HEDGES.

Heat of hydration and energy content of *cis*- and *trans*-*cyclo*hexane-1 : 2-dicarboxylic acids and of the primary ions. A. WASSERMANN (Z. physikal. Chem., 1930, **151**, 113—128; cf. A., 1930, 524).—The heats of dissolution and of the first and second stages of ionisation of the *cis*- and *trans*-acids have been determined, and from these and other existing data the energy content of the primary anions has been calculated. The *trans*-ion is the more heavily hydrated, and the behaviour of the ions of the *cyclo*hexane-1 : 2-dicarboxylic acids therefore agrees with that of the ions of fumaric and maleic acids. Thermochemical data afford no more support to a "*meso-trans*" configuration than do the dissociation constants or the adsorption behaviour. There is no measurable difference in the hydration of the undissociated molecules.

F. L. USHER.

Thermal data for organic compounds. IX. Effect of unsaturation on the heat capacities, entropies, and free energies of hydrocarbons and other compounds. G. S. PARKS and H. M. HUFFMAN (J. Amer. Chem. Soc., 1930, **52**, 4381—4391).—The following heats of fusion (g.-cal./g.) are recorded: β-methyl-Δ^{β}-butene, 25·74; *n*-pentane, 27·75; di*iso*butylene (probably βδδ-trimethyl-Δ^{β}-pentene), 16·83; *cyclo*hexene, 9·57; methyl*cyclo*hexane, 16·24. *cyclo*Hexene exhibits a solid transition at 138·7° Abs.; the heat of transition is 11·86 g.-cal./g. The specific heats of the above hydrocarbons, Δ^{β}-pentene, fumaric, maleic, and succinic acids, stilbene, dibenzoylethane, and dibenzoylethylene have been measured over a wide range of temperature by the method previously used (A., 1925, ii, 491). The molar entropies at 25°, calculated from the heat capacity data, show that for a given unsaturated compound the value is appreciably less than that for the corresponding saturated substance. The entropies of liquid olefines agree fairly well with the values calculated from the equation $S_{298}=25{\cdot}0+7{\cdot}7n-4{\cdot}5r-2{\cdot}7e+19{\cdot}5p$ (cf. A., 1930, 677), where e is the number of double linkings in the acylic portions of the compounds. The free energy change (ΔF_{298}) for the conversion of maleic into fumaric acid is −6600 g.-cal. The free energy change for the formation of olefinic compounds from the corresponding saturated derivatives varies considerably. H. Burton.

Method of measuring the resistance of electrolytes at low frequencies. J. A. C. Teegan (Indian J. Physics, 1930, 5, 463—471).—A new method of measuring metallic and electrolytic resistances at audio frequencies is described, using a Hartley oscillator circuit. The results obtained by this method with copper sulphate and sodium chloride solutions are the same as those measured by Dowling's method at frequencies of 10^6 cycles. When copper electrodes are substituted for the gold electrodes, however, apparent changes of the resistance with frequency are observed, but these are probably due to polarisation or chemical effects. J. W. Smith.

Conductivity and density of chromic acid solutions. H. R. Moore and W. Blum (Bur. Stand. J. Res., 1930, 5, 255—264).—The density of chromium trioxide solutions from $2M$ to $10M$ is an approximately linear function of the concentration; at 25° $d=1{\cdot}00644+0{\cdot}06606c$, where c is the molar concentration. The conductivity of the solution is a maximum at 4—$5M$, and increases with rise of temperature at the rate of 1—1·5% per degree.
H. F. Gillbe.

Electrical conductivity of potassium perrhenate solutions. N. A. Pushin and P. S. Tutundžić (Z. anorg. Chem., 1930, 193, 420—424).—The conductivities of 0·0005—$0{\cdot}04M$-potassium perrhenate solutions have been measured at 18°, 25°, 30°, and 40°; the values of λ_∞ at these temperatures are 111·5, 125·7, 141·8, and 169, respectively, and the mobility of the ReO_4' ion is at 18° 46·9 and at 25° 57·3. The temperature coefficient of the conductivity between 18° and 40° is 0·0247—0·0248, and the degree of ionisation in $0{\cdot}01M$ solution rises from 0·905 at 18° to 0·92 at 40°. H. F. Gillbe.

Conductivity of some uni-univalent salts in ethyl alcohol. E. D. Copley, D. M. Murray-Rust, and (Sir) H. Hartley (J.C.S., 1930, 2492—2498).—A method of preparing pure ethyl alcohol for conductivity work is described. The electrical conductivity of solutions of nine uni-univalent salts in ethyl alcohol has been measured at 25° over the concentration range 0·0001—$0{\cdot}002N$. In each case the curve relating equivalent conductivity to the square root of the concentration consists of a straight line, and an indication of the relative amounts of ionic association is given by comparing the slopes of these lines with the theoretical slopes calculated from the Debye–Hückel–Onsager equation. In spite of its large size, the perchlorate ion has a greater mobility in ethyl alcohol than chloride, bromide, iodide, or nitrate ions. E. S. Hedges.

Mobility of the perchlorate ion in methyl alcohol. E. D. Copley and (Sir) H. Hartley (J.C.S., 1930, 2488—2491).—The electrical conductivities of solutions of the perchlorates of lithium, sodium, and silver have been measured in methyl alcohol at 25° at concentrations varying from $0{\cdot}0001N$ to $0{\cdot}002N$. The variation of conductivity with concentration is in each case in close agreement with the Debye–Hückel–Onsager theory. The mobility of the perchlorate ion is found to be 70·85, and that of the silver ion 50·3. Attention is directed to the surprisingly high mobility of the perchlorate ion, which may be due to slight solvation in consequence of the weaker electrical field in its neighbourhood, due to its large size. E. S. Hedges.

Conductivity of very dilute solutions in antimony trichloride. Z. Klemensiewicz and Z. Balówna (Rocz. Chem., 1930, **10**, 481—491).—The conductivity curves for 10^{-2} to $5\times10^{-5}N$ solutions of potassium, rubidium, ammonium, thallous, and mercuric chlorides, and of ammonium, potassium, thallous, and mercuric bromides in fused antimony trichloride are of the same type as those found by Klemensiewicz (A., 1925, ii, 40) for more concentrated solutions; the results obtained are in complete conformity with Ghosh's theory (A., 1922, ii, 125) for solutions containing uni- but not multi-valent ions.
R. Truszkowski.

Theory and technique of the thermionic valve potentiometer for the measurement of *E.M.F.* I. F. Müller (Z. Elektrochem., 1930, 36, 923—934).—The general theory of the thermionic valve is given in relation to its application to the measurement of *E.M.F.* The valve potentiometer may be employed especially in those cases where difficulties are met with in the ordinary compensation method, *e.g.*, when no current must be taken from the cell studied, or if this has a very high internal resistance. Either a deflexion or a null-point method may be used. According to the first, the curve connecting grid potential and anode current must be known; the unknown potential is inserted in the grid circuit, and the new anode current determined. In the null-point method the anode current is maintained at a fixed value and the deflexion produced by the unknown potential is compensated for by a potentiometer also in the grid circuit, so that the same point of the characteristic curve is adhered to throughout. A detailed description is given of such an instrument which is capable of measuring potentials of 10^{-2} to 10^2 volts with an accuracy of 0·5 millivolt.
J. R. I. Hepburn.

Glass electrode studies. I. Oxy-acids of phosphorus. C. Morton (Quart. J. Pharm., 1930, 3, 438—449).—The neutralisation curves of hypophosphorous and phosphorous acids have been determined by means of the glass electrode (Haber and Klemensiewicz, A., 1909, ii, 785) and those of glycerylphosphoric, phenylphosphoric, pyrophosphoric, and orthophosphoric acids by means of the hydrogen electrode. The curves of phosphorous, glycerylphosphoric, and phenylphosphoric acids are similar in form to the well-known phosphoric acid curve; in each case there are inflexions at p_H 3·4—4·5 and at p_H 8·4—9·2, corresponding with mono- and di-sodium salts, respectively. The curve of hypophosphorous acid is that of a strong monobasic acid, whilst in that of pyrophosphoric acid inflexions corresponding with $Na_3HP_2O_7$ and $Na_2H_2P_2O_7$ are discernible.

The apparent dissociation constants of the six acids have been calculated by the method of the author (Trans. Faraday Soc., 1928, **24**, 1). The effect of the addition of neutral salts on the p_H changes of phenylphosphoric acid enables a mean value of 6·11 to be calculated for the thermodynamic second dissociation constant, pk_2 (cf. A., 1928, 840), of this acid.

From the results of the electrometric titrations, it is shown that phosphorous and phosphoric acids, if present, will be included in the result obtained by the B.P.C. method for the volumetric determination of hypophosphorous acid. Correct results may be obtained by titration with dimethylaminoazobenzene, and then with cresolphthalein; the extra alkali required to reach the cresolphthalein end-point represents phosphorous (and phosphoric) acid and is deducted from the titre to the first end-point.

R. CHILD.

Measurement of the Peltier effect at tungsten–molybdenum [junctions]. E. BLUMENTHAL (Ann. Physik, 1930, [v], **7**, 470—488).—The Peltier effect at a tungsten–molybdenum junction has been measured at the ordinary temperature by a differential calorimetric method and at temperatures up to 2000° by optical measurement of the temperature change at the junction when the current, which serves both to heat the junction and to produce the effect, is reversed in direction. At the ordinary temperature the Peltier coefficient π is $4{\cdot}69\times10^{-3}$ g.-cal., in fair agreement with that calculated from thermoelectric data. At 1290° Abs. π is $29{\cdot}3\times10^{-3}$ g.-cal., and rises to about 59×10^{-3} g.-cal. at 1600° Abs.; thereafter the coefficient diminishes slowly, in accordance with earlier thermoelectric data. For molybdenum–tantalum junctions the coefficient at 1100° is about four times as great as for tungsten–molybdenum, but exact measurements are difficult owing to the considerable difference of resistance of the two metals.

H. F. GILLBE.

Gaseous combustion in electric discharges. VI. Effect of diluents on the cathodic combustion of carbon monoxide "detonating gas." VII. Effect of dilution with hydrogen on the cathodic combustion of carbon monoxide–oxygen mixtures. G. I. FINCH and W. L. PATRICK (Proc. Roy. Soc., 1930, **A**, **129**, 656—671, 672—685; cf. Finch and Hodge, A., 1929, 890, 1401).—VI. An electric discharge can be passed through a dry or moist carbon monoxide–oxygen mixture diluted with nitrogen, helium, argon, carbon monoxide, or oxygen so that the rate of combustion of carbon monoxide is determined solely by and is directly proportional to the current passed by the discharge. At a non-sputtering cathode (tantalum) the rate is only slightly affected by dilution of the dry "detonating gas" with either of its constituents, between the limits of 88% CO_2 and 83% O_2, a slight decrease being shown with increasing oxygen concentration. The rate at a freely sputtering cathode (gold) is inversely proportional to the amount of dilution with nitrogen, helium, or argon, and increases on dilution with oxygen up to 70—80% O_2. For moist "detonating gas" the rate at a non-sputtering cathode increases on dilution with carbon monoxide (up to 80%), but decreases with increasing pressure, whilst at a freely-sputtering cathode the rate is independent of pressure, but increases on dilution with either carbon monoxide (negative pressure effect) or oxygen (positive pressure effect). Both hydrogen and hydrogen peroxide have been detected in the cathodic combustion of moist "detonating gas," the amount of the former being greater at a sputtering cathode, and of the latter at a non-sputtering cathode. It is concluded that autoxidation of carbon monoxide occurs, the carbon formed being burnt directly by oxygen. The fundamental mechanism of the direct oxidation of carbon monoxide by oxygen consists in the union of carbon monoxide molecules with oxygen atoms in either pure or (chiefly) indirect triple collisions. Sputtered metal atoms also interact with oxygen molecules to form loose complexes, which readily oxidise carbon monoxide.

VII. Mixtures of carbon monoxide with oxygen and hydrogen containing just sufficient oxygen for complete combustion burn cathodically at either tantalum or gold, so that the relative proportion of carbon dioxide to steam in the combustion products is greater than the corresponding proportion of carbon monoxide to hydrogen in the original mixture. This preferential combustion of carbon monoxide becomes more marked with decreasing pressure and at a freely sputtering cathode. The rate of combustion of dry detonating gas at a non-sputtering cathode is less than one sixth of that of dry electrolytic gas. When electrolytic gas, or a $(CO+O_2+H_2)$ mixture, or moist detonating gas is burnt cathodically, at least three times as much hydrogen peroxide can be recovered from the products leaving a non-sputtering cathode as when a freely-sputtering cathode is used. From these and a number of further experimentally established facts it is concluded that in the cathodic combustion of carbon monoxide–oxygen–hydrogen mixtures hydrogen first burns to active steam and hydrogen peroxide, both of which then oxidise carbon monoxide more readily than does oxygen; active steam is thereby reduced to an active form of hydrogen and hydrogen peroxide to inactive steam. Increasing pressure and/or oxygen concentration favours the combustion of hydrogen to hydrogen peroxide, whilst decreasing pressure and/or decreasing oxygen concentration and/or increasing hydrogen concentration favours its combustion to active steam.

L. L. BIRCUMSHAW.

Ignition of carbon monoxide–oxygen mixtures: effect of impurities. A. K. BREWER and W. E. DEMING (J. Amer. Chem. Soc., 1930, **52**, 4225—4233).—In an extension of previous work (Brewer, A., 1927, 1147) it is found that for mixtures of oxygen with ethyl alcohol, ether, or carbon disulphide vapours the product of the ignition voltage, *V*, and the total pressure, P, is a constant which is different for each mixture. Hence the voltage, V, or the quantity of electricity, Q ($Q \propto V$ in this investigation), required to ignite an explosive mixture is inversely proportional to the number of molecules in the path of the spark. In all cases, the relation between V and $1/P$ leads to $V=15$—20 volts when $1/P=0$. This indicates that ionisation is necessary for ignition.

Impurities may increase (negative catalysis) or decrease (positive catalysis) V for carbon monoxide–oxygen mixtures. The relative inhibiting effects are almost directly proportional to the number of atoms composing each molecule of impurity. Ether and ethyl alcohol, and to a smaller extent hydrogen, may be positive or negative catalysts, according as to whether or not sufficient additional oxygen is added for their complete combustion. The positive catalysis is attributed to the formation of water (Bone and Weston, A., 1926, 480) which precedes the general ignition of the mixture. The efficiency of a positive catalyst is, over a wide range, proportional to the number of catalyst molecules in the path of the discharge. J. G. A. Griffiths.

Slow combustion of ethane. W. A. Bone and S. G. Hill (Proc. Roy. Soc., 1930, **A**, **129**, 434—457).—The "hydroxylation" and "peroxidation" theories of hydrocarbon combustion are discussed. Experiments have been carried out to determine if a peroxide is formed during the slow combustion of ethane, and if so, at what stage in the process. The investigation covered a temperature range of 290—323° and initial pressures between 440 and 780 mm. The results indicate that the oxidation proceeds homogeneously throughout the medium, being greatly retarded by increasing the surface exposed to the gases, that it is preceded by a well-marked induction period, during which no oxidation occurs, and that it is accompanied by a steady pressure rise and the production chiefly of aldehydes, steam, and oxides of carbon, but of neither hydrogen nor free carbon. The induction period can be considerably reduced by the addition of small amounts (say 1%) of moisture, iodine, nitrogen peroxide, ethyl alcohol, formaldehyde, etc. to a dry $C_2H_6+O_2$ medium without altering the non-explosive nature of the combustion. The addition of 1% of acetaldehyde, however, causes an instantaneous inflammation of the medium. A rise of temperature or an increase of pressure shortens the induction period. A rise of temperature also shortens the "reaction period," and an increase in pressure tends to shorten it. Both the induction and the reaction periods are much shorter for a $(2C_2H_6+O_2)$ than for a $(C_2H_6+O_2)$ mixture, and are rapidly lengthened by an increase in oxygen content beyond an equimolecular proportion. This is consistent with the "hydroxylation," but not with the "peroxidation," theory. Although inconsiderable amounts of a "peroxide" appear to be formed at the acetaldehyde stage of the combustion, no evidence was obtained of any earlier peroxide formation. Indirect experimental evidence supports the view that ethyl alcohol or some lower "oxyethane," rather than $C_2H_6O_2$, is primarily formed in the slow combustion of ethane.

L. L. Bircumshaw.

Combustion of carbon disulphide in oxygen. H. W. Thompson (Z. physikal. Chem., 1930, **B**, **10**, 273—295).—The curve showing the relationship between the ignition temperature and pressure for mixtures of carbon disulphide vapour and oxygen in the volume ratio 1 : 3 resembles closely that for hydrogen–oxygen mixtures; the temperature minimum is 140° at 100 mm., and at higher temperatures the pressure interval becomes increasingly greater. The transition from the slow reaction which takes place at low temperatures or outside the critical pressure range to explosive combustion is abrupt at both pressure limits. As with hydrogen–oxygen mixtures, the explosion is initiated at the walls of the vessel; if streams of the two gases impinge in a free space combustion does not take place at temperatures below 250—290°, but on contact with a glass rod combustion occurs at much lower temperatures.

H. F. Gillbe.

Velocity of polymerisation. I. Polymerisation of diethylenic hydrocarbons. II. Polymerisation of isoprene. E. N. Gapon (J. Russ. Phys. Chem. Soc., 1930, **62**, 1385—1393, 1395—1406).—I. A theoretical consideration of the polymerisation of diethylenic compounds leads to the assumption that the activation of substrate molecules depends on the opening of a double linking with the formation of tervalent carbon; the energy necessary for this process represents the energy of activation. The polymeride is formed by combination of active with inactive molecules.

II. The ratios of the values of the velocity coefficients of the reaction of polymerisation of isoprene to dipentene, to 1 : 3-dimethyl-3-ethenyl-Δ^6-*cyclo*hexene, and to the polymeride are 530 : 41 : 1. Three types of activated molecules may be formed in the polymerisation of isoprene, explaining the variety of products. The temperature coefficients of the above reactions of polymerisation diminish in the order given, as do also the heats of activation and the activity constants of the active molecules.

R. Truszkowski.

Influence of neutral salts on reaction velocity in alcoholic solution. A. Kailan and A. Irresberger (Monatsh., 1930, **56**, 428—446).—The effect of lithium, calcium, and mercuric chlorides on the velocity of esterification of benzoic acid with alcoholic hydrogen chloride has been studied. With alcohol containing 0·05 mol. of water per litre, addition of the salts causes a retardation; the differences in the individual salts are small. When the alcohol contains 1 mol. of water per litre, addition of the salts causes an increase in the coefficient (except with mercuric chloride in concentrations below 0·668N); calcium chloride has the greatest accelerating action, probably owing to its greater capacity for hydrate formation.

H. Burton.

Velocity of intramolecular transformation of β-naphthylacetylchloroamine. A. P. J. Hoogeveen (Rec. trav. chim., 1930, **49**, 1093—1106).—β-Acetnaphthalide is converted by the action of bleaching-powder solution and a small amount of acetic acid on its solution in 96% alcohol at 0° into N-*chloroacet*-β-*naphthylamide*, m. p. 80°. Similar chlorination in glacial acetic acid at 20° yields 1-chloro-

2-acetnaphthalide (cf. Franzen and Stäuble, A., 1922, i, 450), complete isomerisation of the chloroamine taking place under these conditions. The velocity of conversion of the chloroamine into 1-chloro-2-acetnaphthalide was determined by a method similar to that employed in the case of the corresponding α-compound (A., 1930, 866). In aqueous alcohol containing 100 c.c. of *N*-hydrochloric acid per litre, the mean value of the unimolecular coefficient $k\times10^4$ at 25° in 5, 10, 20, 30, 40, 50, 60, and 70% alcohol is, respectively, 46, 40, 39, 45, 70, 124, 233, and 500, the corresponding value when the concentration of hydrochloric acid is doubled being —, 94, 102, 146, 245, 423, 808, and 1670, respectively. The values of $k\times10^4$ in the corresponding series, water–acetic acid containing 100 c.c. of *N*-hydrochloric acid (no value for 5% acetic acid), are, 39, 38, 56, 92, 185, 489, and 1832, respectively. The occurrence of a minimum reaction velocity observed in the case of the α-compound with 50% of the organic solvent (*loc. cit.*) is thus also observed, but to a much smaller extent, with the β-compound, minimum values being obtained in 20% alcohol or acetic acid. In the alcohol series, doubling the concentration of the acid increases the reaction velocity 3·5 times except in 10 and 20% mixtures, when the velocity is only doubled. Comparison of these results with those obtained for the velocity of conversion of *N*-chloroacetanilide and *N*-chloroacet-β-naphthylamide shows that the velocity with the β-compound is approximately 50% greater than that observed in the other two cases. Similar migrations from the β- to the α-position in β-naphthylamine derivatives are discussed. J. W. Baker.

Phenomena of corrosion. XVII. A. Thiel (Z. physikal. Chem., 1930, **151**, 103—104; cf. A., 1928, 376).—The explanation of the "difference effect" by Straumanis (A., 1930, 1125) is considered unsatisfactory. F. L. Usher.

Quartz. R. Weil (Compt. rend., 1930, **191**, 935—937).—Contrary to the results obtained with *L*-quartz (A., 1930, 1240) the action of hydrofluoric acid on a slip of *S*-quartz normal to the ternary axis produces numerous "hairs" over the entire surface which, at the limits of the regions of birefringence, appear as stellar tufts or fissures in the planes normal to the prism faces. Similar hairs are formed at 150° by the action of sulphuric acid on calcium fluoride, but at 300° they are shorter. A detailed study has been made, enabling the corrosion figures to be distinguished from those of *L*-quartz. Corrosion parallel or perpendicular to the ternary axis is obtained by the production of a cylindrical hole by the action of acid on a portion of the crystal surrounded by paraffin wax, the acid being renewed at intervals over several weeks. *L*-Quartz then shows true negative crystals with the rounded $(10\bar{1}0)$ prism below two rounded rhombohedra $(10\bar{1}1$ and $01\bar{1}1)$, 2—3 mm. long. The *S*-quartz, however, shows complete disaggregation resulting from accentuation of the corrosion phenomena observed for a section normal to Λ^3.

J. Grant.

Passivity of metals. W. J. Müller (Korrosion u. Metallschutz, 1929, 5, 8—15; Chem. Zentr., 1930, i, 3483).—A discussion. A. A. Eldridge.

Effect of amount of catalyst on combination of hydrogen and oxygen. C. Kröger (Z. anorg. Chem., 1930, **194**, 73—88).—The rate of formation of water when a mixture of hydrogen and oxygen in the stoicheiometric ratio is passed over various catalysts at a fixed rate has been studied with the object of finding the connexion between the percentage reaction, *Y*, and the weight of catalyst, *m*. With silver as catalyst the experimental data can be represented satisfactorily by the equation $\log\{100/(100-Y)\}=km$, where *k* is a constant for a fixed temperature. This equation can also be deduced theoretically on the assumption that the hydrogen reacts only with adsorbed oxygen free from adsorbed water (cf. Benton and Elgin, A., 1929, 274). For a given weight of catalyst the Arrhenius equation is valid for the effect of temperature on the velocity coefficient, but the heat of activation, *Q*, increases as *m* decreases. When antimony is the catalyst, on the other hand, *Q* does not vary with *m*, which is taken as indicating that here the mechanism of catalysis is chemical, probably consisting in alternate oxidation and reduction of the metal. The effect of variations in *m* when nickel or copper is the catalyst is qualitatively similar to that observed with silver, but is ascribed to the equilibrium ratio of oxide to metal in the catalyst being dependent on the amount of catalyst initially taken (cf. Smith, A., 1928, 719). In the case of nickel, however, it seems that the reaction is not entirely heterogeneous; a homogeneous reaction is probably brought about by reaction chains propagated from the catalyst. Reaction over a nickel oxide catalyst seems to depend on the rate of reduction and oxidation of a higher oxide, and with increase in *m* the amount of this oxide, and therefore *Y*, increases. At the same time, however, the water vapour exerts a retarding influence, and the net result can be represented by the equation $\log\{100/(100-Y)\}=a\log m+\log(100/k)$, where *a* and *k* are constants, the former depending on the temperature. When copper oxide is the catalyst, *Y* is only slightly affected by variations in *m*, apparently because the equilibrium ratio of metal to oxide in the catalyst varies very little with *m* (cf. Pease and Taylor, A., 1922, ii, 148).

R. Cuthill.

Effect of water on the decomposition of ethyl alcohol at the surface of nickel. W. W. Russell and R. F. Marschner (J. Physical Chem., 1930, **34**, 2554—2566).—The addition of water to ethyl alcohol reacting at a nickel surface at 200±2° increases the amount of alcohol undergoing reaction and decreases the percentage of aldehyde decomposed over a wide concentration range. At 80 mol.-% of water a dilution effect begins to predominate. The 10% nickel catalyst was prepared by igniting and reducing at 350° the nitrate supported on pumice. The deactivation of such catalysts is reduced by the presence of water in the alcohol and reactivation is achieved by treatment with hydrogen at 350°. An approximately linear relationship between time of contact and amount of reaction exists for a certain range of space velocities. An explanation of the observed results is discussed.

L. S. Theobald.

Nickel as a catalyst for hydrogenation. H. Adkins and H. I. Cramer (J. Amer. Chem. Soc., 1930, **52**, 4349—4358).—Details, for which the original must be consulted, are given for the reduction of 45 compounds by hydrogen in presence of a nickel catalyst, prepared by a modification of the method of Rather and Reid (A., 1915, i, 933), at 100—200° and pressures up to 200 atm. The reductions are carried out both in absence and presence of solvents such as ether, alcohol, heptane, or methyl*cyclo*hexane. Aldehydes and ketones usually furnish the corresponding alcohols; cyanides give the corresponding amines; aromatic compounds are usually hydrogenated completely (or in distinct stages at different temperatures). The alcoholic hydroxyl group is not replaced by hydrogen except when it is on a carbon atom attached directly to a benzenoid ring. Quinoline is reduced to the 1 : 2 : 3 : 4-tetra- and deca-hydro-derivatives at 150°/160 atm. and 175°/175 atm., respectively.

H. BURTON.

Inversion of sucrose by platinised charcoal saturated with hydrogen. B. BRUNS and M. WANJAN (Z. physikal. Chem., 1930, **151**, 97—102; cf. Miller and Bandemer, A., 1927, 821).—When charcoal (2 g.) containing 0·2—1·0% Pt and saturated with hydrogen is introduced into 50 c.c. of a 5% solution of sucrose at 50°, about 97% of the sucrose is inverted in 48 hrs., whilst no detectable inversion occurs under the same conditions with degassed platinised charcoal. The presence of oxygen leads to oxidation of the sucrose. The result is attributed to catalytic action of the hydrogen ions of the double layer.

F. L. USHER.

Cathodic separation forms of tin. F. FOERSTER and H. DECKERT (Z. Elektrochem., 1930, **36**, 901—923; cf. B., 1929, 685).—The influence of crude *m*-cresolsulphonic acid in determining the form of tin separating at the cathode during electrolysis of sulphuric acid solutions (0·15*M*) of stannous sulphate (0·25*M*) is due to the presence of small quantities of by-products, more especially a resin (0·4%), which exerts a specific influence, being adsorbed at the metal surface. With small adsorption there is a tendency towards the formation of needle-like aggregates or slimes, changing to white tin, and finally to a milky-white structureless deposit, with maximum adsorption. The action of the purely adsorbed material is prolonged, whilst that of the colloidal by-products formed when the *m*-cresolsulphonic acid is prepared above 120° is transitory, the colloid being deposited on the cathode through electrophoresis. Pure *m*-cresol gives in high concentrations separation forms similar to those of the resin by-product, and is itself adsorbed at the cathode. The effect is diminished with rise of temperature and increased with fall of temperature in accordance with the adsorption law, whilst other adsorbable materials, including other phenols, sulphates of aniline and pyridine, and gelatin, are also active. Experiments on electrodeposition of cadmium from ammoniacal solution in presence of pyridine indicate the occurrence of a similar effect with this metal corresponding with that of phenols on tin in acid solution. Stannous chloride in hydrochloric acid solution shows the same effect as the sulphate in a very much smaller degree, having a greater tendency to the formation of the needle-like aggregates. A large number of photographs illustrating the forms of the metal which are obtained under varying conditions is given. It is suggested that the polarisation effect in electrodeposition is connected with changes in the hydration of ions at the moment of deposition, rather than with electric forces in the formation of the crystal lattice. In agreement with this it is shown that the observed adsorption effect is at a maximum at the points and edges of the crystals, and at a minimum on the plane surfaces. It is concluded that the tendency of tin to form needle-like aggregates, and the small polarisation value, make the metal particularly sensitive to adsorption effects.

J. R. I. HEPBURN.

Theory of the lead accumulator. L. JUMAU.—See B., 1930, 1116.

Effect of anodic impurities on the electrodeposition of gold. R. W. HARBISON.—See B., 1930, 1114.

Variations in thickness of metal electrodeposits. E. L. GRANT and V. E. GRANT.—See B., 1930, 1114.

Displacement by ultra-violet light of the explosion limit in a chain reaction. C. N. HINSHELWOOD and K. CLUSIUS (Proc. Roy. Soc., 1930, A, **129**, 589—598).—At atmospheric temperatures mixtures of oxygen and phosphine explode within a sharply defined pressure region, above or below which reaction is negligibly slow. This can be explained on the assumption that the oxidation is a chain reaction. Both limits are affected by exposing the gas mixture to ultra-violet light, and the present work deals with the lower limit. The apparatus used was similar to that described by Dalton and Hinshelwood (A., 1929, 1243), the reaction tube being of fused silica coated internally with a thin layer of phosphoric acid. When illuminated, the gases explode at a lower limit than normally, and the increased sensitiveness persists for a time when the light is extinguished. The increased explosibility appears to be due to the formation of a definite substance which exists for an appreciable time. Its formation was observed experimentally in two ways: (*a*) by exposing the mixture to radiation and then compressing to the explosion point, the total time of illumination, including the time required for compression, being measured, and (*b*) by compressing the gases to some suitable pressure and then illuminating, when explosion occurs after a definite time-interval. The decay curves for mixtures which had been illuminated for 1·5 and 3 min., respectively, show that a stationary state is set up in the light, the action of the substance produced being comparable with that of a trace of nitrogen peroxide in the combination of hydrogen and oxygen. The value for the maximum concentration in the photostationary state is deduced, and the efficiency of collisions with the vessel wall in destroying this substance is calculated. It is considered that the oxidation provides an example of "material" rather than "energy" chains.

L. L. BIRCUMSHAW.

Photochemical combination of chlorine and hydrogen. II. T. ICHIKAWA (Z. physikal. Chem., 1930, **B**, **10**, 299—336).—The photochemical reaction between hydrogen and chlorine has been studied under various conditions of pressure and time of illumination. The total reaction velocity does not immediately fall to zero when the illumination is removed, and on re-illumination after a short interval the resulting increase of velocity commences apparently instantaneously from a higher value than that to which it had fallen. The velocities of the primary and secondary reactions have been calculated, and the kinetics of the reaction are discussed. A suggested new type of mechanism for the combination involves the formation of a complex molecule H_2O,Cl_2, which is decomposed by light, yielding H_2O,Cl groups and chlorine atoms; the reactions $H_2O,Cl+H_2=HCl+H_2O+H$, and $H+Cl_2=HCl+\mathit{Cl}$ ensue, where *Cl* is a high-velocity chlorine atom capable of causing dissociation on collision with a chlorine molecule, and thus aiding the further formation of H_2O,Cl groups. H. F. GILLBE.

Photochemical formation of chlorine dioxide from chlorine monoxide in carbon tetrachloride solution. R. G. DICKINSON and C. F. P. JEFFREYS (J. Amer. Chem. Soc., 1930, **52**, 4288—4297).—The absorption coefficients of chlorine, chlorine monoxide, and chlorine dioxide in carbon tetrachloride are recorded for light of wave-lengths 4358 and 4047 Å. The photo-decomposition of chlorine monoxide in carbon tetrachloride by light of λ 4358 Å. is accompanied by the formation of considerable quantities of chlorine dioxide. For 0·014—0·054*M* solutions of chlorine monoxide, the initial rate of formation of chlorine dioxide is 0·35 mol. per quantum absorbed, and the yield of chlorine dioxide for a given number of quanta absorbed is greater the higher is the initial concentration of chlorine monoxide. The rate of decomposition of the latter falls slightly, with increasing exposure, from an initial value greater than 1·8 mols. per quantum absorbed by the monoxide.

J. G. A. GRIFFITHS.

Directional distribution of the relative velocity of the decomposition products in the optical dissociation of sodium iodide. A. C. G. MITCHELL (Physical Rev., 1929, [ii], **33**, 279).—Sodium iodide can be dissociated by ultra-violet light of wave-length 2450 Å. into an excited sodium and a normal iodine atom. With wave-lengths less than 2450 Å. the excess energy goes into relative kinetic energy of the two atoms as they part, and the excited sodium atom emits *D*-lines with a corresponding Doppler broadening. The atoms fly apart in either direction to that of the electric vector with equal probability.

L. S. THEOBALD.

Decomposition of thiocyanates in ultra-violet light. K. JABŁCZYŃSKI and H. JABŁCZYNSKA (Rocz. Chem., 1930, **10**, 579—600).—Ammonium, sodium, or potassium thiocyanate is decomposed in aqueous solution on irradiation with wave-lengths of less than 3000 Å.; the reaction products are cyanide and sulphur. The reaction is in all cases exothermic. It is autocatalysed by sulphur, the velocity coefficient K being expressed by $K=\log (x+d)/d(1-x)/(1+d)t$, where x represents the relative opacity of the liquid at time t and d is a constant for the given system. The velocity–concentration curves exhibit a maximum at 0·991*N* for ammonium, 1·09*N* for potassium, and 0·271*N* for sodium thiocyanate. The equilibrium point is displaced in the direction of disintegration by raising the temperature, and for this reason the velocity of reaction is greater at higher temperatures. The addition of hydrochloric acid has the same effect, as a result of the greater instability of free thiocyanic acid. The velocity of reaction is retarded by the addition of potassium chloride or zinc or nickel sulphate to potassium thiocyanate solutions.

R. TRUSZKOWSKI.

Action of light on silver hydrosols containing particles of uniform size. A. GAŁECKI and R. SPYCHALSKI (Rocz. Chem., 1930, **10**, 492—500).—The velocity of decolorisation of silver hydrosols conforms to that of a unimolecular reaction. The temperature coefficient is 1·3. R. TRUSZKOWSKI.

Photochemistry of the associated state. F. WEIGERT (Z. physikal. Chem., 1930, **B**, **10**, 241—263). —Franck's views of the photochemical dissociation of non-polar molecules is applied to the consideration of possible changes in associated systems produced by the action of light, and the conditions under which excitation of the electron systems of individual molecules of the associated complexes and micelles can lead to partial opening up are discussed. On examination of the influence of light on silver chloride emulsions it is shown that the lack of proportionality between the energy absorbed and the effect produced, and the anomalous additive effect of radiations of different wave-lengths, are evidence for the occurrence of photomicellary processes, as opposed to photomolecular processes, in which a large number of energy quanta are absorbed by one micelle. Other systems discussed are those of gelatin and collodion films containing light-sensitive dyes, the visual purple of the retina, and systems in which it is impossible directly to observe the nature of the phenomena which take place, such as highly mobile gaseous and liquid associated systems, systems containing solid micelles dispersed in gaseous or liquid media, and certain types of solid micro-crystalline media. The occurrence of primary and induced photodichroism is an indication that the form of the "opened" particles within the micelles is dependent on the wave-form of the exciting radiation, and although the physical significance of such a phenomenon is obscure, it appears that a quantitative study of photodichroism, by revealing the nature of the opening-up process, would give much information relating to the structure of associated systems and to many biological problems.

H. F. GILLBE.

Laying bare of ripening centres. LÜPPO-CRAMER (Z. wiss. Phot., 1930, **29**, 5—7).—The surface centres on the grains of a series of layers of negative (bromide) and chloride emulsions were removed by treatment with chromic acid, and the internal centres were then revealed by physical development after opening up the grains by treatment with a solution of potassium iodide. A much greater number of internal centres was found in the grains of the chloride emulsion, which is in agreement with the easy reducibility of silver chloride, and the ready formation and comparatively greater stability of the silver–silver chloride adsorption complexes. J. W. GLUSSETT.

Photochemical polymerisation of acetylene. S. C. LIND and R. S. LIVINGSTON (J. Amer. Chem. Soc., 1930, **52**, 4613—4614; cf. Reinicke, A., 1928, 1340).—The polymerisation of acetylene at pressures less than 30 cm. in the complete radiation of a quartz mercury lamp is proportional to the pressure. The velocity approaches a constant value at higher pressures. The 10° temperature coefficient between 12° and 39° is 1·25, but this may be due to a temperature coefficient of light absorption. Light of wavelength 2537 Å. or longer is inactive; the quantum efficiency for shorter wave-lengths is about 7·4±2·5. Mercury vapour was excluded from the reaction system. J. G. A. GRIFFITHS.

Composition of deposit forming on zinc immersed in cupric sulphate solutions. II. A. GAŁECKI and J. TOMASZEWSKI (Rocz. Chem., 1930, **10**, 601—629; cf. B., 1930, 822).—The copper content of the deposit diminishes with rise of temperature from 18° to 50°; this effect is most marked in dilute solutions (0·02—0·1N). The appearance of the deposits is unaffected by temperature. The addition of zinc sulphate to the solution similarly depresses the copper content of the deposits; at the same time these become less coherent in stirred systems. The copper content of the deposits diminishes as the concentration of zinc in solution increases. Zinc is present in the deposits probably exclusively as oxide or hydroxide. R. TRUSZKOWSKI.

Cupriammines. II. Ammines of cupric perchlorate. R. PORTILLO (Anal. Fís. Quím., 1930, **28**, 1125—1144).—*Pentamminoaquocupric perchlorate* has been prepared as a blue crystalline powder by addition of ammonia solution to a solution of cupric perchlorate; it has d_4^{25} 1·657 and molecular heat of dissolution −17·9 kg.-cal. At the ordinary temperature it readily passes into the violet tetramminocupric perchlorate, which has d_4^{25} 1·952, mol. heat of dissolution −18·30 kg.-cal. (480 mols. of water), −20·95 kg.-cal. (1600 mols. of water), heat of formation 181·7 kg.-cal. On hydration this compound yields the pale blue *tetramminodiaquocupric perchlorate*. *Tetramminoaquocupric perchlorate*, blue, d_4^{25} 1·83, mol. heat of dissolution −17·9 kg.-cal., results from the recrystallisation of tetramminocupric perchlorate dihydrate; the last-named compound has no definite m. p., but commences to liquefy at 50—54°, and when heated at 100—105° it solidifies to a greenish-black mass of *triamminocupric perchlorate*, which is produced also by heating any of the other complexes mentioned at 180°. The dihydrated tetrammine has d 1·60, mol. heat of dissolution −20·38 kg.-cal., and decomp. 82°. *Hexamminocupric perchlorate*, which has been prepared, although not in a pure state, by the action of ammonia on the tetrammine, has d_4^{25} 1·60, mol. heat of dissolution −20·38 kg.-cal.

H. F. GILLBE.

Cupric perchlorate. R. PORTILLO and L. ALBEROLA (Anal. Fís. Quím., 1930, **28**, 1117—1124).—Pure *cupric perchlorate*, $Cu(ClO_4)_2,7H_2O$, has been prepared by dissolution of copper carbonate in 30% perchloric acid solution, and concentration of the solution. Dehydration over phosphorus pentoxide at the ordinary temperature yields the hexahydrate, which is more stable than the heptahydrate; when heated at 70° in a current of dry air it yields the tetrahydrate. The almost colourless *dihydrate* is produced by heating at 80—100°, but further dehydration causes decomposition with evolution of perchloric acid. The heptahydrate forms pale blue, extremely deliquescent triclinic crystals, m. p. 82°; the hexahydrate has d_4^{25} 2·2255, mol. heat of dissolution −4·6 kg.-cal., and heat of formation in solution 64·7 kg.-cal. The saturated solution at 0° contains 54·3% of anhydrous salt. The classical degree of ionisation falls from 1·02 in 0·024M solution to 0·93 in 0·198M solution. H. F. GILLBE.

Ammonium, potassium, and sodium cuprous thiosulphates. I. G. SPACU and I. G. MURGULESCU (Bull. Soc. Stiinte Cluj, 1929, **5**, 61—107; Chem. Zentr., 1930, i, 3422—3423).—In the titration of 0·1—0·2M-cupric nitrate with ammonium thiosulphate the addition of alcohol (75—86%) affords a yellow, crystalline precipitate, or (with more alcohol) a white, amorphous precipitate; the potentiometric curve indicates the formation of the *compound* $(NH_4)_2[Cu_2(S_2O_3)_2]$, and in a 0·5M-solution with more than 50% of alcohol, the *compound* $(NH_4)_4[Cu_2(S_2O_3)_3]$ results. Other cupric *salts*, similarly obtained, are $(NH_4)_7[Cu(S_2O_3)_4],2NH_4NO_3$, $(NH_4)_5[Cu(S_2O_3)_3]$, and $(NH_4)_7[Cu(S_2O_3)_4],2NH_4ClO_3$. A. A. ELDRIDGE.

Metallic hydroxy-acid complexes. V. Neutral α-cupritartrates. E. E. WARK and I. W. WARK (J.C.S., 1930, 2474—2478).—Dumanski and Chalisev (A., 1929, 259) have questioned the existence of the α-cupritartrates described by Packer and Wark (J.C.S., 1921, **119**, 1348), suggesting that the supposed compounds are merely colloidal solutions of copper hydroxide in neutral or alkaline tartrate solutions. Copper tartrate is completely soluble in sufficient sodium tartrate and it is claimed that lack of appreciation of this fact has led to the criticism, incorrect stoicheiometric relationships for the action of sodium hydroxide on copper tartrate being obtained. As the end-point of the reaction is difficult to determine, a potentiometric method has now been applied and the results confirm the existence of the α-cupritartrates. Similar results were obtained for the copper salts of salicylic, lactic, and glycollic acids.

E. S. HEDGES.

Extraction of rubidium and cæsium from carnallite. III. G. JANDER and F. BUSCH (Z. anorg. Chem., 1930, **194**, 38—46; cf. A., 1930, 435).—The cæsium in a mixture containing rubidium chloride and a little cæsium chloride, such as is obtained in working up carnallite for these metals, may be concentrated by taking advantage of the fact that if silicomolybdic acid is gradually added to the solution precipitation of the cæsium is practically complete when considerably less precipitant than would be required for complete precipitation of the mixture has been added. At the same time, therefore, a considerable proportion of the rubidium compound can be obtained in a state of purity. The mixed precipitate is then boiled with barium hydroxide to eliminate the silicomolybdic acid as barium silicate and molybdate, and the excess of barium is removed as carbonate by saturating the filtrate with carbon dioxide and boiling. By boiling the barium molybdate with sodium carbonate solution, the molybdic acid is recovered as the sodium salt. R. CUTHILL.

Rubidium and cæsium nitrides. K. CLUSIUS (Z. anorg. Chem., 1930, **194**, 47—50).—The residues obtained on heating rubidium and cæsium azides contain the nitrides Rb_3N and Cs_3N, respectively. R. CUTHILL.

Thermal decomposition of mixtures of calcium sulphide and sulphate. J. ZAWADZKI and I. KOWALCZEWSKI (Rocz. Chem., 1930, **10**, 501—509).—Calcium sulphite is converted into sulphide and sulphate only at very high temperatures, and even then very slowly, whence it follows that sulphite is not one of the products of the thermal decomposition of gypsum. The reaction $CaS+3CaSO_4 \longrightarrow 4CaO+4SO_2$ is complicated by secondary reactions occurring between the products of this reaction, and leading to the liberation of sulphur. The partial pressure of sulphur rises from 2·3 mm. at 820° to 115·1 mm. at 1060°; over the same range that of sulphur dioxide rises from 8·8 to 149·0 mm. R. TRUSZKOWSKI.

Formation and composition of bleaching powder. B. NEUMANN (Z. Elektrochem., 1930, **36**, 934—936).—Polemical against Ditz (A., 1930, 1138). The assumption of Ditz that his formulæ for bleaching powders types I and II correspond with those for the hydrates of bleaching powder established experimentally by Neumann and Haebler (*ibid.*, 176) is incorrect. J. R. I. HEPBURN.

Röntgenographic study of the products obtained by the action of the halogen acids on mercuric sulphates, and fusion diagram of the system HgI_2–$HgSO_4$. M. PAIĆ (Compt. rend., 1930, **191**, 941—943).—The halogen acids in the gaseous state or in aqueous solution react with the compounds $HgSO_4$ and $3HgO,SO_3$ to form sulphuric acid and the corresponding mercuric halide. Neither concentrated sulphuric acid nor H_2SO_4,H_2O reacts with mercuric chloride or bromide, but at 300—350° the former reacts with mercuric iodide, forming mercuric sulphate and hydriodic acid. The compound $HgSO_4,HgI_2$ (pale yellow crystals) was shown by *X*-ray, chemical, and thermal analysis to be formed under the latter conditions. Contrary to the results of previous workers, no evidence was obtained of the existence of the compounds $HgSO_4,2HCl$, $HgSO_4,2HBr$, $3HgO,SO_3,6HCl$, $3HgO,SO_3,6HBr$, $HgSO_4,HCl$, $HgSO_4,2HCl,H_2O$, and $HgSO_4,HBr$. J. GRANT.

Boron hydrides. XIV. B_4H_{10}. A. STOCK, E. WIBERG, and H. MARTINI (Ber., 1930, **63**, [*B*], 2927—2937).—The stability of the compound B_4H_{10} varies within wide limits and appears to be influenced by the glass of the apparatus. In the presence of hydrogen chloride, a part of the hydride remains unchanged; a small proportion is decomposed into boron trichloride and a similar amount to non-volatile chlorinated derivatives. The remainder decomposes in the usual manner mainly into B_2H_6 and $(B_5H_4)_n$. The auto-decomposition is not impeded by the presence of an excess of hydrogen chloride in spite of neutralisation of the alkali of the glass. With deficiency of sodium amalgam, the hydride B_4H_{10} yields the non-volatile substance $B_4H_{10},2Na$, decomposed by water into hydrogen and a sodium hypoborate. Treatment of the hydride with an excess of sodium amalgam and subsequently with hydrogen chloride or diborane affords evidence of the production of compounds richer in sodium than $B_4H_{10},2Na$. With an excess of ammonia at −70° the hydride B_4H_{10} yields a colourless, non-volatile *compound*, $B_4H_{10},4NH_3$, which decomposes at the ordinary temperature with evolution of ammonia and hydrogen and without production of recognisable intermediate compounds. At 180° the product $B_3H_6N_3$ is formed, and is thus conveniently obtained. It appears doubtful whether the addition of hydrogen chloride to the compound $B_3H_6N_3$ is a simple case of salt formation. With ammonia and an excess of B_4H_{10} products poorer in ammonia than $B_4H_{10},4NH_3$ appear to be formed, but their precise nature has not been ascertained. Apart from unimportant side reactions, the interaction of $B_4H_{10},4NH_3$ and hydrogen chloride proceeds according to the scheme $B_4H_{10},4NH_3+8HCl=7H_2+B_4H_4Cl_8,4NH_3$. Electrolysis of solutions of the substance $B_4H_{10},4NH_3$ in liquid ammonia between platinum electrodes at −70° is accompanied by evolution of nitrogen and hydrogen at the cathode and a substance, $B_4H_{15\cdot5}N_{5\cdot5}$, is produced. It is therefore probable that the initial material is a salt, $(B_4H_6)''''4(NH_4)^{\cdot}$. In the hydride B_4H_{10} it is certain that four hydrogen atoms differ in their behaviour from the remaining six. H. WREN.

Peraluminates of the alkali and alkaline-earth metals. J. PRÁŠEK (Coll. Czech. Chem. Comm., 1930, **2**, 653—664).—*Sodium* and *potassium peraluminates*, $M_2Al_2O_5,8H_2O$ and $M_2Al_2O_6,8H_2O$, have been prepared as soluble white crystalline powders by addition of hydrogen peroxide to a cold solution of the corresponding aluminate, and precipitation by alcohol; by heating at 105° the normal aluminates are formed. The stability of the solutions, which readily undergo hydrolysis and deposit aluminium hydroxide, decreases with increase of the active oxygen content. Normal lithium peraluminate has not been prepared, but the *compound* $Li_2Al_4O_9,28H_2O$ separates on addition of hydrogen peroxide to a solution of lithium aluminate; dehydration causes decomposition to hydrated acid aluminates. By the action of potassium aluminate on a solution of lithium chloride and hydrogen peroxide the *compound* $Li_2Al_8O_{17},25H_2O$ is formed. Insoluble *magnesium*, *calcium*, *strontium*, and *barium peraluminates*, of the general formula $MAl_2O_6,10H_2O$, are precipitated on addition of potassium aluminate solution to a solution containing the appropriate chloride and hydrogen peroxide, whilst $Ca_4Al_2O_9,15H_2O$, $Sr_3Al_2O_8,20H_2O$, and $Ba_3Al_2O_8,20H_2O$ are formed by shaking these compounds with the hydroxide of the metal and water. The magnesium and alkaline-earth peraluminates are relatively stable, but at temperatures above 100° they decompose, yielding aluminates. The reactions of all these substances are typical of per-compounds; concentrated sulphuric acid liberates oxygen, whereas dilute acids liberate hydrogen peroxide. Consideration of the structure of the peraluminates based on f.-p. determinations indicates that the anions formed in solution are $[Al(OH)_3{\cdot}O{\cdot}OH]'$ and $[Al(OH)_4]'$. H. F. GILLBE.

Halides of the rare earths. IV. Samarium di-iodide and the thermal decomposition of samarium tri-iodide. G. JANTSCH and N. SKALLA (Z. anorg. Chem., 1930, **193**, 391—405).—Reduction of completely anhydrous samarium tri-iodide in a current of hydrogen, which must be free from oxygen and water, commences at 350°; by raising the temperature gradually to 760° pure samarium di-iodide has been prepared. If the tri-iodide is heated in a vacuum at 800° for 50 min. and then at 900° for 15 min., a 90% yield of pure samarium di-iodide is obtained, but if the tri-iodide is heated slowly decomposition commences at 560°. Since at about 680° the di-iodide begins to decompose according to the equation $3SmI_2 \longrightarrow 2SmI_3 + Sm$, the initial rate of heating should be as high as possible. The compound forms dark green, nearly black, very hygroscopic crystals, m. p. 840° (decomp.), which dissolve in water to a deep red solution with evolution of hydrogen and gradual deposition of a basic salt; the solution is more stable than that of samarium dichloride, but on shaking with air or on addition of acid hydrogen is rapidly evolved and the solution becomes colourless. The equivalent conductivity of the solution at 0° falls with time according to a linear law, until complete decolorisation and formation of the basic salt has occurred. Sulphate, chromate, or phosphate ions precipitate from a neutral solution of samarium di-iodide stable orange-yellow crystals of the corresponding salt; the sulphate, which has been isolated in the solid form, is sparingly soluble in water, and its solution in acid rapidly decomposes with evolution of hydrogen. Samarium tribromide, m. p. 665±2° when heated in a vacuum, commences to decompose at 700°, and at 800—850° the dibromide formed decomposes with separation of metallic samarium, but even with rapid heating only a poor yield of impure samarium dibromide is obtained.

H. F. GILLBE.

Rare earths. XXXVI. Separation of ytterbium by electrolytic reduction. R. W. BALL [with L. F. YNTEMA] (J. Amer. Chem. Soc., 1930, **52**, 4264—4268).—Ytterbium sulphate, $YbSO_4,xH_2O$, containing only 1—2% of other rare-earth metals, is precipitated as greenish-white crystals from a sulphuric acid solution of the mixed chlorides of the metals of the yttrium group by prolonged electrolytic reduction with a current of density 0·025 amp. per cm.^{2} at the mercury cathode. The solution becomes green during the reduction, but on stopping the current hydrogen is evolved throughout the solution, which turns colourless, probably owing to the reaction $2Yb^{\cdot\cdot}+2H^{\cdot}\longrightarrow 2Yb^{\cdot\cdot\cdot}+H_2$. The precipitate dissolves in dilute acid with the evolution of hydrogen and in nitric acid with the evolution of oxides of nitrogen.

J. G. A. GRIFFITHS.

Preparation of lanthanum from cerite from Suecia. Separation of ammonium lanthanum nitrate, and spectral analysis of the lanthanum oxide produced. R. LLORD Y GAMBOA (Anal. Fís. Quím., 1930, **28**, 1145—1152).—Details are given of the separation of lanthanum from cerite by extraction with nitric acid, conversion into the double ammonium nitrate, fractional crystallisation of the salt, and ignition to oxide. The method is reported to be very satisfactory, especially as regards the quantity of material which can be handled. Spectroscopic analysis of the product shows it to be entirely free from metals of the yttrium group, although containing traces of cerium, praseodymium, neodymium, europium, and samarium. H. F. GILLBE.

Reduction of zinc oxide by carbon monoxide in a gaseous cycle, and the mechanism of the reaction. O. DONY (Bull. Acad. roy. Belg., 1930, [v], **16**, 881—892).—The reduction has been investigated at about 1000°. When the zinc oxide is mixed with carbon, the only function of the latter is to reduce the carbon dioxide formed.

C. W. GIBBY.

Anhydrous lower bromides of titanium. R. C. YOUNG [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1930, **52**, 4233—4239).—By applying the hot-cold tube technique to a mixture of hydrogen and titanium tetrabromide vapour, *titanium tribromide* is obtained as bluish-black needles and plates which have been examined crystallographically. The tribromide decomposes at 400° into a mixture of titanium tetrabromide and a black powder, *titanium dibromide*. The reaction is reversed by passing the tetrabromide over the dibromide at 280—380°. Titanium dibromide decomposes slowly at 500° and more rapidly at 650° into titanium and titanium tetrabromide; the dibromide ignites when exposed to moist air, and dissolves in water with the evolution of hydrogen.

Titanium tetrabromide and hydrogen are produced by passing hydrogen bromide over titanium tribromide at 250—350°. Similarly, at 160° the dibromide is converted into the tribromide and some tetrabromide. A mixture of the bromides containing a higher proportion of the non-volatile substances is produced at 300° than 450° by the action of hydrogen bromide on metallic titanium. Titanium tetrabromide at 300° is reduced to the tribromide by titanium metal, mercury, and silver. J. G. A. GRIFFITHS.

Oxides of lead and their reduction by charcoal. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1419—1442).—Two types of lead dioxide exist; one gives three breaks on the temperature–time curve, *viz.*, with absorption of heat at 275—409°, with evolution of heat at 525—535°, and with absorption of heat at 602—620°, whilst the other type gives only two breaks, both of an endothermic character. The first break is due to loss of oxygen, with production of litharge, the second to formation of Pb_3O_4, and the third to loss of oxygen by the latter oxide. Oxides of type I (α) are solid solutions of monoxide and dioxide, whilst the second type consists of the β form, of composition PbO—$PbO_{1\cdot01}$, and the γ form, $PbO_{1\cdot31}$—$PbO_{1\cdot93}$; the character of combination with oxygen is of the zeolite type. Up to 1·01% of water may also be present in solid solution. Reduction of oxides of lead by sugar or wood charcoal takes place in two stages, the first probably corresponding with reduction to a suboxide, and the second to metal.

The transformation of red to yellow lead dioxide does not involve any thermal effect.

R. Truszkowski.

Structure of nitroamide and Hantzsch's arguments. A. Angeli (Gazzetta, 1930, 60, 665—668).—Hantzsch's abandonment (A., 1930, 1032) of his view that nitroamide and hyponitrous acid are stereoisomerides is discussed. T. H. Pope.

Interaction between nitrogen trichloride and nitric oxide at $-150°$. II. Further evidence for formation of nitrogen dichloride and mono-oxygen dinitrogen dichloride. W. A. Noyes (J. Amer. Chem. Soc., 1930, **52**, 4298—4301; cf. A., 1929, 158).—The reaction at $-150°$ in chloroform and carbon tetrachloride is represented, approximately, by the equation $NCl_3+3NO=2NOCl+N_2O+Cl$. It is thought that the reaction proceeds in four stages: (i) $NCl_3+NO=ClNO+NCl_2$, (ii) $NCl_2+NO=Cl_2N_2O$, (iii) $Cl_2N_2O+NO=ClNO+ClN_2O$, (iv) $2ClN_2O=Cl_2+2N_2O$, although the intermediate compounds could not be isolated. The difference between the reaction at $-80°$ (*loc. cit.*) and $-150°$ is attributed to the occurrence of stage (iii) which is made possible by the greater stability of the unstable mono-oxygen dinitrogen dichloride at the lower temperature. Attempts to carry out the reaction at $-185°$ to $-191°$ were not successful. J. G. A. Griffiths.

Quadrivalent vanadium cyanide complex. A. Yakimach (Compt. rend., 1930, **191**, 789—790).—*Potassium vanadicyanide*, $K_4V(CN)_6$, was prepared as netted green prisms by slowly mixing concentrated solutions of potassium cyanide and vanadium tetra-acetate and stirring (cf. A., 1930, 558). It decomposes in air or water, in excess of either reagent and at 150°, and should be washed rapidly with alcohol and recrystallised from a dilute solution of potassium cyanide. Cyanogen was determined by distillation (Liebig–Denigès), vanadium by titration with potassium permanganate solution before and after reduction with sulphur dioxide, and by precipitation with cupferron, and the potassium was weighed as sulphate. J. Grant.

Displacement of "metallic" arsenic from alkaline solutions of arsenic acid by hydrogen at a high pressure and temperature. II. V. N. Ipatiev, G. A. Razubaiev, and V. S. Malinovski (Ber., 1930, **63**, [*B*], 2812—2817; cf. A., 1930, 306).—Reduction of arsenic acid by hydrogen in the presence of alkali occurs in two stages, $Na_2HAsO_4+2H\longrightarrow Na_2HAsO_3+H_2O$ and $Na_2HAsO_3+3H\longrightarrow As+2NaOH+H_2O$. After 24 hrs. at 200° only the first change has occurred, whereas under similar conditions at 250° the separation of "metallic" arsenic also commences. At 350°, the maximum separation of arsenic (96%) is observed. At this temperature, displacement of "metallic" arsenic occurs most completely in the absence of alkali. With increase in the amount of the latter, between 0·0 and 0·3 mol. per 50 c.c., the yield of precipitated arsenic decreases, but between 0·3 and 0·4 mol. there is a marked increase in yield. Variation between 43 and 47 atm. in the initial pressure of hydrogen has no effect. The production of arsine is not observed.

H. Wren.

Preparation and physical properties of sulphur hexafluoride. W. C. Schumb and E. L. Gamble (J. Amer. Chem. Soc., 1930, **52**, 4302—4308).—Monel metal is used in place of magnesium in the construction of the fluorine generator (cf. Bancroft and Jones, A., 1929, 658). Sulphur hexafluoride is prepared by passing fluorine over sulphur in a copper tube, and the subsequent purification of the gas is described. The vapour pressure has been determined at temperatures between $-72°$ and $-46°$, and is 760 mm. at $-63·8°$. The vapour density (air=1) is 5·106. The m. p., $-50·8\pm0·2°$, is higher than values previously recorded. J. G. A. Griffiths.

Preparation of tetra- and tri-thionate from thiosulphate and sulphurous acid. A. Kurtenacker and K. Matejka (Z. anorg. Chem., 1930, **193**, 367—384).—By passing sulphur dioxide into a mixture of 25 g. of ammonium thiosulphate and 15 c.c. of water at 13·5° crystals of ammonium tetrathionate of 99·1% purity separate; they contain only small quantities of the trithionate and of hydrogen sulphite. The mother-liquor retains about 24% of tetrathionate and 34% of trithionate. With mixtures containing less thiosulphate sulphur alone separates, whilst at higher concentrations the precipitate contains decreasing quantities of tetra- and increasing quantities of tri-thionate. The reaction proceeds largely, although not entirely, in accordance with the equation $2S_2O_3''+3SO_2=S_3O_6''+S_4O_6''$. The precipitate obtained from mixtures of potassium thiosulphate with water by the action of sulphur dioxide contains not more than 40% of tetrathionate, but from relatively dilute mixtures the precipitate contains up to 91% of trithionate; the mother-liquor contains varying proportions of thiosulphate, and tri-, tetra-, and penta-thionate. Sodium thiosulphate solutions yield precipitates containing up to 90% of tetrathionate, but by addition of a small quantity of arsenious acid solution both the yield and the quality of the product are improved; a 98% pure tetrathionate, containing tri-thionate but no free sulphur, may be obtained by this procedure. For the preparation of tetra- and tri-thionate the following procedure is recommended: 200 g. of sodium thiosulphate and 1 c.c. of saturated arsenious acid solution are added to 40 c.c. of saturated sulphur dioxide solution, and the cooled mixture is saturated with sulphur dioxide; the clear solution is alternately shaken and treated with the gas, and the resulting precipitate of sodium tetrathionate is separated and washed with ether. The mother-liquor, after passage of sulphur dioxide for a few minutes, is treated with a solution of 100 g. of potassium acetate in 120 c.c. of water, and after a short time the crystalline precipitate of potassium trithionate is removed and washed with a mixture of alcohol and ether. Both products are 95—98% pure, and may be further purified by dissolving in warm water, filtering the solution from sulphur, and precipitating the salt with alcohol. H. F. Gillbe.

Action of fluorine on wood charcoal. M. p. and b. p. of carbon tetrafluoride. P. Lebeau and A. Damiens (Compt. rend., 1930, **191**, 939—940).—The mixture of fluorides of carbon obtained from purified wood charcoal by the authors' method (A., 1926, 710) was freed from oxygen by the action of white phosphorus, washed with dilute alkali, dried, liquefied at −190°, and the pure carbon tetrafluoride (about 50% of the total yield) obtained by repeated fractional evaporations at a low pressure. The revised b. p. is −126° (760 mm.) and m. p. −191° (cf. *loc. cit.*, and Ruff and Keim, A., 1930, 1387). The residue after fractional evaporation contained hexafluoroethane and octafluoropropane. J. GRANT.

Preparation of pure rhenium compounds. F. KRAUSS and H. STEINFELD (Z. anorg. Chem., 1930, **193**, 385—390).—Potassium per-rhenate solution is not reduced by sulphur dioxide or by hydrogen with simultaneous short-wave irradiation. By the action of zinc and hydrochloric acid, sodium amalgam, or hydrazine hydrate, a brownish-black precipitate is produced; this after being dried at 105° consists of metallic rhenium containing oxide. Although hydrazine yields a product free from other metals, the yield is poorer and the substance contains volatile material. Rhenic acid may be prepared by dissolving the brown precipitate in hydrochloric or nitric acid and evaporating the solution to dryness, but the purity is greatly increased if the precipitate is first heated in a current of hydrogen.

H. F. GILLBE.

Oxides of iron and their reduction by hydrogen and charcoal. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1453—1466).—A halt, ascribed to the formation of an allotrope, occurs on the heating curves of ferric oxide at 745°, whilst above 1280° fluctuations in the curve, due probably to elimination of oxygen, appear. The temperature–time curves of ferric oxide and of various iron ores heated in an atmosphere of hydrogen exhibit two breaks; one, at 300—325°, corresponds with the formation of triferric tetroxide, and the second, at 350—370°, indicates further reduction of the latter to metallic iron. Ferrous oxide does not appear to exist as an intermediate reduction product. Three breaks are found on the temperature–time curves of mixtures of iron oxide or iron ores with charcoal; the first occurs at 400—650°, and is due to the exothermic reaction of reduction to magnetite, whilst the remaining two, occurring at 750—830° and 875—995°, respectively, are ascribed to the endothermic reactions of reduction of magnetite to ferrous oxide, and of the latter to metallic iron. R. TRUSZKOWSKI.

Hydrates of iron oxide. E. J. RODE (J. Russ. Phys. Chem. Soc., 1930, **62**, 1443—1452).—Hydrated ferric oxide is converted when heated into an unstable modification of ferric oxide; this reaction is endothermic. The unstable modification is converted at 320—340° into crystalline oxide, with evolution of heat, and the crystalline oxide undergoes further transformation at 450°. The results obtained for ferric hydroxide gel are substantially the same as those obtained for such natural products as bog iron ore, xanthosiderite, hetite, etc.

R. TRUSZKOWSKI.

Atomic hydrogen occluded in iron nitride. S. SATOH (Bull. Chem. Soc. Japan, 1930, **5**, 292—303).—Iron nitride prepared by the action of nitrogen on iron previously reduced with hydrogen contains atomic hydrogen, as shown by potential measurements on iron nitride in ferrous sulphate solution, and other tests. C. W. GIBBY.

Decomposition of potassium ferrocyanide and ferricyanide by autoclave treatment. T. KATSURAI and T. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 189—192; cf. A., 1930, 289).—*N*-Potassium ferrocyanide when heated for 1 hr. in an autoclave at 120° or 140° becomes alkaline owing to the formation of ammonia, and deposits hydrated ferric oxide. At 160° or 180° the precipitate is a mixture of ferric oxide and Prussian-blue. *N*-Potassium ferricyanide gives rise to an ammoniacal liquid and hydrated ferric oxide (hæmatite) at all four temperatures. F. L. USHER.

Isomerism of radicals. C. DUVAL and (MME.) DUVAL (Compt. rend., 1930, **191**, 843—845).—Persulphatopentamminocobaltic sulphate, $[Co(SO_4)^I(NH_3)_5](SO_4)^{II},H_2O$ (*a*), is prepared by keeping a mixture of solutions of aquopentamminocobaltic hydroxide and excess of ammonium persulphate for 2 days, and then treating the filtered solution with excess of ammonium persulphate. The compound is precipitated as orange crystals by alcohol. This is compared with the red sulphatopentamminocobaltic sulphate, $[Co(SO_4)^{II}(NH_3)_5]HSO_4$ (*b*) (cf. Job, Diss., Paris, 1921), the cation of which is isomeric with that of (*a*). The densities are, respectively, 2·1, 1·7, and magnetic susceptibilities ($\chi \times 10^6$), −588, −212, giving for the susceptibilities of the cations −537, −80. The absorption spectra of solutions of high concentration of the two salts are different, but greater dilution converts both alike into aquopentamminocobaltic sulphate. It is also concluded that persulphuric acid is HSO_4, and not $H_2S_2O_8$. C. A. SILBERRAD.

Univalent palladium. W. MANCHOT and H. SCHMID (Ber., 1930, **63**, [*B*], 2782—2786).—Dilute aqueous solutions of potassium palladocyanide react vigorously with sodium amalgam. The solution, which contains cyanide, has more energetic reducing properties than the corresponding platinum solution (following abstract). When shaken with air it yields hydrogen peroxide. When preserved at the ordinary temperature the initially colourless solution becomes pale yellow and hydrogen is noticeably evolved. The colour gradually deepens and finally black particles of metal separate which slowly increase in number. If the solution is boiled, the metal is deposited copiously and hydrogen vigorously evolved. If the alkaline solution is boiled before or after addition of acetic acid, hydrochloric acid, or potassium cyanide, hydrogen free from carbon monoxide is evolved in amount varying from 0·22 to 0·72 equivalent. A portion of the liberated hydrogen is utilised in other ways, since methylamine is present in the acetic acid solution. Titration with potassium ferricyanide or iodine requires amounts of reagent less than 1 equivalent, thus corresponding sharply with the transformation of univalent into bivalent palladium.

H. WREN.

Univalent platinum. W. MANCHOT and G. LEHMANN (Ber., 1930, **63**, [*B*], 2775—2782).—Treatment of a 1% aqueous solution of potassium platinocyanide with 3% sodium amalgam yield a colourless solution which reduces ammoniacal silver, Nylander's bismuth reagent, cadmium salt solution, mercuric chloride, and, if more concentrated, litmus, anthraquinonesulphonate, and acid indigotin solution. If the solution is exposed to air, its reducing power slowly disappears. Reduction can also be effected by potassium amalgam, calcium filings, electrolytically, or by aluminium and potassium hydroxide. Barium platinocyanide may be used or potassium chloroplatinite or chloroplatinate in presence of the equivalent amount of potassium cyanide. The reduced solution contains free cyanide, but colloidal platinum is not present. The boiling solution slowly evolves hydrogen, the maximum amount observed being 0·83 equivalent. In the presence of acids hydrogen is much more rapidly evolved in quantity much exceeding one equivalent per atom of platinum; a similar result is obtained after addition of potassium cyanide. Possibly the platinum passes into the quadrivalent state and also disproportionation of the univalent metal occurs to multivalent and free metal which dissolves in the potassium cyanide with evolution of hydrogen. Addition of the reduced solution to a strongly acidic iodine solution results in the production of iodoplatinic acid, H_2PtI_6, and titration of it with potassium ferricyanide requires more than one equivalent of the oxidising agent. The potential of the reduced solution measured at a platinised platinum electrode differs from that of a solution containing the same amounts of potassium platinocyanide, sodium hydroxide, and potassium cyanide. In course of time the potential of the second solution approaches that of the first, probably due to dissolution of the electrode in the cyanide with production of univalent platinum. Attempts to concentrate the reduced solution on the water-bath or in a vacuum are accompanied by evolution of gas; potassium platinocyanide separates. H. Wren.

Complex ions. III. Relative stabilities of halogenoplatinates. H. I. Schlesinger and R. E. Palmateer (J. Amer. Chem. Soc., 1930, **52**, 4316—4331).—Light accelerates the attainment in aqueous solution of the equilibrium $6NaY+Na_2PtX_6\rightleftharpoons 6NaX+Na_2PtY_6$, where X and Y are different halogens. It is found colorimetrically that the concentration of chloride ion must be 660 times that of bromide ion for the equilibrium to be shifted 99% in the direction $PtBr_6''+6Cl'\longrightarrow PtCl_6''+6Br'$, and the concentration of bromide ion must be 25×10^3 times that of iodide ion to cause a like shift in the reaction $PtI_6''+6Br''\longrightarrow PtBr_6''+6I'$. These results indicate the relative order of the tendency of halogen ions to enter into co-ordination in the platinates. Molecular extinction coefficients are recorded and the existence of intermediate compounds in solution is demonstrated. The solid intermediate compounds previously reported are mixtures. J. G. A. Griffiths.

Colorimetric analysis. F. F. Hahn and R. Klockmann (Z. angew. Chem., 1930, **43**, 993—995).—The error of a colorimetric determination may be reduced to 1—2% by the following procedure. Two comparison standards are prepared, both of a lighter shade than the solution under test; the latter is diluted with water until its colour lies between those of the standards, and after further dilution is brought back to approximately its original colour by addition of a further quantity of the original solution. By repetition of this cycle a series of figures may be obtained for the volume of water necessary to bring the colour to the intermediate point; the optical mean value should not be regarded as a simple mathematical mean, but must be obtained by calibration with solutions of known concentration. H. F. Gillbe.

Analysis of mixtures of hydrogen, methane, and ethane. (Mlle.) E. M. J. Mulders and F. E. C. Scheffer (Rec. trav. chim., 1930, **49**, 1057—1065).—A phase-rule study of the system hydrogen–methane–ethane at the temperature of liquid air (−190°), which is above the critical temperature of hydrogen, shows that separation of the mixture of these three gases into a solid phase (ethane) and a gaseous phase (hydrogen+methane) is effected at this temperature under diminished pressure, and an apparatus for the accurate analysis of such mixtures on this principle is described in detail. Some methane is occluded by the solid ethane, the quantity being smaller when hydrogen is present, but larger in the absence of hydrogen, since condensation is more rapid in this case. The two fractions obtained in this manner are then separately analysed by oxidation with hot copper oxide, the water and carbon dioxide formed are condensed in liquid air, and the volume of any inert gas is determined. The water is then absorbed by phosphoric oxide and the carbon dioxide collected and measured. From the data thus obtained the composition of the original mixture may be calculated. In the apparatus described the whole determination may be effected in 2 hrs. and the accuracy of the method is proved by analysis of mixtures of known composition. J. W. Baker.

Diphenylamine and diphenylbenzidine as oxidation–reduction indicators. I. M. Kolthoff and L. A. Sarver (J. Amer. Chem. Soc., 1930, **52**, 4179—4191).—The velocity of the oxidation of diphenylamine and diphenylbenzidine to diphenylbenzidine-violet by dichromate is accelerated markedly by rise of temperature and increase of acidity, and is approximately proportional to the quantity of dichromate (indicator constant) and to that of indicator (dichromate constant). Mercuric chloride has a large inhibiting effect which is only partly eliminated by ferrous ion. The mechanism suggested for the oxidation (A., 1930, 706) receives further support. In 0·1—2·0*N*-acid, diphenylamine is oxidised quantitatively to diphenylbenzidine if the potassium dichromate is added slowly. The absorption spectra of oxidised diphenylamine and diphenylbenzidine solutions (diphenylbenzidine-violet) are identical; the maxima of the curves are nearly flat between 5400 and 5700 A. and are shifted towards longer wave-lengths by increase of acidity (cf. Thiel, A., 1929, 836). In electrometric titration of diphenylbenzidine-violet to diphenylbenzidine-green with ferrous sulphate, the colour change, violet to green, occurs at a potential of about 0·51 volt with reference to the saturated calomel electrode, independently of hydrogen-ion concentration and almost independently of temperature. An explanation is offered. J. G. A. Griffiths.

Separation of alkali chlorides, bromides, and iodides; analysis of mixtures. Cousin and Dufour (J. Pharm. Chim., 1930, [viii], 12, 439—444).—In a solution containing equal quantities of chloride, bromide, and iodide the total halogen is determined by titration with silver nitrate and ammonium thiocyanate. The iodine and bromine are then liberated successively from a second sample by distillation with ferric ammonium sulphate and with acetic acid and lead dioxide, respectively. Mixtures of chlorates, bromates, and iodates are first reduced by zinc dust in boiling neutral solution, or, when the last two only are present, by sulphur dioxide. H. E. F. Notton.

Bromo-iodometry. VI. J. H. van der Meulen (Chem. Weekblad, 1930, 27, 618—619; cf. A., 1930, 1542).—In mixtures containing bromate, iodate, and iodide the three anions are determined simultaneously by oxidising the iodide with bromine water in presence of carbonate or borate, reducing the excess of bromine, and titrating the iodine liberated on addition of potassium iodide to the acidified solution; bromate and iodate are determined iodometrically in a second portion of the original solution, and in a third portion the bromate is reduced by hydrobromic acid, the iodide being simultaneously oxidised to iodate, and the total iodate is determined. By appropriate manipulation of the results the quantity of each anion may be calculated. H. F. Gillbe.

Rapid detection and determination of fluorine in mineral waters. J. Casares and R. Casares Anal. Fís. Quím., 1930, 28, 1159—1162).—Fluorine in mineral waters may be detected by evaporating 15 c.c. to dryness on the water-bath in a porcelain basin, and adding to the residue solid silver sulphate, powdered glass, and concentrated sulphuric acid; the basin is covered with a glass plate from which is suspended a drop of barium acetate solution acidified with acetic acid, and the crystals of barium fluosilicate are observed under the microscope. The fluorine may be determined colorimetrically after acidification of the solution with hydrochloric acid, with a solution composed of equal volumes of 0·17% sodium alizarinsulphonate solution and 0·87% zirconium nitrate solution. H. F. Gillbe.

Volumetric determination of active oxygen in mixtures of hydrogen peroxide and persulphuric acid. G. O. Lubarsky and M. G. Dikova.—See B., 1930, 1108.

Optical determination of atmospheric ozone. A. I. Duninowski (Compt. rend., 1930, 191, 859—861).—By focussing a narrow portion of the solar spectrum on a thermo-element, recording photographically the resulting current, and by means of a clockwork arrangement, energy–wave-length curves are obtained for the whole solar spectrum from 4860 to 12,000 Å. A series of such curves for varying thicknesses of air traversed is obtained, whence the value of Δ in the relation $I=I_0\times10^{-m\Delta}$ (m=mass of air traversed) is deduced for various wave-lengths. Thence by the method of Cabannes and Dufay (A., 1926, 1080) the equivalent thickness of ozone (at normal temperature and pressure) is determined, without the necessity for the special arrangements required for observations on ultra-violet light. In this way the thickness of ozone at Montpellier in the autumn of 1929 was found to have varied from 0·20 to 0·36 cm. C. A. Silberrad.

Colorimetric micro-determination of sulphur in sulphides, sulphates, etc. I. S. Lorant (Z. physiol. Chem., 1930, 193, 56—58; cf. A., 1930, 181).—Minor improvements in the method are described. J. H. Birkinshaw.

Determination of nitrous and nitric acids in concentrated sulphuric acid. H. A. J. Pieters and M. J. Mannens.—See B., 1930, 1149.

Reaction of diphenylamine and sulphuric acid with nitrates in the presence of chlorides, with especial reference to its use in the determination of nitrates in arable soil. H. Riehm.—See B., 1930, 1149.

Analysis of red phosphorus. S. A. Tolkatschov and M. A. Portnov.—See B., 1930, 1108.

Determination of phosphorus in aluminium. Steinhäuser.—See B., 1930, 1157.

Volumetric determination of the orthophosphate ion. A. del Campo (Anal. Fís. Quím., 1930, 28, 1153—1158).—The orthophosphate ion, in dilute acetic acid solution, may be determined by precipitation with a 1% solution of benzidine acetate. To 50—150 c.c. of the solution is added with stirring a slight excess of the reagent; the white precipitate is collected after about 20 min., and washed until the water is but feebly acid. The precipitate is then titrated with 0·1N-sodium hydroxide, using phenolphthalein as indicator. If there is more than 10% of free acetic acid in the solution during the precipitation low results are obtained. Sulphates interfere, but sucrose is without influence and the method is therefore well suited to the determination of phosphate in pharmaceutical preparations. H. F. Gillbe.

Precipitation and ignition of magnesium ammonium phosphate. J. I. Hoffman and G. E. F. Lundell (Bur. Stand. J. Res., 1930, 5, 279—293).—Details of the precipitation and ignition of magnesium ammonium phosphate for the gravimetric determination of phosphorus and of magnesium have been studied, and the procedure recommended in each case is described. The temperature of ignition is of particular importance; for accurate work ignition at 1100° is advisable, since at 1000° constancy of weight is attained only slowly, and at 1200° there is a slow loss of weight. Constancy of weight is more readily obtained in determinations of phosphorus than of magnesium. Data are given relative to the loss of weight of platinum crucibles when heated at various temperatures, for which corrections should be made. H. F. Gillbe.

Cap for holding Gutzeit mercuric chloride papers. T. J. Ward (Analyst, 1930, 55, 630).—The cap consists of a piece of glass 2 in. square coarsely ground on the lower surface and cemented to a cardboard cylinder. The cap fits loosely over a flat red rubber bung with one hole over which is placed the mercuric chloride paper; the bung serves to close the upper end of the purifying tube and the gases, after traversing the paper and producing uniformly coloured stains with sharp edges, escape through the interstices of the ground glass surface.

A. R. Powell.

Volumetric determination of silicic acid in silicates. N. A. Tananaev and A. K. Babko.—See B., 1930, 1110.

Micro-determination of potassium in [potable] waters. M. H. Griffon and A. Bernard.—See B., 1930, 1132.

Direct determination of sodium in presence of aluminium and chromium. E. R. Caley and D. V. Sickman (J. Amer. Chem. Soc., 1930, **52**, 4247—4251; cf. Caley and Foulk, A., 1929, 900).—Improved methods for washing the precipitate of magnesium sodium uranyl acetate are described. Aluminium and chromium do not interfere in the determination of sodium, but if the sulphate ion is also present it is desirable to keep the concentration of ammonia low.

J. G. A. Griffiths.

Adsorption indicators for argentometry, together with comparison of their limits of sensitiveness. A. G. Berry and P. T. Durrant (Analyst, 1930, **55**, 613—617).—Tartrazine and safranine (or phenosafranine) are shown to be suitable indicators for the titration of chloride or bromide with silver nitrate or *vice versa*. In the first case the precipitate of silver halide is coloured deep yellow as long as an excess of silver ions is present in solution but immediately all the silver is precipitated the solution becomes greenish-yellow and the precipitate assumes its normal colour. With safranine the precipitate is red until the end-point is reached, when it suddenly becomes blue. Lead does not interfere in either case. Proteins interfere only in so far as they have a protective colloid action; addition of strontium nitrate, however, causes flocculation.

A. R. Powell.

Quantitative precipitation of calcium oxalate in presence of arsenate ion. J. T. Dobbins and W. M. Mebane (J. Amer. Chem. Soc., 1930, **52**, 4285—4288).—It is recommended that the calcium solution ($<0\cdot1N$) at 90—100° be made slightly alkaline with ammonia and after the addition of excess of ammonium oxalate maintained at about 95° for 10 min. After 1 hr. the precipitate is collected and washed with very dilute ammonia solution. A large excess of ammonia or a lower temperature delays the formation of calcium oxalate.

J. G. A. Griffiths.

Application of the filtration method in volumetric analysis, especially in the analysis of Portland cement. H. T. Bucherer and F. W. Meier.—See B., 1930, 1153.

Determination of calcium and magnesium by titration of the same solution. K. L. Maliarov (J. Russ. Phys. Chem. Soc., 1930, **62**, 1529—1531).—Calcium is precipitated as oxalate, and magnesium as hydroxide; the precipitates are collected and washed together, and heated with a known quantity of $0\cdot1N$-sulphuric acid, the excess of which is determined by titration. The calcium oxalate is then treated with 10% sulphuric acid and titrated with $0\cdot05$—$0\cdot1N$-permanganate solution. This method gives accurate results provided that the joint concentration of calcium and magnesium oxides does not exceed 0·03% in the original solution.

R. Truszkowski.

Test papers for detecting magnesium. I. Stone (Science, 1930, **72**, 322).—One drop of slightly acid solution is allowed to dry on dry filter-paper which has been treated with 0·01% alcoholic *p*-nitrobenzeneazoresorcinol. In the presence of magnesium a blue spot in a reddish field develops when the paper is immersed in 1% sodium hydroxide solution. The reaction is sensitive to 1 drop of a solution containing 0·1 mg. of magnesium per c.c.

L. S. Theobald.

Separation of magnesium from sodium and potassium. G. Kalikinski (J. Russ. Phys. Chem. Soc., 1930, **62**, 1355—1356).—The solution, after the elimination of barium, strontium, and calcium, may contain magnesium, sodium, and potassium. Ammonia is added, with sufficient ammonium chloride to prevent precipitation, the solution is heated at 30°, and phosphoric acid is added to complete precipitation of magnesium, the reaction being maintained alkaline. The solution is filtered, and the filtrate is evaporated to one third of its original volume, when excess of calcium carbonate is added to remove excess of phosphoric acid. The solution is then filtered, the filtrate evaporated to dryness, and the residue ignited, sodium and potassium being detected by the usual tests in the solution of the residue.

R. Truszkowski.

Iodometric determination of thallium in cadavers. R. Fridli (Magyar Gyó. Társas. Ert., 1929, **5**, 479—488; Chem. Zentr., 1930, i, 3470—3471).—Thallous ion in the solution is first oxidised with bromine water and the excess of bromine removed with phenol. Sodium monohydrogen phosphate and phosphoric acid are then added, followed by potassium iodide, and the iodine liberated is treated with $0\cdot01N$-sodium thiosulphate. Excess of potassium iodide causes the precipitation of thallous iodide, which may be collected and weighed or reoxidised with chlorine water to iodate and thallic ions which are determined iodometrically. Portions of cadaver are first treated with dilute hydrochloric acid and potassium chlorate; the filtered solution is evaporated, treated with sodium hydroxide, and ashed together with the residue. The ash of the solid matter is extracted several times with dilute sulphuric acid, the solution being used to extract the other ash also. Bromine water is then added to the acid solution and the above method employed.

A. A. Eldridge.

Gravimetric determination of aluminium, chromium, and iron by means of potassium cyanate. B. J. F. Dorrington and A. M. Ward (Analyst, 1930, **55**, 625—628).—Precipitation of aluminium hydroxide by boiling neutral aluminium chloride solution gives good results only when the precipitate is collected next day and washed with feebly ammoniacal ammonium nitrate solution; contrary to Ripan's statement (A., 1928, 499) the precipitate is always gelatinous. Chromic and ferric hydroxides produced in a similar way from slightly acid chloride solutions are, however, granular and filter readily, but the method does not separate these elements from zinc and manganese even in the presence of ammonium chloride, and there is a tendency for a thin film of precipitate to adhere tenaciously to the beaker. A. R. Powell.

Activity of iron. V. Benzidine reaction. A. Simon and T. Reetz (Z. anorg. Chem., 1930, **194**, 89—112; cf. A., 1928, 147).—The benzidine reaction for " active " iron may be used in alcoholic solution just as well as in aqueous solution, and is most sensitive at p_H 3·95; in strongly acid or strongly alkaline solutions the reaction is not obtained. The reaction mechanism of ferrous ions with benzidine-blue is quite similar to that of hæmoglobin and complex ferrous salts, the duration of the blue colour being solely a function of the intensity and velocity of reaction. Complex salts, however, have a stabilising effect on the blue colour. Petow and Kosterlitz's method for comparing the activity of iron compounds by determining the amount of benzidine-blue formed (A., 1929, 1486) is to be rejected, since there are always formed at the same time as benzidine-blue brown oxidation products which are not reduced by hydrogen iodide. Satisfactory results can, however, be obtained by determining the amount of unchanged benzidine by precipitating as sulphate and titrating while hot with alkali. R. Cuthill.

Compound of phosphoric and stannic acids and its precipitation in analysis. A. Krüger (Z. anal. Chem., 1930, **82**, 62—68).—On boiling with fuming nitric acid a solution of stannous nitrate and an excess of phosphoric acid a voluminous precipitate of *stanniphosphoric acid*, $2SnO_2,P_2O_5,8H_2O$, is obtained. The precipitate is insoluble in nitric acid but readily soluble in alkali hydroxides and ammonia, showing it to be a derivative of α-stannic acid. For the removal of phosphoric acid from a chloride solution the chlorides are converted into nitrates by evaporation with nitric acid and the solution is boiled with nitric acid and stannous nitrate in excess until a syrupy liquor is obtained; on dilution with boiling water all the phosphoric acid separates as stanniphosphoric acid together with most of the excess of tin as metastannic acid. The presence of more than 5% of iron prevents precipitation; in this case the iron should previously be separated by the ether method. A. R. Powell.

Iodometric determination of vanadium in special steels and in ferrovanadium. W. Werz. —See B., 1930, 1156.

Electrolytic separation of antimony and copper in hydrochloric acid solution. H. Hölemann (Z. anal. Chem., 1930, **81**, 161—207).—The deposition potentials of antimony and copper from chloride solutions are so close together that a satisfactory separation of the two metals by electrolysis is not to be expected. Addition of hydroxylamine or hydrazine hydrochloride makes the deposition potential of both metals more negative; increase in the concentration of hydrochloric acid has the same effect, but to a much greater extent. In either case the addition has a more pronounced effect on the copper potential, so that by varying the acidity etc. of the solution either one or the other metal may be deposited first. Measurements of the deposition potentials of copper and antimony at various temperatures from solutions of several compositions are tabulated. A. R. Powell.

Analytical chemistry of tantalum, niobium, and their mineral associates. XVIII. Separation of titanium from zirconium and hafnium. A. R. Powell and W. R. Schoeller (Analyst, 1930, **55**, 605—612).—Dittrich and Freund's method (A., 1908, ii, 134) for the separation of zirconia from titania gives fair results in two treatments only by a compensation of errors, some titania being co-precipitated with the zirconia and a corresponding amount of zirconia remaining in solution. An accurate separation may be effected by precipitation of the titania with tannin from a boiling neutral solution of the double oxalates half saturated with ammonium chloride. The mixed oxides obtained from thiosulphate hydrolysis are fused with potassium hydrogen sulphate and the mass is leached with a hot saturated solution of 2—3 g. of ammonium oxalate. The solution is neutralised with dilute ammonia solution, avoiding a permanent turbidity, diluted to 200—250 c.c. with a 15% solution of ammonium chloride, heated to boiling, and treated dropwise with a solution containing tannin equal to twelve times the weight of titania present. The precipitate is collected by suction, using a platinum cone, washed with hot 12% ammonium chloride solution, and ignited to titania. Reprecipitation is advisable when much zirconia is present. The filtrate is made feebly ammoniacal and treated at 100° with more tannin to recover the zirconia, which should be purified by fusion with potassium hydrogen sulphate and subsequent thiosulphate hydrolysis. Alumina and thoria follow the zirconia. A. R. Powell.

Radiation thermopile design. F. A. Firestone (Rev. Sci. Instr., 1930, [ii], **1**, 630—649).—Existing formulæ for the design of thermopiles for use with a Thomson galvanometer are summarised, and new formulæ for designs to be used with d'Arsonval galvanometers developed. A type of thermopile in which the cold almost entirely surround the hot junctions to reduce drifts is described. The whole fits an evacuated case of 10 mm. edge, and can be used in front of an elliptical mirror, which forms a small hot image. By a slight modification of the spectrometer, a thermopile having adjustable compensation can be used, theoretically eliminating drifts due to temperature changes of the optical parts and surroundings. N. M. Bligh.

Comparator for spectroscopic work. E. Bäcklin (Rev. Sci. Instr., 1930, [ii], **1**, 662—666).—An improved comparator for use with both eyes, and suitable for measuring small spectral plates, is described. A magnified real image of the object plate is formed on a screen with the aid of a photographic objective. N. M. Bligh.

Constricted mercury arc. R. H. Crist (J. Amer. Chem. Soc., 1930, **52**, 4337; cf. Forbes and Harrison, A., 1925, ii, 1194).—The air-cooled quartz capillary lamp described may be used at 4—5·5 amp.

and 20—25 volts per. cm.^{2} for about 30 hrs. and yields a constant high light intensity. J. G. A. Griffiths.

Colorimetry without comparative standards by means of the Bloch leukometer. L. Hock and H. T. Müller (Z. wiss. Phot., 1930, **29**, 262—266).—The leukometer consists of the photometer head of a Marten polarisation photometer fitted with a series of coloured filters which may be interposed to cover the two comparison fields. A calibration curve is prepared for each particular substance to be determined by measuring the percentage of light transmitted by a standard thickness of solutions of known concentration, a suitably coloured light being used by interposition of one of the filters. Fairly accurate results were obtained with nickel sulphate, cobalt nitrate, and copper sulphate solutions by measuring the red light transmission. J. W. Glassett.

Measurement of hardness and absorption of *X*-rays by a photographic method. L. Grebe and W. Schmitz (Z. wiss. Phot., 1930, **29**, 129—133).—A photographic plate is exposed to the *X*-ray source behind an aluminium wedge of known gradation and then, in another part of the plate, given a series of time exposures in the ratio 1 : 2 : 3 etc., which corresponds with a series of intensity exposures varying in the same ratio for a standard time. From the latter series a curve can be plotted from which the intensities corresponding with each density in the wedge exposure may be obtained. By substitution of these values in the absorption law $I/I_0=e^{-\mu d}$ (*d* being the wedge constant) a series of values for μ, the absorption coefficient, can be obtained for each pair of consecutive steps, and from these values the mean effective wave-length can be calculated. J. W. Glassett.

Immersion refractometer. A. Dolinek.—See B., 1930, 1095.

Double-pole double-throw mercury switch. G. H. Damon (J. Physical Chem., 1930, **34**, 2627—2628).—A mercury switch eliminating the difficulties attendant on the use of the usual knife-edge switch is described. The contact resistance is constant, and a unique feature is the possession of neutral or no contact position. The switch can be used for small or relatively large currents and can be operated automatically. L. S. Theobald.

Photographing of cooling curves. H. D. Crockford and A. E. Hughes (J. Physical Chem., 1930, **34**, 2624—2626).—An apparatus for photographing cooling curves is described. The method is accurate to 0·1° and the curves are better than the usual thermometric ones for showing the mechanism of supercooling. L. S. Theobald.

Condenser for low-temperature evaporation of water. H. M. Evans, R. E. Cornish, and J. C. Atkinson (J. Amer. Chem. Soc., 1930, **52**, 4334—4335).—By means of the arrangement described, 2—3 c.c. per min. of water may be evaporated from biological fluids (700 c.c.) at 7°. The condenser is a 12-litre flask, filled with a mixture of ice and salt, and kept below −10°; the neck of the flask is closed by a stopper pierced by two concentric tubes, the wider of which makes immediate connexion with the "retort" (1- or 2-litre flask) and the other communicates with a large-capacity high-vacuum oil pump by which the condenser and "retort" are evacuated. A slow stream of air bubbles admitted to the "retort" facilitates distillation and assists the maintenance of ice in the biological fluid. Apparatus for larger-scale operations is discussed. J. G. A. Griffiths.

Inorganic lubricants. III. Mixtures of aqueous liquids with non-reacting solids. W. A. Boughton (J. Amer. Chem. Soc., 1930, **52**, 4335—4336).—Evaporation of water from such mixtures may be prevented by the use of concentrated aqueous solutions of a deliquescent salt or acid. Of the many mixtures tested, the most successful lubricants consisted of kaolin or graphite with calcium chloride solution. J. G. A. Griffiths.

Short manometer. L. Chudožilov (Z. anal. Chem., 1930, **82**, 68—69).—The closed end of the tube is replaced by a stopcock provided with a short bent funnel to facilitate re-filling with mercury. A. R. Powell.

Extracting liquids which form emulsions. W. Weinberger (Amer. J. Pharm., 1930, **102**, 594—595).—A review of laboratory methods. H. E. F. Notton.

Apparatus for the determination of extraction residues. Anon. (Chem.-Ztg., 1930, **54**, 881).—The apparatus comprises a glass-stoppered weighing bottle with a hemispherical bottom supported on three glass legs and provided with an external siphon connecting with the bottom of the hemisphere. The substance to be extracted is placed in a dried and weighed extraction thimble in the tube and, after weighing, the stopper is removed and the tube placed inside a wide glass tube fitting into the neck of a boiling flask and surmounted by a reflux condenser which returns the condensed solvent into the thimble. A. R. Powell.

Applications of the differential ebullioscope fitted with a condenser. W. Swientosławski (Rocz. Chem., 1930, **10**, 570—578).—A differential ebullioscope intended for the analysis of liquid reagents and eutectic and azeotropic systems is described, with examples of its use for the determination of the purity of samples of benzene, toluene, etc., and of the water content of an azeotropic mixture of acetone and carbon disulphide. R. Truszkowski.

Vacuum tube potentiometer applicable for use with glass electrodes of high resistance. D. Dubois (J. Biol. Chem., 1930, **88**, 729—741).—A full description, with diagrams, is given of a potentiometer employing a screen grid valve suitable for use in determining $p_{\rm H}$ values by means of the glass electrode. The plate current is so reduced by lowering the screen grid voltage that it can be carried directly through a sensitive galvanometer. As, when the apparatus is properly adjusted, the grid current is extremely low (less than 5×10^{-15} amp.), there is no drift of glass electrode voltage. Readings can be taken within 5 min. of switching on the batteries and high accuracy is obtainable. W. O. Kermack.

Corrections for Redwood viscosimeters. G. Barr (J. Sci. Instr., 1930, **7**, 359—361).—The equations $\nu=AT-B/T$ and $\nu=A'T'-B'/T'$ are assumed to hold for the standard Redwood viscosimeter and the instrument to be tested respectively (ν=kinematic viscosity, T, T' times of flow for the usual 50 c.c.). Parallel flow tests are made with two oils, and the results are used in a simple graphic method to estimate the corrections, $T'-T$, which should be applied at several stated values of T. C. A. SILBERRAD.

Oil viscosimeter. H. SCHAFFER.—See B., 1930, 1095.

Micro-balance of new design. G. R. STANBURY and N. TUNSTALL (J. Sci. Instr., 1930, 7, 344—349).—The essential difference from the ordinary torsion micro-balance lies in the replacement of the wire by a strip of spring steel which can be stretched by a varying tension. C. A. SILBERRAD.

Apparatus for experiments with gases at pressures of 6000 kg. per cm.^{2} J. BASSET (Compt. rend., 1930, 191, 928—931; cf. A., 1927, 849).—The gas is compressed in a small cylinder by means of a piston, the reaction on which is supported by means of a larger auxiliary piston moving in a larger cylinder and activated by a glycerin pump. The ratio of the surfaces of the two cylinders gives the ratio of the pressures, 500—1000 kg. per cm.^{2} being attainable. Apparatus for continuous experiments with one or more gases at 5000 kg. per cm.^{2} and 1000° is also described; the gases are compressed in two stages and passed through an electrically-heated reaction vessel. J. GRANT.

Platinum resistance thermometry. I. Calibration of the bridge and annealing of the platinum bulb. II. Determination of constants of the platinum bulb and accuracy of resistance thermometry. M. MATSUI and S. KAMBARA (J. Soc. Chem. Ind. Japan, 1930, 33, 401—403B, 403—407B).—I. Details of the calibration and temperature coefficient determination of a Müller bridge are given. A platinum resistance thermometer was found to vary in resistance after being heated at 400—600° until it had been annealed fourteen times.

II. The error of temperature determinations with the platinum resistance thermometer is discussed and the maximum permissible variations in the quantities measured, in order to obtain a given accuracy, are given for temperatures of from 0° to 1000°. The limit of accuracy is 0·01° up to 500°, and 0·1° at higher temperatures. H. F. GILLBE.

Determination of the m. p. of platinum alloys. L. MÜLLER (Ann. Physik, 1930, [v], 7, 9—47).—A new method of measuring temperatures above 1500°, applicable especially to m.-p. determinations with metals and alloys, has been developed. Emission from the heated material, between certain limits of the spectrum, is measured with a photo-electric cell, calibrated by means of the emission from a similar substance. The method has been applied to the determination of the liquidus curves of alloys of platinum with rhodium, iridium, tungsten, and chromium, with an error of less than 5°, the pure metals being used for calibration. Series of mixed crystals exist for alloys containing 0 to 100% Rh, 0 to 100% Ir, 0 to 50% W, and 0 to 10—30% Cr. These results have been confirmed by photomicrographs, and by measurements of the electrical conductivity and of the temperature coefficient of the conductivity. H. F. GILLBE.

Determination of the m. p. of chromium by a thermo-element. L. MÜLLER (Ann. Physik, 1930, [v], 7, 48—53).—The method previously described (cf. preceding abstract) is not applicable to the determination of the m. p. of chromium on account of the ease with which the metal oxidises. The m. p. has been determined using an iridium–rhodium/iridium–ruthenium thermo-element, the chromium being melted in a zirconia crucible in a high-frequency furnace; a single observation gave the m. p. as 1805°. This was not confirmed as the apparent m. p. changes owing to interaction between the crucible material and the chromium; the latter also dissolves iridium from the thermo-element. H. F. GILLBE.

Test-tube. A. KUHN (Chem.-Ztg., 1930, 54, 908).—An unflanged, robust test-tube is preferred. D. F. TWISS.

Geochemistry.

Amount of ozone in the earth's atmosphere, and its relation to other geophysical conditions. IV. G. M. B. DOBSON (Proc. Roy. Soc., 1930, A, 129, 411—433; cf. Dobson, Harrison, and Lawrence, A., 1929, 419).—A year's observations have been made of the distribution of ozone at Arosa (Switzerland), Table Mountain (California), Helwan (Egypt), Kodaikanal (India), and Christchurch (N.Z.). The results are tabulated, and curves are drawn showing the general distribution and annual variations over the greater part of the earth. The low and uniform value of the ozone content throughout the autumn hemisphere is of importance in connexion with the theory of the variation of ozone with pressure conditions. The ozone value in India appears to be unaffected by the setting in of the monsoon. There is fairly clear evidence that the same relationship exists between ozone content and pressure conditions in Egypt and New Zealand as that previously found in N.W. Europe (*loc. cit.*). In Chile and S. India the meteorological conditions are very constant, and no important variations of the ozone value were observed. Reports are submitted by H. H. KIMBALL and E. KIDSON on the relation of variations in the ozone values obtained at Table Mountain to the meteorological conditions, and on the relation between weather and the amount of ozone above Christchurch, respectively. L. L. BIRCUMSHAW.

Carbonates in the sediments of the Lake of Geneva. J. ROMIEUX (Arch. Sci. Phys. Nat., 1930, [v], 12, 244—254; cf. A., 1930, 1155).—In some samples of the sediments of the lake of Geneva sulphate has been found to the extent of 1% SO_3. The distribution of carbonates depends principally on material deposited by rivers, then on currents, and thirdly on the action of organisms. The micaceous muds of the Rhone are the poorest in carbonates and the whitish muds of the Petit Lac the richest. In a horizontal section the variations are small provided the deposits are far enough from the shore. The variations in a vertical section are greater in the Petit Lac than in the Grand Lac, increasing with increasing depth in the deposit near the coast and in shallow water; far from the coast and in deep water the reverse is the case. C. W. Gibby.

Presence of vanadium in Spanish rocks and minerals. S. Piña de Rubies (Anal. Fís. Quím., 1930, **28**, 1110—1116).—Vanadium has been detected spectroscopically in a great variety of rocks and minerals, as well as in sea-sand and meteorites. Titanium appears always to be associated with vanadium, and the greater is the titanium content the more pronounced is the vanadium spectrum; rocks free from titanium show no trace of the presence of vanadium. H. F. Gillbe.

Crystals of gold, titanite, and garnet. H. Buttgenbach (Bull. Acad. roy. Belg., 1930, [v], **16**, 874—880).—Detailed crystallographic descriptions of gold from Kibali (Congo), titanite from Tavetsh, and of garnet from Ala (Piedmont) are given. C. W. Gibby.

Tectites of Indo-China. A. Lacroix (Compt. rend., 1930, **191**, 893—899; cf. A., 1929, 288).—The tectites, which are identical in character, are usually found on the surface of the soil mixed with round quartz pebbles and grains of limonite. Samples from three different portions of the belt were also similar in chemical composition (approximately: SiO_2 71, Al_2O_3 13·2, FeO 5, MgO 1·9, CaO 3, Na_2O 1·5, K_2O 2·7, TiO_2 1, MnO 0·15, Fe_2O_3 0·2, free SiO_2 38%; *d* 2·440—2·422). The artificial glass and volcanic hypotheses of origin are dismissed as doubtful, whilst the presence of grains of quartz in the neighbourhood of the tectites, although not in the tectites themselves, suggests decomposition by laterisation, *i.e.*, by the more or less complete elimination of certain elements (silica, alkalies, lime, magnesia) from the silicated rocks and their replacement by others (iron, titanium, aluminium). There is also strong evidence of meteoric origin; they date probably to Pleistocene times, and must certainly have existed before the 7th century. J. Grant.

"Fibrous lignites" ("fibrous coal") in brown coal and "fibrous coal" in general. W. Gothan and Benade (Braunkohle, 1930, **29**, 274; Fuel, 1930, **9**, 482—488).—Samples of the fibrous lignites which have been known for some time to occur in German brown coals of different localities have been examined microscopically and chemically. They are distinguished by the readiness with which they split into fibres, and by the very tough nature and flexibility of the cells. With few exceptions they are evidently portions of the bark bast of conifers, the rows of bast cells of which, when the specimens fall to pieces, are weathered and split off in the form of very thin bast lamellæ, so that the general appearance is often almost like that of tow. The cork portions of the bark may also exhibit a similar state of preservation. The remarkable toughness and flexibility of the cells is probably due to the large amount of cellulose, more than 30%, still left in the material. These true fibrous coals should be distinguished from fusain, which yields splinters and not fibres. A. B. Manning.

Occurrence of resin in Ruhr coals. E. Hoffmann and H. Kirchberg (Brennstoff-Chem., 1930, **11**, 389—394).—Numerous resin inclusions one or more mm. in thickness and 5—20 cm. long have been found in the coal seams of the Brassert mine, and have been examined chemically and microscopically. From their occurrence it may be concluded at once that the coal has never been subjected to any considerable rise of temperature. The resins are sparingly soluble in alcohol, but readily soluble in warm benzene. Under the microscope they have a streaky appearance, and in transmitted light exhibit an irregular net-like structure. The frequent occurrence of particles of fusain in the resins is regarded as supporting the "forest fire" theory of the origin of fusain. The microstructure of the resins is discussed from the viewpoint of colloid chemistry; the original colloidal material must have undergone a differential coagulation or coacervation (cf. de Jong and Kruyt, A., 1930, 158) to produce the observed structure. A similar theory is applied to other banded coal constituents. A. B. Manning.

Organic Chemistry.

Effect of electrical discharge on gaseous hydrocarbons. V. Condensation of hydrocarbons by electrical discharge. Comparison with condensation by α-rays. S. C. Lind and B. Glockler (J. Amer. Chem. Soc., 1930, **52**, 4450—4461).—When methane, propane, butane, and ethylene are submitted to a silent discharge in an ozoniser, the condensations taking place are similar in all respects to those caused by α-rays (A., 1926, 1077). The results previously obtained (A., 1927, 1039) with ethane are confirmed. The mechanisms of the reactions are discussed. H. Burton.

Production of liquid hydrocarbons from propylene. A. Mailhe and Renaudie (Compt. rend., 1930, **191**, 851—854).—When ethylene is passed over silica gel at 700° (A., 1930, 1157) the production of a deposit of carbon is due to the presence of metallic iron. When this is removed the liquid products, consisting, besides ethylenic hydrocarbons, chiefly of benzene and toluene, are obtained in high yields, methane and its homologues being produced only in small quantities. Some naphthalene and anthracene have been isolated from the tar. When propylene is passed over silica gel at 650° under similar conditions there are formed a liquid condensate, which contains low-boiling olefines together with aromatic hydrocarbons, and a tar in which toluene, *m*-xylene, naphthalene, and anthracene have been detected.

T. H. Morton.

Auto-oxidation of pentenes. J. Hyman and C. R. Wagner (J. Amer. Chem. Soc., 1930, **52**, 4345—4349).—Oxidation of Δ^{α}- and Δ^{β}-pentenes, β- and γ-methyl-Δ^{α}-butenes, and β-methyl-Δ^{β}-butene with oxygen in presence of cobalt oleate as a catalyst in the dark at 15° shows that a double linking in the αβ-position is the least readily oxidised; the amount of oxidation is determined by the liberation of iodine from potassium iodide by the peroxidic oxygen. Δ^{α}-Pentene, prepared from allyl bromide and magnesium ethyl bromide, has b. p. 30° (corr.) (cf. Kirrmann, A., 1926, 934; Norris and Joubert, A., 1927, 440); an unsaturated hydrocarbon, b. p. 20—24°, is formed as a by-product.

H. Burton.

Pyrolysis of allene and propinene. R. N. Meinert and C. D. Hurd (J. Amer. Chem. Soc., 1930, **52**, 4540—4549).—The gases are decomposed by passing through pyrex glass tubes at about 1—2 c.c. per sec. The main reaction with allene at 500° is polymerisation; 80% of the allene reacts when the contact time is 86 sec. and 90% of the products formed consist of liquid polymerides which are essentially the same as those obtained by Lebedev (A., 1913, i, 1285). Reaction proceeds very slowly below 500°, but at 600° (contact time 50 sec.) there is a marked increase in the amount of gaseous products formed; these consist of hydrogen, methane, ethane, ethylene, and small amounts of acetylenes. There is no indication of the formation of aromatic hydrocarbons.

The optimum yield of liquid products obtained from propinene is at 575° and a contact time of 48 sec.; the liquids formed resemble those from allene. At 650°, increased amounts of hydrogen, ethylene, and methane are produced. Pure propinene, prepared from sodium acetylide and methyl sulphate, undergoes pyrolysis at 555°/74·5 sec. yielding some allene, which may be an intermediate in the pyrolysis of propinene. The name "keteno-ynol" is suggested for the tautomeric change $CH⋮CMe \rightleftharpoons C(CH_2)_2$.

H. Burton.

Preparation of substituted acetylenic hydrocarbons. R. Truchet (Compt. rend., 1930, **191**, 854—856).—The interaction of a sodium derivative of an acetylenic hydrocarbon and an ester of benzene- or *p*-toluene-sulphonic acid gives 45—60% of the theoretical yield: $CR⋮CNa+Ph{\cdot}SO_3R'=CR⋮CR'+Ph{\cdot}SO_3Na$. The reaction is complete in 3 hrs. at 80°. In this way there are obtained: Δ^{γ}-*noninene*, b. p. 155—157°, d^{20} 0·763, n_D^{20} 1·429, from ethyl *p*-toluenesulphonate and Δ^{α}-heptinene; Δ^{γ}-*decinene*, b. p. 175—176°, d^{21} 0·765, n_D^{21} 1·433, from ethyl benzenesulphonate and Δ^{α}-octinene; Δ^{ϵ}-*undecinene*, b. p. 195—196°, d^{20} 0·785, n_D^{20} 1·437, from butyl benzenesulphonate and Δ^{α}-heptinene; and the *hydrocarbon* $C_5H_{11}{\cdot}C⋮C{\cdot}CH_2{\cdot}CH⁚CH_2$, b. p. 74·5—75·5°/12 mm., d^{20} 0·788, n_D^{20} 1·445, from allyl benzenesulphonate and Δ^{α}-heptinene.

T. H. Morton.

Preparation of anhydrous alcohol and the detection and determination of water in alcohol. F. Adickes [with W. Brunnert and O. Lücker] (Ber., 1930, **63** [*B*], 2753—2760).—The process consists in dissolving sodium in the alcohol, addition of ethyl formate, and boiling the mixture under a reflux condenser until carbon monoxide ceases to be evolved: $H{\cdot}CO_2Et+NaOEt+H_2O=2EtOH+H{\cdot}CO_2Na$ and $H{\cdot}CO_2Et=CO+EtOH$. The product is distilled, the final portion of the distillate being rejected. The alcohol thus prepared contains 0·03% of water and 0·00015% of ethyl formate. For the detection of water, an ethoxide–ester solution (about 50 c.c. of alcohol, 1 g. of sodium, and 10 g. of ester preserved in an Erlenmeyer flask until subsidence is complete) is filtered into the alcohol; if more than 0·013% of water is contained therein, a precipitate of sodium formate is produced at 0°. Gravimetric determination of water is effected by means of the sodium formate produced. If 2·5—3·0% of water is present, this can be effected directly, since the slight solubility of the salt is unimportant. With a smaller proportion of water, the alcohol and undecomposed ester are distilled from the sodium formate and excess of sodium ethoxide, finally in a vacuum. With very small amounts of water the acid or water content of the ester must be taken into account. The weight of sodium formate is determined from that of the mercurous chloride which it forms by reduction of mercuric chloride; the method is not applicable in presence of alcohol, which slowly reduces mercuric chloride. With larger amounts, the oxidimetric–volumetric process is applicable. If the alcohol contains more than 4—5% of water it must be mixed with a suitable proportion of absolute alcohol of known water content.

A gas-volumetric method, based on the measurement of the carbon monoxide evolved from the unused ethyl formate, is described; it is sufficiently accurate only with alcohol containing at least 1% of water.

H. Wren.

Decomposition of ethylene glycol in presence of catalysts. I. Vanadium pentoxide as catalyst. N. L. Drake and T. B. Smith (J. Amer. Chem. Soc., 1930, **52**, 4558—4566).—When ethylene glycol vapour is passed over vanadium pentoxide at 250—400°, the main decomposition products are acetaldehyde and ethylene; small amounts of carbon oxides and acetic acid (from the acetaldehyde) are also formed. At temperatures up to about 320°, ethylene is the major product; the minimum amount of ethylene is found at about 360°, at which temperature aldehyde formation is at a maximum. Considerable reduction of the vanadium pentoxide occurs during the decomposition. The use of the partly reduced oxide causes a considerable variation in the proportions of the decomposition products.

H. Burton.

Derivatives of propylene glycol. A. Dewael (Bull. Soc. chim. Belg., 1930, **39**, 395—401).—α-Chloro*iso*propyl alcohol (propylene α-chlorohydrin) and methyl sulphate react at 100° affording a mixture of *methyl α-chloro*iso*propyl ether*, b. p. 103—104°/760 mm., d_4^{20} 1·009, n_D^{20} 1·41372, and *di-α-chloro*iso*propyl ether*, b. p. 187—188°/761 mm., d_4^{20} 1·103, n_D^{20} 1·45046. The last-named ether is converted by treatment with potassium acetate and a little acetic acid into *di-α-*

*acetoxy*iso*propyl ether*, b. p. 248°/761 mm., d_4^{20} 1·050, n_D^{20} 1·42654. Propylene α-chlorohydrin and ethyl sulphate give *ethyl α-chloro*iso*propyl ether*, b. p. 117°/760 mm., d_4^{20} 0·9965, n_D^{20} 1·41902, also obtained from allyl chloride, alcohol, and sulphuric acid. Treatment of propylene oxide with an alcohol and a small amount of sulphuric acid furnishes *propylene glycol α-alkyl ethers*, of which the following are described: *ethyl*, b. p. 136°, d_4^{20} 0·9028, n_D^{20} 1·4 (*acetate*, b. p. 158—160°, d_4^{20} 0·9461, n_D^{20} 1·40968); *methyl*, b. p. 126—127°/760 mm., d_4^{20} 0·9260, n_D^{20} 1·40696 (*acetate*, b. p. 147°/762 mm., d_4^{20} 0·9709, n_D^{20} 1·40449); iso*propyl*, b. p. 142—143°/765 mm., d_4^{20} 0·9059, and *β-chloropropyl ethers*, b. p. 204—205°/762 mm., d_4^{20} 1·059. Ethyl α-chloro*iso*propyl ether and potassium acetate in presence of small amounts of acetic acid and potassium iodide afford *β-ethoxypropyl acetate*, b. p. 160—161°, d_4^{20} 1·025, hydrolysed by concentrated potassium hydroxide solution to *propylene glycol β-ethyl ether*, b. p. 140—141°/761 mm., d_4^{20} 0·9044, n_D^{20} 1·41223. *β-Chloropropyl butyrate* has b. p. 184°/741 mm., d_4^{20} 1·031, n_D^{20} 1·42875. Propylene glycol diacetate, b. p. 190—191°/762 mm., d_4^{20} 1·059, n_D^{20} 1·4173, prepared from propylene dibromide and potassium acetate or by acetylation of the glycol, when saturated with hydrogen chloride (or bromide) gives a mixture of chloro(or bromo)propyl acetates. H. Burton.

New form of two enantiomorphous rhamnitols. F. Valentin (Coll. Czech. Chem. Comm., 1930, **2**, 689—696).—Reduction of rhamnose with 3% sodium amalgam and crystallisation of the product from water gives l-*rhamnitol trihydrate*, m. p. 69°, $[\alpha]_D$ +8·83° in water, dehydrated at 100° in a vacuum to *l*-rhamnitol, m. p. 123°, $[\alpha]_D$ +12·4°. d-*Rhamnitol trihydrate* has m. p. 69°, $[\alpha]_D$ −8·89° in water, whilst r-*rhamnitol*, prepared by crystallising equal quantities of the enantiomorphs from water, has m. p. 117° and is anhydrous. Crystallographic data for the *d*- and *l*-rhamnitol trihydrates are given; the crystals exhibit enantiomorphous facets. C. W. Shoppee.

Pentachloromethyl ether. I. Rabcewicz-Zubkowski and S. Chwaliński (Rocz. Chem., 1930, **10**, 686—689).—*Pentachloromethyl ether*, b. p. 158·5—159·5°, $d^{17\cdot3}$ 1·6496, n_D 1·4825, is prepared by chlorinating *s*-dichloromethyl ether under the influence of ultra-violet light. When heated with water it decomposes to yield carbon monoxide and dioxide, hydrogen chloride, and hexachloroethane, whilst with aqueous aniline the product is *s*-diphenylcarbamide. R. Truszkowski.

"Ring contraction" during the formation of internal ethers (oxides) from glycols. αε-Oxidododecane from dodecane-αμ-diol. A. Franke and A. Kroupa (Monatsh., 1930, **56**, 331—346; cf. A., 1923, i, 530; 1929, 1422).—ακ-Dibromodecane is converted by aqueous alcoholic potassium cyanide into the dinitrile of decamethylene-ακ-dicarboxylic acid and the methyl ester of this is reduced by sodium and alcohol to dodecane-αμ-diol (57% yield), also obtained in 21% yield from trioxymethylene and the Grignard reagent from ακ-dibromodecane. Treatment of this diol with 50% sulphuric acid and distillation with superheated (180°) steam yields *αε-oxidododecane*, b. p. 235—237°, in 22% of the theoretical amount. This is oxidised by 1% potassium permanganate solution at 50° mainly to succinic and octoic acids; similar oxidation of the diol affords no fatty acids. αε-Oxidodecane (*loc. cit.*) is also obtained when decane-ακ-diol is heated with 89% phosphoric acid to 200°. H. Burton.

Unsaponifiable matter from oils of elasmobranch fish. VII. Synthesis of α-glyceryl ethers and its bearing on the structure of batyl, selachyl, and chimyl alcohols. G. G. Davies, I. M. Heilbron, and W. M. Owens (J.C.S., 1930, 2542—2546).—The following *alkyl α-glyceryl ethers* are prepared from α-monochlorohydrin and the requisite sodium alkoxide: α-ethyl, b. p. 118—121°/21 mm. (*diphenylcarbimide* derivative, m. p. 103—104°); α-*propyl*, b. p. 118—122°/15 mm., d_4^{18} 1·074, n_D^{18} 1·4400 (*diphenylcarbimide* derivative, m. p. 116°); and α-*butyl*, b. p. 138—140°/22 mm., d_4^{18} 1·002, n_D^{18} 1·4463 (*diphenylcarbimide* derivative, m. p. 94—95°). Higher alkyl α-glyceryl ethers could not be prepared by this method or from sodium glyceroxide and the alkyl chloride. Sodium allyloxide and cetyl chloride in allyl alcohol give *cetyl allyl ether*, m. p. 25°, oxidised by hydrogen peroxide in acetic acid to *α-cetyl glyceryl ether*, m. p. 64—65° (*diphenylcarbimide* derivative, m. p. 93—94°). This ether appeared to be identical with a specimen of chimyl alcohol (cf. Toyama, A., 1924, i, 604; 1925, i, 4) isolated from a Japanese shark liver-oil, but it is stated that the chimyl alcohol is a mixture of batyl alcohol and an unidentified substance. *Octadecyl allyl ether*, m. p. 27·5—28·5°, is converted similarly into *α-octadecyl glyceryl ether*, m. p. 70—71° (*diphenylcarbimide* drivative, m. p. 95—96°), which is not identical with batyl alcohol (A., 1928, 616). This alcohol must, therefore, be β-octadecyl glyceryl ether. Since selachyl alcohol is hydrogenated to batyl alcohol, it must, by analogy, be β-oleyl glyceryl ether. H. Burton.

Dipentaerythritol [di-γ-hydroxydi-ββ-hydroxymethylpropyl ether]. W. Friederich and W. Brün (Ber., 1930, **63**, [*B*], 2681—2690).—Pentaerythritol, obtained by the condensation of acetaldehyde with formaldehyde in presence of alkali hydroxide, contains dipentaerythritol, from which it cannot be separated by crystallisation. Nitration of the crude product affords a mixture of pentaerythritol tetranitrate and *dipentaerythritol hexanitrate*, m. p. 75°, d^{15} 1·630 or 1·617 after fusion, which can be separated from one another by means of acetone. Hydrolysis of the hexanitrate by zinc and hydrochloric acid or, preferably, with alkaline sodium sulphide gives *dipentaerythritol*, $O[CH_2{\cdot}C(CH_2{\cdot}OH)_3]_2$, m. p. 221°. Homogeneous pentaerythritol has m. p. 260°. Examination of the f.-p. curves of pentaerythritol and dipentaerythritol shows that the technical "pure" alcohol, m. p. 235°, contains 10% of the ether. The m.-p. curve of mixtures of tetranitroerythritol and hexanitrodipentaerythritol is given. *Dipentaerythritol hexaformate*, m. p. 56°, from the ether and boiling, concentrated formic acid, *hexaacetate*, m. p. 73°, prepared by use of acetic anhydride and sodium acetate, and *hexabenzoate*, m. p. 183°, according to Schotten–Baumann, are described.

With triphenylmethyl chloride in pyridine, *dipentaerythritol hexatriphenylmethyl ether*, m. p. 173°, is prepared in 97·3% yield. Attempts to increase the yield of dipentaerythritol from acetaldehyde and formaldehyde by use of potassium, barium, lead, or zinc hydroxides or sodium carbonate were unsuccessful and conversion of pentaerythritol into the ether could not be effected by prolonged ebullition with sodium or calcium hydroxide, sodium or calcium formate, or potassium carbonate, or by heating alone or in presence of water at 300°. Condensation of mixtures of glyceraldehyde and dihydroxyacetone does not give a crystalline product. Pentaerythritol is obtained in 64% yield from crotonaldehyde and formaldehyde (1 : 8) in presence of 1 mol. of calcium oxide or in 63·5% yield from acraldehyde and formaldehyde (1 : 3) in presence of 0·5 mol. of calcium hydroxide. The purest specimens of pentaerythritol, m. p. 258°, are obtained in 73·5% yield from acetaldehyde and formaldehyde (1 : 5), whereas those containing most dipentaerythritol (15%) are derived from the aldehydes in the ratio 1 : 3 in presence of 0·5 mol. of calcium hydroxide.

The constitution of dipentaerythritol is established as follows. The formate decomposes almost quantitatively at 270° into carbon monoxide and dipentaerythritol, thus resembling pentaerythritol tetraformate. Oxidation of dipentaerythritol with nitric acid (*d* 1·13) gives a polymerisation product of diglycollaldehyde $O(CH_2{\cdot}CHO)_2$, hydrolysed by 20% sulphuric acid to diglycollaldehyde, isolated as the phenylhydrazone, m. p. 123°. Pure pentaerythritol under similar conditions is not oxidised to an aldehyde, the previous observation of which is due to the presence of dipentaerythritol in the mixture. The action of hydrobromic acid or hydriodic acid (*d* 1·7) on dipentaerythritol does not give crystalline products, whereas hydriodic acid, red phosphorus, and acetic anhydride give a *dipentaerythritol di-iodohydrin*, $C_{10}H_{20}O_5I_2$, m. p. 106—107°. With hydriodic acid (*d* 3·0) in presence of a little red phosphorus and acetic anhydride at 140° α-iodo-αα-di-iodomethylpropane, m. p. 154°, is produced, hydrolysed to pentaglycerol, m. p. 191·5°.
H. WREN.

Structure of synthetic mixed triglycerides. R. BHATTACHARYA and T. P. HILDITCH (Proc. Roy. Soc., 1930, A, 129, 468—476; cf. Collin and Hilditch, A., 1930, 260).—Mixtures of saturated (lauric, palmitic, or stearic) and unsaturated (85% of oleic and 15% of linoleic) fatty acids have been esterified with about 85% of the theoretical amount of glycerol and 0·5% of naphthalene-2-sulphonic acid at 135—145°/about 1 mm. for 6 hrs. The product is examined by the acetone–permanganate process. Under these conditions the whole of the glycerol retained in the product was in the form of triglycerides. A smooth curve was obtained by plotting the molecular proportion of fully-saturated glycerides in the synthetic fats against the molecular percentage of saturated acids present in the mixture of fatty acids esterified. The corresponding values for a number of animal fats and vegetable pericarp fats tend to follow, although they are not coincident with the experimental curve; the animal fats contain as a rule rather more, the pericarp fats rather less, fully-saturated glycerides than the synthetic fats for a given ratio of saturated to unsaturated fatty acids. Vegetable seed fats, on the other hand, are assembled on entirely different principles, the glyceride structure being determined by a tendency to " even distribution " of the fatty acids amongst the glycerol molecules.
L. L. BIRCUMSHAW.

Hexosemonophosphates. Dextrose 3-phosphate, dextrose 6-phosphate, and their bearing on the structure of Robison's ester. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1930, 89, 479—499).—Di*iso*propylideneglucose was treated with phosphoryl chloride and pyridine at a low temperature and the crude product was partly hydrolysed with hydrochloric acid; the resulting hexosemonophosphate, $[\alpha]_D^{27}$ +39·5° (*brucine* salt, $[\alpha]_D^{25}$ −42·3° in pyridine; *barium* salt, $[\alpha]_D^{27}$ +26·5°), forms both a stable and an unstable methylglucoside; the aldonic acid prepared from it by oxidation with hypoiodite forms 1 : 4 and 1 : 5 lactones. The previously-suggested structure of dextrose 3-phosphate (A., 1929, 1278) for this ester is therefore confirmed. Treatment of *iso*propylideneglucose with phosphoryl chloride and pyridine followed by partial hydrolysis afforded *dextrose 6-phosphate*, $[\alpha]_D^{25}$ +25·9° [*brucine* salt, $[\alpha]_D^{25}$ −49·3° in pyridine; *barium* salt, $[\alpha]_D^{25}$ +13·0° in water; *phenylosazone*, m. p. 151—152°, $[\alpha]_D^{25}$ −31·4° (equilibrium in pyridine–alcohol)]. When hydrolysed with intestinal phosphatase both the dextrose 3-phosphate and the hexosemonophosphate of Robison (A., 1923, i, 86) give dextrose (isolated as glucosazone). Differences in the rates of fermentation of these esters and in the physical properties of their derivatives, however, preclude their identity (cf. King and Morgan, Chem. and Ind., 1929, 296). On the other hand, the dextrose 6-phosphate is fermented at the same rate as Robison's ester, but differs from the latter in the m. p. of the phenylosazone. This last discrepancy may be due to insufficient purity of Robison's ester.
C. R. HARINGTON.

Decomposition of mercaptans in alkali solutions. E. C. BILLHEIMER and E. E. REID (J. Amer. Chem. Soc., 1930, 52, 4338—4344).—When aliphatic mercaptans are heated with sodium hydroxide solution at 250—270°, decomposition occurs in the following ways: $SHR+2NaOH=R{\cdot}OH+Na_2S+H_2O$; $2SHR+2NaOH=SR_2+Na_2S+2H_2O$; $SH{\cdot}CH_2{\cdot}CH_2R+2NaOH=CH_2{:}CHR+Na_2S+2H_2O$. The amount of *n*-butyl mercaptan decomposed at 260° increases almost as a linear function of the normality of the alkali, and is 50% with 3*N*-sodium hydroxide after 2 hrs. Under these conditions the amount of *n*- and *sec.*-alkyl mercaptans reacting decreases gradually with increasing number of carbon atoms; the values for the *sec.*-compounds are, however, somewhat higher than those for the *n*-derivatives. The amount of dialkyl sulphide produced is usually of the order of 5 and 10% for the *sec.*- and *n*-mercaptans, respectively. The decompositions are carried out in an apparatus similar to that described by Herndon and Reid (A., 1929, 46).
H. BURTON.

Oxidation of sulphides by perbenzoic acid. IV. β-Chloroethyl β-chlorovinyl sulphide and

β-chloroethyl α-chlorovinyl sulphide. L. N. Levin and J. Tschulkov (J. pr. Chem., 1930, [ii], **128**, 171—179).—β-Chloroethyl β-chlorovinyl (I) and β-chloroethyl α-chlorovinyl (II) sulphides (Lawson and Dawson, A., 1928, 153) have b. p. 99°/4 mm. and 92°/4 mm., respectively (*loc. cit.*, 77—77·7°/4 mm. and 69·5—70·5°/4 mm.; values recorded for d_4^{20} and n agree with Lawson and Dawson's, *loc. cit.*). I and II have been oxidised by means of the perbenzoic acid method previously described (cf. A., 1928, 505, 999; 1930, 1161).

β-*Chloroethyl* α-*chlorovinyl sulphoxide* (from II) has b. p. 104°/6 mm., d_4^{20} 1·4068, n^{20} 1·5511; the corresponding *sulphone* (from II or, better, from the sulphoxide) has b. p. 108—109°/2—2·5 mm. (slight decomp.), d_4^{20} 1·4366, n^{20} 1·5238. β-*Chloroethyl* β-*chlorovinyl sulphoxide*, d_4^{20} 1·3924, n^{20} 1·5416 (prepared similarly from I), cannot be distilled at 4 mm. without decomposition; it solidifies at −14° to −16°; the *sulphone* has b. p. 125—127°/2 mm., d_4^{20} 1·4384, n^{20} 1·5306 (by-products, two crystalline *substances*, m. p. 109—111° and decomp. 160°). R. Child.

Organic sulphonic and sulphinic acids. J. von Braun and K. Weissbach (Ber., 1930, **63**, [*B*], 2836—2847).—The action of phosphorus pentachloride on benzenesulphonethylamide at 100° proceeds sluggishly, leading to a difficultly-separable mixture of non-crystalline products in which chlorination has occurred partly outside the $\cdot SO_2\cdot NH\cdot$ group. With similar compounds which do not contain an aromatic group reaction occurs less readily than with the amides of non-aromatic carboxylic acids, but, without use of extreme measures, leads to the production of the expected compounds $R'\cdot S(\colon O)Cl\colon NR''$. These are stable towards heat and retain chlorine so firmly that they react only very slowly with water and alcohol and not with amines. With excess of phosphorus pentachloride and under more drastic conditions they yield substances, $R'\cdot SCl_3\colon NR''$, in which two of the chlorine atoms are so mobile that they are removed by cold water. The unexpected behaviour of the chloride is explicable on the supposition that the sulphonamides contain the ring ${:}S\overset{O}{\triangle}N{\cdot}$; measurements of the parachor afford no evidence, since the customary parachor constants do not apply with these substances. The amides of the sulphinic acids are converted by phosphorus pentachloride into liquid chloro-compounds which cannot be distilled without decomposition in a high vacuum, react violently with water, and thus completely resemble the imidochlorides of carboxylic acids.

Non-aromatic sulphinic acids undergo disproportionation when heated into sulphonic acids and thiosulphonic esters, $2R\cdot SO_2H + R\cdot SO_2H = R\cdot SO_2\cdot SR + R\cdot SO_3H + H_2O$. The sulphinic acid molecule which undergoes oxidation can be replaced by thiol compounds ($2R\cdot SO_2H + 2HSR' = R\cdot SO_2\cdot SR + 2H_2O + R'S\cdot SR'$), but not by pyrocatechol or quinol. Sulphinic esters and chlorides are relatively stable, but with the last-named substance the rôle of oxygen acceptor can be played by sodium mercaptides or, more conveniently, by salts of dithiocarbamic acid, $2NR_2\cdot CS\cdot SH,NHR_2 + 2R'\cdot SOCl = NR_2\cdot CS\cdot S\cdot S\cdot CS\cdot NR_2 + 2NHR_2,HCl + R'\cdot SO_2\cdot SR'$. With chlorothiols reaction occurs according to the scheme $2NR_2\cdot CS\cdot SH,NHR_2 + 2R'SCl = NR_2\cdot CS\cdot S\cdot S\cdot CS\cdot NR_2 + 2NHR_2,HCl + R'S\cdot SR'$.

The following compounds are described: *butyl* n-*butylthiosulphonate*, b. p. 126—128°/0·2 mm.; n-*butylsulphonic acid*, b. p. 145°/0·2 mm.; n-*butylsulphinyl chloride*, b. p. 38°/0·1 mm., 78°/12 mm., transformed by dry air into n-*butylsulphonyl chloride*, b. p. 90°/11 mm.; *ethyl* n-*butylsulphinate*, b. p. 85°/13 mm.; n-*butylsulphinethylamide*, b. p. 108—110°/10 mm.; iso*amyl* iso*amylthiosulphonate*, b. p. 176—180°/13 mm.; iso*amylsulphonic acid*, b. p. 176—178°/0·2 mm.; iso*amylsulphinyl chloride*, b. p. 60—62°/0·1 mm., 91—92°/13 mm.; *ethyl* iso*amylsulphinate*, b. p. 98°/13 mm.; iso*amylsulphinethylamide*, b. p. 120°/high vac.; cyclo*hexylsulphinic acid monohydrate*, m. p. 33—35°, completely decomposed by distillation in a high vacuum; cyclo*hexyl* cyclo*hexylthiosulphonate*, b. p. 184—186°/0·1 mm.; cyclo*hexylsulphonic acid*, b. p. 178—180°/0·1 mm. [monohydrate, m. p. 92° (cf. Borsche and Lange, A., 1905, i, 765)]; n-*butylsulphonethylamide*, b. p. 120—122°/0·1 mm., and the corresponding chloride, $Bu^{a}\cdot ClS\overset{O}{\triangle}NEt$, b. p. 124—126°/0·2 mm.; iso*amylsulphonethylamide*, b. p. 130—132°/0·2 mm., and the *chloride* $C_7H_{16}ONSCl$, b. p. 128—130°/0·3 mm.; cyclo*hexylsulphonethylamide*, b. p. 183—185°/18 mm., m. p. 72°, and the corresponding *chloride*, b. p. 131—132°/0·7 mm., m. p. 73—74°, converted by more drastic treatment with phosphorus pentachloride into the *substance* $C_8H_{15}NCl_4S$, b. p. 140—150°/1 mm., from which the *compound* $C_8H_{15}ONCl_2S$, m. p. 156°, is derived by the action of water. cyclo*Hexylsulphonpropylamide*, m. p. 78°, and cyclo*hexylsulphon*-n-*heptylamide*, m. p. 72°, are attacked with difficulty by phosphorus pentachloride. H. Wren.

Methanetrisulphonic acid. H. J. Backer [with R. H. Klaassens] (Rec. trav. chim., 1930, **49**, 1107—1117).—The following methods, described in the literature, for the preparation of methanetrisulphonic acid have been re-investigated: (1) sulphonation of methionic (methanedisulphonic) acid with sulphur trioxide in a sealed tube at 170°; (2) sulphonation of acetanilide (Bagnall, J.C.S., 1899, 75, 278), a similar result being obtained by sulphonation of succinanilide; (3) oxidation of thiolmethanetrisulphonic acid with bromine (A., 1930, 1556); (4) the action of potassium sulphite on potassium nitromethionate (solubility in water at 25° 1·6; *strychnine* $+3\cdot 5H_2O$, *sodium*, and *thallous* salts; free *acid* $+2H_2O$), which is prepared by the action of potassium sulphite on chloropicrin in aqueous solution at 80°, and (5) by the action of potassium hydrogen sulphite (as potassium pyrosulphite) on potassium diazomethionate in aqueous solution at 60° (cf. Fantl and Fisch, *ibid.*, 320). Methods 3 and 5 are to be preferred, the former giving a 90% yield. The following salts of methanetrisulphonic acid $+2\cdot 5H_2O$, m. p. 156°, are described: potassium $+H_2O$ (solubility in water at 25°, 1·126; crystallographic data), *thallous* $+H_2O$ (crystallographic data); *silver* $+H_2O$; *barium* $+9H_2O$ (solubility in water at 25°, 0·107); *calcium* $+12H_2O$, and *lanthanum* $+6H_2O$, and the *potassium barium*, $CHO_9S_3KBa,3H_2O$, salt $+3H_2O$, the last-named being obtained by addition of a hot, concentrated solution of barium chloride to a hot, saturated solution of potassium methanetrisulphonate. Potassium diazomethionate is decomposed by water in accordance with the scheme $N_2C(SO_3K)_2+H_2O\longrightarrow CH(OH)(SO_3K)_2+N_2\longrightarrow KHSO_3+SO_3K\cdot CH{:}O$; $SO_3K\cdot CH{:}O+H_2O\longrightarrow KHSO_3+H\cdot CO_2H$, the potassium hydrogen sulphite reacting with more diazomethionate to give potassium methanetrisulphonate. Concentrated hydrochloric acid at 0° converts potassium diazomethionate into potassium chloromethanetrisulphonate with evolution of nitrogen. J. W. BAKER.

Solubility of ethylenic stereoisomerides in solvents themselves ethylenic stereoisomerides. I. LEBRUN (Bull. Soc. chim. Belg., 1930, 39, 423—433).—The solubilities of maleic, fumaric, citraconic, mesaconic, crotonic, *iso*crotonic, β-chlorocrotonic, β-chloro*iso*crotonic, oleic, elaidic, and cinnamic acids in *cis*- and *trans*-dichloroethylenes, *cis*- and *trans*-β-bromo-Δ^{β}-butenes, ethyl β-chloro*iso*crotonate, crotononitrile, and *iso*crotononitrile have been determined at 0—50°. β-Chloro*iso*crotonic, oleic, *iso*crotonic, citraconic, and maleic acids are more soluble in all the solvents than their isomerides; they are the more fusible isomerides. H. BURTON.

Unsaturation phenomena of acetylenic acids and esters. III. Constitution of mercury derivatives. W. W. MYDDLETON, A. W. BARRETT, and J. H. SEAGER (J. Amer. Chem. Soc., 1930, **52**, 4405—4411).—The triacetoxymercuri-derivatives obtained by the action of mercuric acetate on acetylenic compounds containing the $\cdot C{\vdots}CH$ group are probably best represented as $\cdot C(O\cdot HgOAc){:}C(HgOAc)_2$. Treatment of these compounds with hydrochloric acid affords methyl ketones, formed through the enol, $\cdot C(OH){:}CH_2$, whilst the action of bromine in chloroform at 40° affords tribromomethyl ketones, viz., $\cdot C(OBr){:}CBr_2\longrightarrow\cdot CBr(OBr)\cdot CBr_3\xrightarrow{-Br_2}\cdot CO\cdot CBr_3$. Thus, the *triacetoxymercuri*-derivative of Δ^{α}-heptinene furnishes methyl *n*-amyl ketone and *tribromomethyl* n-*amyl ketone*, b. p. 120°/0·5 mm.; the *triacetoxymercuri*-derivative of Δ^{α}-octinene affords methyl *n*-hexyl ketone and *tribromomethyl* n-*hexyl ketone*, b. p. 137°/0·5 mm.; the *triacetoxymercuri*-derivative of phenylacetylene gives acetophenone, and the *triacetoxymercuri*-derivative of Δ^{ι}-undecinoic acid yields (with chlorine) *κκκ-trichloro-ι-ketoundecoic acid.* The last-named compound decomposes on attempted distillation and is reduced by aqueous-alcoholic hydriodic acid to (probably) the corresponding dichloroketo-acid.

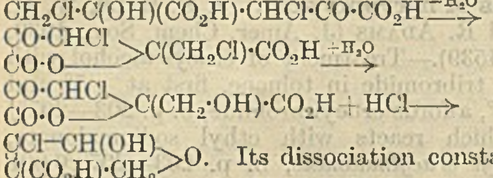
The diacetoxymercuri-derivatives obtained from acetylenes containing the $\cdot C{\vdots}C\cdot$ group are probably best represented as $\cdot C(O\cdot HgOAc){:}C(HgOAc)\cdot$. These are converted by treatment with hydrochloric acid and halogens into keto-derivatives and monohalogenoketo-derivatives, respectively. Thus, the diacetoxymercuri-derivatives of stearolic and behenolic acids are converted into θ-*chloro*- and *-bromo-ι-ketostearic acids* and μ-*chloro*- and *-bromo-ξ-keto-behenic acids*, respectively. The *diacetoxymercuri*-derivative from methyl Δ^{α}-noninoate is converted by hydrochloric acid into methyl β-ketononoate, b. p. 137·5°/28 mm., which is shown by Meyer's method (A., 1911, i, 832) to contain 13·5% of the enol form; the action of bromine causes the formation of a *methyl dibromoketononoate*, b. p. 169°/14 mm. Phenylpropiolic acid yields a *diacetoxymercuri*-derivative convertible into acetophenone and ωωω-tribromoacetophenone (?ωω-dibromoacetophenone). The formation of the dibromo-compounds in these cases probably occurs thus: $\cdot C(O\cdot HgOAc){:}C(HgOAc)\cdot\longrightarrow\cdot C(OBr){:}CBr\cdot\longrightarrow\cdot CBr(OBr)\cdot CBr_2\cdot\xrightarrow{-Br_2}\cdot CO\cdot CBr_2$.
H. BURTON.

Synthesis of nervonic acid. J. B. HALE, W. H. LYCAN, and R. ADAMS (J. Amer. Chem. Soc., 1930, **52**, 4536—4539).—Treatment of erucyl alcohol with phosphorus tribromide in toluene, first at −5° and then at 100°, affords erucyl bromide, b. p. 203—207°/1 mm., which reacts with ethyl sodiomalonate, forming *ethyl erucylmalonate*, b. p. 203—207°/0·001 mm. The corresponding acid decomposes when heated at 175° into a mixture of cis-, m. p. 39—39·5°, and trans-*erucylacetic* (Δ^{ξ}-*tetracosenoic*) *acids*, m. p. 61°; the former of these is identical with the nervonic acid of Klenk (A., 1927, 691). The *cis*-acid is converted into the *trans*-modification when it is melted over nitric acid containing a small amount of nitrous acid. Both isomerides are reduced catalytically (Adams) in alcohol to tetracosoic acid, m. p. 83—84°. Similar reduction of *ethyl* Δ^{ξ}-*tetracosenoate*, b. p. 233—234°/1 mm., affords ethyl tetracosoate, m. p. 55—56° (corr.). H. BURTON.

Transformation of pyruvic acid as a function of time and temperature. M. GARINO, G. BALLETTO, F. DE THIERRY, and C. BECCHI (Gazzetta, 1930, **60**, 592—605).—The published physical data for pyruvic acid vary considerably, and earlier experiments (A., 1923, i, 11, 23, 24) showed that the yields of derivatives prepared from the acid are increased if the acid used is of recent preparation. Numerous fractional distillations of the freshly-prepared acid yield ultimately an acid, m. p. 13·62°, showing 100% purity on titration. Its electrolytic dissociation constant K is 0·00593 and its dilute solutions conduct normally. At about 0° the solid acid is stable, but when kept at 10°, with repeated fusion and recrystallisation, it undergoes change, its electrical conductivity becoming irregular and its m. p. lower, although for some time its titratable acidity remains constant. At 25° the m. p. falls markedly in 24 hrs., owing apparently to the formation of the condensation product, $CO_2H\cdot CO\cdot CH_2\cdot CMe(OH)\cdot CO_2H$, but its acidimetric value remains unchanged; in 20—25 days, it begins to undergo a series of more complex alterations, becoming uncrystallisable and losing about 11% of its titratable acidity and yielding a fluorescent compound not yet identified. In contact with dry air, it gives rise to carbon dioxide. At 40° these changes are accelerated, and contact of the acid with moist air still further accelerates them and sometimes introduces complications into the process of decomposition.
T. H. POPE.

Halogenated derivatives of pyruvic acid. M. GARINO, A. CERESOTO, M. BERNI, and M. BRAMBILLA (Gazzetta, 1930, **60**, 582—592; cf. A., 1923, i, 11, 23, 24).—Chlorine replaces one hydrogen atom of pyruvic acid readily and a second with difficulty, whilst it has not been found possible to replace the third. Bromine replaces either two or three of the hydrogen atoms. Iodine immediately replaces all three hydrogen atoms.

Chloropyruvic acid in anhydrous crystals remains unchanged below 15° and the freshly-prepared acid forms highly dilute solutions without undergoing hydrolysis, but these gradually decompose with formation of hydrogen chloride and carbon dioxide, probably according to the scheme: $2CH_2Cl\cdot CO\cdot CO_2H=$



$$CH_2Cl\cdot C(OH)(CO_2H)\cdot CHCl\cdot CO\cdot CO_2H\xrightarrow{-H_2O}\begin{matrix}CO\cdot CHCl\\CO\cdot O\end{matrix}\!\!>C(CH_2Cl)\cdot CO_2H\xrightarrow{+H_2O}\begin{matrix}CO\cdot CHCl\\CO\cdot O\end{matrix}\!\!>C(CH_2\cdot OH)\cdot CO_2H+HCl\longrightarrow\begin{matrix}CCl{-}CH(OH)\\C(CO_2H)\cdot CH_2\end{matrix}\!\!>O.$$

Its dissociation constant has the value 0·00626. Dichloropyruvic acid is unstable when freshly crystallised, but if kept dry at 10—12° for 10—15 days it becomes more stable and may then be repeatedly crystallised at 20—25° without great loss; its dissociation constant is 0·0078. Dibromopyruvic acid, dissociation constant 0·1527, is moderately stable, but gradually undergoes change in the solid or dissolved state (cf. Grimaux, A., 1874, 887). Chlorobromopyruvic acid, dissociation constant 0·01076, has properties intermediate between those of the dichloro- and dibromo-acids. Tribromopyruvic acid (cf. Grimaux, *loc. cit.*) readily undergoes hydrolysis and above 60—65° is decomposed by water, to form bromoform and oxalic acid. *Chlorodibromopyruvic acid* decomposes without melting and, in aqueous solution, forms chlorodibromomethane at about 80° and lachrymogenic substances at higher temperatures. Dichlorobromopyruvic acid (cf. Hantzsch, A., 1890, 132) melts indefinitely owing to decomposition and becomes more stable if kept, as crystals, in a fairly dry atmosphere. T. H. Pope.

Preparation of δ-ketonic esters. (Mlle.) S. Grateau (Compt. rend., 1930, **191**, 947—949).—The chloride of ethyl hydrogen adipate reacts with benzene in presence of aluminium chloride, forming 80% of the theoretical amount of ethyl δ-benzoylvalerate, b. p. 164°/3 mm. This is reduced by the Clemmensen method to ethyl ε-phenylhexoate, b. p. 162—164°/12 mm. [free acid, b. p. 186—188°/11 mm., m. p. 11° (anilide, m. p. 80°; *p*-toluidide, m. p. 78°)].

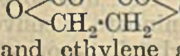
H. Burton.

Bacterial oxidation of oxalates. R. Scholder and C. F. Linström (Ber., 1930, **63**, [*B*], 2730—2737).—The titre of 0·01*N*-sodium oxalate solutions is diminished greatly but somewhat irregularly on exposure to air. The effect is independent of light and the material of the vessel. Since under similar conditions the concentration of sterile solutions remains unchanged, the effect is due to micro-organisms gained from the air. The preparation of cultures from the deposit in an extensively decomposed solution is described, but the pure culture thus obtained does not contain the bacteria responsible for the action. The oxalate is decomposed according to the equation $Na_2C_2O_4+H_2O+O=2NaHCO_3$. In an atmosphere of nitrogen or carbon dioxide the change does not occur. Formate, carbon monoxide, or hydrogen peroxide could not be detected. Sterilisation of solutions by addition of sulphuric acid is not effective unless exposure to bright light is avoided. Mercuric chloride sterilises solutions preserved in brown glass. Sterilised aqueous suspensions of the oxalates of barium, strontium, calcium, zinc, cadmium, manganese, cobalt, or nickel after addition of culture or deposit from a decomposed sodium oxalate solution generally contain carbonate after some months. Copper, mercury, and silver oxalates act bactericidally and remain free from carbonate. An apparatus for the determination of small amounts of carbon dioxide is described. H. Wren.

Partial replacement of the oxalate residue in oxalato-anions of bivalent metals. II. R. Scholder and C. F. Linström (Ber., 1930, **63**, [*B*], 2828—2831; cf. A., 1927, 854).—The compounds are usually prepared by addition of the oxalate of the heavy metal to hot, very concentrated solutions of potassium nitrite, thiocyanate, or thiosulphate. In contrast to the simple oxalato-compounds of bivalent metals, the mixed-complex substances dissolve transitorily in cold water, but the sparingly soluble oxalate separates more or less rapidly from the cold solution; decomposition occurs instantaneously in hot solution. The following *salts* are described: $[Mn(C_2O_4)(NO_2)_2]K_2,H_2O$; $[Zn(C_2O_4)_2]K_2,[Zn(C_2O_4)(NO_2)(H_2O)]K,5H_2O$; $[Mn(C_2O_4)_2]K_2,[Mn(C_2O_4)(CNS)_2]K_2$; $[Zn(C_2O_4)_2]K_2[Zn(C_2O_4)(CNS)(H_2O)]K,5H_2O$; $[Co(C_2O_4)(S_2O_3)]K_2$; $[Mn(C_2O_4)(S_2O_3)]K_2,H_2O$; $[Zn(C_2O_4)_2]K_2$. H. Wren.

Auto-complex formation with oxalates of bivalent, heavy metals. III. Preparation of lead oxalate hydrate; determination of solubility and conductivity of manganese oxalate. R. Scholder and C. F. Linström (Ber., 1930, **63**, [*B*], 2831—2835; cf. A., 1927, 855).—*Lead oxalate dihydrate* is prepared by mixing dilute solutions of lead nitrate and ammonium oxalate at 0°, slowly and with thorough agitation, and preserving the mixture for at least 12 hrs. It loses its water of crystallisation when exposed to air at the ordinary temperature. Its existence tends to explain the abnormal conductivity of saturated and dilute solutions of lead oxalate. Manganese oxalate dihydrate is prepared from manganese chloride and ammonium oxalate in boiling aqueous solution, whereas at 0° the trihydrate is obtained. The solubilities of the di- and tri-hydrate in water at 18° are respectively 0·270 and 0·537 g. per litre. The equivalent conductivity of the two hydrates changes abnormally with increasing dilution. The two curves coincide within the limits of experimental error, showing that the hydrates have the same complex arrangement in solution. H. Wren.

"Superfluous" isomerides. IV. Supposed existence of isomerides of cyclic oxalic esters. E. Bergmann and H. A. Wolff (J. pr. Chem., 1930, [ii], **128**, 229—232; cf. A., 1930, 902, 912).—Ethylene oxalate,



$$O\!<\!\begin{matrix}CO{-}CO\\CH_2\cdot CH_2\end{matrix}\!>\!O$$

(I) (from methyl or ethyl oxalate and ethylene glycol), has m. p. 143° (cf. Bischoff and Walden, A., 1895, i, 17). The alleged isomeride, m. p. 162°, of Tilitschéev (A., 1923, i, 1173) is probably identical with *methyl* β-*hydroxyethyl oxalate*, m. p. 166° (obtained by the interaction of ethylene glycol and methoxalyl chloride), which on distillation in a vacuum is converted into I. R. CHILD.

Preparation of α-alkylpimelic acids from αε-oxido-decane and -dodecane. A. FRANKE and A. KROUPA (Monatsh., 1930, 56, 347—357).—αε-Dibromodecane, b. p. 146—147°/9 mm., prepared from αε-oxidodecane and hydrobromic acid at 100° (cf. A., 1929, 1422), is converted by aqueous-alcoholic potassium cyanide into the corresponding *dinitrile*, b. p. 185—189°/9 mm., which when hydrolysed with aqueous-alcoholic potassium hydroxide solution affords impure α-amylpimelic acid together with α-*amylpimelamic acid*, m. p. 149·5°. The last-named acid is hydrolysed by concentrated potassium hydroxide solution to α-*amylpimelic acid*, m. p. 68° (*amide*, m. p. 186°). αε-Oxidododecane (this vol., 62) is converted as above into αε-*dibromododecane*, b. p. 171°/9 mm., and thence into the corresponding *dinitrile*, b. p. 203—204°/9 mm., which is hydrolysed to α-*heptylpimelamic* and α-*heptylpimelic acids*, m. p. 150·3° and 75°, respectively. H. BURTON.

Course of addition of sodium enol alkylmalonates to αβ-unsaturated esters. A. MICHAEL and J. ROSS (J. Amer. Chem. Soc., 1930, 52, 4598—4609).—Ethyl crotonate and ethyl methylmalonate react in presence of ether containing $\frac{1}{6}$ mol. of sodium ethoxide, forming mainly *ethyl* β-*methylbutane*-αγγ-*tricarboxylate*, b. p. 160°/9 mm., also obtained from ethyl sodio-β-methylpropane-αγγ-tricarboxylate and methyl iodide. When the initial condensation is effected with 1 mol. of sodium ethoxide, a 60% yield of *ethyl* β-*methylbutane*-ααγ-*tricarboxylate*, b. p. 148—150°/3 mm. (free *acid*, m. p. 145°), is obtained; the same ester is also produced from ethyl tiglate and ethyl sodiomalonate. Methylation of this affords *ethyl* γ-*methylpentane*-ββδ-*tricarboxylate*, b. p. 164°/3 mm. (the free *acid*, an oil, when heated, gives *cis*- and *trans*-αβγ-trimethylglutaric acids), whilst similar treatment of its isomeride causes fission to ethyl crotonate and sodiomethylmalonate. When ethyl β-methylbutane-αγγ-tricarboxylate is treated with sodium ethoxide in ether about 50% is isomerised to ethyl β-methylbutane-ααγ-tricarboxylate; the remainder undergoes fission as above. Ethyl tiglate and ethyl sodiocyanoacetate afford ethyl γ-cyano-αβ-dimethylglutarate, methylated to *ethyl* γ-*cyano*-αβγ-*trimethylglutarate*, b. p. 160°/2 mm. Conversion of this nitrile into the corresponding tricarboxylic acid, an oil (lit. m. p. 144—145°), and thermal decomposition of this yields a mixture of trans- (oily) and cis-αβγ-*trimethylglutaric acids*, m. p. 125° after softening at 115° (*anhydride*; *imide*, m. p. 90°) (cf. Ray, A., 1928, 394). β-*Methylpropane*-αγγ-*tricarboxylic acid* has m. p. 139°.

Ethyl methylmalonate condenses with ethyl cinnamate in ether containing 0·2 mol. of sodium ethoxide, furnishing *ethyl* β-*phenylbutane*-αγγ-*tricarboxylate*, b. p. 194—195°/3 mm. [the free *acid* exists in two forms, m. p. 148° (labile) and 188°], also produced by methylation of ethyl β-phenylpropane-αγγ-tricarboxylate, b. p. 187°/4 mm. (free *acid*, m. p. 137°). In presence of 1 mol. of sodium ethoxide the above condensation gives *ethyl* β-*phenylbutane*-ααγ-*tricarboxylate*, b. p. 185—188°/3 mm. (the free *acid* exists in two forms, m. p. 145° and 171°). Ethyl sodiocyanoacetate and ethyl α-methylcinnamate furnish *ethyl* γ-*cyano*-β-*phenyl*-α-*methylglutarate*, b. p. 185—187°/3 mm., hydrolysed by potassium hydroxide solution to the above β-phenylbutane-ααγ-tricarboxylic acids.

These results confirm Thorpe's explanation (J.C.S., 1900, 77, 923) of the course of the addition of ethyl sodio-cyanoacetate and -α-cyanopropionate to αβ-unsaturated esters. H. BURTON.

Composition and structure of mesquite gum. E. ANDERSON and L. OTIS (J. Amer. Chem. Soc., 1930, 52, 4461—4470; cf. B., 1927, 152).—The gum is shown to consist of a salt of a complex acid, *M* 1222, [α] +70·8°, derived from 4 mols. of *l*-arabinose, 3 mols. of *d*-galactose, 1 mol. of *d*-glycuronic acid, and 1 mol. of methyl alcohol by loss of 8 mols. of water; the acid is obtained pure by acidification of an aqueous solution of the gum with hydrochloric acid and repeated precipitation of the acid from its aqueous solution by alcohol. Hydrolysis of the gum with 3% sulphuric acid at 80° for 11 hrs. affords *l*-arabinose, *d*-galactose, and a mixture of methoxydi- and methoxytri-galactosidoglycuronic acids (purified through the *calcium* salts, [α] +16·8° and +38·5°, respectively). The methoxy-group is attached to the acid and not to the sugar residue. Oxidation of the above calcium salts with barium hypoiodite solution gives the corresponding dibasic acids (*calcium* salts, [α] +2·7° and +12·8°, respectively). More prolonged hydrolysis of the gum with 3% sulphuric acid affords, in addition to the above products, a methoxygalactosidoglycuronic acid (*calcium* salt). A structural formula for the complex acid is given. H. BURTON.

Cobalt complexes of thiolacetic acid. L. MICHAELIS and M. P. SCHUBERT (J. Amer. Chem. Soc., 1930, 52, 4418—4426).—When cobalt chloride (1 mol.) is treated with potassium thiolacetate (2 mols.) in alkaline phosphate buffer solutions in absence of oxygen, a green complex is produced. This is oxidised readily to a brown *substance*, $[Co(S{\cdot}CH_2{\cdot}CO_2)_2KH]_2O,5H_2O$, formed as the result of the uptake of 0·5 atom of oxygen per atom of cobalt. Treatment of this with barium chloride solution furnishes the *complex* $Ba[Co(S{\cdot}CH_2{\cdot}CO_2)_2H]_2O,5H_2O$, whilst acidification with hydrochloric acid affords the *complex* $KH[Co(S{\cdot}CH_2{\cdot}CO_2)_2H]_2O,4H_2O$, converted by further acidification into the *substance* $[Co(S{\cdot}CH_2{\cdot}CO_2H)_2]_2O,3{\cdot}5H_2O$. Various structures are suggested for the above complexes. H. BURTON.

α-Oxidation of acetaldehyde and the mechanism of the oxidation of lactic acid. J. B. CONANT and C. O. TONGBERG (J. Biol. Chem., 1930, 88, 701—708).—The main products identified in the oxidation of acetaldehyde by ceric sulphate in dilute acid solutions at 80° are formic acid, carbon dioxide, glyoxylic acid, and glycollaldehyde. When lactic acid is oxidised by ceric sulphate under similar conditions acetaldehyde is formed, but if the acetaldehyde is not allowed to escape from the acid mixture, formic acid, formaldehyde, glyoxylic acid, and glycollaldehyde may be identified. It appears that acetaldehyde is an intermediate in the oxidation of lactic acid in this reaction. The bearing of these results on the oxidation of lactic acid and acetaldehyde in living tissue is discussed. W. O. Kermack.

Production of solutions of methylglyoxal. E. Hofmann and C. Neuberg (Biochem. Z., 1930, **226**, 489—491; cf. A., 1930, 1409).—When oximinoacetone, in aqueous solution, is oxidised first at 0—3°, then at the ordinary temperature, and finally at 30—40° with an equimolecular amount of nitrosylsulphuric acid, unchanged material being then removed by extraction with ether, a solution containing methylglyoxal and sulphuric acid is obtained. When this solution is distilled at 140—150° with occasional addition of water the distillate is an aqueous solution of methylglyoxal. The yield is 56·5% of the theoretical. W. McCartney.

Cracking of acetone under pressure and in presence of zinc chloride. V. N. Ipatiev, A. Petrov, and I. Ivanov (Ber., 1930, **63**, [*B*], 2806—2812; cf. A., 1927, 449, 1172).—Acetone is heated at 300—320° under pressure in the presence of zinc chloride, whereby a very complex mixture of hydrocarbons, b. p. 40—340°, is obtained which is freed from oxygenated compounds by repeated distillation over metallic sodium. Unsaturated hydrocarbons in the mixture are determined by the iodine value, also by treatment with 80% and 100% sulphuric acid. Aromatic hydrocarbons are determined by nitration and by treatment with fuming sulphuric acid. Unsaturated hydrocarbons and mesitylene predominate in the product, whereas naphthenes are present only in minor amount. In the "light petroleum" fraction the unsaturated hydrocarbons belong to the ethylenic series and in the "kerosene" fraction they are polymerised products of diethylenic hydrocarbons and secondary compounds derived therefrom. Attempts to separate the unsaturated hydrocarbons from one another by means of mercuric acetate were unsuccessful; the more volatile portions yield mercury compounds volatile with steam, but partly decomposed during the process, and are also somewhat oxidised by the reagent. The olefines have mainly the *iso*-structure. The question of the structure of the hydrocarbons of the fraction of b. p. 200—300° is provisionally left open. H. Wren.

Polymerisation and condensation. VI. αβ-Dihydroxyhexan-ε-one. P. A. Levene and A. Walti (J. Biol. Chem., 1930, **88**, 771—790).—αβ-Dihydroxyhexan-ε-one, b. p. 120°/0·3 mm., d^{25} 1·118, n^{25} 1·4673, $[M]_D$ 32·81, appears to be a mixture of open-chain and cyclic forms. When the compound is treated with acetic anhydride and pyridine a *diacetyl* derivative is obtained, b. p. 112—114°/0·6 mm. (*semicarbazone*, m. p. 112° decomp.), which predominantly exists in the open-chain form. Treatment of αβ-dihydroxyhexan-ε-one with dry methyl alcohol containing 0·5% of hydrogen chloride yields a *methyl* derivative, b. p. 66—69°/1·5 mm., d^{25} 1·0614, n^{25} 1·4496, apparently possessing the ring structure and giving a *monoacetyl* derivative, b. p. 102—104°/16 mm.; it may be further methylated with silver oxide and methyl iodide to yield *dimethoxy*cyclo*hexan-ε-one*, b. p. 74°/17 mm., d^{25} 0·9922, n^{25} 1·4302. A viscous residue the composition of which corresponded with an anhydrodihydroxyhexan-ε-one was also obtained from the methylation; this when acetylated gave a non-distillable product, the analysis of which corresponded with *hydroxyacetoxyanhydrohexan-ε-one*. When redistilled dihydroxyhexan-ε-one is preserved at 25° or sometimes even at 0° more than 50% may be converted into a *compound*, b. p. 175—180°/0·3—0·4 mm., possessing the composition of a *dihydroxyhexoyldihydroxyhexanone*, $C_{12}H_{22}O_5$ (*diacetyl* derivative, b. p. 170—180°/0·2—0·3 mm.), which when treated with dry methyl alcohol containing 0·5% of hydrogen chloride is apparently hydrolysed with the formation of dihydroxymethyl*cyclo*hexan-ε-one, b. p. 101—103°/15 mm. When dihydroxyhexan-ε-one is allowed to polymerise at 155° in presence of sulphuric acid as catalyst (Hibbert and Timm, A., 1924, i, 16) the product $(C_6H_{10}O_2)_x$ yields a *monoacetate*, $(C_8H_{12}O_3)_x$, and therefore cannot have the formula postulated by Hibbert and Timm, which contains no free hydroxyl group. When αβ-dihydroxyhexan-ε-one is heated intermittently at 150° for 9 hrs. an *anhydride*, $C_6H_{10}O_2$, b. p. 40°/20 mm., 55°/42 mm., d^{25} 1·0423, n^{25} 1·4356, parachor 259·2, apparently containing two oxygen bridges, results. If the condensation product is acetylated before distillation a *monoacetyl* derivative, b. p. 58°/2 mm., d_4^{25} 1·0575, n^{25} 1·4490, parachor 352·6, is obtained probably containing a double linking and an oxygen bridge. Further, when acetylanhydro-αβ-dihydroxyhexan-ε-one is hydrogenated in presence of Adams' catalyst it absorbs 1 mol. of hydrogen to form a *compound*, $C_8H_{14}O_3$, b. p. 95°/12 mm. The hard brown resin sometimes obtained on heating αβ-dihydroxyhexan-ε-one intermittently at 150° for 10½ hrs. lost only water at 230° under reduced pressure to yield a solid *polymerised anhydrodihydroxyhexan-ε-one*, $(C_6H_{10}O_2)_x$, which when acetylated yielded an *acetyl* derivative, $(C_8H_{12}O_3)_x$, indicating that the hydroxyl group of the anhydride is not involved in the polymerisation. The substance $(C_6H_{10}O_2)_x$ is unchanged by 0·5% of hydrogen chloride at the ordinary temperature and on refluxing is methylated only to the extent of one methyl group to five groups of the ketone. In presence of Adams' catalyst it absorbed 1 mol. of gas for every 7 mols. of anhydride. It is therefore probable that the double linking is involved in the polymerisation. The conclusion of Hibbert and Timm (*loc. cit.*) that polymerised αβ-dihydroxyhexan-ε-one is analogous to the polymerisation of hexoses to form polysaccharides is adversely criticised. When the solid polymeric anhydride was heated in a bath at 230—290°/high vac., a small quantity of yellow viscous distillate, $(C_6H_{10}O_2)_x$, b. p. 130—180°/0·5 mm., was obtained which yielded an ill-defined monoacetyl derivative, $(C_8H_{12}O_3)_x$. When freshly-distilled αβ-dihydroxyhexan-ε-one in acetic acid solution is reduced by hydrogen in presence of Adams' catalyst, a *compound*, $C_6H_{12}O_2$, b. p. 70—73°/14 mm. (*monoacetyl* derivative, $C_8H_{14}O_3$, b. p. 88°/13 mm., d^{25} 1·0175, n^{25} 1·4321), is formed, the most probable structure of which is that of a tetrahydrofuran or a tetrahydropyran derivative.

W. O. Kermack.

Osazonogenic groups. E. Votoček (Coll. Czech. Chem. Comm., 1930, 2, 681—688).—The following groups by treatment with phenylhydrazine under ordinary conditions yield osazones: $\cdot CO\cdot CH_2Cl$, $\cdot CO\cdot CHCl\cdot$, $\cdot CO\cdot CHCl_2$ (cf. Nastvogel, A., 1889, i, 237), and chloroacetaldehyde, chloroacetone, and α-monochlorodiethyl ketone give respectively the osazones of glyoxal, methylglyoxal, and acetylpropionyl. The corresponding reaction with $\cdot CO\cdot CH_2\cdot NH_2$ or $\cdot CO\cdot CH(NH_2)\cdot$ is prevented by alkylation, and no osazone could be obtained from diethylaminoacetone. The known replacement in oximes by treatment with phenylhydrazine $\cdot C\!:\!NOH \longrightarrow \cdot C\!:\!N\cdot NHPh$ also occurs with glyoximes, dimethylglyoxime giving the osazone of diacetyl. Oximes and semicarbazones of reducing sugars with phenylhydrazine yield osazones under the same conditions as the free sugars. α-Ketol ethers and tertiary α-ketols do not give osazones. Secondary α-ketols, $\cdot CO\cdot CH(OH)\cdot$, react readily with secondary hydrazines, $NRR'\cdot NH_2$, to form osazones; thus acetoin with phenylmethyl-, phenylbenzyl-, and diphenyl-hydrazine gives *diacetylphenylmethylosazone*, m. p. 96—97°, *diacetylphenylbenzylosazone*, m. p. 110—111°, both also obtained from diacetyl, and *diacetyldiphenylosazone*, m. p. 187°. C. W. Shoppee.

Synthesis of a methoxyketose. E. F. Hersant and W. H. Linnell (Nature, 1930, **126**, 844).—A 5-methoxyketose has been prepared by the condensation of dihydroxyacetone and α-methoxyglyceraldehyde. The method of synthesis proves the position of the methoxyl group, and such a structure cannot form a furan ring. The *acetal* of α-methoxyglyceraldehyde has been obtained as a colourless liquid, b. p. 100—102°/6 mm. Osazones considered to be r-5-*monomethoxyfructosazone*, m. p. 183° and r-5-*monomethoxysorbosazone*, m. p. 130°, have been prepared. Experiments which show that the synthesised 5-methoxyhexose and its derivatives have properties similar to those of the methylated derivatives of normal fructose and that the hexose is the racemic form of 5-monomethoxyfructose are described. Normal fructose and its derivatives cannot possess a furanose structure and the accepted pyranose constitution is supported. L. S. Theobald.

Alcoholysis of αγ-diketones and β-ketonic esters. W. M. Kutz and H. Adkins (J. Amer. Chem. Soc., 1930, **52**, 4391—4399).—When a mixture of sodium ethoxide (0·5 mol.) and ethyl acetate (6 mols.) is boiled for 10—96 hrs., approximately the same amount of ethyl acetoacetate is produced as that remaining when ethyl acetoacetate (0·5 mol.) is heated with alcohol (0·5 mol.), sodium ethoxide (0·5 mol.), and ethyl acetate (6 mols.). Attempts to obtain similar equalities in the synthesis and alcoholysis of αγ-diketones have been unsuccessful owing to the non-homogeneous reaction conditions.

The rates of alcoholysis of diacetyl-, diacetylethyl-, benzoylacetyl-, diacetylbenzyl(?)-, benzoylacetylbenzyl-, and dibenzyldiacetyl-methane, ethyl acetoacetate, ethyl ethyl-, benzyl-, diethyl-, and dibenzylacetoacetate have been measured in alcohol containing varying amounts of sodium ethoxide at 60°. The esters undergo slower alcoholysis than the diketones for a given ratio ethoxide : reactant. The rates for both esters and diketones are increased by introducing ethyl or benzyl groups into the molecule (on the carbon atom between the carbonyl groups). The rates of alcoholysis of diacetyl- and dibenzoyl-methanes are approximately the same; these are increased by 100% when the ratio ethoxide : diketone is changed from 1 : 5 to 1 : 2. The order of increasing reactivity of the above αγ-diketones towards sodium ethoxide is as quoted; this is the reverse order of their reactivity towards alcoholic hydrogen chloride (A., 1930, 1273), except in the case of benzoylacetylmethane. These results support Bradley and Robinson's hypothesis that alkaline fission of diketones occurs through the keto-form. H. Burton.

Action of methylglyoxal on acetoacetic acid. II. M. Henze and R. Müller (Z. physiol. Chem., 1930, **193**, 88—96; cf. A., 1930, 1022).—Hexan-γ-ol-βε-dione exists in two modifications, b. p. 113·5°/12 mm. and m. p. 95°. When oxidised by alkaline hypobromite, it yields bromoform and malic acid. Derivatives were obtained: di-*p*-bromophenylhydrazone, m. p. 181°; p-*di*-p-*nitrophenylhydrazone*, m. p. 198°, dehydrated by boiling nitrobenzene to form a *pyrazole* compound, $C_{18}H_{18}O_4N_6$, m. p. 254°; *disemicarbazone*, $C_8H_{16}O_3N_6$, m. p. 210° (*anhydride*, m. p. 254°, decomp.). J. H. Birkinshaw.

Dextrose and the structure of the cycloses. A. L. Patterson (Nature, 1930, **126**, 880—881).—The assumption that the cycloses and their methyl derivatives have their origin in dextrose or at least are closely related to it structurally is discussed.

L. S. Theobald.

Carbazole reaction for carbohydrates and related compounds. J. S. Hepburn and M. Lazarchick (Amer. J. Pharm., 1930, **102**, 560—564).—The colours given under standard conditions by 1 c.c. of 1—0·0001% solutions of typical monosaccharides, disaccharides, polysaccharides, glucosides, and hydroxy-acids with 0·1 c.c. of 0·5% alcoholic carbazole and 2 or 4 c.c. of sulphuric acid (cf. Dische, A., 1927, 1213) are tabulated. The limiting concentration at which a positive reaction is obtained varies from 0·01% with maltose and β-hydroxybutyric acid to 0·0001% with salicin and calcium gluconate, and both the sensitivity and the colour obtained sometimes vary considerably with slight changes in technique. The reaction forms a useful general test, but none of the compounds examined gives a sufficiently characteristic colour to permit its identification.

H. E. F. Notton.

Sugar anhydrides. II. Action of trimethylamine on acetobromo-*l*-rhamnose. F. Micheel and H. Micheel (Ber., 1930, **63**, [*B*], 2862—2866; cf. A., 1929, 543).—Acetobromo-*l*-rhamnose is slowly converted by trimethylamine in alcohol and benzene into *diacetylrhamnose anhydride*, $C_{10}H_{14}O_6$, m. p. 124—125°, $[\alpha]_D^{20}$ —21° in chloroform, which reduces boiling Fehling's solution slowly, very rapidly after hydrolysis by acids, and is stable towards bromine and permanganate. Under apparently identical conditions, β-triacetylrhamnose, m. p. 108—115°, $[\alpha]_D^{18}$ —26·7° in chloroform, is sometimes the main product of the reaction. A strongly-reducing syrup is always formed as by-product. Formation of the anhydride appears to be preceded by loss of acetyl bromide from acetobromorhamnose, since, in benzene solution, the unstable additive *compound*, $CH_3\cdot COBr,NMe_3$, m. p. about 100° (decomp.), is precipitated. H. Wren.

Composition of Salkovski's araban. C. L. Butler and L. H. Cretcher (J. Amer. Chem. Soc., 1930, 52, 4509—4511).—The araban of Salkovski (A., 1902, i, 593) is not a simple polymeride of arabinose, since it contains arabinose, galactose, rhamnose, and glycuronic acid. H. Burton.

Sugars with branched carbon chains. II. Constitution and configuration of apiose. O. T. Schmidt (Annalen, 1930, **483**, 115—123).—Crude apiose is obtained by hydrolysis of apiin (Vongerichten, A., 1901, i, 646) with dilute sulphuric acid and removing admixed dextrose from the partly purified sugar by fermentation. Decomposition of apiosephenylbenzylhydrazone, m. p. 137—138°, $[\alpha]^{20}_{5461}$ −94° in pyridine (cf. Vongerichten, A., 1906, i, 143), with aqueous-alcoholic formaldehyde affords pure apiose, $[\alpha]^{15}_{D}$ +5·6° in water. This is oxidised by Goebel's method (A., 1927, 647) to apionic acid, $[M]^{10}_{5461}$ −33·2° in water [calcium salt (+$2H_2O$); potassium salt, $[M]^{25}_{5461}$ −2·45° in water; *phenylhydrazide*, m. p. 127°, $[M]^{25}_{5461}$ +76·8° in water]; the calcium salt is reduced by phosphorus and hydriodic acid (*d* 1·9) to *iso*valeric acid. The optical data for apionic acid show that it possesses the same configuration as *d*(—)-lactic acid. Apiose has, therefore, the constitution $(CH_2\cdot OH)_2C(OH)\cdot CH(OH)\cdot CHO$. *p*-Bromophenacyl *n*-valerate has m. p. 74° (lit. 63·5°). H. Burton.

Anhydro-sugars. I. Constitution of anhydro-sugars. II. Action of superheated water on anhydro-sugars. C. Tanaka (Mem. Coll. Sci. Kyoto, 1930, A, 13, 239—263, 265—280).—I. From comparative observations of ultra-violet absorption spectra and heats of combustion of simple and anhydro-sugars, modified formulæ are proposed for the latter. The following heats of combustion (g.-cal. per g.) have been determined: lævan, 4300; lævulosan, 4183; α-, 4186, β-glucosan, 4184; chitose, 4148; triacetyl-1 : 2-glucosan, 4593; triacetylglucal, 4949; tetra-acetyl-1 : 2-glucosen, 4647; triacetyl-β-glucosan, 4527; glycerol, 4312; glycide, 5610; allyl alcohol, 7626; glycide acetate, 5490; allyl acetate, 6549. The absorption spectra of some acetylated simple and anhydro-sugars are described, the general effect of acetylation being to displace the absorption end towards the red.

II. Lævulosan, α-glucosan, and lævan are gradually hydrolysed by water in a closed vessel at 100°; progress of hydrolysis leads to increasing reducing power, increasing amounts of humus and hydroxymethylfurfuraldehyde, and decreasing rotatory power and p_H value of the solution. β-Glucosan is not hydrolysed at 120°, but at 150° about 50% is converted into dextrose in 24 hrs., whereas heterolævulosan is unaffected. It is suggested that the p_H of the original sugar may determine the rate of hydrolysis. Chitose is easily hydrolysed to hydroxymethylfurfuraldehyde, which is simultaneously polymerised to humus and degraded to acids. With water at 150°, chitose, β-glucosan, and lævulosan give formic and lævulic acids and hydroxymethylfurfuraldehyde; lævulosan also gives lævulose, and β-glucosan dextrose (no trace of γ-glucose). The humus obtained from anhydro-sugars, dextrose, lævulose, and hydroxymethylfurfuraldehyde under the same conditions is similar in composition. It is suggested that the anhydro-sugars examined (except chitose, hydrolysed directly) give hydroxymethylfurfuraldehyde by way of a hexose and, subsequently, a chitose-like intermediate.

The absorption spectra of furfuraldehyde, its hydroxymethyl and methyl derivatives, and hydroxymethylpyromucic acid are formally similar; the heats of combustion (g.-cal. per g.) of furfuraldehyde and hydroxymethylfurfuraldehyde are 5816 and 5320, respectively. C. W. Shoppee.

Degradation of sugars in alkaline medium and with simultaneous action of oxidising agents. F. Fischler and J. Reil (Biochem. Z., 1930, **227**, 140—155).—When the ratio of cuprous oxide to dextrose is plotted against the mg. of sugar in determinations of sugars by Ost's method, a curve and not a straight line is obtained, due to the sensitivity of the methylglyoxal formed to alkali. If an alkaline solution containing sugar is distilled in presence of sufficient oxygen, acet- and form-aldehydes and acetic and formic acids are obtained, and if methylglyoxal is treated in the same way, the same products are obtained. Distillation in presence of oxidising agents (hydrogen peroxide, hypochlorite, hypoiodite, and permanganate) also gives the same results, and it appears probable that alkaline oxidative degradation of sugars proceeds by way of the formation and further oxidation of methylglyoxal. P. W. Clutterbuck.

Relationship of methylglyoxal to alkaline degradation of dextrose. F. Fischler, H. Hauss, and K. Täufel (Biochem. Z., 1930, **227**, 156—170).—Solutions of pure methylglyoxal, obtained by distilling solutions of crude methylglyoxal over barium carbonate under reduced pressure, show an absorption maximum at 2840 and minimum at 2400 Å. Pure dextrose solutions show no absorption, but after treatment with very dilute alkali show absorption characteristic for methylglyoxal. The formation of caramel does not account for the absorption. The absorption is lost almost completely on adding small amounts of acid. Addition of alkali to pure methylglyoxal solutions causes an immediate formation of caramel together with lactic, acetic, and formic acids. These results are followed quantitatively.

P. W. Clutterbuck.

Action of animal charcoal on dextrose in the presence of dehydrogenated intermediate products. F. Zuckerkandl and L. Messiner-Klebermass (Biochem. Z., 1930, **226**, 395—400).—Although dextrose in aqueous solution is not decomposed when boiled with animal charcoal, if the hydrochloride of an aromatic amine such as *p*-phenylenediamine or aniline (but not dimethylaniline) or an amino-acid such as tyrosine, alanine, phenylalanine, or histidine is also present, decomposition both of the sugar and of the amino-compound or amino-acid takes place, and in the case of *p*-phenylenediamine a sparingly soluble condensation product can be obtained. The process can be explained by supposing that the amines or amino-acids are converted by loss of hydrogen into intermediate imino-compounds which then attack the dextrose molecule, and it is possible that a similar process occurs in the animal organism.

W. McCartney.

Carbohydrates. X. 1 : 2-Derivatives of dextrose. P. Brigl and R. Schinle (Ber., 1930, 63, [*B*], 2884—2887; cf. A., 1929, 1043).—Tetrabenzoylglucose diethylmercaptal (cf. Brigl and Mühlschlegel, A., 1930, 1022) is very readily transformed by silver oxide and methyl iodide into the corresponding 2-*methyl* derivative, m. p. 88—89°, $[\alpha]_D^{18}$ +64·57° in acetone, from which sodium ethoxide removes the benzoyl groups, giving 2-methylglucose diethylmercaptal, m. p. 178°, $[\alpha]_D^{20}$ −25·0° in pyridine, identical with the product described by Papadakis (A., 1930, 1274). Treatment of the mercaptal with aqueous mercuric chloride affords 2-*methylglucose*, m. p. 158° after softening, $[\alpha]_D^{20}$ +56·6° to +65·6° in water, which reduces Fehling's solution very slowly when freshly prepared, but normally after repeated crystallisation. With phenylhydrazine in cold acetic acid it gives 2-methylglucosephenylhydrazone, m. p. 177°, whereas in hot solution glucosephenylosazone, m. p. 205°, is produced.

H. Wren.

Acetone [*iso*propylidene] compounds of the sugars and their derivatives. XVII. Conversion of *iso*propylideneglucose into a new amino- and anhydro-hexose; acyl migration. H. Ohle and R. Lichtenstein (Ber., 1930, 63, [*B*], 2905—2912).—The action of methyl-alcoholic ammonia on 5-*p*-toluenesulphonyl-6-benzoylglucose *iso*propylidene ether proceeds very slowly at the ordinary temperature and is incomplete after 3 weeks. If the change is interrupted after 14 days, the main products are 1 : 2-iso*propylideneidosyl*-6-*amine* p-*toluenesulphonate*, m. p. 173—174° (decomp.), $[\alpha]_D^{20}$ −23·49° in water, and a nitrogen-free material (see later). Removal of the *iso*propylidene group leaves a material which does not give a crystalline phenyl-hydrazone or -osazone, but affords *idosyl*-6-*amine*-p-*nitrophenylosazone*, m. p. (indef.) 227° [*phenylhydrazine* p-*toluenesulphonate*, m. p. 183—184° (decomp.), is incidentally described]. With benzoyl chloride in pyridine at 37°, the *p*-toluenesulphonate affords *tribenzoylidosyl*-6-*amine* iso*propylidene ether*, m. p. 192°, $[\alpha]_D^{20}$ −19·30° in chloroform; the corresponding acetyl and *p*-toluenesulphonyl derivatives have not been obtained crystalline. Sodium nitrite transforms the *p*-toluenesulphonate into 3 : 6-*anhydroidose* iso*propylidene ether*, m. p. 105°, $[\alpha]_D^{20}$ +24·94° in water, hydrolysed by *N*-sulphuric acid to 3 : 6-*anhydroidose*, m. p. 105—106°, $[\alpha]_D^{20}$ +25·36° in water. For purposes of comparison the following derivatives of dextrose have been prepared: *triacetylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 86°, $[\alpha]_D^{18}$ +18·35° in chloroform, from *iso*propylideneglucosyl-6-amine *p*-toluenesulphonate, pyridine, and acetic anhydride at 37°; *tribenzoylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 198—199°, $[\alpha]_D^{20}$ −76·43° in chloroform; *di*-p-*toluenesulphonylglucosyl*-6-*amine* iso*propylidene ether*, m. p. 172° (decomp.), $[\alpha]_D^{19}$ −2·54° in chloroform; *hexabenzoylglucosyl*-6-*amine*, (+C_6H_5Me), m. p. 188°, $[\alpha]_D^{20}$ +22·89° in chloroform.

Acetylation of the nitrogen-free syrup (see above) yields an *acetyldi*-p-*toluenesulphonylhexose* iso*propylidene ether*, m. p. 112°, $[\alpha]_D^{19}$ −28·76°, which is not identical with 3-acetyl-5 : 6-di-*p*-toluenesulphonylglucose *iso*propylidene ether. It is remarkably resistant to dilute mineral acid. Its constitution is not established, but its formation is accompanied by the wandering of a *p*-toluenesulphonyl group.

H. Wren.

Ring structure of methylglucodesoside. P. A. Levene and L. A. Mikeska (J. Biol. Chem., 1930, 88, 791—798; cf. Bergmann and Breuers, A., 1929, 797).—2-Deoxy-*d*-glucose (glucodesoside; cf. Bergmann, Schotte, and Lechinsky, A., 1922, i, 227) was oxidised according to the method of Goebel (A., 1927, 647) to yield 2-*deoxy*-d-*gluconic acid*, $C_6H_{12}O_6$, m. p. 145°, $[\alpha]_D^{25}$ +2·4° in water (*barium* salt), converted in aqueous solution at 100° into the *lactone*, m. p. 95—97°, $[\alpha]_D^{25}$ +68·0° in water, which when methylated with methyl iodide and silver oxide yields *trimethyl*-d-*glucodesonolactone*, m. p. 62°, $[\alpha]_D^{25}$ +21·5° in benzene. Methyl-2-deoxy-*d*-glucoside (Bergmann, Schotte, and Lechinsky, *loc. cit.*) was methylated with methyl sulphate and sodium hydroxide to yield *trimethyl*-d-*methylglucodesoside*, b. p. 86—90°/0·35 mm., $[\alpha]_D^{25}$ varying from +64° to +97° in chloroform from which *trimethyl*-d-*glucodesose*, m. p. 58—61°, $[\alpha]_D^{25}$ +59·5° to +33·1° in water, was obtained by treatment with 0·1*N*-hydrochloric acid at 100°. *Trimethyl*-d-*glucodesonic acid* (*barium* salt, $[\alpha]_D^{25}$ +18·1° in water), obtained from the last compound by oxidation by the method of Goebel, yields a *lactone*, b. p. about 137°/0·02 mm., $[\alpha]_D^{25}$ +87·5° in chloroform, $[\alpha]_D^{25}$ +88·2° in benzene. From the non-identity of these two trimethyl-*d*-glucodesonic lactones it is concluded that as the one formed by direct methylation of *d*-desonolactone probably has the 1 : 4 ring structure, a 1 : 5 ring structure is to be assigned to the other and therefore to the 2-deoxyglucoside from which it was formed. The instability of this compound is therefore to be attributed, not to its possessing a furanose structure, but to the reduced state of carbon atom 2. W. O. Kermack.

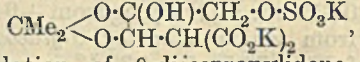
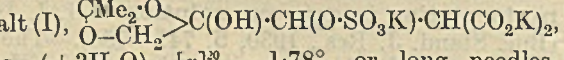
α-*d*-Gulose calcium chloride, its rotation and mutarotation in aqueous solution. H. I. Isbell (Bur. Stand. J. Res., 1930, 5, 741—755).—The solution of crude *d*-gulose from reduction of gulonolactone (Fischer and Stahel, A., 1891, 667) is purified through the phenylhydrazone (cf., Blanksma and van Ekenstein, A., 1908, i, 951); treatment of the pure syrup so obtained with calcium chloride affords α-d-*gulose calcium chloride* (+H_2O), decomp. 205°, initial $[\alpha]_D^{20}$ +37·7° (by extrapolation), mutarotation constant k_1+k_2, 0·0193, equilibrium $[\alpha]_D^{20}$ −15·4°+0·78*c* (*c*=concentration in g. per 100 c.c.).

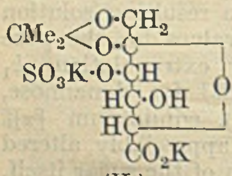
Calcium chloride is rapidly and quantitatively removed from solutions of the above compound by means of silver oxalate, and the resulting solution of *d*-gulose gives the following values for the pure sugar: initial $[\alpha]_D^{20}$ +61·6° (by extrapolation), $k_1 + k_2$ 0·0206 (cf. the value found for *d*-mannose, 0·019, by Dale, A., 1929, 1280), equilibrium $[\alpha]_D^{20}$ −26·4°. The last value is not appreciably altered by variations in the concentration of the sugar itself, although the equilibrium rotation of the calcium chloride compound is greatly altered by variations in concentration (cf. the equation above, which may be modified to express the equilibrium rotation of *d*-gulose in presence of calcium chloride to $[\alpha]_D^{20}$ $-26{\cdot}4°+3{\cdot}73m$, where m=g. of anhydrous calcium chloride per 100 c.c. of solution); concentrated solutions of the compound on dilution with water show a mutation rate approximately equal to that of *d*-gulose. A different equilibrium is reached in alcoholic solution.

R. CHILD.

Individualities of anhydrofructose and difructose anhydride. R. F. JACKSON and S. M. GOERGEN (Bur. Stand. J. Res., 1930, 5, 733—734).—Difructose anhydride, m. p. 162—164° (A., 1929, 1280) has the mol. wt. required for a double hexose molecule, and is thus not identical with the anhydrofructose of Irvine and Stevenson (A., 1929, 1046); the latter is deliquescent, whilst the former will crystallise from aqueous solutions at the ordinary temperature.

R. CHILD.

Model experiments based on the theory of alcoholic fermentation. III. Degradation of α-di*iso*propylidenefructose sulphate. H. OHLE and G. COUTSICOS (Ber., 1930, 63, [*B*], 2912—2927; cf. A., 1929, 913; 1930, 70).—The constitution of the potassium salt,  $CMe_2{<}\begin{matrix}O{\cdot}C(OH){\cdot}CH_2{\cdot}O{\cdot}SO_3K\\O{\cdot}CH{\cdot}CH(CO_2K)_2\end{matrix}$, obtained by the oxidation of β-di*iso*propylidenefructose hydrogen 1-sulphate by potassium permanganate in neutral, aqueous solution is confirmed by determination as the basic lead salt of glycollic acid produced by its hydrolysis. The observations are extended to *potassium* di*iso**propylidenefructose 3-sulphate*, $C_{12}H_{19}O_9SK,0{\cdot}5H_2O$, decomp. about 165°, $[\alpha]_D^{20}$ $-124{\cdot}3°$ in water, which causes alcohol to gelatinise markedly; the corresponding *sodium* salt $(+H_2O)$, decomp. about 170°, has $[\alpha]_D^{20}$ $-128{\cdot}3°$ in water. The oxidation graph shows that the substance is completely degraded to optically inactive compounds when 12 atoms of oxygen are used. The graph of hydrolysis shows that the maximum possibility of isolating intermediate products containing sulphur occurs when 6 atoms of oxygen are used, and under these conditions, the *potassium* salt (I),  $\begin{matrix}CMe_2{\cdot}O\\O{-}CH_2\end{matrix}{>}C(OH){\cdot}CH(O{\cdot}SO_3K){\cdot}CH(CO_2K)_2$, prisms $(+3H_2O)$, $[\alpha]_D^{20}$ $-1{\cdot}78°$, or long needles, $4{\cdot}5H_2O$, $[\alpha]_D^{20}$ $-2{\cdot}72°$, is obtained. It is decomposed by dilute mineral acid into acetone, sulphuric acid, methylglyoxal, glycollic acid, and carbon dioxide. Partial hydrolysis of potassium α-di*iso*propylidenefructose 3-sulphate affords *potassium* α-iso*propylidenefructose* 3-*sulphate*, decomp. about 150°, $[\alpha]_D^{20}$ $-112°$ in water (corresponding *sodium* salt, decomp. 140°, $[\alpha]_D^{20}$ $-118{\cdot}6°$ in water). When oxidised with 5 atoms of oxygen it yields large amounts of the tripotassium salt I (see above) and smaller quantities of the *fructuronate* II $(+4H_2O)$, $[\alpha]_D^{20}$ $-45{\cdot}68°$ in water, which is hydrolysed to acetone, carbon dioxide, and sulphuric acid. The oxidation graph of β-di*iso*propylidenefructose resembles in some respects that of the corresponding 1-sulphate and indicates a possibility of isolating intermediate compounds by use of 6 atoms of oxygen. Since an optically inactive product is not obtained when 12 atoms of oxygen are employed, it appears that a portion of the liberated acetone must be oxidised. This is also the case with α-di*iso*propylidenefructose, with which also the reproducible scattering of the experimental values around the graph indicates the production of a series of intermediate compounds formed along different lines, some of which are closed by the introduction of the sulphuric acid residue. α-*iso*Propylidenefructose with 2—9 atoms of oxygen appears mainly to suffer direct conversion into acetone, carbon dioxide, and water without marked accumulation of intermediate compounds.



(II.)

The selective influence of the sulphuric acid residue is most apparent in the case of α-*iso*propylidenefructose and its 3-sulphate, and obviously depends on its proximity to the masked ketonic group, the hydrate form of which is stabilised by the strongly electronegative character of the acid residue. This stabilisation strengthens the union of the acetone residue and thus withdraws the upper half of the molecule from attack by the oxidising agent. The conclusion is reached that degradation of dextrose in the sense of Neuberg's fermentation scheme is possible only by a detour through lævulose.

H. WREN.

Action of mercury salts on acetohalogenosugars. IV. Direct preparation of alkylbiosides of the α-series. G. ZEMPLÉN and A. GERECS (Ber., 1930, 63, [*B*], 2720—2729; cf. A., 1929, 683; 1930, 456, 1167).—Re-examination of the action of mercuric acetate and ethyl alcohol on acetobromocellobiose in benzene shows that α-ethylcellobioside hepta-acetate is obtained with certainty when about 100% excess of ethyl alcohol is used; with a 200% excess the product is reasonably homogeneous, but the yield is unsatisfactory. The reducing power of the products increases sharply when more than about a 300% excess of ethyl alcohol is used, and with between 300 and 400% excess there is marked transition to the production of the β-form. With *iso*propyl alcohol α-*iso*propylcellobioside hepta-acetate is obtained in good yield and excellent optical purity by the use of a 40—200% excess of the alcohol; with increase in the amount of the alcohol a maximum in the reducing power of the product is observed. With *n*-propyl, *n*-butyl, *iso*butyl, *sec.*-butyl, *sec.*-amyl, *n*-hexyl, and β-phenylethyl alcohols the highest observed specific rotation of the α-forms is attained with an approximate excess of 100% of the alcohol. For the production of the β-alkylcellobioside hepta-acetates a large excess of the requisite alcohol is advisable. With the lower members it is advantageous to use alcohol as solvent, whereby completely non-reducing products which are optically homogeneous only after repeated crystallisation are obtained. In benzene the majority of the β-alkylcellobioside hepta-acetates can be obtained provided that a sufficiently large excess of the alcohol is used. They may also be prepared from acetobromocellobiose in the necessary alcohol or in benzene with the aid of mercury cyanide, which is not very successful in the production of the α-compounds. The following α-alkylcellobioside hepta-acetates are described. The rotations are the highest observed, all being measured in chloroform: ethyl, $[\alpha]_D^{23}$ $+57{\cdot}23°$; n-*propyl*, $[\alpha]_D^{20}$ $+58{\cdot}79°$; iso*propyl*, $[\alpha]_D^{22}$ $+59{\cdot}29°$; n-*butyl*, m. p. 172°, $[\alpha]_D^{23}$ $+52{\cdot}40°$; iso*butyl*, m. p. 174°, $[\alpha]_D^{21}$ $+45{\cdot}51°$; sec.-*butyl*, m. p. 193°, $[\alpha]_D^{25}$ $+55{\cdot}76°$; sec.-*amyl*, m. p. 193°, $[\alpha]_D^{23}$ $+52{\cdot}23°$; n-*hexyl*, m. p. 182°, $[\alpha]_D^{21}$ $+53{\cdot}42°$; β-*phenylethyl*, m. p. 207°, $[\alpha]_D^{21}$ $+54{\cdot}16°$. The following β-alkylcellobioside hepta-acetates are described: *methyl*, $[\alpha]_D^{26}$ $-25{\cdot}0°$; iso*propyl*, $[\alpha]_D^{25}$ $-22{\cdot}7°$; n-*butyl*, $[\alpha]_D^{23}$ $-24{\cdot}60°$; iso*butyl*, $[\alpha]_D^{25}$ $-23{\cdot}04°$; sec.-*butyl*, $[\alpha]_D^{23}$ $-23{\cdot}20°$; *hexyl*, $[\alpha]_D^{23}$ $-24{\cdot}37°$; β-*phenylethyl*, $[\alpha]_D^{23}$ $-25{\cdot}28°$.

H. WREN.

Preparation and m. p. of β-maltose anhydride. J. GILLIS (Natuurwetensch. Tijds., 1930, **12**, 193—199).—Contrary to the results obtained by de Bruyn and van Leent (A., 1895, i, 7), β-maltose hydrate may be dehydrated below 100° in a vacuum; the m.-p. curves show that the anhydride melts at 108°, and the hydrated form at 102—103°. The product obtained by de Bruyn and van Leent is probably a supercooled mixture of about 56% of β- and 46% of α-maltose.

S. I. LEVY.

Thio-sugars and their derivatives. XV. Nature of the sugars of mustard oil glucosides. W. SCHNEIDER, H. FISCHER, and W. SPECHT (Ber., 1930, **63**, [*B*], 2787—2793; cf. A., 1929, 913).—Aqueous solutions of sinigrin are smoothly and rapidly decomposed by silver nitrate in presence of barium or silver carbonate (to neutralise the liberated nitric acid) in accordance with the equation $C_{10}H_{16}O_9NS_2K+H_2O+2AgNO_3 \longrightarrow C_4H_5O_4NS_2Ag_2+C_6H_{12}O_6+KNO_3+HNO_3$. The liberated dextrose exhibits downward mutarotation attaining the equilibrium value, $[\alpha]_D^{20}$ $+53{\cdot}3°$. Similar results are obtained with sinalbin. Precisely analogous results are obtained when mercury salts are used with the glucosides, thus apparently confirming the conclusion of Wrede (A., 1923, i, 589) that these are α-glucosides. Since, however, α-glucose is liberated by the action of silver nitrate in presence or absence of barium carbonate on the sodium compound of β-glucothiose, it appears that in all cases the reaction is accompanied by a Walden inversion and that the glucosides are β-compounds. Experimental confirmation of this view is found in the production of octa-acetyl-ββ-diglucosyl disulphide, m. p. 142—143°, $[\alpha]_D^{21}$ $-158{\cdot}7°$ in *s*-tetrachloroethane (cf. A., 1928, 872) from sinigrin and 0·1*N*-aqueous sodium hydroxide with subsequent treatment of the neutralised solution with iodine, evaporation to dryness, and treatment of the residue with pyridine and acetic anhydride.

H. WREN.

Chellol glucoside. P. FANTL and S. I. SALEM (Biochem. Z., 1930, **226**, 166—179).—Kellin, $C_{14}H_{12}O_5$, the supposed glucoside of *Ammi Visnaga* (A., 1897, 1041), is not a single substance. Alcoholic extraction of the seeds (in the absence of lime) gave β-d-*chellol glucoside*, $C_{19}H_{20}O_{10},2H_2O$, m. p. 175°, α_D^{20} $-31{\cdot}88°$, containing one methoxyl group and giving a *tetra-acetyl* derivative, m. p. 153°. Hydrolysis of the glucoside with hydrochloric acid gave dextrose and *chellol*, $C_{13}H_{10}O_5$, m. p. 179°, which contains one methoxyl group and gives a *monoacetyl* derivative, m. p. 105°. Hydrolysis of the glucoside with dilute alkalis gave β-*d*-glucosidoglycollic acid, $C_8H_{14}O_8$, m. p. 163°, together with a *substance*, $C_{11}H_{10}O_4$, m. p. 111° (*methyl* derivative, m. p. 136—137°; *benzoyl* derivative, m. p. 115°; *oxime*, m. p. 144°).

P. W. CLUTTERBUCK.

Natural glucosides. II. Constitution of æsculin. F. S. H. HEAD and A. ROBERTSON (J.C.S., 1930, 2434—2444; cf. Glaser and Kraus, A., 1923, i, 820).—Prolonged treatment of æsculin with methyl iodide in presence of acetone and potassium carbonate affords 7-O-*methylæsculin* ($+2H_2O$), m. p. 230° (decomp.), hydrolysed by 5% sulphuric acid to 7-*O*-methylæsculetin, m. p. 185° (Tiemann and Will, A., 1883, 199; Bargellini and Monti, A., 1915, i, 84). This is converted by treatment with ethyl iodide in presence of acetone and potassium carbonate into 7-*methoxy*-6-*ethoxycoumarin*, m. p. 120°, which on repeated treatment with methyl sulphate and 20% sodium hydroxide solution gives the *methyl* ester, m. p. 80°, of 2 : 4-*dimethoxy*-5-*ethoxycinnamic acid*. When this acid is heated it passes (at 117—118°) into a yellow solid, m. p. 128°, which when kept in contact with benzene reverts to the original colourless form. 5-Nitro-2-ethoxyanisole is reduced by aqueous sodium sulphide to the corresponding amine, convertible by the usual method into 3-*methoxy*-4-*ethoxyphenol*, m. p. 58°. When a solution of this in ether containing hydrogen and zinc cyanides is saturated with hydrogen chloride and the resulting product hydrolysed, 2-*hydroxy*-4-*methoxy*-5-*ethoxybenzaldehyde*, m. p. 112—113°, is obtained. Methylation of this with methyl iodide in presence of acetone and potassium carbonate affords 2 : 4-*dimethoxy*-5-*ethoxybenzaldehyde*, m. p. 110°, which could not be converted into the above cinnamic acid but into a pale yellow *modification*, m. p. 132—133°, by condensation with malonic acid in presence of pyridine and a small amount of piperidine. Oxidation of both cinnamic acids with aqueous potassium permanganate in acetone furnishes the above dimethoxyethoxybenzaldehyde, which is oxidised further to 2 : 4-*dimethoxy*-5-*ethoxybenzoic acid*, m. p. 137°. 7-Methoxy-6-ethoxycoumarin could not be prepared from 2-hydroxy-4-methoxy-5-ethoxybenzaldehyde.

4-Aminoveratrole is converted by the usual method into 3 : 4-*dimethoxyphenol* ($+H_2O$), m. p. 46°, and thence by Gattermann's reaction into 2-*hydroxy*-4 : 5-*dimethoxybenzaldehyde*, m. p. 105°, which is methylated to asarylaldehyde. Methoxyquinol, m. p. 89° (lit. 82—84°), affords similarly 2 : 5-*dihydroxy*-4-*methoxybenzaldehyde*, m. p. 209° (slight decomp.) (also methylated to asarylaldehyde), which with acetic anhydride and sodium acetate at 120—180° gives a small amount of 7-*O*-methylæsculetin. Æsculin, therefore, contains the glucose residue in the 6- and not the 7-position as suggested by Glaser and Kraus (*loc. cit.*).

4-*Methoxy*-3-*ethoxyphenol* ($+H_2O$), m. p. 92—93° after sintering at 85°, is converted into 2-*hydroxy*-5-*methoxy*-4-*ethoxybenzaldehyde*, m. p. 91° (*phenylhydrazone*, m. p. 157—158°), and thence by the usual methods into 2 : 5-*dimethoxy*-4-*ethoxy-benzaldehyde*, m. p. 110°, -*benzoic acid*, m. p. 130°, and -*cinnamic acid*, m. p. 178—179° after sintering at 170°.

H. BURTON.

***Digitalis* glucosides. II. Digoxigenin, the aglucone of digoxin.** S. Smith (J.C.S., 1930, 2478—2482).—When digoxigenin (A., 1930, 583) [*diacetyl* derivative, m. p. 221°, $[\alpha]^{20}_{5461}$ +61·3° (all rotations are in methyl alcohol)], is heated with aqueous-alcoholic sulphuric acid, *anhydrodigoxigenin*, $C_{23}H_{32}O_4$, m. p. 182°, $[\alpha]^{20}_{5461}$ +16·3° (*diacetyl* derivative, m. p. 199°, $[\alpha]^{20}_{5461}$ +38·6°), is obtained. These results indicate that digoxigenin contains three hydroxyl groups; the remaining oxygen atoms are present in a lactone group as shown by hydrolysis and titration. Reduction of digoxigenin with hydrogen in presence of palladium-black and 80% alcohol affords *dihydrodigoxigenin*, $C_{23}H_{36}O_5$, m. p. 215°, $[\alpha]^{20}_{5461}$ +20·5° (*diacetyl* derivative, m. p. 222°, $[\alpha]^{20}_{5461}$ +29·8°), and since digoxigenin gives a red colour with alkaline sodium nitroprusside (cf. Jacobs, Gustus, and Hoffmann, A., 1926, 430, 1250), it is probably a trihydroxy-$\Delta^{\beta\gamma}$-unsaturated lactone. When digoxigenin is treated with 10% methyl-alcoholic potassium hydroxide solution, iso*digoxigenin* (+C_5H_5N), m. p. 280°, m. p. (solvent-free) 260° (decomp.), $[\alpha]^{20}_{5461}$ +13·6° [*diacetyl* derivative, m. p. 280° (all m. p. except this are corr.)], is produced. This does not give Legal's test, is not reduced under the above conditions, and is converted by successive treatment with warm 10% sodium hydroxide solution and acetic acid into iso*digoxigeninic acid*, $C_{23}H_{36}O_6$, m. p. 228° (decomp.). H. Burton.

Digitalinum verum. H. Kiliani (Ber., 1930, 63, [*B*], 2866—2869).—To avoid the formation of ethylated sugars during the hydrolysis of digitalinum verum, the ethyl-alcoholic hydrochloric acid is replaced by a mixture of glacial acetic acid, water, and concentrated hydrochloric acid (vol. ratio 35 : 55 : 10). Digitaligenin is readily isolated in satisfactory yield, but the digitalose could not be caused to crystallise. It is therefore oxidised with bromine, thus giving digitalonolactone (yield 40%) and *d*-gluconic acid isolated as the barium salt. H. Wren.

Constitution of starch. Critical review. M. Schœn (Bull. Soc. Chim. biol., 1930, 12, 1033—1099).

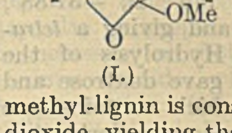
Action of hydrofluoric acid on starch. B. Helferich, A. Starker, and O. Peters (Annalen, 1930, 482, 183—188).—When hydrofluoric acid is allowed to interact with anhydrous potato-starch under the conditions described in the case of cellulose (cf. A., 1930, 72) *amylan*, $[\alpha]^{16}_{D}$ +145° in water, is produced. It resembles cellan in all properties except that it is precipitated from an aqueous solution by alcohol. When heated with acetic anhydride and pyridine, an *acetyl* derivative $(C_6H_7O_5Ac_3)_x$, $[\alpha]^{17}_{D}$ +141·5° in chloroform, results, from which the amylan can readily be regenerated in a state of purity, $[\alpha]^{17}_{D}$ +144·2° in water, +110° in hydrofluoric acid. Identical treatment of anhydrous maltose gives *maltan*, $[\alpha]^{21}_{D}$ +145° (*acetyl* derivative, $[\alpha]^{17}_{D}$ +141·3° in chloroform), indistinguishable in all its properties from amylan. Mercerised cotton has $[\alpha]^{14}_{D}$ +1·2°, +0·4° in hydrofluoric acid, as has raw cotton. H. A. Piggott.

Supposed depolymerisation of glycogen. E. Berner (Ber., 1930, 63, [*B*], 2760—2764; cf. A., 1930, 1025).—Glycogen, $[\alpha]^{20}_{D}$ +194·5°, ash content less than 0·02%, causes depressions of the f. p. of water which become smaller as the substance is more completely dried, thus indicating the probable presence of alcohol. Complete dehydration of glycogen requires heating at 100—110°/vac. Dried glycogen precipitated by alcohol from solutions in anhydrous solvents such as acetamide, formamide, and ethylene glycol retains the substances, the amount of amide depending on that of alcohol employed. The precipitates lose alcohol slowly over calcium chloride in a vacuum; when exposed to air the loss is more rapid, owing to the absorption of atmospheric moisture. Cryoscopic determinations of the mol. wt. of the glycogen precipitates in water gives values corresponding with those observed by Reilly, Pringsheim, and Donovan (A., 1930, 895). Analysis discloses the presence of amide and alcohol in amount sufficient to explain the low values. Addition of alcohol to solutions of glycogen in ethylene glycol yields a product giving, after desiccation for 2 days, a high depression of the f. p. It contains 9·4% of alcohol. The observation of Reilly, Pringsheim, and Donovan (*loc. cit.*) that its aqueous solution exhibits opalescence and gives the same colorations with iodine as pure glycogen solutions is in harmony with the author's view that depolymerisation has not occurred. H. Wren.

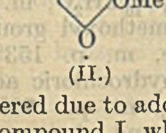
Constitution of cellulose nitrates and acetates and their passage to colloidal film. J. J. Trillat.—See this vol., 27.

Cellulose xanthate. III. T. Lieser (Annalen, 1930, 483, 132—139).—Treatment of methylcellulose (A., 1929, 799) with a mixture of acetic acid and anhydride containing sulphuric acid at 25—30° for 7—20 days gives about 50% of cellobiose octa-acetate, indicating that some of the glucose anhydride units in the original product are not methylated. No methylcellobiose acetate could be detected; it is probably decomposed during acetolysis. H. Burton.

Lignin and cellulose. XV. Lignin and nitrogen dioxide. K. Freudenberg and W. Dürr (Ber., 1930, 63, [*B*], 2713—2720).—Lignin reacts very rapidly with gaseous nitrogen dioxide and, after a short period, the initial absorption is succeeded by evolution of nitric oxide due to a secondary oxidation. With methyl-lignin only the initial, rapid absorption is observed. During the reaction the lignin becomes partly demethylated with production of methyl alcohol. The observations are most readily explained on the assumption that substitution has occurred. Under favourable conditions the ratio of nitrogen introduced to original aromatic methoxyl approaches 1 : 1. Double linkings are not involved to an important extent, since nitrolignin and nitromethyl-lignin can be brominated and bromomethyl-lignin can be nitrated. Loss of methyl alcohol from lignin or methyl-lignin is considered due to addition of nitrogen dioxide, yielding the compound I, which in part loses



(I.)



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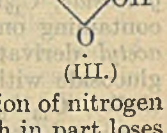


(III.)

nitric acid to give the substance II and in part eliminates methyl nitrite giving a quinol derivative passing into the nitrophenol III.

Dehydrodivallin is very violently attacked by nitrogen dioxide owing to the presence of free phenolic hydroxyl groups. Its dimethyl ether resembles lignin in being nitrated with loss of about 2% of methyl as methyl alcohol. Veratric acid is nitrated with production of traces of methyl alcohol, and veratrylcellulose behaves similarly. H. Wren.

Two syntheses of heptamethyleneimine. A. Müller and P. Bleier (Monatsh., 1930, 56, 391—406).—Reduction of suberone*iso*oxime (α-ketoheptamethyleneimine) with sodium and alcohol (cf. A., 1929, 194) affords 1·5% of the theoretical amount of slightly impure heptamethyleneimine, b. p. 162—164°, d_4^{17} 0·869, n_D^{17} 1·5262 (*chloroaurate*, m. p. 188° after sintering at 173° and slight decomp. at 183—185°; *picrate*, m. p. 147—148°), together with high-boiling products. Oxidation of N-*benzoylheptamethyleneimine*, b. p. 196—197°/13 mm., with aqueous potassium permanganate at about 65° furnishes 41·3% of ζ-benzamido-*n*-heptoic acid, dimorphous, m. p. 86° and 90° (lit. 81—82°), prepared also by Zemplén and Csürös' method (A., 1929, 1283) and by benzoylating ζ-amino-*n*-heptoic acid [hydrochloride, m. p. 112° (lit. 97—99°)]. The last-named acid is obtained when suberone*iso*oxime is heated with 20% hydrochloric acid at 150°.

Hydrolysis of the reaction product from αη-dibromo-*n*-heptane and *p*-toluenesulphonamide in presence of alcoholic potassium hydroxide with hydrochloric acid at 160° yields slightly impure heptamethyleneimine (0·8% yield) and αη-diamino-*n*-heptane.

Improved methods of preparation of suberic acid, suberone, and suberone*iso*oxime are given. All m. p. are corr. H. Burton.

Asymmetric nitrogen atom. LVIII. Decomposition of active and inactive quaternary ammonium nitrates under the influence of amines; solvate formation by ammonium salts. E. Wedekind and F. Feistel (Ber., 1930, 63, [*B*], 2743—2753; cf. Wedekind and Uthe, A., 1925, i, 536, 1059).—Examination by the conductivity method of a number of quaternary ammonium halides and the corresponding nitrates shows that the halides which are stable in chloroform solution are stable also after addition of aniline. Decomposition of the halides takes place only if a phenyl or benzyl or an allyl group is present. With phenylmethylallylammonium nitrate decomposition occurs in chloroform in presence of aniline or methylaniline, but not of dimethylaniline, the secondary base having the more profound influence. Triethylamine and methylethylaniline are ineffective. The action of the various bases is shown by the half period in minutes for drop in activity and mean velocity coefficient as deduced from the conductivity: *iso*amylamine, 25, 0·0182; *iso*butylamine, 45, 0·0072; *n*-propylamine, 47, 0·0065; *n*-butylamine, 88, 0·0064; benzylamine, 90, 0·0037; aniline, 250, 0·0032; diethylamine, 26, 0·0259; benzylethylamine, 42, 0·0176; dibenzylamine, 80, 0·0077; methylaniline, 90, 0077; ethylaniline, 150, 0055: benzylaniline, 195, 0·0014; diphenylamine, ∝. Confirmation of the hypothesis that reaction occurs in accordance with the scheme $NR^1R^2R^3R^4{\cdot}NO_3+H{\cdot}NHX=NR^1R^2R^3+R^4{\cdot}NHX+HNO_3$, is found in the isolation of *p*-toluidine nitrate, decomp. 199°, from phenylmethylallylammonium nitrate in molten *p*-toluidine. The possible preliminary formation of solvates is examined by placing weighed amounts of amine, nitrate, and amine +nitrate in a high vacuum at a temperature not exceeding 36° until the solvent is removed, and then raising the temperature in stages until, at 111°, constancy in weight is observed. A final weight lower than the original weight (owing to removal of volatile bases formed as shown above) is observed with those nitrates which are known by the decrease in conductivity to decompose in chloroform solution after addition of aniline. The method does not indicate solvate formation with tertiary bases. Further evidence of solvate formation is deduced from measurements of specific rotation, the lowest values being observed in "indifferent" solvents, the highest in those which cause decomposition. In indifferent media the specific rotation is affected slightly by variation in concentration, but shows great dependence thereon in "active" solvents. Cryoscopic measurements of the mol. wt. of phenylbenzylmethylallylammonium nitrate in bromoform show only that the salt is associated in this medium. In *p*-toluidine decomposition of the nitrate appears to occur, a constant minimum value being reached when the solution has been preheated at 45—50° for a lengthy period. With the non-decomposing phenyldimethylethylammonium perchlorate in *p*-toluidine, the apparent mol. wt. diminishes with increasing concentration, thus indicating solvate formation. H. Wren.

Purely aliphatic *strepto*pentamethine dyes. W. König and W. Regner (Ber., 1930, 63, [*B*], 2823—2827; cf. A., 1926, 522).—ε-Methylanilinopentadienal is converted by dimethylamine in presence of alcohol and perchloric acid into methylaniline and *αε-tetramethyldiaminopentamethinium perchlorate*, m. p. 165°, obtained similarly from ethylanilino- or tetrahydroquinolino-pentadienal; it may be prepared in poor yield and accompanied by much other substance by addition of dimethylamine followed by perchloric acid to a mixture of piperidine and cyanogen bromide in alcohol and ether. *αε-Dipiperidinopentamethinium perchlorate*, m. p. 111°, is described. The new compounds give yellowish-green solutions in water or alcohol and give shades on mordanted cotton similar to those of auramine G. The absorption curves of the aliphatic dyes are nearly identical with one another. The shades on cotton are as fast to light as those of the auramines and superior in resistance to acids and alkalis. The solid compounds exhibit very marked luminescence when exposed to the Hanau lamp. H. Wren.

Reaction of choline and lecithin. J. A. Sanchez (Semana méd., 1930, i, 1416).—When heated with iodine and sodium hydroxide, choline and lecithin (the latter after saponification with sodium hydroxide) afford iodoform. Chemical Abstracts.

Glycine and its neutral salt additive products. J. V. Dubský and A. Rabas (Pub. Fac. Sci. Univ. Masaryk, 1930, No. 123, 1—18).—The zinc salt of glycine, $ZnX_2,2HX,4H_2O$ $(X=NH_2{\cdot}CH_2{\cdot}CO_2)$ (cf. Kraut, A., 1892, 294), is hydrolysed under special conditions to the normal *salt*, ZnX_2,H_2O, decomp. 319°, a neutral *salt*, $ZnX_2,3HX,H_2O$, decomp. 245°, being simultaneously produced. The following neutral salts are described : $ZnCl_2,2HX,2H_2O$, m. p. 100°, decomp. 230° ; $ZnCl_2,3HX,2H_2O$, decomp. 228° ; $ZnBr_2,2HX,2H_2O$, m. p. 98°, decomp. 335° ; $ZnSO_4,HX,5H_2O$, m. p. 82°, decomp. 320° ; $CuCl_2,CuX_2,2H_2O$, decomp. 195° ; $CuCl_2,CuX_2,HCl$, decomp. 190° ; $CuCl_2,(HCl,HX)_2,2H_2O$, m. p. 96°, decomp. 120°. Analogous compounds with cobalt, nickel, or stannic chlorides were not obtained.

R. Child.

Preparation of ω-amino-acids. B. Flaschenträger. **I. κ-Benzenesulphonylmethylamino-undecoic acid from κ-undecenoic acid.** B. Flaschenträger, F. Halle, and T. Hosoda. **II. Degradation of sebacic acid to δ-aminononoic acid by the Jeffreys–Hofmann method.** B. Flaschenträger and F. Gebhardt. **III. Degradation of normal dicarboxylic acids of high mol. wt. to ω-amino-acids by the Naegeli–Curtius method. Degradation of sebacic acid to δ-aminononoic acid.** B. Flaschenträger and F. Halle. **IV. Degradation of αϕ-heneicosane-dicarboxylic acid to ϕ-aminobehenic acid.** B. Flaschenträger, B. Blechman, and F. Halle (Z. physiol. Chem., 1930, **192**, 245—248, 249—252, 253—257, 257—263).—I. κ-Bromoundecoic acid when heated with alcoholic methylamine at 90—110° (under pressure) yields *κ-methylaminoundecoic acid*, m. p. 136—137°, which forms *κ-benzenesulphonylmethylaminoundecoic acid*, m. p. 47—48°.

II. When sebacamic acid is treated with bromine in methyl alcohol followed by sodium methoxide, it forms *θ-carbomethoxyaminononoic acid*, m. p. 77°. The latter when heated with concentrated hydrochloric acid furnishes *θ-aminononoic acid hydrochloride*, which is isolated as *θ-benzenesulphonamidononoic acid*, m. p. 85°.

III. θ-Carbethoxynonoyl chloride when heated with sodium azide in xylene yields *ethyl θ-carbimidononoate*. The latter when boiled with concentrated hydrochloric acid furnishes *ethyl θ-aminononoate hydrochloride*. Hydrolysis of the ester and removal of the by-product, *carbamido*-NN′-*di*-θ-*nonoic acid*, m. p. 158° (corr.), gives θ-aminononoic acid, isolated as the benzenesulphonyl compound.

IV. *Ethyl hydrogen heneicosanedicarboxylate*, m. p. 83·3° (corr.), obtained by heating together in alcohol the free acid and the normal ester, yields successively by the Naegeli–Curtius method *α-carbethoxyheneicosane-ϕ-carboxyl chloride*, m. p. 59·9° (corr.) ; *ϕ-aminobehenic acid*, m. p. 167° (corr.) ; *ϕ-benzenesulphonamidobehenic acid*, m. p. 114·5° (corr.). *Carbamido*-NN′-*di*-*ϕ-behenic acid*, m. p. about 110°, is obtained as by-product.

J. H. Birkinshaw.

***N*-Alkylation of β-amino-esters.** J. Décombe (Compt. rend., 1930, **191**, 945—947).—Treatment of β-amino-esters with alkyl iodides causes decomposition to ammonia and αβ-unsaturated esters. When an equimolecular mixture of αβ-amino-ester and acetaldehyde is reduced catalytically (Adams) in alcohol, the ethylamino-ester is obtained together with resinous material. The following are prepared : *ethyl β-ethylaminobutyrate*, b. p. 74—75°/12 mm. (*hydrochloride*, m. p. 125° ; free *acid*, m. p. 169—170°) ; *ethyl β-ethylaminohexoate*, b. p. 110—111°/20 mm. (*hydrochloride*, m. p. 79°) ; *ethyl β-ethylamino-octoate*, b. p. 130—132°/20 mm. (*hydrochloride*, m. p. about 60° ; free *acid*, m. p. 140—141°). Similar treatment of a mixture of butaldehyde and ethyl β-ethylaminobutyrate gives a small amount of *ethyl β-ethylbutylaminobutyrate*, b. p. 118—119°/15 mm.

Ethyl β-aminobutyrate has b. p. 68—69°/17 mm., and not 82°/20 mm., as previously reported (A., 1930, 328).

H. Burton.

Synthesis of *dl*-aspartic acid. M. S. Dunn and B. W. Smart (J. Biol. Chem., 1930, **89**, 41—50).—Ethyl sodiophthalimidomalonate (conveniently prepared by the action of sodium on ethyl phthalimidomalonate in boiling toluene) was condensed with ethyl chloroacetate to give *ethyl ethane-α-phthalimido-ααβ-tricarboxylate*, which was hydrolysed with aqueous-alcoholic hydrochloric acid to *dl*-aspartic acid (33%) together with a small amount of glycine. β-Chloropropionitrile and other halogen compounds (except trimethylene bromide) failed to condense with ethyl sodiophthalimidomalonate.

C. R. Harington.

Reduction of cystine in liquid ammonia by metallic sodium. V. du Vigneaud, L. F. Audrieth, and H. S. Loring (J. Amer. Chem. Soc., 1930, **52**, 4500—4504).—Cystine (1 mol.) is reduced to cysteine when a solution in liquid ammonia is treated with sodium (4 atoms). The resulting solution is evaporated, the residue extracted with alcoholic hydrochloric acid, the cysteine hydrochloride crystallised from 20% hydrochloric acid, and then decomposed with ammonia in alcohol, whereby practically pure cysteine is obtained. Treatment of the liquid ammonia solution with benzyl chloride affords α-amino-β-benzylthiolpropionic acid.

H. Burton.

Reduction of *l*-cystine to *l*-cysteine. E. Gebauer-Fülnegg (J. Amer. Chem. Soc., 1930, **52**, 4610—4611).—Cystine is reduced by 1—1·5 parts of aluminium amalgam (Wislicenus, A., 1896, i, 671) in carbon dioxide-free aqueous solution to *l*-cysteine, which is isolated in the usual manner.

H. Burton.

Action of alkali on cystine and cysteine. H. T. Clarke and J. M. Inouye (J. Biol. Chem., 1930, **89**, 399—419).—When cystine or cysteine is boiled in alkaline solution in presence of lead acetate and of phenylhydrazine or of phenylhydrazine-4-carboxylic acid, the phenylhydrazone or *p*-carboxyphenylhydrazone (m. p. 259°) of pyruvic acid is formed in a yield of about 60% from cystine and 80% from cysteine. Pyruvic acid given an orange colour when warmed with salicylaldehyde in alkaline solution ; the same colour is obtained by interaction of salicylaldehyde with alkaline solutions of cystine, cysteine, αβ-dibromopropionic acid, and β-chlorolactic acid. When boiled in alkaline solution in presence of lead cystine yields 75% (larger amounts in presence of reducing agents, *e.g.*, stannite and arsenite) and cysteine the whole of its sulphur as sulphide ; the remainder of the cystine sulphur appears as thiosulphate. Deamination of cystine tends to lag behind desulphurisation.

C. R. HARINGTON.

Optical rotation of *l*-cystine. G. TOENNIES and T. F. LAVINE (J. Biol. Chem., 1930, **89**, 153—166).—Cystine, after careful purification by fractional precipitation, has, in 1% solution in *N*-hydrochloric acid, $[\alpha]^{20}_{5461}$ −241·87° ±0·15° and $[\alpha]^{20}_{D}$ −205·1° ±0·2°. Over the temperature range 20—30° the relationships, $[\alpha]^{t}_{5461}$ = (2·431*t*—312·37) ±0·2° and $[\alpha]^{t}_{D}$ −(2·061*t*—264·84) ±0·2° hold good. C. R. HARINGTON.

***N*-Carbomethoxyformamide.** I. J. RINKES (Rec. trav. chim., 1930, **49**, 1126).—When methyl carbamate is refluxed with 100% formic acid and the product is distilled at 90° in a vacuum *N*-carbomethoxyformamide, identical with the product obtained by ozonolysis of methyl styrylcarbamate (A., 1929, 1296), is obtained. J. W. BAKER.

Action of magnesium ethyl bromide on chloroacetdiethylamide. S. P. TI (Compt. rend., 1930, **191**, 943—945).—Decomposition of the reaction product from chloroacetdiethylamide (1 mol.) and magnesium ethyl bromide (3 mols.) with alkali furnishes diethylamine, 20% of *α-diethylamino-α-ethylbutyl alcohol*, b. p. 90°/18 mm. [*picrate*, m. p. 99°; *chloroplatinate*, m. p. 140—141°; *acetate*, b. p. 97—98°/13 mm. (*picrate*, m. p. 130—131°)], together with small amounts of an unsaturated *base*, $C_{10}H_{21}N$, b. p. 169° (*picrate*, m. p. 74°; *chloroplatinate*, m. p. 142—143°), diethylaminoacetdiethylamide, b. p. 125—126°/20 mm. [picrate, m. p. 121° (lit. 133°); *chloroplatinate*, m. p. 164—165°], and a basic *compound*, $C_{16}H_{34}O_2N_2$, b. p. 160—162°/14 mm. H. BURTON.

Derivatives of *dl*-asparagine. II. S. BERLINGOZZI and G. CAROBBI (Gazzetta, 1930, **60**, 573—582; cf. A., 1928, 158).—Although it has not been found possible to prepare the racemic modification of asparagine, such modifications are obtainable for various derivatives of asparagine. Chloroacetyl-*d*(or *l*)-asparagine, m. p. 150°, d^{15} 1·538, forms monoclinic crystals, $a:b:c$=0·7876 : 1 : 0·4281, β 96° 22′. *Chloroacetyl*-dl-*asparagine*, m. p. 105°, d^{15} 1·560, forms triclinic (pinacoidal) crystals (+H_2O), $a:b:c$= 0·9068 : 1 : 0·8617, α 63° 29′, β 113° 20′, γ 117° 15′. *Benzoyl*-dl-*asparagine*, m. p. 184°, d^{15} 1·433, forms monoclinic crystals, $a:b:c$=0·8865 : 1 : 0·5929, β 92° 12′. *Benzenesulphonyl*-d(or l)-*asparagine*, m. p. 163°, d^{15} 1·434, forms monoclinic crystals, $a:b:c$= 0·7557 : 1 : 0·7105, β 104° 42′, and is optically inactive as sodium salt in aqueous solution. *Benzenesulphonyl*-dl-*asparagine*, m. p. 172°, d^{15} 1·559, forms monoclinic crystals. T. H. POPE.

Adipheptadecylamic acid and sebacheptadecylamic acid. B. FLASCHENTRÄGER and H. LACHMANN (Z. physiol. Chem., 1930, **192**, 268—273).—Heptadecylamine hydrochloride, m. p. 163° (corr.), is converted into the following compounds; *heptadecylamine*; *heptadecyl carbamate*, m. p. 99·5—102·5°; *benzenesulphonylheptadecylamine*, m. p. 64·7°; *heptadecylamine gluconate*, m. p. 140° (decomp.) after softening at 105°; *adipheptadecylamic acid*, m. p. 120° (*ethyl* ester, m. p. 77—77·5°; *barium* salt, decomp. 198°); *sebacheptadecylamic acid*, m. p. 115° (*ethyl* ester, m. p. 82°; *barium* salt, decomp. 204°).

J. H. BIRKINSHAW.

Biuret reaction. II. Di-acid amides. M. M. RISING, J. S. HICKS, and G. A. MOERKE (J. Biol. Chem., 1930, **89**, 1—25).—Biuret, malonamide, and oxamide, together with certain mono- and *s*-dialkyl derivatives of these amides give the biuret reaction with formation of coloured compounds having the general formula $Na_2Cu(amide)_2,nH_2O$. That the copper of these compounds is contained in an electronegative ionic complex is proved by the fact that electrolysis of the alkaline solution leads to the accumulation of the colour in the anodic region and only after long periods to the cathodic deposition of copper. The same applies to the previously described (A., 1929, 196) sodium copper diethylbarbiturate, and structural formulæ are now given which represent the complex ions as consisting of copper united by auxiliary valencies with the nitrogen atoms of four imide or amide groups, respectively; this accounts for the fact that 4 mols. of imide (*loc. cit.*) and only 2 mols. of diamide take part in the formation of the coloured compounds. By treatment of the appropriate amide in aqueous solution with sodium hydroxide (4 mols.) and cupric acetate (1 mol.) the following *compounds* were obtained: *sodium copper biuret*, $Na_2Cu(C_2H_3O_2N_3)_2,2H_2O$; *sodium copper malonamide*, $Na_2Cu(C_3H_4O_2N_2)_2,2H_2O$; *sodium copper oxethylamide*, $Na_2Cu(C_4H_6O_2N_2)_2,4H_2O$; *sodium copper oxdiethylamide*, $Na_2Cu(C_6H_{10}O_2N_2)_2$. The last-named compound is blue, whilst the hydrated salts are pink; those of them, however, which lose their water over phosphoric oxide (*e.g.*, sodium copper oxethylamide) become blue during dehydration. Using nickel acetate, there was obtained *sodium nickel oxethylamide*, $Na_3Ni_2C_{12}H_{37}O_{14}N_6$. *Malonethylamide*, obtained by treatment of ethyl malonamate with ethylamine, had m. p. 122°; it gave the biuret reaction, but the coloured product could not be isolated. C. R. HARINGTON.

Interaction between alkyl Grignard reagents and arsenic trichloride. W. J. C. DYKE and W. J. JONES (J.C.S., 1930, 2426—2430).—Magnesium alkyl halides react with arsenic trichloride forming trialkylarsines; free arsenic is always produced owing to the reducing action of the arsine. The paraffin formed during the preparation of the Grignard reagent can be isolated by shaking the pre-arsine fraction in the final distillation with sulphuric acid. The following are prepared: trimethylarsine; triethylarsine; tri-*n*-butylarsine; *triisobutylarsine*, b. p. 119°/31 mm., d^{25}_4 0·9590, n^{25}_D 1·4627; *tri*-dl-*β-methylbutylarsine*, b. p. 160°/28 mm., d^{25}_4 0·9563, n^{25}_D 1·4696; *tri-γ-methylbutylarsine*, b. p. 167—168°/28 mm., d^{25}_4 0·9504, n^{25}_D 1·4694, and *tri-δ-methylamylarsine*, b. p. 158—160°/5 mm., d^{25}_4 0·9309, n^{25}_D 1·4669. The mean value for the atomic refractivity of arsenic is calculated from these values to be 11·84 for the *D* line.

No arsine could be obtained from magnesium *tert*.-butyl chloride. H. BURTON.

Boron. II. Action of lithium on ethylamminoboron trifluoride. C. A. KRAUS and E. H. BROWN (J. Amer. Chem. Soc., 1930, **52**, 4414—4418).—Ethylamminoboron trifluoride (A., 1929

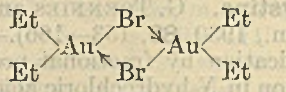
1250) is completely aminolysed in ethylamine solution. Treatment of such a solution with lithium affords hydrogen, lithium fluoride, and *boron triethylimine*, $BF_3+3NH_2Et+3Li=1{\cdot}5H_2+3LiF+B(NHEt)_3$. Boron triethylimine is a liquid which is volatile at the ordinary temperature and readily hydrolysed by water vapour. H. BURTON.

Tin methyl derivatives. VI. Reaction between chloroform and tin sodium trimethyl in liquid ammonia. C. A. KRAUS and A. M. NEAL (J. Amer. Chem. Soc., 1930, 52, 4426—4433).—Tin sodium trimethyl and chloroform react in liquid ammonia forming tin trimethyl and s-*di*(*trimethylstannyl*)*ethylene*, $SnMe_3{\cdot}CH{:}CH{\cdot}SnMe_3$, b. p. 194—195°, separable by successive treatment of an ethereal solution of the mixture with iodine and ammonia whereby the tin trimethyl is precipitated as the compound $SnMe_3I,NH_3$. The ethylene derivative is not affected by bromine at the ordinary temperature, but in boiling carbon tetrachloride tin dimethyl dibromide is produced slowly. When treated with sodium in liquid ammonia it furnishes methane, sodamide, and a mixture of tin sodium trimethyl and sodium dimethylvinylstannide, $CH_2{:}CH{\cdot}SnMe_2Na$. The last-named compound is produced by the action of sodium and ammonia on the intermediately formed trimethylvinylstannane according to the equation $CH_2{:}CH{\cdot}SnMe_3+2Na+NH_3\longrightarrow CH_4+NaNH_2+CH_2{:}CH{\cdot}SnMe_2Na$. Treatment of the above mixture with methyl iodide affords tin tetramethyl and trimethylvinylstannane; the latter has not been obtained pure.

Carbon tetrachloride reacts with sodium tin trimethyl and triethyl forming mainly tin trimethyl and triethyl, respectively. H. BURTON.

Thermal decomposition of gaseous germanium tetraethyl. R. L. GEDDES and E. MACK, jun. (J. Amer. Chem. Soc., 1930, 52, 4372—4380).—Decomposition of germanium tetraethyl, usually in quartz vessels at 420—450°, is followed by measurement of pressure changes; quartz and pyrex glass membrane manometers are used. The reaction is almost wholly homogeneous and is unimolecular at pressures above 80 mm. The velocity coefficient increases with rise of temperature and in presence of 0·1—0·2% of oxygen; the rate is decreased by carbon dioxide, but nitrogen, helium, and argon have little or no effect. Added hydrogen and ethylene enter into hydrogenation and polymerisation reactions, respectively. The products formed by the decomposition are germanium and the pyrolysis compounds of butane (Hurd and Spence, A., 1930, 58). The reactions $GeEt_4\longrightarrow Ge+4Et$ and $2Et\longrightarrow C_4H_{10}$ may occur. H. BURTON.

Organic compounds of gold. I. Diethylgold bromide and derivatives. C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1930, 2531—2536).—Determinations of the mol. wt. of diethylgold bromide (Pope and Gibson, J.C.S., 1907, **91**, 2061) (complete details given for its preparation from magnesium ethyl bromide and gold tribromide) by the cryoscopic method in benzene show that it has the composition $(AuEt_2Br)_2$; it is represented as (I). The bromide is acted on slowly by water with the production of ionisable bromine, probably owing to the tendency of formation of the salt (II). Treatment of the bromide with methyl-alcoholic pyridine furnishes *pyridinodiethylgold bromide* $[AuEt_2Br,C_5H_5N]$, m. p. 59—60° (decomp.; explosive decomp. at about 79°), which, like the ammino-derivative (*loc. cit.*), darkens rapidly when exposed to light. With ethylenediamine in light petroleum, *ethylenediaminodiethylgold bromide* (III), becomes red at 182° and then decomposes gradually, is obtained. Thallous acetylacetone and diethylgold bromide in alcohol give *diethylgold acetylacetone* (IV), m. p. 9—10°, which with bromine in carbon tetrachloride regenerates the bromide. Treatment of IV with sodium iodide in alcohol furnishes *diethylgold iodide*, m. p. 67—68° (vigorous decomp. at 70—71°), which with ethylenediamine in light petroleum gives *ethylenediaminodiethylgold iodide*, m. p. 162° (decomp.). In all the above compounds gold has a co-ordination number of 4. H. BURTON.



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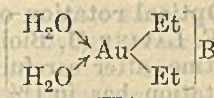

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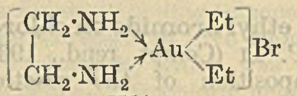

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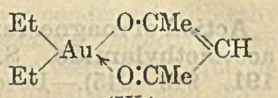


(IV.)

Distillation of Grignard reagents. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 4480—4483).—Magnesium alkyl halides (or their equivalents MgR_2+MgX_2) can be distilled by the method previously used for organoberyllium compounds (A., 1928, 50). Magnesium phenyl bromide could not be distilled; during the process, some diphenyl is formed (possibly by the change $RMgX\longrightarrow R{\cdot}+{\cdot}MgX$). High-vacuum sublimation of magnesium alkyl halides gives magnesium dialkyls. H. BURTON.

Determination of constitution by the displacement of groups from the benzene nucleus. J. W. DIENSKE (Rec. trav. chim., 1930, 49, 1096—1081).—A theoretical paper in which cases of the replacement of one substituent in an aromatic compound by another are systematically summarised. The structure of *p*-thiocyanoaniline (cf. A., 1927, 454) is confirmed by the fact that *p*-chloro(or bromo)thiocyanobenzene is obtained by the appropriate Sandmeyer reaction on either *p*-thiocyanoaniline or *p*-chloroaniline. The observation of Challenger and Collins (A., 1924, i, 953) that *p*-iodothiocyanobenzene is not obtained by the action of cuprous thiocyanate on diazotised *p*-iodoaniline is confirmed. J. W. BAKER.

Behaviour of benzenoid hydrocarbons in the Tesla discharge. J. B. AUSTIN and I. A. BLACK (J. Amer. Chem. Soc., 1930, 52, 4552—4557).—When vapours of aromatic hydrocarbons are excited by the Tesla discharge (cf. A., 1930, 660) two types of compounds are produced: (*a*) shellac-like substances containing oxygen, probably condensed molecules of a phenolic type and (*b*) simple crystalline products. The crystalline products formed from the following substances are quoted in parentheses: benzene (diphenyl), toluene (dibenzyl and di-*o*-tolyl), *p*-xylene (di-*p*-tolylethane), and chlorobenzene (diphenyl; in this case benzene and chlorine are also produced). The low and high refractive indices of dibenzyl are 1·53 and 1·74, respectively.

H. BURTON.

Action of sodium methoxide on derivatives of o-dichlorobenzene. G. M. KRAAY (Rec. trav. chim., 1930, 49, 1082—1092).—The action of sodium methoxide at 180° on the following halogenobenzene derivatives has been investigated: 1 : 2-dichloro-4-nitrobenzene, 3 : 4-dichloroaniline, 3 : 4-*dichlorofluorobenzene* (A., 1929, 1170), 1 : 2 : 4-trichlorobenzene, 3 : 4-dichlorobromobenzene (best obtained by the Sandmeyer reaction from 3 : 4-dichloroaniline), 3 : 4-*dichloroiodobenzene*, b. p. 117°/15 mm., m. p. 30·5° (obtained in 83% yield from 1 : 2-dichloroaniline by the Sandmeyer reaction), 3 : 4-dichlorobenzenesulphonic acid, 3 : 4-*dichlorobenzonitrile*, m. p. 71·8—72·1° (obtained by the action of cuprous cyanide on 3 : 4-dichlorobenzenediazonium chloride), 3 : 4-dichlorophenol (converted by dissolving in concentrated sulphuric acid into its 6(?)-*sulphonic acid*, m. p. 75—76°), 3 : 4-dichlorotoluene, 3 : 4-*dichloronitrosobenzene*, m. p. 88° (prepared by oxidation, with potassium dichromate and sulphuric acid, of 3 : 4-dichlorophenylhydroxylamine, the latter being converted, in alcoholic solution, by atmospheric oxidation into 3 : 4 : 3′ : 4′-*tetrachloroazoxybenzene*, m. p. 139—139·5°), 3 : 4-dichlorobenzophenone, 3 : 4-dichlorobenzaldehyde, m. p. 38° (lit. m. p. 77°), and 3 : 4-dichlorobenzoic acid, m. p. 208—209° (lit. m. p. 204·1—206·5°). The product of the action of sodium methoxide on these compounds is, respectively, I 1-chloro-group replaced, II a resin, III 3 : 4-dichloroanisole, converted into the phenol by prolonged action, IV 2 : 5-dichlorophenol (Holleman, A., 1916, i, 22), V 2-*chloro*-5-*bromophenol*, m. p. 57°, identical with a specimen obtained by the diazo-reaction from 2-chloro-5-bromoaniline, prepared by reduction of the corresponding nitro-compound, VI 3 : 4-dichlorophenol and 2-*chloro*-5-*iodophenol*, m. p. 56·5°, identical with a specimen synthesised by the action of potassium iodide on diazotised 4-chloro-3-nitroaniline to yield 1-*chloro*-4-*iodo*-2-*nitrobenzene*, m. p. 74·5°, reduction of this with titanous chloride to 2-*chloro*-5-*iodoaniline*, m. p. 61·6°, and conversion into the phenol by diazotisation; VII 2-chlorophenol-4-sulphonic acid, converted by nitric acid (*d* 1·52) into 2-chloro-4 : 6-dinitrophenol; VIII hydrolysis of the nitrile group; IX no action; X 4-chloro-*m*-cresol, m. p. 46° (Gibson, A., 1926, 832, gives m. p. 57°), identical with a specimen obtained from 4-chloro-*m*-toluidine by the diazo-reaction; XI 3 : 4 : 3′ : 4′-tetrachloroazoxybenzene; XII—XIV, chlorine partly replaced, but the products were not identified. Under comparable conditions the amount of the halogen replaced is as follows: I 83(F) and 4(Cl); II 72; III 83(Cl) and a trace of bromine; IV 94(Cl+I); V 79; VI 3; VII 20; and VIII 0%, respectively.

J. W. BAKER.

Direct *meta*-substitution in the toluene nucleus. J. B. SHOESMITH and J. F. MCGECHEN (J.C.S., 1930, 2231—2236).—*tert.*-Butyl chloride reacts with toluene in presence of aluminium chloride at 0—5° forming 46% of the theoretical amount of a mixture of *m*- (6·5—7 parts) and *p*-*tert.*-butyltoluenes (3—3·5 parts); in presence of nitrobenzene the yield is improved to 70% without affecting the ratio. Baur's statement (A., 1891, 1464) that only the *m*-derivative is produced is, therefore, incorrect. A similar mixture is produced from *sec.*-butyl bromide and toluene in presence of aluminium chloride or from the above reactants in presence of ferric chloride (cf. Bialobrzeski, A., 1897, i, 514, who states that only the *p*-compound is formed). The amounts of isomerides produced are determined either by treating the mixture with sulphuric acid at the ordinary temperature, extracting the unaffected *p*-derivative, and regenerating the *m*-*tert.*-butyltoluene from its sulphonic acid by distillation with superheated steam, or by complete sulphonation of the mixture at 100° and fractional crystallisation of the *barium* salts of the sulphonic acids produced. Toluene and *n*-butyl chloride in presence of aluminium chloride give 45% of the theoretical amount of a mixture of *m*- (75 parts) and *p*-*sec.*-butyltoluenes (25 parts); the latter is unaffected by sulphuric acid at the ordinary temperature.

Magnesium *m*- and *p*-tolyl bromides react with methyl ethyl ketone forming the corresponding carbinols, which are dehydrated with boiling acetic anhydride to β-*m*- and β-*p*-tolyl-Δ^{β}-butenes, respectively. The former of these is reduced with sodium and alcohol to *m*-*sec.*-butyltoluene, b. p. 194—198° (*sulphonyl chloride*, b. p. 164—165°/11 mm.; *sulphonanilide*, m. p. 119·5—120·5°), and the latter with red phosphorus and hydriodic acid (b. p. 127°) to *p*-*sec.*-butyltoluene (*sulphonyl chloride*, b. p. 162—164°/12 mm.; *sulphonanilide*, m. p. 124·5—125°). These unoriented sulphonic acid derivatives were also prepared from the hydrocarbons obtained in the Friedel–Crafts reaction.

The observations (lit.) that toluene and acetyl chloride in presence of aluminium chloride give *p*-tolyl methyl ketone are confirmed.

H. BURTON.

Diphenyl-2 : 2′-disulphonic acid. VIII. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 4471—4476).—Reduction of azobenzene-3 : 3′-disulphonic acid with stannous chloride and hydrochloric acid gives 4 : 4′-diaminodiphenyl-2 : 2′-disulphonic acid [*strychnine* salt, m. p. 310—318° (decomp.), $[\alpha]_D^{20}$ −22·4° in water; *brucine* salt, m. p. 311—314° (decomp.), $[\alpha]_D^{20}$ −24·6° in water], convertible by the usual method into diphenyl-2 : 2′-disulphonic acid [*brucine* salt, m. p. 245—248°, $[\alpha]_D^{20}$ −33·2° in chloroform; *quinine* salt, m. p. 189—192°, $[\alpha]_D^{20}$ −83·5° in chloroform; *morphine* salt, m. p. 261—267° (decomp.), $[\alpha]_D^{20}$ −75·1° in water]. No evidence of resolution was obtained, although the size of the sulphonic acid group is sufficiently large to interfere with the 6(6′)-hydrogen atom.

H. BURTON.

Reaction between triphenylmethyl, magnesium, and a small amount of magnesium halide. Composition of the Grignard reagent. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 4412—4413).—Magnesium reacts with triphenylmethyl in presence of a small amount of magnesium iodide (not in its absence) in ethereal benzene in an atmosphere of nitrogen forming magnesium triphenylmethyl, which is hydrolysed to triphenylmethane. The reactions taking place are: $2CPh_3+Mg+MgI_2\longrightarrow 2CPh_3\cdot MgI\rightleftharpoons(CPh_3)_2Mg+MgI_2$, *i.e.*, a small amount of magnesium iodide causes continuous reaction. Magnesium triphenylmethyl is also produced when triphenylmethyl and magnesium react in presence of a small amount of triphenylmethyl bromide; in this case, the bromide is converted into triphenylmethyl and magnesium bromide with subsequent reaction as above. H. BURTON.

***s*-Diphenyldi-*n*-alkylethanes and their stereoisomerism.** A. LEEPIN (Latvij. Univ. Raksti, 1930, **1**, 145—232).—α-Bromoethylbenzene is converted by treatment with magnesium into a mixture of *dl*-, b. p. 283—284°/752 mm., 140°/10 mm., m. p. 8°, d_4^{20} 0·9757, n^{20} 1·55516, and *meso*-, m. p. 126°, -βγ-diphenyl-*n*-butanes. Sodium reacts with α-halogenoalkylbenzenes, $CHXPh\cdot CH_2Alk$, forming mixtures of *s*-diphenyldi-*n*-alkylethanes, $(CHPh\cdot CH_2Alk)_2$, structural isomerides of these, the ethylenes, $CHPh{:}CHAlk$, and the alkylbenzenes, $CH_2Ph\cdot CH_2Alk$. The following *s*-diphenyldi-*n*-alkylethanes are described: *dl*-, b. p. 297—298°/767 mm., d_4^{20} 0·9591, n^{20} 1·54622, and *meso*-, m. p. 90°, -γδ-diphenyl-*n*-hexanes; *dl*-, b. p. 178—179°/13 mm., d_4^{20} 0·9452, n^{20} 1·53663, and *meso*-, m. p. 98°, -δε-diphenyl-*n*-octanes; *dl*-, b. p. 183—184°/10 mm., d_4^{20} 0·9337, n^{20} 1·52857, and *meso*-, m. p. 79·5°, -εξ-diphenyl-*n*-decanes; *dl*-, b. p. 223—224°/10 mm., d_4^{20} 0·9174, n^{20} 1·51770, and *meso*-, m. p. 59°, -ηθ-diphenyl-*n*-tetradecanes. The m. p. of the *meso*-forms decrease (with alternation) with increasing length of the carbon chain, whilst for the *dl*-modifications, the density decreases with increased carbon content. Both *dl*- and *meso*-forms are oxidised to phenyl *n*-alkyl ketones; the m. p. of the semicarbazones decrease (with alternation) with the length of the alkyl group. The same equilibrium mixture is obtained when either modification is heated at 230—300° in presence of a catalyst such as iodine.

The mechanism of the formation of the structural isomerides of the above stereoisomeric hydrocarbons is discussed and various observations are made regarding the Wurtz–Fittig reaction. An explanation of the mechanism of racemisation is made from the viewpoint of the chemical theory of catalysis. Racemisation and the Walden inversion are considered from a common viewpoint as two phenomena identical in principle. H. BURTON.

Synthesis of alkylnaphthalenes. II. 1:3:5- and 1:3:8-Trimethylnaphthalenes. I. M. HEILBRON and D. G. WILKINSON (J.C.S., 1930, 2537—2542).—2 : 4-Dimethylbenzaldehyde condenses with ethyl acetate in presence of sodium wire forming *ethyl* 2 : 4-*dimethylcinnamate*, b. p. 135—137°/5 mm., reduced by sodium and alcohol to γ-2 : 4-*dimethylphenylpropyl alcohol*, b. p. 126°/5 mm. (*phenylcarbimide* derivative, m. p. 81°). This is converted by way of the *bromide*, b. p. 147°/18 mm., and nitrile, b. p. 175—177°/23 mm., into γ-2 : 4-*dimethylphenylbutyric acid*, m. p. 78—79° (*amide*, m. p. 128—129°, formed as a by-product during the preparation of the nitrile); the *acid chloride*, b. p. 136—138°/9 mm., is then converted by treatment with aluminium chloride under the conditions previously described (A., 1930, 593) into 5-*keto*-1 : 3-*dimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 160°/14 mm. [*semicarbazone*, m. p. 243—246° (decomp.)]. The carbinol from this ketone and magnesium methyl iodide is dehydrated by boiling acetic anhydride to 1 : 3 : 5-*trimethyl*-7 : 8-*dihydronaphthalene*, b. p. 143—145°/18 mm., which is dehydrogenated by selenium to 1 : 3 : 5-*trimethylnaphthalene*, m. p. 47° (*picrate*, m. p. 141—142°; *styphnate*, m. p. 138°).

2 : 4-Dimethylacetophenone and ethyl bromoacetate react in presence of zinc and benzene forming mainly impure *ethyl* β-*hydroxy*-β-2 : 4-*dimethylphenylbutyrate*, b. p. 170—180°/20 mm. (free *acid*, m. p. 70—72°), dehydrated by treatment with phosphoryl chloride in benzene to *ethyl* β-2 : 4-*dimethylphenylcrotonate*, b. p. 160—170°/20 mm. Reduction of this gives a mixture of γ-2 : 4-*dimethylphenylbutyl alcohol*, b. p. 152—153°/19 mm. (*bromide*, b. p. 143°/17 mm.), and β-2 : 4-*dimethylphenylbutyric acid*, m. p. 69°, the *ethyl* ester, b. p. 168—170°/25 mm., of which is reduced by sodium and propyl alcohol at 130° to the alcohol. The *chloride*, b. p. 157—160°/18 mm., of γ-2 : 4-*dimethylphenylvaleric acid*, b. p. 175°/9 mm. (*amide*, m. p. 91—92°), when treated with aluminium chloride in light petroleum (b. p. 90—100°) affords 5-*keto*-1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 174—176°/20 mm. (*semicarbazone*, m. p. 220—222°), reduced by Clemmensen's method to 1 : 3 : 8-*trimethyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. 133—136°/18·5 mm. This is dehydrogenated by selenium at 300° to 1 : 3 : 8-*trimethylnaphthalene*, m. p. 48° (*picrate*, m. p. 125°; *styphnate*, m. p. 140·5°). H. BURTON.

Unsaponifiable matter from oils of elasmobranch fish. VIII. Structure of the naphthalene hydrocarbon derived from squalene. I. M. HEILBRON and D. G. WILKINSON (J.C.S., 1930, 2546—2554).—The naphthalene hydrocarbon previously obtained (A., 1927, 130) by dehydrogenation of tetra*cyclo*squalene with sulphur or, better, with selenium at 300° is 1 : 2 : 5-trimethylnaphthalene, since it is not identical with the 1 : 3 : 8-isomeride (preceding abstract) and is oxidised to a series of products which can arise only from either the 1 : 2 : 5- or 1 : 3 : 8-derivatives. Prolonged oxidation of the hydrocarbon with potassium ferricyanide in potassium hydroxide solution at 60° affords *naphthalene*-1 : 2 : 5-*tricarboxylic acid*, m. p. 270—272° (*methyl* ester, m. p. 89°), whilst oxidation with chromic acid in 80% acetic acid at 60° furnishes a mixture of the following substances: a 1 : 2 : 5-*trimethyl*-β-*naphthaquinone*, decomp. 130—135°, isolated in appreciable amount only when oxidation is arrested before completion; 1 : 6-dimethyl-α-naphthaquinone, m. p. 94° (*phenylhydrazone*, m. p. 226°); (?)5 : 8-*diacetoxy*-1 : 6-*dimethylnaphthalene*, m. p. 70—71°; 3-*methylacetophenone*-2-*carboxylic acid*, m. p. 126° {*semicarbazone*, m. p. 177° (decomp.); *methyl* ester, m. p. 47—48° [*semicarbazone*, m. p. 215° (decomp.)]}, oxidised by sodium hypobromite to 3-methylphthalic acid; 4-*methylacetophenone*-2-*carboxylic acid*, m. p. 125—126° [*semicarbazone*, m. p. 182° (decomp.); *methyl* ester, m. p. 71—72°]; 3 : 4-*dimethylacetophen*-

one-2-carboxylic acid, m. p. 105° [*semicarbazone*, m. p. 217° (decomp.); *methyl* ester, m. p. 78—79°]. 3-Methylacetophenone-2-carboxylic acid crystallises from the acid fraction; the other acids are separated from the residue by fractionation of the mixed methyl esters. During the oxidation with chromic acid scission of the hydrocarbon occurs in both rings.

The formation of 1 : 2 : 5-trimethylnaphthalene from a sesquiterpene of the farnesene type can be formulated; two methyl groups must be eliminated on passing from the hydroaromatic to the aromatic condition.

H. Burton.

Purification of phenanthrene. F. L. Cohen and U. Cormier (J. Amer. Chem. Soc., 1930, 52, 4363—4364).—Crude phenanthrene is crystallised from 95% alcohol and this material (1 kg.) heated with alcohol (6 litres) and concentrated nitric acid (120 g.). The resultant solution (freed, if necessary, from insoluble oxidation products) is cooled, the crystalline material distilled in portions of 500 g., and finally crystallised from alcohol. The overall yield of pure phenanthrene, m. p. 99—99·5°, is 30—45% of the crude product.

H. Burton.

Pyrolysis of allylanilines. F. L. Carnahan and C. D. Hurd (J. Amer. Chem. Soc., 1930, 52, 4586—4595).—When allylaniline [p-*toluenesulphonyl* derivative, m. p. 69·3° (corr.)] is heated at 275°, aniline, propylene, and resinous material are produced (cf. Dains and others, A., 1923, i, 62). At 600°, propylene, ethylene, hydrogen, carbon monoxide, nitrogen, gaseous paraffin hydrocarbons, a small amount of benzene, aniline, and unidentified products are formed; at 700°, a small amount of quinoline is also obtained. Diallylaniline decomposes at 275° to a mixture of products similar to that obtained from allylaniline. *Diallyl*-p-*phenetidine*, b. p. 164—165°/23 mm., d_4^{23} 0·9921, n_D^{22} 1·5458, affords similarly mainly propylene, *p*-phenetidine [p-*toluenesulphonyl* derivative, m. p. 110° (corr.)], and resinous material. Various mechanisms are suggested for the changes; allene is not a product of the pyrolysis.

H. Burton.

Rhythmic phenomena in the combination of methylethylaniline with ethyl iodoacetate. P. Freundler and (Mlle.) Pilaud (Bull. Soc. chim., 1930, [iv], 47, 1151—1157).—When equimolecular quantities of ethyl iodoacetate and diethyl- or methyl-*iso*butyl-aniline are mixed the clear mixture gradually becomes turbid and a coloured syrup accumulates at the bottom of the vessel which in some cases has the consistency of a gel. The surface of separation is sharp and after a rapid initial increase the volume of syrup gradually becomes constant, the syrup then containing, in the case of diethylaniline, the quaternary iodide with about 20% of iodoacetate, whilst the supernatant liquid consists of nearly pure tertiary amine.

With methylethylaniline turbidity first appears after about 2 hrs. 20 min. and the limit is reached in 4 days, the rate of combination decreasing rapidly after 12 hrs. No sensible heat of reaction is observed and there is a final contraction of about 6% by volume, the viscosity of the suspended drops increasing as the volume of syrup increases. A periodic stratification of coloured zones appears at intervals of 24 hrs. and persists for 1—2 months until diffusion gradually renders the surface of separation less sharp. The stratification is intensified when the tube is surrounded with silver. The phenomenon is regarded as due to the nature of the material, in particular the nitrogen atom, and not to external factors.

R. Brightman.

Reduction of Schiff's bases. L. Zechmeister and J. Truka (Ber., 1930, 63, [*B*], 2883—2884).—The Schiff's base is dissolved in nearly anhydrous methyl alcohol and treated with at least five times the theoretical quantity of magnesium; the mixture is heated or cooled as required. After disappearance of the metal, the alcohol is mainly recovered by distillation; the residue is treated with ice-water and sufficient 30—50% acetic acid to dissolve the magnesium hydroxide. The following bases are obtained in 70—90% yield: benzylaniline, m. p. 37—38°; *p*-methoxybenzylaniline, m. p. 64·5°; γ-phenylpropylaniline, b. p. 193—195°; *o*-hydroxybenzylaniline, m. p. 108°; phenylpiperonylamine, m. p. 78°; *p*-dimethylaminobenzylaniline, m. p. 62°; benzyl-*p*-toluidine, b. p. 318—320°; methoxybenzyl-*p*-toluidine, m. p. 65°; benzyl-α-naphthylamine, m. p. 67°; methoxybenzyl-α-naphthylamine, m. p. 80°; benzyl-β-naphthylamine, m. p. 68°; methoxybenzyl-β-naphthylamine, m. p. 104·5°.

H. Wren.

αγ-Migration of [aryl]amino-groups. Mechanism. Applications to other analogous reactions. J. Robin (Compt. rend., 1930, **191**, 1013—1015; cf. A., 1930, 1571).—In addition to that named in the title, two mechanisms are suggested for the transformation $\mathrm{NHPh{\cdot}CPh_2{\cdot}C⋮CPh \longrightarrow CPh_2{:}CH{\cdot}CPh{:}NPh}$; the first, involving αγ-migration of a phenyl group and subsequent rearrangement, is disproved, since $\mathrm{NHPh{\cdot}CPh_2{\cdot}C⋮C{\cdot}C_7H_7}(p)$ yields, not $\mathrm{NPh{:}CPh{\cdot}CH{:}CPh{\cdot}C_7H_7}(p)$, but $\mathrm{CPh_2{:}CH{\cdot}C({:}NPh){\cdot}C_7H_7}(p)$. The second mechanism involves addition of hydrogen chloride to the triple linking followed by simultaneous elimination of aniline and condensation with an external aniline molecule. In support, it is found that compounds $\mathrm{CAr_2Cl{\cdot}C⋮CAr}$ give unstable but well-defined hydrochlorides, which are very sensitive to water, being converted into unsaturated ketones, $\mathrm{CAr_2Cl{\cdot}CH{:}CClAr \longrightarrow CAr_2{:}CH{\cdot}COAr}$. This mechanism is adopted (the aniline and water acting similarly) and the αγ-migration of arylamino-groups is therefore only apparent. It is suggested that a similar mechanism should apply to other transformations, apparently involving αγ-migration, of acetylenic compounds. The *hydrochlorides* of diphenyl-β-naphthyl- and diphenyl-*p*-bromophenyl-ethinyl chloride have m. p. 155° and 100°, respectively.

C. W. Shoppee.

Acenaphthene series. V. G. T. Morgan and H. A. Harrison (J.S.C.I., 1930, 49, 413—421T).—The substances previously described as 1-nitro- and 1-amino-acenaphthene and derivatives (A., 1925, i, 1144) are impure forms of the 3-nitro-compounds (cf. J.S.C.I., 1928, 47, 16T). Nitration of acenaphthene with benzoyl nitrate or diacetylorthonitric acid under carefully regulated conditions does, however, give 1-*nitroacenaphthene*, m. p. 151°, characterised by the greyish-blue colour of its solution in cold concentrated sulphuric acid, which rapidly changes to bright red; this test serves for its detection in the products of nitration under ordinary conditions. On oxidation it gives 1-*nitro*-7 : 8-*dihydroxyacenaphthene*, orange-red, m. p. 137—139°, and 2-*nitronaphthylic acid*, m. p. 173—175° (as anhydride, m. p. 190—200°). 1-*Aminoacenaphthene*, m. p. 81·5° (*hydrochloride*; *sulphate* (+1H_2O), m. p. 235°; *picrate*, decomp. 221°: *formyl*, m. p. 151—152°; *acetyl*, m. p. 192—193°; *benzoyl*, m. p. 209—210°; *benzylidene*, m. p. 65—66°; o-*nitrobenzylidene*, m. p. 143·5—144·5°; m-*nitrobenzylidene*, m. p. 142·5—143·5°; and p-*nitrobenzylidene*, m. p. 157—158°, derivatives) is formed on reduction, accompanied by a little 1 : 6-*diaminoacenaphthene*, m. p. 167—168°, when the crude 3-nitro-compound is employed. 1-*Chloro*-, m. p. 76—77°, 1-*bromo*-, m. p. 78°, 1-*iodo*-, m. p. 87°, and 1-*hydroxy-acenaphthene*, m. p. 151—151·5°, are prepared through the diazo-compound, and 1-*amino-acenaphthenemono*-, -di-, and -tri-sulphonic acids by direct sulphonation.

Nitration of 1-formamidoacenaphthene in acetic acid at 12° gives 3-*nitro*-, m. p. 260—262° (decomp.), and 2(?)-*nitro*-1-*formamidoacenaphthene*, m. p. 193—196°; the former is readily hydrolysed to 3-*nitro*-1-*aminoacenaphthene*, m. p. 199—200° (*hydrochloride*, decomp. 235°). No similar product was obtained from 1-acetamidoacenaphthene, but 1-benzamidoacenaphthene gave the 3(?)-*nitro*-derivative, m. p. 215—216°. 1 : 4-*Dinitro*-, decomp. 205—206°, and a little 1 : 6-*dinitro-acenaphthene*, m. p. 155—156°, are obtained by dissolving the 1-nitro-compound in nitric acid; the latter is more readily prepared by use of diacetylorthonitric acid; this reagent with 3-nitroacenaphthene appears to give a mixture of 1 : 4- and 3 : 4-dinitroacenaphthenes. Partial reduction of the appropriate dinitro-compound with stannous chloride and hydrochloric acid in glacial acetic acid gives 4-*nitro*-1-*aminoacenaphthene*, m. p. 181°. The action of excess of nitric acid, followed by hydrochloric acid at 70°, on acenaphthene dissolved in glacial acetic acid gives 4-chloro-3-nitro- and the 4-chloronitro-acenaphthene of Farnell (J.C.S., 1923, **123**, 60); from the reduction product of the former 3 : 4-*dichloroacenaphthene*, m. p. 169—170°, may be obtained by the Sandmeyer reaction. It is more conveniently prepared from 3-chloroacenaphthene and sulphuryl chloride, and is converted by fuming nitric acid at 10° into a *mono*-, m. p. 157—160°, and *di-nitro*-derivative, m. p. 248—250°. Reduction of 3-nitro- with zinc dust and alcoholic calcium chloride gives 3-*azoxy-acenaphthene*, m. p. 180°. *Di*-3-*acenaphthenyl ether*, m. p. 210—215°, is prepared by heating 3-chloroacenaphthene with methyl-alcoholic alkali at 200—210°, or from the sodium 3-sulphonate with aqueous alkali under identical conditions. The following also are described: *acenaphthene*-3-*diazonium chloroaurate*; 3-*acenaphthenylazoimide*, m. p. 66—68° (from sodium azide and the diazonium salt); 3′-*acenaphthene*-2-*azo*-3-*acenaphthenol*, m. p. above 305° (by diazotisation of 3-aminoacenaphthene under special conditions); 3 : 3′-*diamino*-2 : 2′-*diacenaphthenylmethane*, brick-red, m. p. 226—229°, and an *acenaphtheneacridine*, m. p. above 300° (from 3-aminoacenaphthene hydrochloride and formaldehyde in alcoholic solution); 2-*iodoacenaphthene*, m. p. 88—90°; p-*nitrobenzenediazo*-1-*amino*-, m. p. 140—142°, and -3-*amino-acenaphthene*, m. p. 170—173°. The oxidation of acenaphthene and its 3-nitro- and 3-chloro-derivatives by a variety of agents to the quinone and naphthalic acid, and the preparation of resins from acenaphthene or its 3-chloro- (but not 3 : 4-dichloro-)derivative and formaldehyde are described. The acenaphthene resin can be oxidised to a tricarboxylic acid, probably $C_{13}H_8O_6$, m. p. 265—268°.

H. A. Piggott.

p-Aminophenylguanidine hydriodide. C. E. Braun (J. Biol. Chem., 1930, **89**, 97—108).—Equimolecular proportions of *S*-methyl*iso*thiocarbamide hydriodide and *p*-phenylenediamine, when heated together in aqueous or alcoholic solution, yield p-*aminophenylguanidine hydriodide*, m. p. 209—210°. Solubility data are given for this salt. In doses of 5—10 mg. per kg. the compound exercised a definite hypoglycæmic effect in rabbits without apparent toxic action.

C. R. Harington.

Constitution and reactions of isomeric diazohydroxides. A. Angeli (Atti R. Accad. Lincei, 1930, [vi], **11**, 923—929).—Polemical against Hantzsch (A., 1930, 1032).

T. H. Pope.

Double linking. II. Spatial configuration of aromatic azo-compounds. E. Bergmann, L. Engel, and S. Sándor (Ber., 1930, **63**, [*B*], 2572—2575).—The dipole moments of azobenzene and 4 : 4′-dibromoazobenzene are zero, whereas 4-chloro- and 4-bromo-azobenzene have exactly the dipole moments of chlorine and bromine as deduced from chloro- and bromo-benzene. The azo-hydrocarbons have therefore the *trans* structure.

H. Wren.

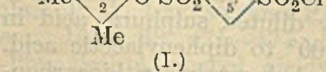
Group influence on the colours of substituted benzeneazophenols, including o-azophenols. H. H. Hodgson and W. Rosenberg (J.S.C.I., 1930, **49**, 405—408T; cf. B., 1929, 1008; A., 1930, 906).—The results obtained are discussed from the viewpoint of modern electronic theory under five headings. (*a*) Differences between the isomeric *o*- and *p*-hydroxy-azo-dyes. Here in all the cases investigated, coupling in *o*-position produces a deeper (redder) dye than does coupling in *p*-position. (*b*) Influence of groups on the colours of substituted *o*-hydroxyazo-dyes. (*c*) Influence of halogeno-substitution in *o*-position to the hydroxyl group in the *p*-hydroxyazo-dyes. Each of the aniline→*o*-halogenophenol dyes is found to be redder than unsubstituted benzeneazophenol, which establishes that in all cases ionisation has been promoted by the general effect of the halogen. The order of electronic restraint being Cl>Br>I, the consequent order of electronic mobility with attendant ease of photo-activation will be I>Br>Cl as observed. (*d*) Influence of the nitro- and sulphonic acid groups when in the aniline (first) component. An electronic explanation is given for the effect of the nitro-group in *p*-position greatly exceeding that in the *o*- and *m*-positions, respectively. (*e*) Influence of chlorine, especially in positions adjacent to the azo-group. Here certain additive relationships are indicated and an explanation is given for the greater effect of two chlorine atoms *ortho-* to the azo-group when in the phenolic than when in the other nucleus.

Action of ferric chloride on acyl esters of phenol. H. Huber and K. Brunner (Monatsh., 1930, **56**, 322—330).—When phenyl acetate is heated with an equal weight of anhydrous ferric chloride at 100° (bath), *p*-hydroxyacetophenone is obtained in 10% yield (on ester used); at 65° the yield is improved to 25%. Similar treatment of phenyl *iso*butyrate affords p-*hydroxyphenyl* iso*propyl ketone* (16% yield), m. p. 56°, and a small amount of the o-*isomeride*, an oil, b. p. about 110°/10 mm. (*oxime*, m. p. 129°; *dibromo*-derivative, m. p. 97°), whilst phenyl benzoate gives a mixture of 2- and 4-hydroxybenzophenone (28% yield; *phenylhydrazone*, m. p. 144°; *semicarbazone*, m. p. 194°). Diphenyl derivatives were not isolated in any of the above experiments. H. Burton.

Action of aromatic alcohols on aromatic compounds in presence of aluminium chloride. V. Benzylation of *o*-cresol. R. C. Huston, H. A. Swartout, and G. K. Wardwell (J. Amer. Chem. Soc., 1930, **52**, 4484—4489).—Benzyl alcohol (1 part) reacts with *o*-cresol (1 part) in presence of aluminium chloride (0·65 part) and light petroleum (2 parts) at 30—35°, forming mainly 5-*benzyl*-o-*cresol*, b. p. 167—169°/5 mm., m. p. 49·5—50·5° (*benzoate*, m. p. 54—55°; 3-*bromo*-derivative, b. p. 182—184°/5 mm.), together with small amounts of 3-benzyl-*o*-cresol, b. p. 150—152°/5 mm., m. p. 49·5—50·5° (*benzoate*, b. p. 216—218°/5 mm.; 5-*bromo*-derivative, b. p. 187—189°/5 mm., m. p. 63—64°, prepared also from benzyl chloride and sodium 5-bromo-*o*-tolyloxide in toluene), and 3 : 5-*dibenzyl*-o-*cresol*, b. p. 225—227°/5 mm. Benzyl chloride and sodium *o*-tolyloxide in toluene afford the above 3-benzyl-*o*-cresol (cf. Schorigin, A., 1925, i, 1404). 5-Benzyl-*o*-cresol, zinc ammonium chloride, and ammonium chloride at 330° give a small amount of 4-amino-3′-methyldiphenylmethane, which after elimination of the amino-group and subsequent oxidation with potassium dichromate and sulphuric acid yields *m*-benzoylbenzoic acid. H. Burton.

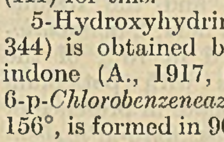
Action of chlorosulphonic acid on phenols. VI. Xylenol-sulphonyl chlorides and -sulphonylides. E. Katscher (Monatsh., 1930, **56**, 381—390).—The action of chlorosulphonic acid on five xylenols is investigated.

[With H. Lehr, A. Harnisch, and L. Steinhardt.] Treatment of *vic.-o*-xylenol with 10 parts of chlorosulphonic acid at −5° to 0° (bath) gives water-soluble products; at 110° a mixture of approximately equal amounts of the 4 : 6-*disulphonyl chloride*, m. p. 104—105° (*disulphonanilide*, m. p. 232°), and 2 : 3 : 2′ : 3′-*tetramethyldiphenyl*-1 : 6 : 1′ : 6′-*sulphonylide*-4 : 4′-*disulphonyl chloride* (I), decomp. 295° (*disulphonanilide*, m. p. 273°). *o*-4-Xylenol is converted similarly at the ordinary temperature into probably the 3 : 5-*disulphonyl chloride*, m. p. 72° (*disulphonanilide*, m. p. 160°), since the corresponding acid couples with diazotised *p*-nitroaniline in neutral or alkaline solution. *p*-Xylenol and chlorosulphonic acid at 110—150° give p-*xylenol*-3 : 6-*disulphonyl chloride*, m. p. 58° (*disulphonanilide*, m. p. 173°; the free acid couples with diazotised *p*-nitroaniline), together with an unidentified substance, m. p. 104—105°. Two *disulphonyl chlorides*, m. p. 89—91° and 117—119° (corresponding *disulphonanilides*, m. p. 160—161° and 205—207°), are obtained from *m*-5-xylenol and 10 parts of chlorosulphonic acid at the ordinary temperature; when the reaction is carried out with a mixture of chlorosulphonic acid and sulphur trioxide at 60—70°, the former chloride is the sole product. *m*-4-Xylenol and chlorosulphonic acid at the ordinary temperature yield a mixture of probably m-4-*xylenol-5-sulphonyl chloride*, m. p. 93—95°, and 3 : 5 : 3′ : 5′-*tetramethyldiphenyl* 1 : 6 : 1′ : 6′-*sulphonylide*, decomp. above 300°. The former of these derivatives gradually changes to a water-soluble oil; an aqueous solution contains free sulphuric acid and gives a colour with ferric chloride. It is suggested that the chloride may be *m*-4-xylenol-*O*-sulphonyl chloride. H. Burton.

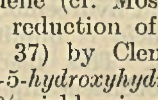


(I.)

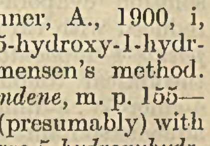
Stereochemical influences on aromatic substitution. Substitution derivatives of 5-hydroxyhydrindene. W. H. Mills and I. G. Nixon (J.C.S., 1930, 2510—2524).—It is argued, on stereochemical grounds, that of the two possible configurations of hydrindene required by the Kekulé formula, I is the more stable, and that 5-hydroxyhydrindene should be substituted by bromine and diazonium salts mainly in the 6-position. For details of the reasoning the original should be consulted. Application of these criteria to *o*-4-xylenol (II; cf. Diepolder, A., 1909, i, 786) and 4-acetamido-*o*-xylene indicates that the *o*-methyl groups produce an effect similar to that of the five-membered ring in hydrindene, but the reactivity of the 1-position in *ar*-tetrahydro-β-naphthol (cf. Schroeter, A., 1922, i, 123; Smith, J.C.S., 1904, **85**, 730) is in favour of the alternative configuration (III) for this.



(I.)



(II.)



(III.)

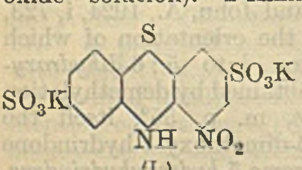
5-Hydroxyhydrindene (cf. Moschner, A., 1900, i, 344) is obtained by reduction of 5-hydroxy-1-hydrindone (A., 1917, i, 37) by Clemmensen's method. 6-p-*Chlorobenzeneazo-5-hydroxyhydrindene*, m. p. 155—156°, is formed in 90% yield, mixed (presumably) with 10% of 4-isomeride. 6-p-*Tolueneazo-5-hydroxyhydrindene*, m. p. 132·5°, is reduced by alcoholic stannous chloride to 6-*amino-5-hydroxyhydrindene*, m. p. 185—186° (described by Borsche and John, A., 1924, i, 723, as the 4-amino-compound), the orientation of which follows from its conversion into 5 : 6-*dihydroxyhydrindene*, m. p. 116°, also obtained by demethylation of 5 : 6-*dimethoxyhydrindene*, m. p. 55°, itself the reduction product of 5 : 6-dimethoxy-1-hydrindone (J.C.S., 1907, **91**, 1079). 6-*Bromo-5-hydroxyhydrindene*, m. p. 37·7°, b. p. 143°/14 mm., is the product of direct bromination of the hydroxy-compound, and may also be obtained from 6-amino-5-hydroxyhydrindene by the Sandmeyer reaction.

Bromination of 4-acetamido-*o*-xylene in acetic acid gives the 5-*bromo*-derivative, m. p. 164°, hydrolysed by 50% sulphuric acid to 5-*bromo*-o-4-*xylidine*, m. p. 84·5°, converted by Sandmeyer's reaction into 4 : 5-dibromo-*o*-xylene (A., 1885, 142). H. A. PIGGOTT.

β-Naphthol-3-sulphonic acid. S. HOLT and F. A. MASON (J. Soc. Dyers and Col., 1930, 46, 270—271).—The synthesis of β-naphthol-3-sulphonic acid, hitherto the only one of the seven possible β-naphtholsulphonic acids not prepared, is announced but not described. It couples smoothly with diazo-components to give dyes of slightly redder shade than the corresponding dyes from Schaeffer acid, and having similar dyeing properties. The *aniline* and α-*naphthylamine* salts of the 2 : 3-acid prepared by the method of Forster and Keyworth (J.S.C.I., 1924, 43, 166T, 299T) have m. p. 241—242° and 247—248°, respectively. A. J. HALL.

Nitration of substituted diaryl ethers. Phenyl *p*-tolyl ether. J. REILLY, P. J. DRUMM, and T. GRAY (Sci. Proc. Roy. Dublin Soc., 1930, 19, 461—465).—Nitration of phenyl *p*-tolyl ether with nitric acid (*d* 1·51) at —20° to —10° affords (?) 4-*nitrophenyl* 3-*nitro*-p-*tolyl ether*, m. p. 101—102°, which when treated with boiling piperidine does not undergo appreciable scission. Nitration of the ether in presence of acetic acid gives a *nitro*-derivative, b. p. 204°/21 mm. Partial scission of the ether occurs during nitration (cf. A., 1927, 239). *Phenyl* 3-*nitro*-p-*tolyl ether*, b. p. 224—225°/24 mm., 2 : 4-*dinitrophenyl* p-*tolyl ether*, m. p. 93°, and *phenyl* 3 : 5-*dinitro*-p-*tolyl ether*, m. p. 70°, are synthesised by the usual methods. 2 : 4 : 6-*Trinitrophenyl* p-*tolyl ether*, m. p. 103°, is obtained from picryl chloride and potassium *p*-tolyloxide in cold alcohol; in the hot, potassium picrate is the sole product. The 2 : 4-dinitro- and 2 : 4 : 6-trinitro-derivatives are readily decomposed by piperidine yielding 2 : 4-dinitro- and 2 : 4 : 6-trinitro-phenylpiperidine, respectively. H. BURTON.

Preparation of an *o*-aminothiophenolsulphonic acid. J. POLLAK and K. DEUTSCHER (Monatsh., 1930, 56, 365—380).—When potassium 4-chloro-3-nitrobenzenesulphonate is heated with an aqueous solution of potassium hydrogen sulphide, the resulting solution evaporated to dryness, and the residue reduced with tin and hydrochloric acid, 2-*aminothiophenol*-4-*sulphonic acid* is obtained in 75% of the theoretical amount. This reacts with potassium 4-chloro-3 : 5-dinitrobenzenesulphonate in presence of aqueous sodium acetate, forming *potassium* 5-*nitrophenthiazine*-3 : 8-*disulphonate* (I) (+$2H_2O$) (isolated by treating the reaction mixture with potassium hydroxide solution). 2-Aminothiophenolsulphonic acid and sodium nitrite afford a phenylenediazosulphidesulphonic acid (or its sodium salt) which does not couple with β-naphthol. Numerous attempts to prepare the above acid using other sulphur-containing salts were unsuccessful.



(I.)

Potassium 4-chloro-3-nitrobenzenesulphonate and sodium disulphide in 96% alcohol give *potassium* 2 : 2′-*dinitrodiphenyl disulphide*-4 : 4′-*disulphonate*; in aqueous solution reduction occurs with either sodium sulphide or disulphide. Barium 4-chloro-3-nitrobenzenesulphonate and potassium xanthate react in aqueous solution according to Blanksma's scheme (A., 1902, i, 281), forming alcohol, ethyl xanthate, carbon disulphide, barium carbonate, and *barium* 2 : 2′-*dinitrodiphenyl sulphide*-4 : 4′-*disulphonate* (II) (+$5H_2O$). In presence of ammonium acetate only a small amount of the sulphide is produced. Treatment of II with phosphorus pentachloride gives 2 : 2′-*dinitrodiphenyl sulphide* 4 : 4′-*disulphonyl chloride* (+$0{\cdot}5C_6H_6$), m. p. (solvent-free) 195°, oxidised by fuming nitric acid to 2 : 2′-*dinitrodiphenylsulphone*-4 : 4′-*disulphonic acid* [*lead* salt (+$3H_2O$); *barium* salt (+$3H_2O$), obtained by similar oxidation of II]. Reduction of II with tin and hydrochloric acid affords 2 : 2′-*diaminodiphenyl sulphide*-4 : 4′-*disulphonic acid* (+$3H_2O$), which oxidises readily in air. Treatment of the reaction product from sodium 4-chloro-3-nitrobenzenesulphonate and aqueous sodium thiosulphate with phosphorus pentachloride also furnishes the above chloride; when the potassium sulphonate is treated similarly *sodium* 2 : 2′-*dinitrodiphenyl sulphide*-4 : 4′-*disulphonate* is produced [in one case a modification (?) of potassium 4-chloro-3-nitrobenzenesulphonate was produced].

2 : 2′-Diaminodiphenyl disulphide is decomposed by chlorosulphonic acid at —20° and by fuming sulphuric acid under various conditions. Phenylenediazosulphide is unaffected by fuming sulphuric acid (25—70% SO_3) at 160—170°, and *o*-aminothiophenol could not be sulphonated. H. BURTON.

Characteristic colour reactions of certain diamino- and nitroamino-diphenyl-mono- and -di-sulphides. H. H. HODGSON and W. ROSENBERG (J. Soc. Dyers and Col., 1930, 46, 267—270).—Characteristic colour reactions are tabulated for the identification of a number of products obtained in the thionation of aniline (B., 1924, 901) and related substances, including 2 : 2′-diaminodiphenyl disulphide, 4 : 4′-diaminodiphenyl disulphide, 2 : 2′-diaminodiphenyl sulphide, 2 : 4′-diaminodiphenyl sulphide, 4 : 4′-diaminodiphenyl sulphide, 2′-nitro-2-aminodiphenyl sulphide, 2′-nitro-4-aminodiphenyl sulphide, 4′-nitro-2-aminodiphenyl sulphide, 4′-nitro-4-aminodiphenyl sulphide. The preparation of these substances from *p*-aminothiophenol and the requisite chloronitrobenzene is described. A. J. HALL.

Action of compounds of the diazomethane series on thio-esters. Synthesis of ketenmercaptols, -acetal chlorides, and -thioacetal chlorides. Diphenyldiazomethane as a "free radical." A. SCHÖNBERG and L. VON VARGHA (Annalen, 1930, 483, 176—189).—Diphenyldiazomethane reacts with diphenyl trithiocarbonate in ether at the ordinary temperature, forming ββ-*diphenylthiol*-αα-*diphenylethylene sulphide*, m. p. 135°, which on treatment with copper bronze in boiling benzene affords ββ-*diphenylthiol*-αα-*diphenylethylene*, m. p. 112°. This is very stable towards alkalis, but is hydrolysed by slightly diluted sulphuric acid in acetic acid solution at 100° to diphenylacetic acid. Di-*p*-tolyldiazomethane and di-*p*-tolyl trithiocarbonate give similarly ββ-*di*-p-*tolylthiol*-αα-*di*-p-*tolylethylene* *sulphide*, m. p. 134—135°, which when heated at 200° or acted on by copper bronze passes into ββ-*di*-p-*tolylthiol*-αα-*di*-p-*tolylethylene*, m. p. 122—123°. Diphenylenediazomethane and phenyl chlorodithioformate furnish β-*chloro*-β-*phenylthioldiphenylene-ethylene sulphide*, m. p. 110°, convertible as above into β-*chloro*-β-*phenylthioldiphenylene-ethylene*, m. p. 133°, which is hydrolysed by sulphuric and acetic acids to fluorene-9-carboxylic acid. Diphenylenediazomethane and phenyl chlorothioformate, Cl·CS·OPh, react slowly in benzene at the ordinary temperature, yielding β-*chloro*-β-*phenoxydiphenylene-ethylene*, m. p. 114—115°, also hydrolysed to fluorene-9-carboxylic acid. Diphenyldiazomethane and 2 : 4 : 6-*trichlorophenyl chlorothioformate*, b. p. 146—147°/12 mm., prepared from 2 : 4 : 6-trichlorophenol and thiocarbonyl chloride in presence of chloroform and aqueous sodium hydroxide, react in ether forming β-*chloro*-β-2 : 4 : 6-*trichlorophenoxy*-αα-*diphenylethylene*, m. p. 91°.

The self-decomposition of diphenyldiazomethane and its reactions with diphenyl disulphide, oxygen, sulphur dioxide, and iodine are compared with the similar reactions of triphenylmethyl. The results are readily explicable on the assumption that diphenyldiazomethane reacts as the di-radical, $^{-}CPh_2{\cdot}N_2^{-}$.

H. BURTON.

Structure of *iso*anethole. G. D. GOODALL and R. D. HAWORTH (J.C.S., 1930, 2482—2487).—Oxidation of *iso*anethole with potassium permanganate gives anisic acid and α-*p*-methoxyphenyl-*n*-propyl methyl ketone; the constitution p-MeO·C_6H_4·CH:CMe·CHEt·C_6H_4·OMe-p' is therefore assigned to it. The ketone was identified by comparison with the synthetic product and with the isomeric α-*p*-methoxybenzyl ethyl ketone: its structure is confirmed by oxidation with sodium hypobromite to give (probably) α-3-*bromo*-4-*methoxyphenyl*-n-*butyric acid*, m. p. 123—125°.

Ethyl p-*methoxybenzylacetoacetate*, b. p. 172°/0·25 mm., and di-*p*-methoxybenzylacetoacetate, prepared from *p*-methoxybenzyl bromide and ethyl sodioacetoacetate, are hydrolysed by 10% aqueous potassium hydroxide to p-*methoxybenzylacetone*, b. p. 177°/25 mm. (*semicarbazone*, m. p. 172—173°: *oxime*, m. p. 77°), and *di*-p-*methoxybenzylacetone*, m. p. 96—97°. *Ethyl* p-*methoxybenzylmethylacetoacetate*, b. p. 180°/0·5 mm., is similarly hydrolysed to α-p-*methoxybenzylethyl methyl ketone*, b. p. 175°/20 mm. (*semicarbazone*, m. p. 135°). *p*-Methoxyphenylacetonitrile (*benzylidene* compound, m. p. 96°) condenses with ethyl acetate in presence of sodium ethoxide to *acetyl*-p-*methoxyphenylacetonitrile*, m. p. 80°, hydrolysed by 50% sulphuric acid to p-*methoxybenzyl methyl ketone*, b. p. 150°/20 mm. (*semicarbazone*, m. p. 173°), which with ethyl iodide and sodium ethoxide gives α-p-*methoxyphenyl*-n-*propyl methyl ketone*, b. p. 125—128°/0·7 mm. (*semicarbazone*, m. p. 189°: *oxime*, m. p. 84—85°).

H. A. PIGGOTT.

Hydrogenation of α-phenylethyl and α-phenyl-*n*-propyl alcohol. Reduction of aromatic carbinols. P. A. LEVENE and P. G. STEVENS (J. Biol. Chem., 1930, 89, 471—477; cf. A., 1930, 1178).—*l*-α-Phenylethyl alcohol yields, with hydrogen and platinum oxide, *cyclo*hexylethane together with d-α-cyclo*hexylethyl alcohol*, b. p. 88°/11 mm., $[\alpha]_D^{20}$ +4·7°; α-phenyl-*n*-propyl hydrogen phthalate was resolved with brucine, the d-*hydrogen phthalate*, $[\alpha]_D^{21}$ +41·5° in alcohol, giving the d-*carbinol*, b. p. 105·5—107°/15 mm., $[\alpha]_D^{20}$ +28·3°, which was hydrogenated to d-α-cyclo*hexyl*-n-*propyl alcohol*, b. p. 105—106°/18 mm., $[\alpha]_D^{20}$ +20·0°. It follows that *l*-α-phenylethyl and *d*-α-phenyl-*n*-propyl alcohols are configuratively related. When reduced with hydrogen and platinum oxide, benzyl alcohol yields chiefly *cyclo*hexylmethane, benzhydrol 60% of di*cyclo*hexylcarbinol together with di*cyclo*hexylmethane, and triphenylcarbinol almost exclusively diphenyl*cyclo*hexylmethane; aliphatic *tert.*-carbinols are not reduced under these conditions.

C. R. HARINGTON.

Methylation of alcoholic hydroxyl groups on the basis of the electronic theory. J. VON BRAUN, E. ANTON, and K. WEISSBACH (Ber., 1930, 63, [*B*], 2847—2861).—Attempts are made to explain the varied behaviour of the hydroxyl groups towards methylation on the basis of the electronic theory from which the following consequences are deduced. The inductive action of a benzene nucleus or double linking must diminish greatly with its distance from the hydroxyl group, since it is distributed over each intermediate carbon atom. An effect equal to or more pronounced than that of the benzene nucleus or double linking must be exerted by each dipole with the + side directed towards the hydroxyl group, for example, $\overset{-}{O}{=}\overset{+}{C}{<}$, $\overset{-}{N}{\equiv}\overset{+}{C}{-}$. The effect must be most marked when hydroxyl is attached to a chain in which an element is present with the character of a positively charged ion.

The compound to be methylated is dissolved or suspended in ten times its weight of water at 5° and 6 mols. of methyl sulphate and 14 mols. of sodium hydroxide in 10% solution are added. The mixture is shaken for 5 min. while cooled in ice and then set aside. The temperature rises spontaneously to 50—55° and is maintained at this point for 15 min. With the simpler alcohols the mixture is extracted with ether; after removal of solvent and distillation, the product is analysed, particularly according to Zerewitinov. With more complex products individual methods are used for isolation. With the following alcohols, the percentage of methyl ether produced is placed within parentheses; benzyl (64); β-phenylethyl (19); γ-phenylpropyl (5); ε-phenylamyl (0); phenyldimethylcarbinol (0); cinnamyl (53); furfuryl (70); allyl (more than 20); *n*-propyl (0); *iso*amyl (0); *n*-heptyl (0). The marked influence of the cyano- and sulpho-groups is shown by the production of more than 50% and 100% of methyl ether from β-cyanoethyl alcohol and β-ethylsulphonylethyl alcohol, respectively. In compounds with basic nitrogen the influence is stronger than in the fatty-aromatic alcohol, as shown by the data: β-piperidinoethyl alcohol (100); γ-dimethylaminopropyl alcohol (100); γ-methylanilinopropyl alcohol (almost 100); δ-piperidinobutyl alcohol (about 50); ε-piperidinoamyl alcohol (0); ε-dimethylaminoamyl alcohol (0); 2-dimethylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene (100); 2-β-hydroxyethylpiperidine (100); 2-dimethylamino-5-methylbenzyl alcohol (60); dihydrocodeine (almost 100). Tropine and γ-dimethylamino-β-hydroxy-γ-methylbutane are almost unaffected. With hydroxy-acids the following percentages of methyl ether are obtained : lactic (?15); mandelic (70); tropic (40).

The following observations appear new : N-β-hydroxyethylpiperidine methiodide, m. p. 238° (corresponding *chloroplatinate*, m. p. 228; and *chloroaurate*, m. p. 243°), transformed by methylation into a non-crystalline *methiodide* [corresponding *chloroplatinate*, $C_{18}H_{40}O_2N_2Cl_6Pt$, m. p. 234° (decomp.), and *chloroaurate*, m. p. 108° after softening at 100°]; *methyl γ-dimethylaminopropyl ether methiodide*, m. p. 221° (corresponding *chloroplatinate*, m. p. 222°; *chloroplatinate* of the non-methylated compound, decomp. 235°); N-*methyl*-N-*γ-hydroxypropylaniline methiodide*, m. p. 132°, and N-*methyl*-N-*γ-methoxypropylaniline methiodide*, m. p. 119—121°; 2-dimethylamino-3-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 31°, and 2-*dimethylamino*-3-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene methiodide*, m. p. 223° (corresponding *methochloride*, m. p. 230°, and *chloroplatinate*, m. p. 229°); 1-*methyl*-2-β-*methoxyethylpiperidine chloroplatinate*, $C_{20}H_{44}O_2N_2Cl_6Pt$, m. p. 212°; 1-*methyl*-2-β-*hydroxyethylpiperidine methiodide*, decomp. about 235°, and the corresponding *chloroplatinate*, m. p. 204°; *methyl 2-dimethylamino-5-methylbenzyl ether*, m. p. 120—125°/12 mm. [*picrate*, m. p. 155°; *chloroplatinate*, m. p. 172°; *methiodide*, m. p. 115° (decomp.)]; *γ-dimethylamino-γ-methylbutan*-β-*ol methiodide*, m. p. 172° (decomp.); *benzenesulphonmethyl-γ-hydroxypropylamide*, b. p. 167°/0·3 mm.; *methylephedrine*, $OMe\cdot CHPh\cdot CHMe\cdot NMe_2$, b. p. 116°/16 mm. (*picrate*, m. p. 166—168°; *methiodide*, m. p. 190°); *methyldihydrocodeine methiodide*, m. p. 207—209°; β-*methoxy* - α - *dimethylamino* - α - *methylenedioxyphenylpropane methiodide* and the corresponding *chloride* and *chloroplatinate*, m. p. 216°, and the *methiodide* of the corresponding β-hydroxy-compound, m. p. 190° (corresponding *chloroplatinate*, m. p. 198°); β-*ethylsulphonylethyl alcohol*, b. p. 193—195°/12 mm., m. p. 40°, and *methyl* β-*ethylsulphonylethyl ether*, b. p. 142—144°/12 mm.; *dimethyl*-β-*hydroxyethylsulphonium iodide*, m. p. 60—62° (*platinum* salt, m. p. 80—81°); *dimethyl-γ-hydroxypropylsulphonium iodide*, m. p. 52—55° (corresponding *platinum* salt, m. p. 115°); β-*methoxy*-α-*phenylpropionic acid*, b. p. 134—136°/0·3 mm., m. p. 62°, and the corresponding *chloride*, b. p. 88°/0·5 mm.; *phenyl* β-*methoxy*-α-*phenylethyl ketone*, b. p. 139—141°/0·2 mm. (non-crystalline *oxime* and *semicarbazone*); *phenyl* β-*chloro*-α-*phenylethyl ketone*, b. p. 139—140°/0·5 mm. (slight decomp.); o-*methoxymethylbenzoic acid*, b. p. 121—125°/0·5 mm., m. p. 93—94°, converted by thionyl chloride into phthalide; α-*methoxybenzylsuccinic anhydride*, b. p. about 155°/0·5 mm., m. p. 95—96°, and α-*methoxybenzylsuccinic acid*, m. p. 140°.

H. Wren.

Quinonoid structure of triphenylmethyl salts. L. C. Anderson (J. Amer. Chem. Soc., 1930, **52**, 4567—4572; cf. A., 1928, 219, 285; 1929, 977).—Curves are given for the absorption spectra of solutions of triphenylcarbinol, triphenylmethyl chloride, sulphate, and perchlorate in methyl sulphate, triphenylmethyl hydrogen sulphate in sulphuric acid, and triphenylmethyl perchlorate in perchloric acid. These show that all the above solutions (except triphenylcarbinol and triphenylmethyl chloride in methyl sulphate) are similar, probably because they are present in solution as quinonoid compounds.

H. Burton.

Action of hydrogen sulphide on acid chlorides. I. Hydrogen sulphide and benzoyl chloride. L. Szperl [with A. Smolańska] (Rocz. Chem., 1930, **10**, 510—522).—The following products are found after passing hydrogen sulphide through benzoyl chloride at 180—185°: hydrogen chloride, sulphur, benzoic acid, dibenzoyl disulphide, ethylidene dithiobenzoate, and an unidentified, sulphur-containing *substance*, m. p. 28—30°. The last-named substance was not found when the reaction was carried out in decalin solution, whilst in xylene solution at 145° the products are hydrogen chloride, benzoic acid, and dibenzoyl mono- and di-sulphide. Dibenzoyl disulphide gives an intense red coloration on fusion in the presence of traces of sodium silicate or sodium, lithium, or strontium carbonates, whilst with cadmium or silver carbonates sulphides of the metal are precipitated. Attempts to isolate the red product from the former reaction were not successful, the only product identified being thiobenzoic acid. Dibenzoyl sulphide can be prepared by adding thiobenzoic acid to benzoyl chloride in ethereal solution. A violet coloration is obtained by fusing the monosulphide with the above salts.

R. Truszkowski.

Hydrolysis of benzoylated amino-acids and polypeptides. S. Goldschmidt and W. Füner (Annalen, 1930, **483**, 190—216).—The hydrolysis of various benzoylated mono- and di-amino-acids, aminohydroxy-acids, and polypeptides with sodium hydroxide solution (2% unless stated otherwise) at 25° and 100° and sulphuric acid at 100° is studied (cf. A., 1929, 1188). The rate of the alkaline hydrolysis of the benzoylated monoamino-acids increases with rise in temperature and hydroxyl-ion concentration; for a definite hydroxyl-ion concentration, the coefficient decreases with increasing length of the carbon chain. Alkaline hydrolysis of hippuric acid is increased both at 25° and 100° by the addition of sodium chloride, but is decreased by added glycine. The *O*-benzoyl group is eliminated from *ON*-dibenzoylserine and -tyrosine at 25°; at 100°, both benzoyl groups are readily eliminated from the former compound. Alkaline hydrolysis of dibenzoylarginine causes the very ready elimination of one benzoyl group with the production of α-benzoylornithine; the velocity of hydrolysis of the second benzoyl group is measurable when 8% sodium hydroxide solution is used. Similarly, αε-dibenzoyl-lysine is first hydrolysed to the α-benzoyl derivative. With benzoylated glycyl-, diglycyl-, and alanylglycylglycines, the peptide linkings are rapidly broken; during this hydrolysis little benzoic acid is produced.

The rate of hydrolysis of benzoylated monoamino-acids by 70% sulphuric acid at 100° increases with the length of the carbon chain. Dibenzoylarginine behaves similarly with acidic hydrolytic agents as with alkaline, but the behaviour of αε-dibenzoyllysine is reversed, *i.e.*, the α-benzoyl group is eliminated first. The peptide linkings are first broken when the above benzoylated peptides are hydrolysed with 70% sulphuric acid. The velocity of hydrolysis of benzoylproteins is greater with 30% sulphuric acid than with more concentrated acid; the rate corresponds with the specific conductivity of the acid. The velocity of hydrolysis of hippuric acid by 70% sulphuric acid at 100° is increased by the addition of glycine. H. Burton.

Dynamic isomerism involving hydrocarbon radicals. II. Intramolecular character of the amidine rearrangement. A. W. Chapman. **III. Effects of substitution on velocity of interchange and position of equilibrium of isomeric triarylbenzamidines.** A. W. Chapman and C. H. Perrott (J.C.S., 1930, 2458—2462, 2462—2468).—II. The interconversion of isomeric triarylbenzamidines (cf. A., 1929, 1294) is shown by velocity measurements (see below) to follow a unimolecular course; it does not need a catalyst, and is not accompanied by side reactions. Thus symmetrical amidines, *e.g.*, triphenyl- and tri-*p*-tolyl-benzamidines, are unchanged when heated (at 345° for 2 hrs., and 335° for 1 hr., respectively). Further evidence for the intramolecular nature of the change is afforded by the absence of phenyl-*p*-tolylamine from the hydrolysis products of a mixture of triphenyl- and tri-*p*-tolyl-benzamidines after rearrangement by heating. *Triphenyl-*, m. p. 168—169°, *tri-*p*-tolyl-*, m. p. 188—189°, and *tri-*p*-chlorophenyl-benzamidine*, m. p. 147—148°, are prepared by the method previously described (*loc. cit.*). The product of chlorination of benzoyldiphenylamine (Claus and Schaare, A., 1882, 1060) is *pp'*-dichlorodiphenylamine, as is proved by its preparation from N-p-*chlorophenylbenzimino*-p-*chlorophenyl ether*, m. p. 68—69°.

III. A kinetic study of the reaction $RN{:}CPh{\cdot}NRR'$ (I) $\rightleftharpoons$ $R'N{:}CPh{\cdot}NR_2$ (II) indicates that its mobility is affected by the nature of R′ in the order *p*-tolyl<phenyl<*p*-chlorophenyl, and by R in the order *p*-tolyl>*p*-chlorophenyl. The proportions of I in the equilibrium mixtures are estimated as 69% [$R=Ph$, $R'=C_7H_7(p)$], 53% [$R=C_7H_7(p)$, $R'=Ph$], 59% [$R=Ph$, $R'=C_6H_4Cl(p)$], and 71% [$R=C_6H_4Cl(p)$, $R'=Ph$]. In view of its similarity to this change, a modified explanation of the rearrangement of imino-ethers into amides, based on these results, is advanced (cf. A., 1927, 874). *NN'-Di*-p-*tolyl*-N-*phenyl-*, m. p. 133°; N-*di*-p-*tolyl*-N'-*phenyl-*, m. p. 149·5—150°; NN'-*diphenyl*-N-p-*chlorophenyl-*, m. p. 150—152°; N-*diphenyl*-N'-p-*chlorophenyl-*, m. p. 167·5—168·5°; NN'-*di*-p-*chloro-diphenyl*-N-*phenyl-*, m. p. 132—133°, and N-*di*-p-*chlorodiphenyl*-N'-*phenylbenzamidine*, m. p. 101—103°, are described.

H. A. Piggott.

Esterification of 3 : 5-diamino- and iodobenzoic acids with alcoholic hydrogen chloride. A. Kailan and A. Irresberger (Monatsh., 1930, 56, 407—427).—The unimolecular velocity coefficients of esterification of 3 : 5-diamino-, and *o*-, *m*-, and *p*-iodo-benzoic acids with alcoholic hydrogen chloride in absence and presence of water have been determined at 25°. With alcohol containing little water, the coefficients for all the acids are proportional to the concentration of the hydrogen chloride; in moist alcohol, the coefficients increase much more rapidly. The values for 3 : 5-diaminobenzoic acid show that the introduction of a second *m*-amino-group into benzoic acid has a much smaller effect than the first (cf. A., 1907, ii, 158). The retarding action of the halogen atom is most marked with the *o*-iodobenzoic acid and least with the *m*-isomeride. For the *o*-halogenobenzoic acids, the coefficient decreases with increasing atomic weight of the halogen atom (cf. A., 1929, 1244). All the *m*-halogenobenzoic acids have approximately the same coefficient, which is less than that for benzoic acid. H. Burton.

Di- and tri-arylamine derivatives. R. Joszt and W. Leśniański (Rocz. Chem., 1930, 10, 523—540).—A number of attempts to synthesise 4-*nitro*-2-*diphenylaminobenzoic acid*, m. p. 200°, by condensation were unsuccessful. Thus condensation of 5-nitro-2-anilinobenzoic acid or its ethyl ester with iodobenzene yielded either the original products or 5-nitrotriphenylamine, and similar reactions took place with 5-nitro-2-aminobenzoic acid and iodobenzene and with 2-*iodo*-5-*nitrobenzoic acid*, m. p. 197—198°, and diphenylamine. The required acid is produced by oxidation with chromic acid of 4-*nitro*-2-*methyltriphenylamine*, m. p. 130·5—131·5°, prepared by the condensation of diphenylamine with 2-iodo-4-nitrotoluene or of 4-nitro-2-methyldiphenylamine with iodobenzene. The following compounds have been prepared: 4-*nitro*-2-*methyldiphenylamine*, m. p. 140—141°, by the condensation of 5-nitro-*o*-toluidine with nitrobenzene and iodobenzene, 6-*diphenylamino*-m-*toluidine*, m. p. 94—99° (*hydrochloride*, m. p. 217°; *acetyl* derivative, m. p. 144—145·5°), and 4-*amino*-2-*methyldiphenylamine*, m. p. 49—50° (*hydrochloride*, m. p. 185—187°; *acetyl* derivative, m. p. 139—140·5°), by the reduction of the corresponding nitro-derivatives; the former amine yields, on diazotisation and coupling with β-naphthol, a red *dye*, m. p. 186—188°. R. Truszkowski.

Behaviour of condensation products of *p*-dimethylaminobenzaldehyde towards bromine and nitrous acid. K. H. Bauer and M. Seyfarth (Ber., 1930, 63, [*B*], 2691—2695).—Addition of bromine to α-phenyl-*p*-dimethylaminocinnamonitrile in chloroform affords α-*phenyl*-3-*bromo*-4-*dimethylaminocinnamonitrile*, $NMe_2{\cdot}C_6H_3Br{\cdot}CH{:}CPh{\cdot}CN$, m. p. 102°, identical with the substance obtained by condensing 3-bromo-4-dimethylaminobenzaldehyde with phenylacetonitrile in alcohol containing a little potassium hydroxide. Similarly, treatment of α-phenyl-*p*-dimethylaminocinnamonitrile with sodium nitrite in glacial acetic acid yields α-*phenyl*-3-*nitro*-4-*dimethylaminocinnamonitrile*, m. p. 128°, also derived from 3-nitro-4-dimethylaminobenzaldehyde and phenylacetonitrile. *Ethyl* α-*cyano*-3-*bromo*-4-*dimethylaminocinnamate*, m. p. 107°, is prepared from 3-bromo-4 dimethylaminobenzaldehyde and ethyl cyanoacetate or from bromine and ethyl α-cyano-*p*-dimethylaminocinnamate. *Ethyl* α-*cyano*-3-*nitro*-4-*dimethylaminocinnamate*, m. p. 172—173°, is obtained by analogous methods, which are also applied in the production of 3-*bromo*-4-*dimethylaminobenzylidenemalononitrile*, $NMe_2{\cdot}C_6H_3Br{\cdot}CH{:}C(CN)_2$, m. p. 123—124°, and

3-*nitro*-4-*dimethylbenzylidenemalononitrile*, m. p. 147—148°. In these compounds the introduction of a basic group into the phenyl residue does not so far neutralise the accumulation of negative groups that addition occurs, but facilitates substitution in the phenyl nucleus. Similarly, phenyl 4-dimethylaminostyryl ketone and bromine yield *phenyl* 3-*bromo*-4-*dimethylaminostyryl ketone*, m. p. 82° (*hydrochloride*, m. p. 145—146°), obtained also from 3-bromo-4-dimethylaminobenzaldehyde and acetophenone, whereas methyl *p*-dimethylaminostyryl ketone and bromine give *methyl* α-*bromo*-4-*dimethylaminostyryl ketone*, m. p. 92°. The constitution of the last-named compound follows from the conversion of its *phenylhydrazone*, m. p. 127°, into 1-*phenyl*-5-p-*dimethylaminophenyl*-3-*methylpyrazole*, m. p. 148—150°. In this instance, therefore, reaction consists in addition of bromine followed by loss of hydrogen bromide.

H. WREN.

Preparation of α-naphthonitrile from α-naphthylamine. J. A. McRAE (J. Amer. Chem. Soc., 1930, **52**, 4550—4552).—Contrary to the statement of Whitmore and Fox (A., 1930, 99), a 25—35% yield of α-naphthonitrile can be obtained by the Sandmeyer reaction from α-naphthylamine. The yield is improved to 58—65% when potassium nickel cyanide solutions containing sufficient sodium hydroxide to neutralise the diazonium solution are used (cf. Korczynski and others, A., 1920, i, 643; 1926, 1037).

H. BURTON.

Reactions of salicylic acid and salol. L. EKKERT (Pharm. Zentr., 1930, **71**, 744).—Superposition of a solution of sodium nitrite and salicylic acid, salicylates, or *o*-acetoxybenzoic acid on sulphuric acid gives a red ring and, after mixing, a blood-red solution, becoming green when basified with sodium hydroxide. Phenyl salicylate gives a red ring and, on mixing, a green solution which becomes red when diluted with water and greenish-blue and bluish-green with sodium hydroxide and ammonia, respectively.

H. E. F. NOTTON.

Keto-enol equilibrium of ethyl α-phenylacetoacetate. H. W. POST and G. A. MICHALEK (J. Amer. Chem Soc., 1930, **52**, 4358—4362).—The enol content of ethyl α-phenylacetoacetate, prepared by a modification of the method of Beckh (A., 1899, i, 211), is found to be 28·6% in pyrex glass vessels at 20°, by the indirect method of Meyer (A., 1911, i, 832). The electronegative phenyl group facilitates ionisation of the α-hydrogen atom. Abnormal results are obtained when the amount of enol is calculated from refractometric data.

H. BURTON.

Minjak pelandjau, the exudation from the wood of *Pentaspadon motleyi*, Hook f. III. P. VAN ROMBURGH, A. G. VAN VEEN, and A. J. H. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**. 690—693).—When the phenol (A., 1930, 1434), obtained by the decarboxylation of pelandjauic acid, is hydrogenated in the presence of a large amount of acetic acid, with palladium-black as the catalyst, a *tetrahydrophenol*, $C_{24}H_{42}O$, m. p. 58—59°, is obtained, which when distilled with zinc dust yields a small quantity of 1-methylnaphthalene. If the original phenol is distilled in the same manner with
zinc, a mixture of naphthalene and 1-methylnaphth
ene is produced in a larger yield. A sample of dec
hydropelandjauic acid, obtained from crystalli
pelandjauic acid, m. p. 25°, after decarboxylation
330—350°, and vigorous reduction in acetic acid wi
platinum oxide as the catalyst, yields a hydrocarb
identical with rationally synthesised heptadecyl*cyc*
hexane. The decahydrophenol (*loc. cit.*), after trea
ment with zinc chloride to remove water, and hydroge
ation with platinum oxide in acetic acid, yields t
same hydrocarbon. It is therefore suggested that t
crude pelandjauic acid is a mixture of a least tv
similar substances; the crystalline acid, m. p. 25°,
formulated as 3-hydroxy-2-heptadecadienylbenzo
acid, and the liquid acid as 3-hydroxy-2-heptadec
dienyl-*p*-toluic acid. T. H. MORTON.

**Action of hydrogen sulphide on acid chlor
anhydrides. II. Hydrogen sulphide and
phthalyl chloride.** L. SZPERL. **III. Hydrog
sulphide and naphthalyl chloride.** L. SZPE
and H. MORAWSKI (Rocz. Chem., 1930, **10**, 652
656, 657—666).—II. *o*-Phthalyl chloride reacts wi
hydrogen sulphide at 195—200° to yield hydrog
chloride, phthalic acid, *o*-phthalyl sulphide, and *di*-
phthalyl disulphide, m. p. 330—331·5°.

III. Naphthalyl chloride in benzene solution reac
with hydrogen sulphide at 80° to yield hydrog
chloride, naphthalic acid, and *naphthalic thioanhydri*
m. p. 205—206° (decomp.). R. TRUSZKOWSKI.

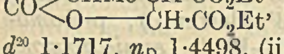
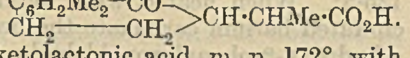
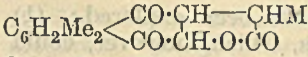
Naphthalene-2:3-dicarboxylic acid. H. WAL
MANN (J. pr. Chem., 1930, [ii], **128**, 150—152).—T
preparation of 3-*cyano*-2-*naphthoic acid*, m. p. 273
274°, from the corresponding amino-acid by San
meyer's method, and its hydrolysis to naphthalen
2 : 3-dicarboxylic acid, are described.

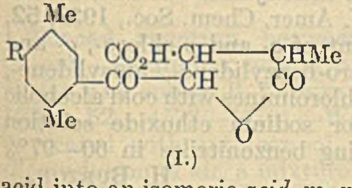
H. A. PIGGOTT.

**Resolution of γ-truxillic hydrogen esters in
their optical components.** F. SCHENCK (Be
1930, **63**, [*B*], 2706—2712; cf. Stoermer and Fr
wurst, A., 1926, 291).—Treatment of γ-truxil
anhydride with the requisite boiling alcohol in t
presence of a small amount of anhydrous sodiu
carbonate affords *methyl*, m. p. 183·5—184°, *eth*
m. p. 173—174·5°, n-*propyl*, m. p. 170—171°, a
n-*butyl hydrogen* dl-γ-*truxillates* (*hydrated sodiu*
n-*butyl* γ-*truxillate* is described). The optically acti
hydrogen esters are obtained by successive treatme
of the racemic compounds with morphine and bruci
and from the active γ-truxillamic acids by the acti
of nitrous fumes in glacial acetic acid. The followi
compounds are described, all rotations being measur
in acetone: *methyl* d-γ-*truxillamate*, m. p. 153—154
ethyl *d*-γ-truxillamate, m. p. 168°; n-*propyl* d-
truxillamate, m. p. 159—160°, $[\alpha]_D^{20}$ −17·70°; n-*bu*
l-γ-*truxillamate*, m. p. 141·5—143°, $[\alpha]_D^{20}$ +18·33
di-n-*butyl* γ-*truxillate*, m. p. 85—86°; *methyl hydrog*
l(—)-γ-*truxillate*, m. p. 145·5—147°; *methyl hydrog*
d-(+)-γ-*truxillate*, m. p. 145·5—147°, $[\alpha]_D^{18}$ +6·48
ethyl hydrogen l-(—)-γ-*truxillate*, m. p. 142·5—14
$[\alpha]_D^{19}$ −16·48°; *ethyl hydrogen* d(+)-γ-*truxillate*, m.
142·5—143°, $[\alpha]_D^{19.5}$ +19·14°; *n*-propyl hydrogen l(—
γ-*truxillate*, m. p. 148—149°, $[\alpha]_D^{21}$ −21·35°; n-*pro*
hydrogen d(+)-γ-*truxillate*, m. p. 148—149°; n-*bu*
hydrogen l(—)-γ-*truxillate*, m. p. 151—152°, [α]

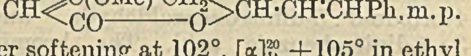
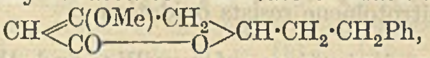
$-25{\cdot}70°$, and d(+)-*γ-truxillate*, m. p. 151—152°, $[\alpha]_D^{21}$ $+26{\cdot}14°$. H. Wren.

Chlorophenol-red. W. C. Harden (J. Amer. Chem. Soc., 1930, **52**, 4611).—Pure chlorophenol-red is obtained by repeated dissolution of the dye in water, acidifying with hydrochloric acid, and evaporating until crystallisation begins. The colour of the pure product with alkali is more blue and less red than that with a commercial sample. H. Burton.

Syntheses of santonin derivatives. A. E. Tschitschibabin and M. N. Schtschukina (Ber., 1930, **63**, [*B*], 2793—2806).—Ethyl methylsuccinate condenses with ethyl oxalate in ether under the influence of sodium ethoxide to ethyl oxalylmethylsuccinate, which is completely decomposed into ethyl propanetricarboxylate and carbon dioxide when distilled under diminished pressure. Reduction of the crude ester by aluminium amalgam in moist ether affords three stereoisomeric lactonic *esters*,  $CO<\begin{array}{l}CHMe\cdot CH\cdot CO_2Et\\ O\text{———}CH\cdot CO_2Et\end{array}$, (i) b. p. 182—183°/13 mm., d^{20} 1·1717, n_D 1·4498, (ii) b. p. 186—187°/13 mm., d^{20} 1·1747, n_D 1·4507, and (iii) b. p. 200—204°/13 mm., m. p. 70°. Hydrolysis of the ester (i) with hydrochloric acid affords an *acid*, $C_7H_8O_6$, m. p. 181—182°, which is transformed by acetyl chloride into a mixture of dimethylmaleic anhydride and *methylbutanolidedicarboxylic anhydride*, m. p. 162°. The *anilide* of acid i has m. p. 212—214°. The ester, b. p. 186—187°/13 mm., is hydrolysed to an *acid*, m. p. 186°, mainly unchanged by warming with acetyl chloride, but to a small extent isomerised to the anhydride of acid i. The *acid* from the solid ester has m. p. 185° and passes into an *anhydride*, m. p. 201° (with a small amount of anhydride, m. p. 162°), from which the original acid is regenerated by water. Isomerisation of the anhydride, m. p. 201°, to anhydride, m. p. 162°, is caused by distillation. Both anhydrides yield the same anilide with boiling aniline. Condensation of the anhydride, m. p. 162°, with *p*-xylene in presence of aluminium chloride gives the *ketolactonic acid* (I, R=H), m. p. 171—173°, transformed by short treatment with warm, concentrated sulphuric acid into an isomeric *acid*, m. p. 150°; the second acid is obtained directly by the successive action of thionyl chloride and aluminium chloride and *p*-xylene on 3-methylbutanolide-1 : 2-dicarboxylic acid, m. p. 181—182°. Reduction of the two stereoisomeric acids by amalgamated zinc and concentrated hydrochloric acid affords ε-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 161—163°, whereas reduction of the acid, m. p. 150°, with amalgamated zinc and acetic acid yields ε-*keto*-ε-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 169—172°. The acid, m. p. 161—163°, is transformed by ring closure into a *substance*, m. p. 130°, which probably has the structure  $\begin{array}{l}C_6H_2Me_2\text{—}CO\text{—}\\ CH_2\text{———}CH_2\end{array}>CH\cdot CHMe\cdot CO_2H$. Treatment of the ketolactonic acid, m. p. 172°, with thionyl chloride followed by heating of the residue in a vacuum at 160—185° gives the *diketone*,  $C_6H_2Me_2<\begin{array}{l}CO\cdot CH\text{——}CHMe\\ CO\cdot CH\cdot O\cdot CO\end{array}$, m. p. 137—139°. Condensation of the anhydride, m. p. 162°, with methoxy-*p*-xylene in presence of aluminium chloride yields the *ketolactonic acid* (I, R=OMe), m. p. 207—208°, and an unidentified *product*, m. p. 156°. Reduction of the ketolactonic acid by Clemmensen's method yields ε-*methoxy*-p-*xylylpentane*-βγ-*dicarboxylic acid*, m. p. 131—132°, transformed by successive demethylation and ring closure into an unsaturated lactone, m. p. 250—252°, identical with the product of Clemo, Haworth, and Walton (A., 1930, 919). H. Wren.



(I.)

Constituents of kawa root. X. Kawain and dihydrokawain. W. Borsche and W. Peitzsch (Ber., 1930, **63**, [*B*], 2414—2417; cf. A., 1929, 442, 1453).—Technical kawa resin is dissolved in ether and the solution is extracted with 3% sodium hydroxide; after desiccation of the ethereal solution and removal of the ether the residue is subjected to prolonged fractional extraction with hot hexane. Slow evaporation of ethereal solutions of suitable solid extracts yields *kawain*,  $CH\ll\begin{array}{l}C(OMe)\cdot CH_2\\ CO\text{———}O\end{array}>CH\cdot CH{:}CHPh$, m. p. 105—106° after softening at 102°, $[\alpha]_D^{20}$ +105° in ethyl alcohol. It is isomerised by boiling 2*N*-sodium hydroxide to kawaic acid, m. p. 184—185°, and catalytically reduced to a mixture of much *dihydrokawain*,  $CH\ll\begin{array}{l}C(OMe)\cdot CH_2\\ CO\text{———}O\end{array}>CH\cdot CH_2\cdot CH_2Ph$, m. p. 56—58°, $[\alpha]_D^{19}$ +30° in ethyl alcohol, and little tetrahydrokawaic [β-methoxy-ζ-phenyl-Δ^α-heptenoic] acid. Dihydrokawain is transformed by 10% sodium hydroxide into *dihydrokawaic* [β-*methoxy*-ζ-*phenyl*-Δ^α-*heptadienoic*] *acid*, m. p. 139—140° (decomp.); the acid can be obtained by treatment of purified kawa resin dissolved in methyl alcohol with hydrogen in presence of palladium.

[With J. Niemann.] Dihydrokawain is isolated from the initial fractions of the extraction of kawa resin with hexane. H. Wren.

Constituents of kawa root. XI. Syntheses of methystic acid and kawaic acid. W. Borsche and B. R. Blount (Ber., 1930, **63**, [*B*], 2418—2420).—*allo*Methysticin is converted by methyl orthosilicate in presence of methyl alcohol containing a trace of hydrogen chloride into methyl methystate, m. p. 162—164°, hydrolysed by sodium hydroxide to methystic acid, m. p. 187—188°. Methyl α-acetyl-γ-cinnamylideneacetoacetate is transformed by ammonia in presence of ether at the ordinary temperature into *allo*kawain [methyl γ-cinnamylideneacetoacetate], m. p. 93°, in nearly 80% yield; it is converted by methyl orthosilicate and subsequent hydrolysis into kawaic [β-methoxy-ζ-phenyl-Δ^αγ-heptadienoic] acid, m. p. 186° (decomp.). H. Wren.

Nitration of substituted benzaldehydes and stability of the aldehyde group. H. H. Hodgson and E. W. Smith (J.S.C.I., 1930, **49**, 408—410T).—The introduction of a 5-nitro-group into *m*-nitrobenzaldehyde by direct nitration has so far proved to be impracticable on account of oxidation taking place under the severe conditions employed. To modify the deactivation of the nuclear carbon atoms, due to the combined symmetrical effect of the two nitro-groups, two routes have been explored: (1) the use of substituted anils, which, however, could be nitrated only in the aniline portion of the molecule, and (2) the introduction of *op*-directing groups into the *m*-nitrobenzaldehyde nucleus. Of the various groups available, the amino-group was unsuitable because of its facile decomposition, although when protected, as in 3-nitro-4-acetamidobenzaldehyde, even acetyl nitrate failed to introduce a second nitro-group. When the hydroxyl group was present, as in 3-nitro-4-hydroxybenzaldehyde, dinitration readily occurred with formation of 3 : 5-dinitro-4-hydroxybenzaldehyde, although the hydroxyl group now resists methylation. Starting from 4-methoxy- or 4-ethoxy-benzaldehyde, the 3-nitro-group was introduced without difficulty, but attempts at further nitration resulted in the formation of 2 : 4-dinitro- and 2 : 4 : 6-trinitro-anisole. Attempts to dinitrate *o*-anisaldehyde produced 3 : 5-dinitro-2-methoxybenzoic acid. *p*-Chlorobenzaldehyde mononitrates and then oxidises only when the nitration conditions are made more stringent *p*-Bromobenzaldehyde gives both 4-bromo-3 : 5-dinitrobenzaldehyde and 4-bromo-3 : 5-dinitrobenzoic acid. The bromine atom in 4-bromo-3 : 5-dinitrobenzaldehyde is readily replaced by the amino- and methoxy-groups. 3 : 5-Dinitro-4-aminobenzaldehyde resists diazotisation and 3 : 5-dinitrotoluene resists oxidation.

Chloro-derivatives of vanillin and their reactions. L. C. Raiford and J. G. Lichty (J. Amer. Chem. Soc., 1930, 52, 4576—4586).—2-*Chlorovanillin* (2-*chloro*-4-*hydroxy*-3-*methoxybenzaldehyde*), m. p. 128—129° (*oxime*, m. p. 157—158°; p-*bromophenylhydrazone*, m. p. 144—146°; *semicarbazone*, m. p. 220—221°), prepared by the usual method from 2-aminovanillin, condenses with benzidine forming *bis*-2-*chlorovanillylidenebenzidine*, m. p. 224—226°. Chlorination of vanillin with rather more than 1 mol. of chlorine in chloroform below 60° affords 5-chlorovanillin, m. p. 163° (lit. 165°) (*oxime*, m. p. 172°; p-*bromophenylhydrazone*, m. p. 161°; *semicarbazone*, m. p. 201°), converted by treatment with acetic anhydride and sodium acetate into the *acetyl* derivative, m. p. 201°, of 5-*chloro*-4-*hydroxy*-3-*methoxycinnamic acid*, m. p. 235—236° after previous shrinking. *Bis*-5-*chlorovanillylidenebenzidine* has m. p. 252—254°. Chlorination of 4-acetoxy-3-methoxybenzylidene diacetate, m. p. 90—91° (lit. 88—89°), in acetic acid containing sodium acetate at about 40°, gives the 6-*chloro*-derivative, m. p. 143—144°, hydrolysed by dilute potassium hydroxide solution to 6-*chlorovanillin*, m. p. 167—168° (*oxime*, m. p. 178°; p-*bromophenylhydrazone*, m. p. 174°; *semicarbazone*, m. p. 241°); *bis*-6-*chlorovanillylidenebenzidine*, decomp. 263°, is also described. Bromination of 6-chlorovanillin in acetic acid containing sodium acetate furnishes 6-*chloro*-5-*bromovanillin*, m. p. 214°, and chlorination of 6-bromovanillin in chloroform at about 40° yields 5-*chloro*-6-*bromovanillin*, m. p. 202°.

Nitration of 6-chloro-4-acetoxy-3-methoxybenzylidene diacetate with fuming nitric acid at 20—30° affords the 2-*nitro*-derivative, m. p. 81—82°, hydrolysed to 6-*chloro*-2-*nitrovanillin*, m. p. 155—157°. This is reduced by ferrous sulphate and ammonia to 6-*chloro*-2-*aminovanillin*, m. p. 192—193° after softening at 190°, converted by the usual method into 2 : 6-*dichlorovanillin*, m. p. 139—140° (*oxime*, m. p. 141°; *semicarbazone*, m. p. 213°); *bis*-2 : 6-*dichlorovanillylidenebenzidine* has m. p. 232°. The *acetyl* derivative, m. p. 67°, of 5-chlorovanillin yields with nitric acid (*d* 1·5) below 20° the *acetyl* derivative (+EtOH), m. p. 95—96°, m. p. (alcohol-free) 112°, of 5-*chloro*-2-*nitrovanillin*, m. p. 137°. The last-named compound is reduced by ferrous hydroxide to 5-*chloro*-2-*aminovanillin*, m. p. 136—137°, convertible into 2 : 5-*dichlorovanillin*, m. p. 179° (*oxime*, m. p. 158°; p-*bromophenylhydrazone*, m. p. 158°; *semicarbazone*, m. p. 228°), also formed in small amount during the chlorination of vanillin. *Bis*-2 : 5-*dichlorovanillylidenebenzidine* has m. p. 254—255°. Chlorination of 5-*chloro*-4-*acetoxy*-3-*methoxybenzylidene diacetate*, m. p. 115—116°, in acetic acid containing sodium acetate yields 5 : 6-*dichloro*-4-*acetoxy*-3-*methoxybenzylidene diacetate*, m. p. 117—118°, hydrolysed by boiling with 10*N*-potassium hydroxide to 5 : 6-*dichlorovanillin*, m. p. 192° [*oxime*, m. p. 203° (decomp.); p-*bromophenylhydrazone*, m. p. 163—164°; *semicarbazone* (+EtOH), m. p. (alcohol free) 237°], also obtained by direct chlorination of 6-chlorovanillin. *Bis*-5 : 6-*dichlorovanillylidenebenzidine*, decomp. 289°, is also described.

Treatment of a saturated solution of 2 : 6-dichlorovanillin in chloroform with sulphuryl chloride at the ordinary temperature furnishes 2 : 5 : 6-*trichlorovanillin*, m. p. 154° (*oxime*, m. p. 173°; *semicarbazone*, m. p. 219°). 2 : 6-*Dichloro*-5-*bromovanillin* has m. p. 167°.

One oxime only is obtained from each chlorovanillin examined and this (? *anti*) derivative could not be isomerised by hydrogen chloride (cf. Brady and Dunn, J.C.S., 1915, 107, 1859; Raiford and Stoesser, A., 1928, 1246). H. Burton.

Chloroimines. III. Decomposition of aromatic aldchloroimines to form nitriles. Preparation of nitriles from aldehydes. C. R. Hauser and A. G. Gillaspie (J. Amer. Chem. Soc., 1930, 52, 4517—4519).—Treatment of *o*- and *p*-chloro-, *o*- and *m*-nitro-, 2-chloro-5-nitro-benzylidene-, anisylidene-, and piperonylidene-*N*-chloroimines with cold alcoholic potassium hydroxide or sodium ethoxide solution affords the corresponding benzonitriles in 60—97% yield. H. Burton.

Isomerisation of hydroxyaldehydes. IV. Transformation of benzylbromoacetaldehyde and benzylglycollaldehyde. S. Danilov and E. Venus-Danilova (Ber., 1930, 63, [*B*], 2765—2775; cf. A., 1929, 1448).—β-Phenylpropaldehyde in carbon disulphide at −5° is transformed by the gradual addition of bromine into the unstable α-*bromo*-β-*phenylpropaldehyde*, which readily becomes resinified and polymerised. It yields a crystalline *monohydrate*, m. p. 87·5—88°. With semicarbazide it yields α-*hydroxy*-β-*phenylpropaldehydesemicarbazone*, m. p. 136·5°. When heated with water and freshly precipitated barium carbonate the bromoaldehyde gives α-hydroxy-β-phenylpropaldehyde in moderate yield with 4% of β-phenylpropionic acid and halogenated condensation products. With silver oxide and hot

water, the products are 20% of α-hydroxy-β-phenylpropaldehyde, 9·4% of α-hydroxy-β-phenylpropionic acid, 5·6% of a condensation product of the bromoaldehyde, and 31% of β-phenylpropionic acid. Lead oxide and water afford mainly condensation products of the bromoaldehyde and 22·6% of β-phenylpropionic acid. α-*Hydroxy-β-phenylpropaldehyde*, m. p. 51·5—52°, gives an *oxime*, m. p. 123°, semicarbazone, m. p. 136·5° (see above), *phenylosazone*, $C_{21}H_{20}N_4$, m. p. 137°, and *benzoate*, m. p. 70°. Oxidation of the aldehyde by permanganate in presence of pyridine gives phenylacetaldehyde and α-hydroxy-β-phenylpropionic acid; similar treatment of the benzoate and hydrolysis of the product affords α-hydroxy-β-phenylpropionic acid unaccompanied by neutral products. The hydroxyaldehyde is isomerised by sulphuric acid in the presence of alcohol at 130—135° to a mixture of α-phenylpropane-αβ-dione (*dioxime*, m. p. 238—239°) and acetylphenylcarbinolsemicarbazone, m. p. 194°, accompanied by a small amount of (?) *p*-diphenylbenzoquinone, m. p. 230°. The structure of the hydroxyketone is established by its conversion by magnesium phenyl bromide into methylhydrobenzoin, m. p. 103°, oxidised to benzoic acid and acetophenone.
H. WREN.

Mixed catalysts in the Friedel–Crafts reaction. Yield of benzophenone from benzoyl chloride and benzene using ferric chloride–aluminium chloride mixtures as catalysts. W. A. RIDDELL and C. R. NOLLER (J. Amer. Chem. Soc., 1930, **52**, 4365—4369; cf. Boswell and McLaughlin, A., 1930, 170).—Optimum yields (more than 90%) of benzophenone are obtained when 1·1 mols. of pure aluminium chloride are used per 1 mol. of benzoyl chloride in the Friedel–Crafts reaction. When mixtures (=1·1 mols.) of aluminium and ferric chlorides are used, the yields are approximately the mean of those obtained using the individual chlorides. Addition of ferric chloride to 1·1 mols. of aluminium chloride also causes a diminution in the yield. In all experiments with ferric chloride an iron-containing by-product is formed.
H. BURTON.

Forced reaction between anils and *p*-thiocresol. Reducing action of the thiol grouping. H. GILMAN and J. B. DICKEY (J. Amer. Chem. Soc., 1930, **52**, 4573—4576).—When benzophenoneanil is treated with *p*-thiocresol in boiling xylene with the exclusion of air, a mixture of di-*p*-tolyl disulphide and benzhydrylaniline is obtained; the last-named substance is isolated mainly as the additive *compound* (1 : 1), m. p. 83—84°, with benzophenoneanil. Benzylideneaniline and *p*-thiocresol afford similarly di-*p*-tolyl disulphide and benzylaniline; azobenzene is reduced to hydrazobenzene, which under the experimental conditions decomposes to aniline (and azobenzene). Nitrobenzene and benzophenone are not reduced by *p*-thiocresol.

Magnesium *p*-tolylthiol iodide (A., 1925, i, 810) does not react with benzophenoneanil or benzylideneaniline in ethereal toluene solution.
H. BURTON.

ωω-Dihalides of aliphatic-aromatic ketones of the type Ar·CO·CHX₂, in particular ωω-chlorobromo-derivatives of the type Ar·CO·CHClBr. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1930, **10**, 541—554).—The following substances have been prepared: *p-tolyl chlorobromo-* and *dichloro-methyl ketones*, m. p. 87° and 55·5—56°, respectively, o-4-*xylyl chlorobromo-* and *dichloro-methyl ketones*, m. p. 25·5—26° and b. p. 145—146°/10·5 mm., respectively, 4-*methoxy-*, 4-*bromo-*, and 4-*iodo-phenyl chlorobromo-methyl ketones*, m. p. 88—89°, 82°, and 78·5—79°, respectively. The halogen of the side-chains is transferred to the nucleus on oxidation with dilute nitric acid; thus *p*-tolyl dibromomethyl ketone yields 3-bromo-4-methylbenzoic acid.
R. TRUSZKOWSKI.

Ketonitriles and ketothiocyanates of the type $Ar\cdot CO\cdot CH_2\cdot CN$ and $Ar\cdot CO\cdot CH_2\cdot SCN$. I. RABCEWICZ-ZUBKOWSKI and H. KAFLIŃSKA (Rocz. Chem., 1930, **10**, 555—569).—The following substances have been prepared by the action of potassium cyanide or thiocyanate on the appropriate chloro- or bromo-derivative: 4-*bromophenyl*, m. p. 162·4—163·4°, 4-*iodophenyl*, m. p. 187·4—188·4°, 3-*nitrophenyl*, m. p. 152—153°, p-*tolyl*, m. p. 104·6—105·2°, m-4-*xylyl*, m. p. 80·1—81°, and β-*naphthyl*, m. p. 127·6—128·2°, *cyanomethyl ketones*; *phenyl*, m. p. 74·1—74·6°, 4-*chloro-*, m. p. 138·6—139·2°, 4-*bromo-*, m. p. 148·8—149·2°, 4-*iodo-*, m. p. 154—155°, p-*tolyl*, m. p. 106·2—106·8°, p-*anisyl*, m. p. 124·2—124·8°, 3-*nitrophenyl*, m. p. 123·6—124·2°, m-4-*xylyl*, m. p. 80·8—81·0°, and β-*naphthyl*, m. p. 109·4—110°, *thiocyanomethyl ketones*. Bromination of cyanoacetophenone yields *benzoyldibromoacetamide*, m. p. 181·6—182·4°, whilst thiocyanoacetophenone gives an unstable *dibromide*, m. p. 132—134°, which loses hydrogen bromide on recrystallisation from alcohol, yielding a *substance*, $(C_9H_5ONS)_x$, m. p. 208—208·5°.
R. TRUSZKOWSKI.

Reactivity of the positive hydrogen atom. V. Preparation of tetraphenyl*cyclo*pentadienone. W. DILTHEY and F. QUINT (J. pr. Chem., 1930, [ii], **128**, 139—149).—The condensation of benzil with dibenzyl ketone in cold alcoholic solution under the influence of alkali leads to 3-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ^4-*cyclo*penten-1-one, previously obtained by use of aqueous alkali (J.C.S., 1901, 79, 1256), and probably identical with Löwenbein and Ulich's product from benzylidenediphenylmaleide and magnesium phenyl bromide (A., 1926, 171). It is converted by reduction with zinc and acetic acid into 2 : 3 : 4 : 5-*tetraphenyl-*Δ^4-cyclo*penten-1-one*, m. p. 162—163°, also obtained by replacing benzil by benzoin in the above condensation. At the b. p., 2 : 3 : 4 : 5-tetraphenyl-$\Delta^{2:4}$-*cyclo*pentadien-1-one (Löwenbein and Ulich, *loc. cit.*) [*dibromide*, m. p. 169—170° (decomp. into the ketone and bromine: similarly decomposed by warming in a suitable solvent)] is formed by further elimination of water in the original condensation. It is also produced by the action of bromine in acetic acid at 100° on tetraphenyl*cyclo*penten-1-one, to which it is reduced by hydrogen and palladium, and also to some extent by zinc and acetic acid, being accompanied in the latter case by 2 : 3 : 4 : 5-*tetraphenyl-*$\Delta^{2:4}$-cyclo*pentadien-1-ol* (+1AcOH), m. p. 139—140°, an unstable substance which is readily re-oxidised to the ketone. Unidentified substances of m. p. 163°, 220°, and 144°, obtained by catalytic hydrogenation of 3-hydroxy-2 : 3 : 4 : 5-tetraphenyl-Δ^4-*cyclo*penten-1-one, are described.
H. A. PIGGOTT.

Tautomerism of α-diketones. H. Moureu (Ann. Chim., 1930, [x], **14**, 283—405).—A detailed account of work previously reviewed (A., 1922, i, 843; 1923, i, 113; 1924, i, 405; 1925, i, 937; 1927, 246, 571, 884, 1173; 1928, 180, 419, 1334; 1929, 189, 448, 883, 929). H. Burton.

4-Alkyl derivatives of 1-phenyl*cyclo*hexane-3 : 5-dione. I. H. el-S. Mattar, J. J. H. Hastings, and T. K. Walker (J.C.S., 1930, 2455—2458).—The synthesis of derivatives of *cyclo*hexane-1 : 3-dione by addition of ethyl sodiomalonate to ketones of the type $>C{:}CH{\cdot}CO{\cdot}CHR$ (R=H; cf. Vorländer, A., 1894, i, 527) is also applicable where R=alkyl. The following are prepared from the appropriate styryl alkyl ketones: *ethyl* 1-*phenyl*-4-*methyl*cyclo*hexane*-3:5-*dione*-2-*carboxylate* $(+0{\cdot}5H_2O)$, m. p. 121—123°; 1-*phenyl*-4-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 212—213°; 1-*phenyl*-4-*ethyl*-, m. p. 200° (oxidises and resinifies in air); 1-*phenyl*-4-n-*propyl*-, m. p. 185°; 1-*phenyl*-4-n-*amyl*-cyclo*hexane*-3 : 5-*dione*, m. p. 191°; *ethyl* 1-*phenyl*-4-*benzyl*cyclo*hexane*-3 : 5-*dione*-2-*carboxylate*, m. p. 146°, and 1-*phenyl*-4-*benzyl*cyclo*hexane*-3 : 5-*dione*, m. p. 169—170°. Ethyl phenylacetate condenses with styryl ethyl ketone (but not styryl β-phenylethyl ketone) in presence of sodium ethoxide, and the product on decarboxylation gives 1 : 2-*diphenyl*-4-*methyl*cyclo*hexane*-3 : 5-*dione*, m. p. 167°. An improved preparation of styryl β-phenylethyl ketone (Harries and Gollnitz, A., 1904, i, 427) by alkaline hydrolysis of ethyl benzylacetoacetate, followed by decarboxylation of the product, is described. H. A. Piggott.

Reduction of *p*-dimethylaminobenzil. S. S. Jenkins [with J. S. Buck and L. A. Bigelow] (J. Amer. Chem. Soc., 1930, **52**, 4495—4499).—Reduction of *p*-dimethylaminobenzil by the method previously described (A., 1929, 1072) affords either *p*-dimethylaminobenzoin (*p*-dimethylaminobenzoylphenylcarbinol) or p-*dimethylaminohydrobenzoin*, m. p. 112°, according to the amount of hydrogen consumed. The hydrobenzoin is dehydrated by heating with a 4 : 1 mixture of acetic and hydrochloric acids to α-p-*dimethylaminodeoxybenzoin* (*benzoyl*-p-*dimethylaminophenylmethane*), m. p. 128° (*oxime*, m. p. 139°), reduced catalytically (Adams) in alcohol at 60° to α-*phenyl*-β-p-*dimethylaminophenylethyl alcohol*, m. p. 78°. Reduction of *p*-dimethylaminobenzoin with tin and alcoholic hydrochloric acid containing a small amount of copper sulphate gives a mixture of α-(above) and β-p-*dimethylaminodeoxybenzoin* (p-*dimethylaminobenzoylphenylmethane*), m. p. 164° (*oxime*, m. p. 142°). The β-compound is reduced catalytically to β-phenyl-α-*p*-dimethylaminophenylethyl alcohol, m. p. 60° (Sachs and Sachs, A., 1905, i, 202). The last-named substance and its isomeride are dehydrated with acetic and hydrochloric acids to *p*-dimethylaminostilbene, which is reduced catalytically to α-*phenyl*-β-p-*dimethylaminophenylethane*, m. p. 63° [*methiodide*, m. p. 260—262° (all m. p. except this are corr.)]. H. Burton.

Valency tautomerism in unsaturated systems. G. Wittig and W. Wiemer (Annalen, 1930, **483**, 144—156).—The following dibenzoylnaphthalenes are prepared from magnesium phenyl bromide and the requisite dicyanonaphthalene: 1 : 5-dibenzoyl-, m. p. 185—186°; 1 : 6-dibenzoyl-, m. p. 175—176°; 2 : 6-*dibenzoyl*-, m. p. 184—186°, and 2 : 7-*dibenzoyl*-, m. p. 171—172°. The 1 : 5- and 2 : 6-derivatives react with magnesium phenyl bromide yielding 1 : 5-, m. p. 280° (decomp.), and 2 : 6-*di*(*hydroxydiphenylmethyl*)*naphthalene*, m. p. 279—281° (decomp.), respectively; crystalline compounds could not be obtained from the 1 : 6- and 2 : 7-compounds. Treatment of the above carbinols with hydrogen chloride in boiling dioxan solution furnishes 1 : 5-, m. p. 250—251°, and 2 : 6-*di*(*chlorodiphenylmethyl*)*naphthalene*, m. p. 250—253°, respectively. Treatment of these dichlorides with copper bronze (Naturkupfer C) in xylene in an atmosphere of nitrogen affords red solutions of 1 : 5- and 2 : 6-di(diphenylmethylene)napthalene, which are decolorised by oxygen only after many hours' treatment. The red solution of the 2 : 6-derivative when treated with phenyl iodochloride regenerates the corresponding dichloro-compound. The number of conjugated unsaturated linkings between the methylene carbon atoms is, in the above cases, four. In compounds of similar types containing five (Tschitschibabin, A., 1907, i, 503; Schlenk, A., 1915, i, 518) and six conjugated unsaturated linkings (see below), decolorisation by treatment with oxygen is rapid. This can be ascribed to the existence of the radical form of the hydrocarbon,

$$CPh_2{:}R{:}CPh_2 \rightleftharpoons \overset{|}{C}Ph_2{\cdot}R{\cdot}\overset{|}{C}Ph_2.$$

αβ-Di-*p*-benzoylphenylethane (A., 1928, 642) is treated with bromine in boiling nitrobenzene whereby hydrogen bromide is evolved and 4 : 4′-*dibenzoylstilbene*, m. p. 234—235°, is produced. This reacts with magnesium phenyl bromide forming 4 : 4′-*di*(*hydroxydiphenylmethyl*)*stilbene*, m. p. 208—212°, which with hydrogen chloride in benzene containing a little acetyl chloride gives 4 : 4′-*di*(*chlorodiphenylmethyl*)*stilbene*, m. p. 213—216° with darkening. Treatment of a suspension of this dichloride in chloroform with copper bronze in an atmosphere of nitrogen yields a blue solution of 4 : 4′-di(diphenylmethylene)-stilbene, which is decolorised by oxygen; the solid di-radical decomposes rapidly in air to a yellow substance. Treatment of the blue solution with phenyl iodochloride regenerates the above dichloride, which is readily hydrolysed to the dicarbinol. H. Burton.

Syntheses of phenolic ketones according to Hoesch. IV. W. Borsche and K. Diacont (Ber., 1930, **63**, [*B*], 2740—2743; cf. A., 1929, 1309).—Benzoylformic acid and resorcinol in presence of zinc chloride and ether are transformed by hydrogen chloride into 2 : 4 : 2′ : 4′-tetrahydroxytriphenylacetolactone, whereas phloroglucinol does not afford a crystalline product. Under similar conditions, acetyl cyanide and resorcinol give α-2 : 4-*dihydroxyphenylpropane*-αβ-*dione*, m. p. 159° (decomp.) [*disemicarbazone*, m. p. 243—245°; *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 249—250°]; the corresponding *monoketimine hydrochloride* is described. With phloroglucinol, acetyl cyanide appears to yield a *trihydroxyphenylpropanediol*. Resorcinol and propionyl cyanide give the *monoketimine hydrochloride* $C_{10}H_{12}O_3NCl$, hydrolysed to α-2 : 4-*dihydroxyphenyl*-

butane-αβ-dione, m. p. 150° (*disemicarbazone*, m. p. 205°; *bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 245°).
H. WREN.

Reduction of substituted *p*-benzoquinones by sulphur dioxide alone and in presence of alkali. J. W. DODGSON (J.C.S., 1930, 2498—2502; cf. *ibid.*, 1914, **105**, 2435).—The sulphonation that accompanies reduction of a quinone by sulphur dioxide in aqueous solution increases as the proportion of alkali is increased to a maximum which corresponds approximately with the formation of alkali hydrogen sulphite, and then steadily decreases. In the case of monochlorobenzoquinone, chlorine is not liberated until the ratio of alkali to sulphur dioxide is greater than 1 : 1, some disulphonic acid being then produced. Displacement of chlorine from dichlorobenzoquinone, with consequent sulphonation, is more marked, and from tetrachlorobenzoquinone aqueous sulphur dioxide alone displaces a considerable proportion of chlorine, sulphonation occurring to a corresponding degree. *Barium toluquinolsulphonate*, p-*xyloquinolsulphonate*, *chloroquinolsulphonate*, 2 : 5-*dichloroquinolsulphonate*, and 2 : 3-*dichloroquinolsulphonate* are described, the last two being apparently contaminated by disulphonate.
H. A. PIGGOTT.

Anthraquinhydrone. O. BALLY (Ber., 1930, **63**, [*B*], 2938).—The green colour observed when anthraquinone is treated with potassium hydroxide is probably due to the formation of the potassium derivative of anthraquinhydrone (cf. Scholl and Böttger, A., 1930, 1438).
H. WREN.

Action of nitric oxide on caoutchouc. A. GORGAS (Ber., 1930, **63**, [*B*], 2700—2705).—Total caoutchouc prepared from "revertex" according to the method of Pummerer and Pahl (A., 1927, 1193), sol and gel caoutchoucs give iodine values corresponding with the absorption of 1 mol. of iodine per isoprene residue when treated by the author's modification of Hanus' process. With bromine iodide a somewhat low iodine value is observed. Differing thiocyanogen values are not observed for the differing varieties of caoutchouc.

Treatment of purified caoutchouc in carbon tetrachloride at 0° with nitrogen peroxide, prepared from formaldehyde and concentrated nitric acid, followed by the action of oxygen and repeated crystallisation and fractional distillation, does not lead to the formation of a homogeneous product. Addition of the peroxide is invariably accompanied by oxidation. In the material produced after 24 hrs.' action, about one third of the added nitrogen is evolved as ammonia by heating with concentrated alkali hydroxide, thus indicating the presence of an oximino-group and decomposition of the liberated hydroxylamine, $3NH_2{\cdot}OH{=}NH_3{+}3H_2O{+}N_2$. Addition of nitric oxide to caoutchouc proceeds more slowly than that of nitrogen peroxide and yields a heterogeneous product containing the oximino-group. Dilute nitric acid transforms caoutchouc into a nitrogenous product soluble in acetone and a non-nitrogenous material insoluble in this medium. Ammonia is evolved when the former substance is boiled with alkali hydroxide. If carbamide is added to the nitric acid, the product of the change is a yellow, friable mass free from nitrogen.
H. WREN.

Isoprene and caoutchouc. XXII. *iso*Caoutchouc nitron. H. STAUDINGER and H. JOSEPH (Ber., 1930, **63**, [*B*], 2888—2899; cf. Pummerer and Gündel, B., 1928, 793).—A review of the literature shows that almost invariably the primary action of reagents on caoutchouc consists in fission of the labile macro-molecules into smaller fragments of hemicolloidal character which then react further with the reagent with rupture of the double linking. Treatment of purified caoutchouc in 0·2*M*-solution with nitrosobenzene in amount varying from 0·01 to 3 mols. and with nitrogen peroxide or benzoyl peroxide causes diminution in the viscosity of the solutions which is more marked with nitrogen peroxide than with nitrosobenzene and least obvious with benzoyl peroxide. Since with 0·01—0·02 mol. of nitrosobenzene the viscosity is but little diminished, the change cannot be due to initial oxidative degradation to hemicolloidal products and reaction of the latter with nitrosobenzene, but oxidative fission and nitron formation must occur simultaneously. Analyses of *iso*caoutchouc nitron disclose a deficiency of 1·5—2·0% of carbon and, assuming the determination of mol. wt. by Pummerer and Gündel (*loc. cit.*) to be correct, agree with an octameric nitron which has acquired by oxidation 2 atoms of oxygen or 1 mol. of hydrogen peroxide. The mol. wt. of the product in benzene is approximately twice as great as in nitrobenzene; the values in the latter medium vary considerably, but, on the average, are only slightly higher than those recorded by Pummerer and Gündel. The action of oxides of nitrogen on caoutchouc is accompanied by marked degradation of the hydrocarbon molecule, and the nitrosate is richer in oxygen than a caoutchouc nitrosite. *iso*Caoutchouc nitron is a polymeric-homologous mixture, since it can be separated by cold benzene into more and less freely soluble portions which differ in viscosity when dissolved in chloroform; the composition of the fractions is approximately the same. The oxidative degradation of the long caoutchouc molecule to hemicolloidal products of relatively similar order of magnitude instead of to those of widely varying length is attributed to the incomparably less stable condition of the longer molecules. The formation of a relatively simple, hemicolloidal *iso*caoutchouc nitron is thus not incompatible with the view that caoutchouc has a very high mol. wt.
H. WREN.

Isoprene and caoutchouc. XXIII. Cryoscopic measurements with caoutchouc solutions. H. STAUDINGER and H. F. BONDY (Ber., 1930, **63**, [*B*], 2900—2905).—The viscosity of solutions of caoutchouc in benzene is much greater with the fresh material than with that which has been dissolved in molten camphor. Treatment of caoutchouc with the last-named substance involves a profound degradation of the caoutchouc molecule and renders camphor an unsuitable medium for the determination of mol. wt. The observations of Pummerer and others (A., 1929, 1455) on the behaviour of caoutchouc and benzene are readily explicable, since they used gel solutions; the molecules are freely mobile only in much less concentrated solution than those employed. The statement of Pummerer and Gündel (B., 1928, 793) that the authors' product is contaminated by nitrogen is not supported by experiment. Their values for the mol. wt. of sol caoutchouc in menthol do not appear to be established firmly, since considerably higher data are given by the method of isothermal distillation. The mol. wts. recorded by Pummerer for intact caoutchouc cannot be accepted, since they are identical with those observed for degraded products which have properties differing widely from those of caoutchouc. H. WREN.

Sclareol and its derivatives. M. M. JANOT (Compt. rend., 1930, **191**, 847—849).—Sclareol has *M* 250—265 in benzene, acetic acid, and camphor, $[\alpha]_D$ −3·3° in chloroform (rotations in other solvents are given). It is probably a tertiary alcohol, $C_{17}H_{30}O_2$ (cf. Volmar and Jermstad, A., 1928, 524). Sclareol distils at 188—189°/3 mm. or 218—220°/19 mm. to give a crystalline product, m. p. 104—105°, is not hydrolysed by alcoholic potassium hydroxide, may be acetylated and benzoylated only with difficulty and incompletely, and suffers a loss in weight of 45% when heated for 72 hrs. at its m. p. When heated with phenylcarbimide at 150° it gives carbon dioxide and diphenylcarbamide.

Bromination in carbon disulphide in presence of silver carbonate affords a *bromide* (Br 35·33%), m. p. 122—124°, and two other *substances*, m. p. 140—143°, and m. p. 134—135°, $[\alpha]_D$ +12·4° in pyridine. Sclareol is hydrogenated in alcohol, with palladium-black as catalyst, to a crystalline *derivative*, m. p. 114—115°, *M* 270 in camphor, $[\alpha]_D$ −10·1°, Silver sclareolate (*loc. cit.*) melts at 152—154°. Sclareol possesses no marked ultra-violet absorption. T. H. MORTON.

Resin acid of the *iso*sylvic acid group. O. ASCHAN (Annalen, 1930, **483**, 124—132).—The preparation of an *iso*sylvic acid (cf. A., 1924, i, 533) is described and suggestions are made regarding its structure and that of pinabietic acid.

[With O. M. GADD.] Pinabietic acid dihydrobromide, m. p. 192—194° (Virtanen, A., 1921, i, 669), is converted by potassium hydroxide in 90% alcohol into *pin*iso*sylvic acid*, $C_{20}H_{30}O_2$, m. p. 82° (*silver* salt; *tetrabromide*, m. p. 87°). Reduction of the dihydrobromide with zinc dust and acetic acid affords *dihydropin*iso*sylvic acid*, m. p. 92° (impure *dibromide*, m. p. about 92°), which with hydrogen bromide in presence of ether and acetic acid gives a *hydrobromide*, m. p. 163—165°. When pinabietic acid dihydrobromide is boiled with acetone, hydrogen bromide is eliminated and a *monohydrobromide*, m. p. 186°, is formed. Pinabietic acid hydrochlorides could not be prepared. H. BURTON.

Reactions of *g*-strophanthin (ouabain) and *k*-strophanthin. L. EKKERT (Pharm. Zentr., 1930, **71**, 724—725).—To about 0·005 g. of substance is added a drop of a 1% alcoholic solution of furfuraldehyde, followed by a drop of sulphuric acid; ouabain shows under these conditions only a pale greenish- to greyish-brown colour, whilst strophanthin gives a deep indigo blue. If more (5 drops) of sulphuric acid be employed, the respective colorations are red to brown, and dark green (cf. Helbing, A., 1887, 1001; Richaud, 1921, ii, 601). R. CHILD.

Menthone series. VII. Condensation of menthylamines with *d*- and *l*-oxymethylenecamphor. J. READ and (MISS) C. S. STEELE (J.C.S., 1930, 2430—2434).—*d*-*neo*Menthylamine condenses with *d*- and *l*-oxymethylenecamphor to yield, respectively, *d*-neo*menthylamino*-d-, m. p. 105°, $[\alpha]_D$ +317·8° (all rotations in alcohol unless otherwise stated), and -l-, m. p. 94°, $[\alpha]_D$ −129·8°, *-methylenecamphor*. *dl*-*neo*Menthylamine condenses similarly with *d*-oxymethylenecamphor, and the crude product, m. p. 92°, is separated into *d*-*neo*menthylamino-*d*-methylenecamphor (insoluble) and l-neo*menthylamino*-d-*methylenecamphor*, m. p. 92°, $[\alpha]_D$ +130°, which are converted by bromine in alcohol into d-, not melting below 220°, $[\alpha]_D$ +18·6° in water, and l-, $[\alpha]_D$ −18·5° in water, -neo*menthylamine hydrobromide*, respectively. Similarly, from the active components are obtained: d-iso*menthylamino*-d-, m. p. 110°, $[\alpha]_D$ +281·3—257·5° (constant) in 48 hrs., and -l-, m. p. 99—100°, $[\alpha]_D$ −212·9° to −160·8° in 48 hrs., *-methylenecamphor*; l-*menthylamino*-d-, m. p. 90°, $[\alpha]_D$ +196·7—125·0° in 16 hrs., and -l-, $[\alpha]_D$ −170·2°, *-methylenecamphor*. In both these cases, however, the condensation product of the *dl*-base with *d*-oxymethylenecamphor, $[\alpha]_D$ +162·2—155·2° in 48 hrs., and $[\alpha]_D$ +140·2—145·6° in 16 hrs., respectively, is too soluble to effect resolution by fractional crystallisation, nor could any optical activity be detected in the unchanged base arising from a possible difference in the reaction velocity of the *d*- and *l*-forms. *l*- and *d*-*iso*Menthylamino-*d*-methylenecamphor appear to form a partial racemate which retains its stability when dissolved in alcohol, since the observed value, $[\alpha]_D$ +162·2°, for the *dl*-condensation product differs considerably from the mean of the values of the individual components (+247·1°). J. W. BAKER.

Autoxidation of piperitone in alkaline solution. W. TREIBS (Ber., 1930, **63**, [*B*], 2423—2428).—In alcoholic, alkaline solution, oxygen is absorbed most rapidly by the unsaturated ketones, carvone, piperitone, and carvenone, less rapidly by pulegone, *cyclo*hexenone, and verbenone, and not by dihydrocarvone. Benzylideneacetone reacts energetically, methylheptenone and mesityl oxide only very slowly. With 0·1 mol. of ketone in 40—60 c.c. of solvent, the amount of oxygen absorbed increases to a maximum of 1 mol. per mol. of ketone when the mol. ratio of alkali hydroxide to ketone is 1 : 1. In more dilute solution up to 2 mols. of oxygen are absorbed with formation of lower fatty acids derived from the alcohol by autoxidation. In acetone solution oxidation occurs only if alcohol is added; the presence of the latter in mol. ratio 1 : 1 suffices to complete the change in the same manner as in alcoholic solution. With aliphatic alcohols the rate of reaction appears to increase with increasing length of the hydrocarbon chain, but the total absorption is substantially independent of the nature of the alcohol. In the concentration 0·1 mol. in 40—60 c.c. and in presence of not more than 0·1 mol. of alkali hydroxide, *p*-benzoquinone, phenanthraquinone, β-naphthaquinone, and orcinol absorb 1 mol. of oxygen per mol., pyrocatechol and quinol 2 mols., benzylideneacetone and resorcinol about 0·5 mol. Gold chloride greatly accelerates the absorption of oxygen by pulegone, but retards that by resorcinol. Salts of platinum and palladium are without action.

Piperitone dissolved in methyl-alcoholic potassium hydroxide is subjected to autoxidation and then distilled with steam whereby a small amount of phenolic material, probably containing thymol, is obtained. After acidification, the residual solution is again distilled with steam, thus leading to the isolation of an unsaturated *acid*, $C_{10}H_{16}O_2$, m. p. 57—59° (*calcium* salt), and a *lactone*, $C_{10}H_{16}O_2$, b. p. 246—248°/atm. pressure, 118—120°/13 mm., d_{15}^{20} 1·010, transformed slowly by 20% potassium hydroxide into the *hydroxy-acid* $C_{10}H_{18}O_3$, m. p. 113—114° (*sodium* and *potassium* salts). Reduction of the lactone by sodium in methyl or ethyl alcohol affords a *glycol*, $C_{10}H_{20}O_2$, b. p. 150—152°/13 mm. Digestion of the hydroxy-acid with 25% sulphuric acid yields mainly lactone with some unsaturated acid, $C_{10}H_{16}O_2$. Treatment of the lactone with methyl- or ethyl-alcoholic hydrogen chloride or sulphuric acid gives the *methyl* ester, b. p. 94—95°/15 mm., d_{15}^{20} 0·9450, and *ethyl* ester, b. p. 102—105°/14 mm., d_{15}^{20} 0·9467, of the unsaturated acid.

The residue from the distillation with steam is a brown resin; its solubility in alkali hydroxide increases with the amount of alkali used in its preparation. The soluble and insoluble portions have the same composition. H. WREN.

Photopolymerisation of piperitone. W. TREIBS (Ber., 1930, 63, [*B*], 2738—2740).—Irradiation of piperitone dissolved in glacial acetic acid or alcohol and water by the mercury-vapour lamp yields three *dimerides*: (1) needles, m. p. 162°, which do not yield a semicarbazone, (2) needles, m. p. 142—144°, giving a *semicarbazone*, needles or cubes, m. p. 228—235° (decomp.) according to the rate of heating, and (3) rhombic leaflets, m. p. 157—159°, which do not give a semicarbazone. Insolation appears to yield only the first-named of the dimerides. H. WREN.

Hydratation of nopinene. V. Hydratation by nascent acids. G. AUSTERWEIL (Bull. Soc. chim., 1930, [iv], 47, 1157—1159).—When a mixture of *l*-nopinene and alcohol is added to a solution of phthalic anhydride in xylene at 135—140° and the bornyl ethyl phthalate obtained is hydrolysed with sodium hydroxide in presence of sodium sulphoricinoleate, about 41% of *l*-borneol, m. p. 211°, is obtained (or 64% if the xylene is replaced by pinene), the remaining unhydrated nopinene being converted mainly (75%) into pinene, the residual 25% giving limonene, [α] −80°, dipentene, and terpinene but not terpinolene; a little *d*-fenchyl alcohol is also formed (cf. A., 1926, 619; 1927, 156, 1082; 1928, 69).

R. BRIGHTMAN.

Sulphur compounds of terpenes. I. Action of sulphur on *d*-limonene and α-pinene. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1930, 33, 408—409B).—*d*-Limonene was heated with sulphur (25%) at 160° for 28 hrs., and the product was distilled under reduced pressure. *p*-Cymene (cf. Ruzicka, B., 1922, 482A) was obtained, together with a *sulphide*, $C_{10}H_{16}S$, m. p. −26·79°, b. p. 104·5—105·5°/16·8 mm., $[\alpha]_D^{25\cdot1}$ −12·31°, $n_D^{27\cdot6}$ 1·51534, $d_4^{27\cdot6}$ 0·9948 (*chloroaurate*, $C_{10}H_{16}SAuCl_3$). Probably sulphur is attached at the position of the double linking in the side-chain. Similar treatment of α-pinene yielded a polymerised product and a very small amount of a sulphide which was isolated as the methiodide (cf. Budnikov and Schilov, A., 1923, i, 118), and may or may not be identical with that described above.

E. LEWKOWITSCH.

Condensation products of pernitrosocamphor with amines. P. SACCARDI (Annali Chim. Appl., 1930, 20, 489—494).—Condensation of pernitrosocamphor with anæsthesin, *m*-anisidine, and *p*-aminobenzoic acid respectively yields 2-*camphoranæsthesin*, $\begin{matrix}CH_2\\C_8H_{14}\end{matrix}\!\!>\!C{:}N{\cdot}C_6H_4{\cdot}CO_2Et$, m. p. 85°; 2-*camphor*-m-*anisidine*, b. p. 246—249°/35 cm., n^{18} 1·401, and 2-*camphor*-p-*aminobenzoic acid*, m. p. 238—239° (decomp.). Anthranilic acid condenses with pernitrosocamphor only as sodium salt, the resulting salt being unstable; *lead* 2-*camphor*-o-*aminobenzoate* is, however, stable and was analysed (cf. Saccardi and Romagnoli, A., 1927, 1196; Romagnoli, A., 1929, 72).

T. H. POPE.

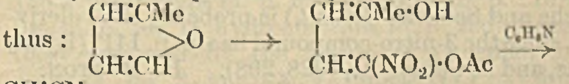
Spatial structure of *apo*cyclene and of other more simple tricyclic hydrocarbons. V. Stereochemistry of alicyclic compounds. S. S. NAMETKIN and L. G. BOGATSCHEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1335—1342).—*apo*Cyclene prepared from *l*-fenchene is optically inactive; this result is explicable on the basis of the space formula given.

R. TRUSZKOWSKI.

Oxidation of acetylenic glycols. The *o*-diketones of the tetrahydrofuran series. T. I. TENUIKOVA and P. A. TICHOMOLOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1217—1222).—Oxidation of tetratolylbutinenediol, m. p. 156°, with chromic acid gave 2 : 2′ : 5 : 5′-*tetratolyl*-3 : 4-*diketotetrahydrofuran*, deep purple, m. p. 182°, which on further oxidation yielded ditolyl ketone, m. p. 93°; a *phenylhydrazone*, m. p. 184—186°, *oxime*, m. p. 226°, and *quinoxaline*, m. p. 220—221°, were also obtained.

M. ZVEGINTZOV.

Furan derivatives. I. J. RINKES (Rec. trav. chim., 1930, 49, 1118—1125).—Nitration of 2-methylfuran (Reichstein, A., 1930, 783) with nitric acid (*d* 1·51) and acetic anhydride below −5° and treatment of the product with pyridine affords 5-*nitro*-2-*methylfuran*, m. p. 43·5°, b. p. 104°/12 mm., probably thus:



$$\begin{matrix}CH{:}CMe\\|\qquad\quad\\CH{:}CH\end{matrix}\!\!>\!O \longrightarrow \begin{matrix}CH{:}CMe{\cdot}OH\\|\qquad\qquad\quad\\CH{:}C(NO_2){\cdot}OAc\end{matrix} \xrightarrow{C_5H_5N}$$

$\begin{matrix}CH{:}CMe\\|\qquad\quad\\CH{:}C(NO_2)\end{matrix}\!\!>\!O$, together with a small yield of (?) the *monoacetate* of *αγ-dinitro-Δ^αγ-pentadiene-αδ-diol*, $OH{\cdot}CMe{:}C(NO_2){\cdot}CH{:}C(NO_2){\cdot}OAc$, m. p. 77—78°, a nitro-derivative of the assumed intermediate. Oxidation of 5-methylfurfuraldehyde (Fenton, J.C.S., 1901, 79, 807) with silver nitrate and sodium hydroxide affords 5-methylfuroic acid, converted by methyl-alcoholic hydrogen chloride into its *methyl* ester, b. p. 98°/15 mm. The latter is similarly nitrated in acetic anhydride to give a small yield of its 4-*nitro*-derivative.

m. p. 81°. Nitration of 5-methylfuroic acid itself affords mainly 5-nitro-2-methylfuran, identical with the product obtained above (replacement of the carboxyl by a nitro-group), together with a small yield of 4-*nitro*-5-*methylpyromucic acid*, m. p. 159—160°. Similar nitration of 4-methylpyromucic acid affords 2-nitro-3-methylfuran, m. p. 32·6°, and an *acid*, m. p. 195°, not obtained in sufficient quantity for analysis. J. W. Baker.

Syntheses with ββ′-dichlorodiethyl ether. I. Derivatives of tetrahydropyran. C. S. Gibson and J. D. A. Johnson (J.C.S., 1930, 2525—2530).—ββ′-Dichlorodiethyl ether, b. p. 66°/12 mm., m. p. −24·5°, is converted by prolonged boiling with 4 mols. of sodium iodide in acetone into ββ′-*di-iododiethyl ether*, b. p. 123·5—124°/10 mm. The dichloro-ether readily condenses with ethyl sodiomalonate to give ethyl tetrahydropyran-4 : 4-dicarboxylate (Kamm and Waldo, A., 1922, i, 105), b. p. 134—135°/12 mm., converted by hydrolysis and decarboxylation at 175—185° into tetrahydropyran-4-carboxylic acid, b. p. 146—147°/15 mm. (acid *chloride*, b. p. 85—86°/16 mm.; *methyl*, b. p. 80·5—81°/16 mm., and *ethyl*, b. p. 82·5°/12 mm., esters; *anilide*, m. p. 163°; *amide*, m. p. 179°). Similar condensation with ethyl sodiocyanoacetate affords *ethyl* 4-*cyanotetrahydropyran*-4-*carboxylate*, b. p. 122—125°/16 mm. This is hydrolysed by boiling aqueous-alcoholic potassium hydroxide to the 4 : 4-dicarboxylic acid, but hydrolysis with cold aqueous methyl-alcoholic potassium hydroxide affords 4-*cyanotetrahydropyran*-4-*carboxylic acid*, m. p. 160—162° (*amide*, m. p. 158°), decarboxylated at 180—200° to 4-*cyanotetrahydropyran*, b. p. 82—85°/10 mm. The dichloro-ether does not form a magnesium compound, whilst the di-iodo-ether gave no isolable product. Various unsuccessful experiments are recorded.

J. W. Baker.

Diphenylene oxide series. II. N. M. Cullinane (J.C.S., 1930, 2267—2269).—Nitration of diphenylene oxide with fuming nitric acid in sulphuric acid solution (cf. A., 1924, i, 534) gives 80% of the theoretical amount of the 2-nitro-derivative (cf. Mayer and Krieger, A., 1922, i, 746; Borsche and Schacke, A., 1924, i, 161). 2-*Chlorodiphenylene oxide*, m. p. 101°, prepared by the usual method from the 2-amino-derivative, is also formed when the diazonium sulphate from 5-*chloro*-2-*aminodiphenyl ether*, m. p. 44°, is heated in 50% sulphuric acid solution.

The 3(?)-nitrodiphenylene oxide, m. p. 110°, of Borsche and Schacke (*loc. cit.*) is probably the 1-derivative, since the 3-nitro-compound has m. p. 141° (Ryan, Keane, and M'Gahon, A., 1928, 298). H. Burton.

Tannins and related substances. XXIV. Catechins from kola nuts. K. Freudenberg and L. Oehler (Annalen, 1930, 483, 140—143).—*d*-Catechin and *l*-epicatechin are the only catechins isolated from fresh kola nuts using the method previously described (A., 1924, i, 868). The names kolatin, kolatein (Goris, A., 1907, i, 631), and cola-catechin (Casparis, A., 1930, 1223) should be deleted from the literature. Contrary to the statement of Casparis (*loc. cit.*), no catechin could be isolated from fresh or dry tormentilla root. H. Burton.

Furfuraldehyde. Preparation of tetraethyldiaminodiphenylfurylmethyl chloride and diphenylfurylmethane. S. A. Mahood and H. F. Aldrich (J. Amer. Chem. Soc., 1930, 52, 4477—4480).—Diethylaniline, furfuraldehyde, and zinc chloride at 100° (bath) give (yield, 31%) *tetraethyldiaminodiphenylfurylmethane*, m. p. 78° after previous sintering, converted by the usual method into the corresponding chloride, green. This dyes silk a yellower and less light-stable shade than does malachite-green.

Magnesium phenyl bromide converts ethyl pyromucate in boiling toluene into diphenylfurylcarbinol, m. p. 91° (corr.), reduced by zinc dust and acetic acid below 70° to *diphenylfurylmethane*, m. p. 51° (corr.), which, after a few days, becomes a gum.

H. Burton.

Diflavone group. V. *m*-Methoxybenzaldehyde and diacetoresorcinol. E. M. Ryan and H. Ryan (Proc. Roy. Irish Acad., 1930, 39 B, 425—433).—4 : 6-Diacetoresorcinol reacts in hot alcoholic sodium hydroxide solution with *m*-methoxybenzaldehyde to form 4 : 6-*di*-m-*methoxybenzylideneacetoresorcinol*, m. p. 157°, which condenses, in alcoholic chloroform solution of hydrogen chloride, with benzaldehyde and piperonal yielding *dibenzylidene*-, m. p. 249—250°, and *dipiperonylidene*-3′ : 3″-*dimethoxyflavanone*, m. p. 245°, respectively. Treatment of the dichalkone with sodium acetate and acetic anhydride affords the *diacetate*, m. p. 122°. This substance in chloroform solution reacts with bromine to yield a *bromide*, which in alcoholic potassium hydroxide solution undergoes cyclisation with the formation of 3′ : 3″-*dimethoxydicoumarone*, m. p. 277—279° (decomp.) after softening at 275°. In a similar manner 4 : 6-diacetoresorcinol dimethyl ether condenses with *m*-methoxybenzaldehyde with the production of 1 : 3-*dimethoxy*-4 : 6-*di*-m-*benzylideneacetobenzene*, m. p. 157—158°. Bromine converts this substance into a *dibromide*, m. p. 213° (decomp.), a *tetrabromide*, decomp. 176°, and a *pentabromide*, m. p. 186° (decomp.).

T. H. Morton.

Synthesis of substituted thioxanthhydrols. J. Reilly, P. J. Drumm, and B. Daly (Proc. Roy. Irish Acad., 1930, 39 B, 515—522; cf. A., 1928, 63).—*p*-Tolyl sulphide condenses with phthalic anhydride in presence of carbon disulphide and aluminium chloride. Decomposition of an intermediate aluminium chloride *compound* by water at 0° affords 2-o-*carboxybenzoyldi*-p-*tolyl sulphide*, m. p. 207° (*oxime*, m. p. 129°; *silver* salt). The constitution is confirmed by a second synthesis from the potassium salts of thio-*p*-cresol and 2-chloro-5-methylbenzophenone-2′-carboxylic acid at 200—210° in presence of copper. Treatment of this substance with concentrated sulphuric acid at 100° for a few minutes, or successively with phosphorus pentachloride and aluminium chloride in benzene solution, results in the formation of 2 : 7-dimethylthiofluoran, m. p. 222°. The application of the Friedel–Crafts reaction, with carbon disulphide as the medium, to benzoyl chloride and *p*-tolyl sulphide affords 9-*phenyl*-2 : 7-*dimethylthioxanthhydrol*, m. p. 207°. This substance reacts with ethereal hydrogen chloride to form a *chloride-hydrochloride*, to which a quinonoid structure is assigned. Reduction with boiling alcoholic hydrogen chloride, or with zinc and acetic acid converts the thioxanthhydrol into 9-*phenyl*-2 : 7-*dimethylthioxanthen*, m. p. 157°; treatment of the same substance with diethylaniline in boiling acetic acid produces 4′-*diethylamino*-9 : 9-*diphenyl*-2 : 7-*dimethylthioxanthen*, m. p. 211°.

p-Tolyl sulphide is conveniently prepared (cf. Otto, A., 1879, 926) by diazotising, at 5—10°, *p*-toluidine dissolved in dilute hydrochloric acid (2 mols.) with the theoretical quantity of sodium nitrite. This solution is added to a solution of thio-*p*-cresol (1 mol.) in dilute sodium hydroxide (1 mol.) at 60—70°. The disulphide, b. p. 186°/16 mm., may be obtained from the crude product by distillation under diminished pressure. The addition of bromine to an ethereal solution of thio-*p*-cresol affords di-*p*-tolyl disulphide (cf. Marcker, Annalen, 1865, **136**, 88). T. H. Morton.

Catalytic dehydrogenation of pyrrolidine. J. P. Wibaut, C. C. Molster, H. Kauffmann, and A. M. Lenssen (Rec. trav. chim., 1930, **49**, 1127—1130).—When pyrrolidine is passed over 30% platinised or palladised asbestos at 360°, slow and partial dehydrogenation to pyrrole occurs, the presence of the latter in the distillate being detected by the pine-splint and other tests. Unchanged pyrrolidine can also be isolated as its picrate. Some decomposition occurs, since, with the above catalysts, 8 and 5%, respectively, of hydrocarbons are mixed with the hydrogen evolved. These results together with those of Zelinski and Jurjev (A., 1929, 1461) indicate that the catalytic reduction of pyrrole is reversible. J. W. Baker.

Catalytic synthesis of phenyl-substituted pyridines from aldehydes and ketones and ammonia. A. E. Tschitschibabin and D. I. Orotschko (J. Russ. Phys. Chem. Soc., 1930, **62**, 1201—1206).—The formation of phenyl-substituted pyridine derivatives by the condensation of aldehydes and ketones with ammonia in the presence of aluminium oxide or china clay as catalyst was investigated. Benzaldehyde and acetaldehyde at 305—310° condense with ammonia to give 4-phenylpyridine (picrate, m. p. 196—197°), together with some 2-phenylpyridine (picrate, m. p. 173—174·5°), the maximum yield being 25%. If acetone is used instead of acetaldehyde, 4-phenyl-2 : 6-dimethylpyridine, m. p. 62—63·5°, is obtained. Phenyl styryl ketone, acetone, and ammonia yield the same product. M. Zvegintzov.

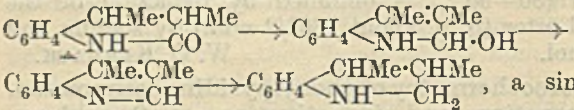
2-Hydroxy-derivatives of quinoline bases. A. E. Tschitschibabin and A. I. Kursanova (J. Russ. Phys. Chem. Soc., 1930, **62**, 1211—1216).—The preparation of 2-hydroxy-derivatives from quinoline bases by heating them with anhydrous potassium hydroxide was investigated. The reaction proceeds smoothly at 250—260°, yields from 40% to 70% being obtained. 8-Methylquinoline gave 2-hydroxy-8-methylquinoline, m. p. 219—220°, and 6-methylquinoline the corresponding 6-compound. α- and β-Naphthoquinolines gave the corresponding hydroxy-derivatives, m. p. 285—286° and 252—253°, respectively, whilst *iso*quinoline yielded *iso*carbostyril, m. p. 209—210°.

The two 2-hydroxymethylquinolines when oxidised with potassium permanganate gave the corresponding methylisatins (m. p. 266° and 186°), together with some oxalylmethylanthranilic acid, m. p. 231°. Oxidation of α-naphthocarbostyril gave a deep red compound, m. p. 290°. M. Zvegintzov.

Synthesis of tryptophol. R. W. Jackson (J. Biol. Chem., 1930, **88**, 659—662).—Reduction of methyl indolyl-3-acetate (b. p. about 180°/2 mm.) according to the method of Marvel and Tanenbaum (A., 1923, i, 2) yields tryptophol, m. p. 57°, purification being effected through the picrate. A better yield (80—90%) is obtained by reduction of the ethyl ester (b. p. about 180°/2 mm.) by sodium and alcohol. W. O. Kermack.

Stereochemistry of phenylpyridine compounds. Preparation and investigation of 2-*o*-chlorophenylpyridine-3 : 6′-dicarboxylic acid and 6-phenyl-3-*o*-carboxyphenylpyridine-2 : 4-dicarboxylic acid. X. C. C. Steele and R. Adams (J. Amer. Chem. Soc., 1930, **52**, 4528—4535).—8-Chloro-α-naphthylamine, m. p. 95—96° (lit. 89—94°), prepared in 97% yield by reducing 8-chloro-1-nitronaphthalene with iron powder and water containing a little hydrochloric acid, is converted by the Skraup reaction into 10-*chloro-α-naphthoquinoline* (20% yield), m. p. 81·5—82°. This is oxidised by aqueous potassium permanganate at 100° to 2-o-*chlorophenylpyridine*-3 : 6′-*dicarboxylic acid*, m. p. 252—256° (decomp.) (*strychnine*, m. p. 171—173°; *brucine*, m. p. 168—170°; *morphine*, m. p. 200—204°; *cinchonine hydrogen*, m. p. 154—156°; *cinchonine*, m. p. 194—196°, and *quinine hydrogen*, m. p. 152—155°, salts). 2-Phenyl-β-naphthoquinoline-3-carboxylic acid (Döbner and Kuntze, A., 1889, 411) is oxidised by Immerheiser's method (A., 1889, 527) to 6-*phenyl*-3-o-*carboxyphenylpyridine*-2 : 4-*dicarboxylic acid*, m. p. 202° (74% yield) [*strychnine hydrogen*, m. p. about 238° (decomp.); *brucine hydrogen*, melts partly at 204° (decomp.), and *cinchonine dihydrogen* salts, m. p. 174—176°, resolidifying with m. p. 200—204° (decomp.); *trichloride*, m. p. 127—130°; n-*butyl* ester; *menthyl* ester, $[\alpha]_D$ −38° in acetone]. Neither of the above acids could be resolved. The various possibilities of optical isomerism in the phenylpyridine series are discussed. H. Burton.

Stereoisomerism in substituted 1 : 2 : 3 : 4-tetrahydroquinolines. II. S. G. P. Plant and R. J. Rosser (J.C.S., 1930, 2444—2455).—Reduction of 3 : 4-dimethylquinoline, m. p. 73—74° (Knorr, A., 1888, 1111, gives m. p. 65°) [picrate, m. p. 215—217° (lit. m. p. 205°); hydrochloride, m. p. 290° (decomp.)] (best prepared by the action of phosphorus oxychloride on 2-keto-3 : 4-dimethyl-1 : 2-dihydroquinoline and reduction of the 2-chloro-3 : 4-dimethylquinoline so formed with red phosphorus and hydriodic acid, *d* 1·7, in a sealed tube at 175—180°), with tin or zinc and alcoholic hydrochloric acid, sodium and boiling alcohol, or electrolytically, occurs slowly and affords only one stereoisomeric form of 3 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, an oil (*picrate*, m. p. 143—145°), isolated as its *phenylcarbamyl* derivative, m. p. 107—108°. Reduction of 2-keto-3 : 4-dimethyl-1 : 2-dihydroquinoline with sodium amalgam and boiling alcohol, however, affords a mixture (6 : 1) of the two stereoisomeric *forms*, *A*, m. p. 127—128° (least soluble), and *B*, m. p. 117°, of 2-*keto*-3 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, separated by fractional crystallisation from the reaction product. The form A is converted by phosphorus oxychloride into 2-chloro-3 : 4-dimethylquinoline. Further reduction of the mixture of stereoisomerides with sodium and boiling alcohol gives only the previously described form of 3 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, together with a little 3 : 4-dimethylquinoline. The presence of the latter product suggests that the mechanism of the reaction is :



$$C_6H_4\!\!<\!\!\begin{array}{l}CHMe\cdot CHMe\\NH\text{——}CO\end{array}\longrightarrow C_6H_4\!\!<\!\!\begin{array}{l}CMe\!:\!CMe\\NH\text{–}CH\cdot OH\end{array}\longrightarrow C_6H_4\!\!<\!\!\begin{array}{l}CMe\!:\!CMe\\N\text{==}CH\end{array}\longrightarrow C_6H_4\!\!<\!\!\begin{array}{l}CHMe\cdot CHMe\\NH\text{——}CH_2\end{array}$$

, a similar mechanism applying equally to the reaction of Blount, Perkin, and Plant (A., 1929, 1312). Reduction of 2 : 4-dimethylquinoline with sodium and boiling alcohol affords a mixture (2 : 3) of two inactive stereoisomeric *forms*, *A* (*hydrochloride*, m. p. 228° ; 1-*acetyl* derivative, m. p. 50—51° ; *picrate*, m. p 139—141° ; 1-*phenylcarbamyl*, m. p. 121—122°, and 1-*benzoyl*, m. p. 115°, derivatives), and *B* (*hydrochloride*, m. p. 178—179° ; *picrate*, m. p. 188—191° ; 1-*phenylcarbamyl* derivative, m. p. 112—113°), isolated from the mother-liquor as its 1-*acetyl* derivative, m. p. 97—98°, of 2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline. The form A is probably the racemate of the *d*- and *l*-forms obtained by Thomas (J.C.S., 1912, **101**, 725). Reduction of 2 : 4-dimethylquinoline with tin and alcoholic hydrochloric acid, electrolytically, and with zinc and alcoholic hydrochloric acid affords a mixture of A and B forms in the ratios 9 : 1, —, and 5 : 1, respectively. A steric explanation of the failure of 3 : 4-dimethylquinoline to yield stereoisomerides is given on the assumption that 3 : 4-dimethyl-1 : 4-dihydroquinoline is an intermediate product. J. W. Baker.

Friedel–Crafts reaction with 8-hydroxyquinoline. K. Matsumura (J. Amer. Chem. Soc., 1930, 52, 4433—4436).—Acetyl chloride and 8-hydroxyquinoline react in presence of nitrobenzene and aluminium chloride, forming 8-*hydroxy*-5-*acetylquinoline*, m. p. 112—112·5° [*hydrochloride* (+3H_2O), m. p. 284—285° (decomp.) ; *hydrogen sulphate*, m. p. 248° (decomp.) ; *picrate* (+H_2O), m. p. 188—189° ; *chloroplatinate*, m. p. 275° (decomp.) ; *methiodide* (+H_2O), m. p. 210° (decomp.)], the *oxime*, m. p. 193°, of which undergoes the Beckmann rearrangement, yielding 5-*acetamido*-8-*hydroxyquinoline*, m. p. 217—218° [*hydrogen sulphate*, m. p. 263° (decomp.)]. Chloroacetyl chloride reacts as above at 90—95° furnishing 8-*hydroxy*-5-*chloroacetylquinoline*, m. p. 158—159° [*hydrochloride*, m. p. 287° (decomp.) ; *hydrogen sulphate*, m. p. 263° (decomp.) ; *picrate*, m. p. 179° ; *chloroplatinate*, m. p. 275° (decomp.)], reduced by iron powder and 80% alcohol containing a little hydrochloric acid to 8-hydroxy-5-acetylquinoline. 8-*Hydroxy*-5-*benzoylquinoline*, m. p. 118—119° [*hydrochloride*, m. p. 252—260° ; *hydrogen sulphate*, m. p. 219—220° ; *picrate*, m. p. 143—145° ; *methiodide*, m. p. 199·5° (decomp.)], is prepared similarly from benzoyl chloride at 110—120° ; its *oxime*, m. p. 147—148°, undergoes the Beckmann transformation yielding 5-*benzamido*-8-*hydroxyquinoline*, m. p. 237—238° [*hydrogen sulphate*, m. p. 221—222° (decomp.)]. Benzoylation of 8-hydroxyquinoline in pyridine in the cold gives 8-benzoyloxyquinoline, m. p. 122—122·5° (lit. 118—120°) (*hydrochloride*, m. p. 124°). H. Burton.

***Py*-Alkylquinolines. Generalisation of the Skraup reaction applied to α-alkylglycerols.** R. Delaby and J. Hiron (Compt. rend., 1930, **191**, 845—847).—The application of a modification (A., 1930, 616) of the Skraup reaction to α-alkylglycerols and aniline leads to a mixture of 2- and (less) 4-alkylquinolines. The intermediate formation of the aldehyde, CHR:CH·CHO, is postulated. In this manner were prepared : 2-ethylquinoline, b. p. 128—131°/13 mm., d_4^{17} 1·050, n_D^{23} 1·5979 [*picrate*, m. p. 148° ; *chloroplatinate*, m. p. 188° ; *chloromercurate*, m. p. 118° ; *iodomercurate*, m. p. 135° ; *iodobismuthate*, m. p. 205° (decomp.)] ; 2-propylquinoline, b. p. 142—145°/13 mm., d_4^{17} 1·038, n_D^{21} 1·5886 (*picrate*, m. p. 159 ; *chloroplatinate* ; *chloromercurate*, m. p. 112° ; *iodomercurate*, m. p. 112° ; *iodobismuthate*, m. p. 186°), and 2-butylquinoline, b. p. 150—155°/13 mm., d_4^{18} 1·020, n_D^{23} 1·5799 (*picrate*, m. p. 143° ; *chloroplatinate*, m. p. 163·5° ; *chloromercurate*, m. p. 163·5° ; *iodomercurate*, m. p. 163·5° ; *iodobismuthate*, m. p. 163°). T. H. Morton.

Quinoline and benzacridine derivatives yielding coloured adsorption compounds with iodine. W. O. Kermack, R. H. Slater, and W. T. Spragg (Proc. Roy. Soc. Edin., 1930, **50**, 243—261).—9-Methyl-3 : 4-benzacridine and 3 : 4 : 5 : 6-dibenzacridine in colloidal suspension give a red or blue coloration with solutions of iodine. Some closely-related benzacridine derivatives are inactive, but certain derivatives of 4-anilinoquinoline (Slater, A., 1930, 937) also develop a colour on treatment with iodine at concentrations of the order of 0·0001*N*. In the case of the active benzacridine compounds, the colour is still apparent at a concentration of 0·00001*N* or even less. The effect of variation of concentration of compound, iodine, and hydrogen ions has been investigated in certain instances. The action of certain inorganic salts has also been investigated, but in low concentrations these are without much effect. The methosulphates of the two active benzacridine bases also develop colours with iodine even with very low concentrations of the latter (less than 0·00001*N*). It is suggested that these methosulphates form micellar, colloidal solutions. The following new compounds have been prepared : 9 : 10-*Dihydro*-9-(3′ : 4′-*methylenedioxyphenyl*)-3 : 4 : 5 : 6-*dibenzacridine*, m. p. 305°, from piperonal, β-naphthylamine, and β-naphthol at 200—230° ; 9-(3′ : 4′-*methylenedioxyphenyl*-)-3 : 4 : 5 : 6-*dibenzacridine*, m. p. 282°, by oxidation of the previous compound in acetic acid solution with an equimolecular quantity of bromine ; 9-*methyl*-3 : 4-*benzacridine methosulphate*, m. p. 205°, and 3 : 4 : 5 : 6-*dibenzacridine methosulphate*, unmelted at 300°. W. O. Kermack.

Action of aniline and derivatives on benzaldehyde and pyruvic acid. H. T. Bucherer and R. Russischwili (J. pr. Chem., 1930, [ii], **128**, 89—138).—A further investigation of Döbner's synthesis of 2-phenylquinoline-4-carboxylic acid (cf. A., 1888, 300). The failure to increase the average yield of 50—55% is correlated with the observed absence of hydrogen among the reaction products. The interaction of benzylideneaniline with pyruvic acid in cold acetic acid gives 4 : 5-diketo-1 : 2-diphenylpyrrolidine (I; cf. A., 1898, i, 489; the previously reported instability is not confirmed) as main product, the proportions of 4-anilo-5-keto-1 : 2-diphenylpyrrolidine and 2-phenylquinoline-4-carboxylic acid (cf Döbner, *loc. cit.*; Borsche, A., 1909, i, 52) simultaneously formed being favoured by ether or alcohol as solvent at higher temperatures. The condensation of *o*-nitroaniline and 2-nitro-*p*-toluidine with benzaldehyde and pyruvic acid leads to 4 : 5-*diketo-2-phenyl-*1-o-*nitrophenylpyrrolidine*, m. p. 154°, and 4 : 5-*diketo-2-phenyl-*1-2′-*nitro*-p-*tolylpyrrolidine*, m. p. 213—214°, respectively (cf. Borsche, *loc. cit.*), the presence of the nitro-group tending to favour pyrrolidine formation. The aniline salt of the solid form of cinnamoylformic acid (A., 1903, i, 608) is converted quantitatively into I by heating alone or in alcoholic solution, thus confirming the *trans*-configuration previously assigned to this acid. Attempts at conversion of I into 2-phenylquinoline-4-carboxylic acid failed. It does not condense with aniline and cannot be regenerated from its 4-anil. Hydrolysis with 80% sulphuric acid gives (probably) *γ-anilino-γ-phenyl-α-keto-*n-*butyric acid*, decomp. 75—85° (*calcium* and other salts described). By heating with phenylhydrazine in presence of a little acetic acid, a *substance*, $C_{16}H_{14}O_2N_2$, m. p. 153·5° (unstable silver and magnesium salts), is formed, the solubility of which in alkali and ready conversion into a p-*nitrobenzeneazo*-derivative, decomp. about 115°, points to its constitution as 1-anilino-4 : 5-diketo-2-phenylpyrrolidine, or, possibly, 4 : 5-diketo-2 : 3-diphenylpyridazine. Use of excess of phenylhydrazine gives, in addition, a *substance*, $C_{16}H_{14}ON_2$(?), decomp. 124—125°, also obtained from the 4-anilo-compound and phenylhydrazine.

The preparation of the following derivatives of *m*-tolylenediamine, and their conversion by condensation with benzaldehyde and pyruvic acid in alcoholic solution into derivatives of 2-phenylquinoline-4-carboxylic acid, accompanied by a little of the corresponding diketopyrrolidine, are described: 4-*nitro*-p′-*toluenesulphon*-o-*toluidide*, m. p. 157°; 4-*amino*-p′-*toluenesulphon*-o-*toluidide*, m. p. 176°, by reduction of the preceding, or hydrolysis of the p-*toluenesulphonyl* derivative, m. p. 182—183°, of 2-aminoaceto-*p*-toluidide; 2-*nitro*-p′-*toluenesulphon*-p-*toluidide*, m. p. 162—163°; 2-*amino*-p′-*toluenesulphon*-p-*toluidide*, m. p. 164—165°, by reduction of the preceding: 7-*amino*-, decomp. indefinitely, 250—270° (*hydrochloride*), 7-*acetamido*-, decomp. 300—302°, by acetylation of the preceding, or from 4-aminoaceto-*o*-toluidide, and 7-p-*toluenesulphonamido-2-phenyl-6-methylquinoline-4-carboxylic acid*, decomp. 273—274° (*methyl* ester, m. p. 224°; *ethyl* ester, m. p. 186—187°), from the appropriate acyl-*m*-tolylenediamine. 5-p-*Toluenesulphonamido-2-phenyl-8-methylquinoline-4-carboxylic acid*, decomp. 98—103°, is prepared similarly. The condensation of resacetophenone and isatin in presence of 33% sodium hydroxide gives 2′ : 4′-*dihydroxy-2-phenylquinoline-4-carboxylic acid*, decomp. 305° (*methyl* ester, m. p. 211—212°; *ethyl* ester, m. p. 195—196°).

H. A. PIGGOTT.

Diazotisation in the pyrazole series. J. REILLY and D. MACSWEENEY (Proc. Roy. Irish Acad., 1930, 39B, 497—504).—Reduction of 4-nitroso-1-phenyl-3 : 5-dimethylpyrazole with tin and hydrochloric acid at 100° affords 4-*amino*-1-*phenyl*-3 : 5-*dimethylpyrazole dihydrochloride*, from which the free *base* (*benzoyl* derivative, m. p. 153—154°; *chloroplatinate*) may be obtained. The base condenses with benzaldehyde (1 mol.) in presence of a trace of piperidine to give the corresponding 4-*benzylideneamino*-derivative, m. p. 90—91°. Diazotisation with ethyl nitrite and hydrochloric acid yields 1-*phenyl*-3 : 5-*dimethylpyrazole*-4-*diazonium chloride*, which may be obtained crystalline by evaporation under diminished pressure. This diazonium salt is exceedingly stable, losing only 20% of its diazo-nitrogen in aqueous solution during 6 hrs. at 100°. The diazonium salts, *chloroplatinate*, and *dichromate hydrochloride*, $(C_{11}H_{11}N_4)_2Cr_2O_7,HCl$, are described. It is suggested that these diazonium compounds can be represented only by a cyclic structure similar to that proposed by Forster and Müller (J.C.S., 1909, 95, 2072) for triazole derivatives. The diazonium chloride couples readily with phenols and aromatic amines. With dimethylaniline, diethylaniline, *p*-toluidine, and α-naphthylamine it gives coloured *azo*-derivatives; with β-naphthol a red *azo*-compound, m. p. 189—190°, and with β-naphthylamine an orange *azo*-derivative, m. p. 195—196°. With α-naphthol-3 : 6-disulphonic acid and β-naphthol-6 : 8-disulphonic acid it yields soluble red *dyes*, and with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid a purple soluble *dye*. With *m*-phenylenediamine a red azo-*dye* of the chrysoidine group is obtained. An aqueous solution of the diazonium chloride reacts with ethyl acetoacetate and acetylacetone, dissolved in alcohol, to produce 1-*phenyl*-3 : 5-*dimethylpyrazole*-4-*azo-ethyl acetoacetate*, m. p. 84—85°, and -4-*azo-acetylacetone*, m. p. 115—116°, respectively.

T. H. MORTON.

Reaction of antipyrine and pyramidone. Detection of antipyrine in pyramidone. M. RIBÈRE (J. Pharm. Chim., 1930, [viii], 12, 444—447).—A white precipitate, soluble in excess, is given by antipyrine, but not by pyramidone, with trichloroacetic acid or perchloric acid. Hot ammoniacal silver nitrate is reduced by pyramidone, but not by antipyrine. A 10% solution of mercury in nitric acid from which nitrous fumes have been almost completely removed gives with antipyrine a white precipitate, soluble at the b. p. and reprecipitated on cooling with a brick-red colour, and with pyramidone a violet coloration. A mixture of this reagent with an equal amount of 20% trichloroacetic acid enables the presence and approximate proportion of antipyrine in pyramidone to be determined. Samples of pyramidone containing (*a*) 25%, (*b*) 10%, and (*c*) 1—0·1% of antipyrine give in 1% aqueous solution: (*a*) the same reaction as with pure antipyrine, (*b*) a white precipitate and a red coloration at the b. p., (*c*) (by superposition) a violet ring and a white cloud extending into the upper layer.

H. E. F. NOTTON.

Pyrimidines. CXVII. Synthesis of nucleosides. G. E. Hilbert and T. B. Johnson (J. Amer. Chem. Soc., 1930, 52, 4489—4494).—Treatment of 2 : 6-dimethoxypyrimidine with acetobromoglucose at 50° affords 2-*keto*-6-*methoxy*-3-*tetra-acetylglucosidopyrimidine*, m. p. 220—221°, together with 2-keto-6-methoxy-3-methylpyrimidine (cf. A., 1930, 928). Hydrolysis of the former compound with alcoholic hydrogen chloride gives 3-*glucosidouracil* (+0·5H_2O), m. p. 195—203° according to the rate of heating, m. p. (anhydrous) 207—209°, $[\alpha]_D^{23}$ +21·4° in water [*tetra-acetyl* derivative, m. p. 154—155°; 5-*bromo*-derivative, m. p. 224° (decomp.), $[\alpha]_D^{25}$ +10·3° in water], which is similar in all its reactions to uridine (Levene and La Forge, A., 1913, i, 211). Catalytic reduction (Adams) of 3-glucosidouracil in 80% alcohol furnishes the 4 : 5-*dihydro*-derivative, decomp. 238° after darkening at 220°, $[\alpha]_D^{24}$ +9·3° in water, hydrolysed by 3% sulphuric acid to 4 : 5-dihydrouracil (cf. *loc. cit.*).

H. Burton.

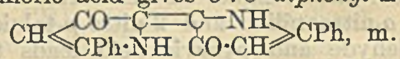
Pyrimidines. CXVIII. Molecular rearrangements in the thymine series. W. Schmidt-Nickels and T. B. Johnson (J. Amer. Chem. Soc., 1930, 52, 4511—4516).—2 : 6-Dichloro-5-methylpyrimidine and methyl-alcoholic sodium methoxide give 2 : 6-*dimethoxy*-5-*methylpyrimidine*, m. p. 61°, passing at 200° into 1 : 3-dimethylthymine. Treatment of the dimethoxy-derivative with methyl iodide affords 2-*keto*-6-*methoxy*-3 : 5-*dimethylpyrimidine*, m. p. 144°, hydrolysed by hydrochloric acid to 3-methylthymine, m. p. 291° (lit. 280—282°). 2 : 6-*Diethoxy*-5-*methylpyrimidine*, m. p. 36°, reacts with methyl and ethyl iodides forming 2-*keto*-6-*ethoxy*-3 : 5-*dimethyl*-, m. p. 111°, and 2-*keto*-6-*ethoxy*-5-*methyl*-3-*ethyl-pyrimidines*, m. p. 78°, respectively. The last-named compound is hydrolysed by hydrochloric acid to 2 : 6-*diketo*-5-*methyl*-3-*ethylpyrimidine* (3-*ethylthymine*), m. p. 223°.

Acetobromoglucose and 2 : 6-dimethoxy-5-methylpyrimidine at 60° afford mainly 3-methylthymine, probably owing to the methyl bromide formed; acetochloroglucose does not react. A small amount of a substance, m. p. 316°, is obtained by similar treatment of 2 : 6-diethoxy-5-methylpyrimidine.

H. Burton.

Action of sodamide on 2 : 5-dimethylpyrazine. A. E. Tschitschibabin and M. N. Schtschukina (J. Russ. Phys. Chem. Soc., 1930, 62, 1189—1199).—The reaction between sodamide and 2 : 5-dimethylpyrazine, b. p. 152—153°, in solution does not proceed readily, but in the pure state the two react, giving 2 : 2′ : 5 : 5′-*tetramethyldipyrazine*, m. p. 68°, and 2 : 5 : 3′-*trimethyldipyrazylmethane*, m. p. 135°. The structure of both was deduced from their oxidation products. On being oxidised with potassium permanganate, the former gave 2 : 5 : 3′-trimethyldipyrazinecarboxylic acid, m. p. 173° (decomp.), and 2 : 5-dimethylpyrazinecarboxylic acid, m. p. 117°. Under similar conditions, the 2 : 5 : 3′-trimethyldipyrazylmethane gave 2 : 5-pyrazinedicarboxylic acid, m. p. 256°, and a dibasic keto-acid, giving a hydrazone, m. p. 173°.

M. Zvegintzov.

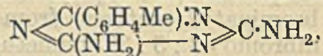
"Bis-5-phenyl-2-pyrroleindigo" [5 : 5′-diphenyl-$\Delta^{2:2'}$-bispyrrol-3-one]. W. Madelung and L. Ubermann (Ber., 1930, 63, [*B*], 2870—2876).—Potassium phenylglycidate and potassium amino-acetate in aqueous solution afford *potassium* β-*carboxymethylamino*-α-*hydroxy*-β-*phenylpropionate trihydrate*, m. p. 96°, and *tetrahydrate*, m. p. 86°, from which the *lead* and *calcium* salts and the free *acid*, $CO_2H\cdot CH_2\cdot NH\cdot CHPh\cdot CH(OH)\cdot CO_2H$, m. p. 235°, are derived. The potassium salt is transformed by boiling acetic anhydride into 1-*acetyl*-3-*hydroxy*-5-*phenylpyrrole*-2-*carboxylic acid*, m. p. 150°, converted by boiling water into 1-*acetyl*-3-*hydroxy*-5-*phenylpyrrole*, m. p. 88°, from which 1-*acetyl*-3-*acetoxy*-5-*phenylpyrrole*, m. p. 181°, is derived. Oxidation of crude 1-acetyl-3-hydroxy-5-phenylpyrrole with ferric chloride and hydrochloric acid gives 5 : 5′-*diphenyl*-$\Delta^{2:2'}$-*bispyrrol*-3-*one*,  $CH{<}\begin{matrix}CO-C=C-NH\\ CPh\cdot NH\quad CO\cdot CH\end{matrix}{>}CPh$, m. p. above 300° (decomp.), which, contrary to Posner's theory (A., 1926, 1155), closely resembles indigotin in absorption spectrum, yields complex compounds with zinc chloride and titanium chloride in benzene, and silver and copper compounds with the metallic acetates in pyridine. The hyposulphite vat has only slight affinity for cotton. The corresponding *acetyl* derivative, m. p. 220°, is described.

H. Wren.

Formation and analysis of some 1 : 3 : 4-triazoles. H. Macurevitsch (Bull. Soc. chim., 1930, [iv], 47, 1160—1183, and J. Russ. Phys. Chem. Soc., 1930, 62, 1137—1163).—Further investigation of the reaction between *o*-toluidine and phenyl-*s*-di(thiocarbamyl)hydrazine has shown that the crystalline substance of m. p. 219—220° (A., 1927, 777) is 3-tolyliminothiourazole (*silver* salt; *acetyl* derivative, $C_9H_9N_4SAc$, m. p. 184—185°) and the substance, m. p. 300°, obtained as a secondary product is identical with Arndt's iminothiourazole, decomp. 303° (A., 1921, i, 813), the product m. p. 370° (*silver* salt) being a further condensation product which does not give the azo-reaction of Arndt (*loc cit.*) when oxidised with potassium ferricyanide. Aniline and *s*-di(thiocarbamyl)-hydrazine yield 3-imino-5-thio-4-phenylurazole, m. p. 263—264·5° (*silver* salt; *acetyl* derivative, m. p. 185—186°; *dibenzyl* derivative, m. p. 189—190°), identical with the 3-amino-5-thiol-4-phenyl-1 : 2 : 4-triazole obtained by Fromm (A., 1924, i, 882) and Arndt (A., 1922, i, 375). *m*-Toluidine similarly affords 3-*imino*-5-*thiol*-4-m-*tolylurazole*, decomp. 309—310° (*silver* salt; *diacetyl* derivative, m. p. 189—190°); *o*-toluidine and *p*-toluidine yield, respectively, 3-imino-5-thiol-4-*o*-tolylurazole, m. p. 229—230° (*silver* salt; acetyl derivative, m. p. 190—191°; dibenzyl derivative, 3-*benzylimino*-5-*benzylthiol*-4-o-*tolylurazole*, an oil), and 3-imino-5-thiol-4-*p*-tolylurazole, decomp. 297—298° (*silver* salt; *dibenzyl* derivative, m. p. 237—238·5°). *m*-Toluidine and phenyl-*s*-di(thiocarbamyl)hydrazine yield a substance, $C_9H_{10}N_4S$, m. p. 247—249° (decomp.), together with 3-imino-5-thiol-4-*m*-tolylurazole; *p*-toluidine similarly yields 3-p-*toluidino*-5-*thio*-1 : 2 : 4-*triazole*, m. p. 263—264° (decomp.) [*silver* salt; *acetyl* derivative, m. p. 191—192° (sinters at 172°)], and a *substance*, decomp. 258—286°, and *m*-2-xylidine gives 3-m-2-*xylylimino*-5-*thiourazole*, m. p. 203—204° (sinters at 196°), and a substance, m. p. above 370°. o-*Tolyl*-s-*di*(*thiocarbamyl*)*hydrazine*, decomp. 168—170°, obtained by condensing *o*-tolylthiocarbimide and thiosemicarbazide in aqueous alcohol, when heated with aniline yields the substance, m. p. 259—260°, obtained from aniline and *s*-di(thiocarbamyl)-hydrazine or phenyl-*s*-di(thiocarbamyl)hydrazine, and 2-anilino-5-thiol-1-phenyl-1 : 3 : 4-triazole, together with a substance, m. p. above 370°.

These triazoles are amphoteric and the monometallic silver salts tend to form complex salts. True chloroplatinates are probably not formed, but unstable complex salts. All these combinations give Arndt's azo-reaction with potassium ferricyanide, but a yellowish coloration is first produced.

R. Brightman.

γ-Triazines. XVIII. Syntheses of *m*- and *p*-tolyl- and benzyl-diaminotriazines. A. Ostrogovich and G. Gheorghiu (Gazzetta, 1930, 60, 648—664).—Condensation of *m*- or *p*-toluonitrile or phenylacetonitrile with cyanoguanidine proceeds similarly to that of acetonitrile (A., 1911, i, 507), but *o*-toluonitrile remains unchanged, the cyanoguanidine being converted into a mixture of ammeline and melamine. m-*Tolyldiamino-γ-triazine*,  $N<\begin{matrix}C(C_6H_4Me):N\\C(NH_2)—N\end{matrix}>C\cdot NH_2$, m. p. 239—240°, forms a *hydrochloride*, m. p. 265°; a *sulphate* (+2H_2O), m. p. 260°; a *picrate*, m. p. 267—268°; a *diacetate*, m. p. 230—232°; a *monoacetyl* derivative, m. p. 248°, and a *diacetyl* derivative, m. p. 232—233°. p-*Tolyldiamino-γ-triazine*, m. p. 240°, forms a *hydrochloride*, m. p. 285°; a *sulphate* (+3H_2O), m. p. 298°; a *picrate*, m. p. 269°; a *diacetate*, m. p. 230—232°; a *monoacetyl* derivative, m. p. 273—274°, and a *diacetyl* derivative, m. p. 264°. Benzyldiamino-γ-triazine, m. p. 238—239° (slight decomp.) (Elzanowski, Diss., Fribourg, 1898, gave m. p. 233°), forms a *hydrochloride*, m. p. 215°; a *sulphate*, m. p. 193—203°; a *monosulphate* (+2H_2O), m. p. 178—183°; a *picrate*, 235° (blackening); a *diacetate*, m. p. 230°; a *monoacetyl* derivative, m. p. 239—240°, and a *diacetyl* derivative, m. p. 145°.

T. H. Pope.

Catalyst for the autoxidation of uric acid. Frèrejacque (Compt. rend., 1930, 191, 949—951).—The autoxidation of uric acid in potassium hydroxide solution (cf. Piaux, A., 1925, i, 592) is accelerated to a very marked extent by active charcoal; allantoin and potassium oxonate are formed at the ordinary temperature, but at 0°, oxonamide is produced. The oxidation of 1- and 7-methyl-, 1 : 3-dimethyl-, and hydroxymethylene-uric acids is catalysed by active charcoal, but xanthine, hypoxanthine, caffeine, and theobromine are not oxidised.

H. Burton.

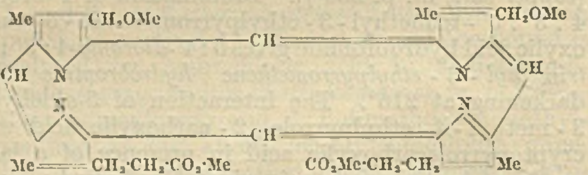
Preparation of 1 : 3 : 9- and 3 : 7 : 9-trimethyluric acid. H. Biltz and H. Pardon (Ber., 1930, 63, [*B*], 2876—2880).—8-Chlorotheobromine is converted by methyl-alcoholic sodium methoxide into 8-*methoxytheobromine*, m. p. 282°, which becomes isomerised at 290° to 3 : 7 : 9-trimethyluric acid, m. p. 373—375° (decomp.). Treatment of the last-named acid with methyl sulphate and sodium hydroxide yields tetramethyluric acid, m. p. 228°. 1 : 3-Dimethyluric acid is transformed into the *potassium* salt, which is treated with methyl *p*-toluenesulphonate in *o*-dichlorobenzene at 150°, whereby 1 : 3 : 9-trimethyluric acid mixed with some 1 : 3-dimethyluric acid results. The trimethyluric acid, decomp. 340°, is obtained by dissolving the product in ammonia solution and boiling or by dissolution in potassium hydroxide solution followed by treatment with carbon dioxide; in either case the more strongly acidic 1 : 3-dimethyluric acid remains in the solution. 8-*Chlorotheophylline*, m. p. indef. 304° (decomp.), obtained by treating theophylline with hydrochloric acid and potassium chlorate, cannot be converted smoothly into the corresponding methoxy-compound.

H. Wren.

Porphyrin synthesis. XXXI. Further pyrroporphyrins. H. Fischer and H. Berg. **XXXII. Introduction of hydroxymethyl, methylmalonic and propionic acid residues into porphyrins.** H. Fischer and H.-J. Riedl. **XXXIII. Synthesis of pyrroætioporphyrins I, II, III, IV, VI, and VIII, and a dimethyldiethylporphin.** H. Fischer and A. Schormüller (Annalen, 1930, 482, 189—213, 214—225, 232—251).—XXXI. Pyrroporphyrins 12, 2, and 3 are synthesised and shown to be different from pyrroporphyrin 15 by mixed-m. p. determinations of their methyl esters. 4-Bromo-5-aldehydo-3-methylpyrrole-2-carboxylic acid when condensed with cryptopyrrole, and the product treated with hydrobromic acid, gives 3-*bromo*-5-*carboxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene hydrobromide*, decomp. 130°, converted by bromine in formic acid into 3 : 5-*dibromo*-4 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene hydrobromide*, (I), m. p. 175° (decomp.). This condenses with 5′-bromo-3 : 5 : 3′-trimethyl-4-ethylpyrromethene-4′-propionic acid in presence of methylsuccinic acid at 130° to give *pyrroporphyrin* 12 [*hæmin*; *methyl* ester, m. p. 242° (*hæmin*, m. p. 260°)] and *bromopyrroporphyrin* 12 [*copper* salt; *methyl* ester, m. p. 304° (*copper* salt, m. p. 259°)]. Bromination of 4′-bromo-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene-5-carboxylic acid hydrobromide gives 5 : 4′-*dibromo*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene hydrobromide* (II), darkening at 215°. The interaction of 5-aldehydo-3-methyl-4-ethylpyrrole-2-carboxylic acid with cryptopyrrolecarboxylic acid in presence of a large excess of hydrobromic acid gives 5-*carboxy*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene*-4′-*propionic acid hydrobromide*, decomp. 170°, which on bromination in formic or acetic acid is converted into 5-*bromo*-4 : 3′ : 5′-*trimethyl*-3-*ethylpyrromethene*-4′-*propionic acid hydrobromide* (III), decomp. 216°. The hydrobromides II and III, when heated at 130° with methylsuccinic acid, condense to *pyrroporphyrin* 2 [*hæmin*; *methyl* ester, m. p. 229° (*hæmin*, m. p. 265°)] and *bromopyrroporphyrin* 2 [*copper* salt; *methyl* ester, m. p. 291° (*copper* salt, m. p. 235°)]. When similarly treated, I and III give *pyrroporphyrin* 3 [*hæmin*; *methyl* ester, m. p. 219° (*hæmin*, m. p. 274°)] and *bromopyrroporphyrin* 3 [*copper* salt; *methyl* ester, m. p. 254° (*copper* salt, m. p. 230°)]. An attractive alternative synthesis of pyrroporphyrin 3 is by heating 5-*carboxy*-4 : 3′ : 5′-*trimethylpyrromethene*-3-*propionic acid hydrobromide* (IV), decomp. 168°, with 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromomethylpyrromethene hydrobromide and succinic acid at 210° for 10 min. It is unnecessary to brominate IV, which is prepared by condensation of 2 : 4-dimethylpyrrole with 5-aldehydo-2-carboxy-3-methylpyrrole-4-propionic acid; consequently the sole by-product is the ætioporphyrin.

Deuteroætioporphyrin II (*hæmin*) and its *mono-bromo*-derivative (*copper* salt) occur as by-products in the above porphyrin syntheses, mixed, in the case of pyrroporphyrins 12 and 3, with the dibromo-derivative, in the case of pyrroporphyrin 12 with mesoporphyrin V, and in that of pyrroporphyrin 2 with mesoporphyrin II. The isolation of the first two from the combined residues from the preparation of pyrroporphyrins 12 and 3, and from that of porphyrin 2 is described. Mesoporphyrin II is readily formed by self-condensation of III in presence of methylsuccinic acid; and may also be synthesised as follows: hæmopyrrole-aldehydecarboxylic acid condenses with opsopyrrole to 4 : 5 : 3′-*trimethyl*-4′-*ethylpyrromethene*-3-*propionic acid hydrobromide*, decomp. 178°, converted by bromine in acetic acid into the 5-*bromo*-derivative, decomp. 204°, which is then fused with methylsuccinic acid. The action of 6% potassium methoxide on 3 : 5 : 3′-trimethyl-4-ethylpyrromethene-4′-propionic acid hydrobromide gives coproporphyrin, identified by its tetramethyl ester, in excellent yield. Spectroscopic observations gave identical results for isomeric pyrroporphyrins.

XXXII. Synthesis of hydroxymethylporphyrins from appropriate pyrromethenes is difficult and unsatisfactory, but the hydroxymethyl group can be introduced into deuterohæmin by the action of a large excess of chloromethyl ether and stannic chloride at 0°, the *O*-methyl groups being removed in the process. The product isolated by crystallisation from acetic acid is the *iron* salt of O-*monoacetyl*-1 : 3 : 5 : 8-*tetramethyl*-2 : 4-*di*(*hydroxymethyl*)*porphin*-6 : 7-*dipropionic acid*, m. p. above 270°. The *ether-ester*,



m. p. 215°, prepared according to Küster (A., 1913, i, 1004) gives 2 : 3 : 4-trimethylpyrrole with hydriodic acid, and with hydrogen bromide in acetic acid the dibromomethyl derivative (*hydrobromide*). With ethyl potassiomalonate this gives (after esterification) *hexamethyl*-1 : 3 : 5 : 8-*tetramethylporphin*-2 : 4-*di*-(*methylmalonate*)-6 : 7-*dipropionate*, m. p. 202° [*iron* salt, m. p. 200° (sinters at 165°); *hexa-ethyl* ester, m. p. 161° (sinters at 122°)], hydrolysed by 1% hydrochloric acid at 180° to (after re-esterification) the tetramethyl ester of coproporphyrin III, identical in all respects with the synthetic material.

XXXIII. The syntheses of a number of ætioporphyrins and of 1 : 5-dimethyl-2 : 6-diethylporphin by fusion of the corresponding pyrromethenes with an equal mixture of succinic and methylsuccinic acids are described. The following new *pyrromethene hydrobromides* are described: 4 : 5 : 4′ : 5′-*tetramethyl*-3′-*ethyl*- (*A*), m. p. 230° (decomp.), from 2 : 3-dimethylpyrrole-5-aldehyde and hæmopyrrole; 4 : 5 : 3′ : 5′-*tetramethyl*-4′-*ethyl*- (*B*), m. p. 233° (decomp.); from the above aldehyde and cryptopyrrole; 3 : 5-*dimethyl*-4-*ethyl*-, m. p. 193° (decomp.) [*dibromo*-compound (*C*), m. p. above 300°], from pyrrole-2-aldehyde and cryptopyrrole; 4 : 5-*dimethyl*-3-*ethyl*-, m. p. 197° [*dibromo*-compound (*D*), m. p. 145°], from pyrrole-2-aldehyde and hæmopyrrole; 3 : 5-*dicarbethoxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethyl*-, m. p. 160—162° (free *base*, m. p. 107°), from ethyl 5-aldehydo-3-methylpyrrole-2 : 4-dicarboxylate (*F*) and cryptopyrrole; and 3 : 5-*dicarbethoxy*-4 : 5 : 3′-*trimethylpyrromethene*-4′-*propionic acid hydrobromide*, m. p. 137—138° (decomp.), from *F* and cryptopyrrolecarboxylic acid; and the *methene hydrobromides*, m. p. 157° (decomp.) and 133°, from cryptopyrrole with furfuraldehyde and thiophen-2-aldehyde, respectively. The last did not form a porphyrin by the usual methods.

The condensation of 3-bromo-5-carboxy-4 : 3′ : 5′-trimethyl-4′-ethyl- and 5′-bromo-3 : 4′-dimethyl-4 : 3′-diethyl-5-bromomethyl-pyrromethene hydrobromides at 145—150° as described above gives *pyrroætioporphyrin I*, m. p. 335°, with some *bromopyrroætioporphyrin I*; *bromoætioporphyrin III* [*copper* salt, m. p. 323° (decomp.)] is similarly prepared from the brominated methene from hæmopyrrole and 4 : 5′-dibromo-3 : 5 : 3′-trimethyl-4′-ethylpyrromethene hydrobromide (A., 1930, 931). The brominated porphins may be debrominated by hydrazine and palladised calcium carbonate in presence of 10% alcoholic potassium hydroxide (*pyrroætioporphyrin III*, m. p. 330°). The following are prepared at 195—210°: *pyrroætioporphyrin II*, m. p. 330—332° (*copper* salt, m. p. 263°), from *A* and 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-diethylpyrromethene hydrobromide (*E*); *pyrroætioporphyrin IV*, m. p. 327° (*iron* salt, decomp. about 330°; *copper* salt, m. p. 333°), from *E* and 3 : 5 : 4′ : 5′-tetramethyl-3′ ethylpyrromethene hydrobromide; *pyrroætioporphyrin VIII*, m. p. 284° (*iron* salt, decomp. about 250°; *copper* salt, m. p. 245°), from *A* and 5 : 5′-dibromo-3 : 3′-dimethyl-4 : 4′-diethylpyrromethene hydrobromide; *pyrroætioporphyrin VI*, m. p. 309° (*iron* salt, m. p. about 325°; *copper* salt, m. p. 260°), from *B* and *E*; and 1 : 5-*dimethyl*-2 : 6-*diethylporphin*, m. p. 310° (*iron* salt; *copper* salt, m. p. 312°; *sulphonic acid*), from *C* or *D* alone (accompanied by a small quantity of a chlorin-like substance). The interaction of *F* with malonic acid in presence of aniline gives 2 : 4-*dicarbethoxy*-3-*methylpyrrole*-5-*acrylic acid*, m. p. 244°, converted by reduction with sodium amalgam into the corresponding -*propionic acid*, m. p. 209°. H. A. PIGGOTT.

Conversion of phæophorbide *a* into phylloerythrin. H. FISCHER and O. SUS (Annalen, 1930, 482, 225—232).—Phæoporphyrin a_6 (A., 1930, 932), on fractionation by the ether–hydrochloric acid method and crystallisation from pyridine and ether, gives a substance which analyses as phæoporphyrin a_5, and the homogeneity of a_6 must provisionally be regarded as doubtful. By heating with hydrogen bromide in acetic acid at 50—55° for 24 hrs., phæophorbide a_6 (purified as above), a_5, and a_4 are all converted into phylloerythrin, identified by its methyl ester and its additive compound with chloroform. This affords a very convenient method of preparing phylloerythrin from chlorophyll. H. A. PIGGOTT.

***iso*Oxazoline oxides. X. Reduction.** E. P. KOHLER and A. R. DAVIS (J. Amer. Chem. Soc., 1930,

52, 4520—4528).—Bromination of γ-nitro-α-anisoyl-βγ-diphenylpropane (I) (A., 1928, 523) in chloroform affords an α-*bromo*-derivative, m. p. 165°, converted by alcoholic pyridine into 5-*anisoyl*-3 : 4-*diphenyl*iso*oxazoline oxide*, m. p. 158°. This is isomerised by treatment with potassium acetate and acetic acid in methyl alcohol to 5-*hydroxy*-5-*anisoyl*-3 : 4-*diphenyl*iso*oxazoline*, m. p. 177° (*benzoate*, m. p. 173°), and converted by treatment with alkali into α-*oximino*-γδ-*diketo*-δ-*anisyl*-αβ-*diphenylbutane* (+Et_2O), m. p. 110° (decomp.). When a methyl-alcoholic solution of this oximino-derivative is heated with potassium acetate and acetic acid, 3-*keto*-4 : 5-*diphenyl*-2-*anisylpyrrolenine oxide*, m. p. 182° (decomp.), is produced. The above bromo-compound, the *iso*oxazoline oxide, the hydroxy*iso*oxazoline, and the oximino-derivative are all converted by weak alkali into 5-*anisoyl*-3 : 4-*diphenyl*iso*oxazole*, m. p. 156°, which is reduced by zinc dust and acetic acid to 3 : 4-*diphenyl*-5-α-*hydroxy*-p-*methoxybenzyl*iso*oxazole*, m. p. 146°. Oxidation of this with sodium dichromate and acetic acid regenerates the anisoyldiphenyl*iso*oxazole.

Catalytic reduction (Adams, Willstätter) of 5-anisoyl-3 : 4-diphenyl*iso*oxazoline oxide in methyl alcohol furnishes a mixture of I (small amount) and two stereoisomeric 3 : 4-*diphenyl*-5-α-*hydroxy*-p-*methoxybenzyl*iso*oxazoline oxides*, m. p. 160° and 170°. Further reduction of these oxides affords α-*amino*-γδ-*dihydroxy*-αβ-*diphenyl*-δ-*anisylbutane*, m. p. 208°, whilst treatment with alcoholic potassium hydroxide solution gives anisaldehyde and 3 : 4-*diphenyl*iso*oxazole*, m. p. 91°. This *iso*oxazole is also obtained by the action of 5% alcoholic potassium hydroxide on 5-anisoyl-3 : 4-diphenyl*iso*oxazole. 3 : 4-Diphenyl*iso*oxazole is degraded further by alkaline treatment to benzonitrile and phenylacetic acid, whilst hydrolysis of the product formed by the action of ozone with sodium hydroxide solution yields β-benzilmonoxime.

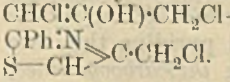
H. Burton.

Dioximes. LXVII. M. Milone (Gazzetta, 1930, **60**, 632—643).—Crystallographic measurements have been made of the glyoxime peroxides already described (A., 1928, 888; 1929, 334, 1072, 1316; 1930, 226) and of certain peroxides existing in two isomeric forms, for purposes of comparison with the furazans, which differ from the peroxides by only one atom of oxygen. The results show that the two peroxides obtained by dehydrogenation of the asymmetric glyoximes, OH·N:CAr·CMe:N·OH, crystallise in different systems. As far as the available data indicate, only one of the two peroxides, viz., that to which a furoxan (furazan oxide) structure is attributable, is isomorphous with the corresponding furazan (monoclinic); the analogy of crystalline form is hence due to the presence in each molecule of the penta-atomic ring, C_2N_2O, characteristic of the furazans. The other peroxide crystallises in the triclinic system, although it exhibits a habit similar to that of the corresponding furoxan and furazan. The furazans and furoxans crystallise in systems of higher degrees of symmetry than the corresponding dioxadiazines.

Phenylmethylfuroxan, m. p. 96°, forms rhombic crystals, $a : b : c = 0{\cdot}59179 : 1 : 0{\cdot}79354$; 5-phenyl-4-methyl-1 : 2 : 3 : 6-dioxadiazine, m. p. 62°, monoclinic, $a : b : c = 1{\cdot}36827 : 1 : 0{\cdot}506001$, β 103° 6′; *p*-anisylmethylfurazan, m. p. 66°, monoclinic, $a : b : c = 1{\cdot}6524 : 1 : 1{\cdot}15384$, β 71° 35′; *p*-anisylmethylfuroxan, m. p. 99°, monoclinic, $a : b : c = 1{\cdot}76427 : 1 : 1{\cdot}52736$, β 72° 33′; 5-*p*-anisyl-4-methyldioxadiazine, m. p. 80—81°, triclinic, $a : b : c = 1{\cdot}299 : 1 : 0{\cdot}9539$, α 71° 18′ 48″, β 61° 59′ 10″, γ 76° 17′ 40″; diphenylfurazan, rhombic, $a : b : c = 0{\cdot}81644 : 1 : 0{\cdot}27766$; 4 : 5-diphenyl-1 : 2 : 3 : 6-dioxadiazine, monoclinic, $a : b : c = 2{\cdot}4803 : 1 : 1{\cdot}0698$, β 86° 16′; phenyloximinoacetonitrile peroxide (α-peroxide), triclinic, $a : b : c = 1{\cdot}7463 : 1 : 0{\cdot}66613$, α 84° 23′ 42″, β 63° 4′ 38″, γ 73° 9′ 22″, and 5-phenyl-1 : 2 : 3 : 6-dioxadiazine (β-peroxide), triclinic, $a : b : c = 1{\cdot}5918 : 1 : 1{\cdot}0314$, α 86° 40′ 30″, β 60° 20′ 40″, γ 73° 37′ 20″.

T. H. Pope.

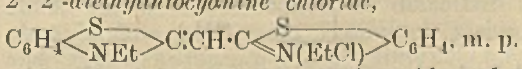
Use of *s*-dichloroacetone for the preparation of thiazoles. III. C. M. Suter and T. B. Johnson (Rec. trav. chim., 1930, **49**, 1066—1068).—*s*-Dichloroacetone reacts readily, in a suitable solvent, with thioamides to yield thiazoles in accordance with the scheme $CHCl{:}C(OH){\cdot}CH_2Cl + SH{\cdot}CPh{:}NH \longrightarrow$

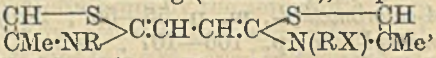


$\begin{matrix} CPh{:}N \\ S{-}CH \end{matrix}\!\!>\!C{\cdot}CH_2Cl$. The following compounds have been prepared in the above manner: 2-*phenyl*-4-*chloromethyl*-, b. p. 155—156°/4 mm., m. p. 51°; 2-p-*anisyl*-4-*chloromethyl*-, m. p. 55—56°; 2-*piperonyl*-4-*chloromethyl*-, m. p. 106—107°, -*thiazole*. The chemical behaviour and reactivity of the chlorine is comparable with that in benzyl chloride, and hence by the action of suitable reagents on the above are obtained: 2-*phenylthiazole*-4-*acetonitrile*, b. p. 180—185°/4 mm., and -4-*acetic acid*, m. p. 90° (*hydrochloride*, m. p. 206—207°), and 2-p-*anisylthiazole*-4-*acetonitrile*, b. p. 220°/5 mm., m. p. 73°. By the action of potassium phthalimide on the appropriate chloromethylthiazole are obtained: 4-*phthalimidomethyl*-2-*phenyl*-, m. p. 151—152°, and -2-p-*anisyl*-, m. p. 186—187°, -*thiazole*, hydrolysed to 2-*phenylthiazole*- (*dihydrochloride*, m. p. 217—219°; *monohydrochloride*, m. p. 188—189°), 2-p-*anisylthiazole*- (*dihydrochloride*, m. p. 224—225°), and 2-p-*hydroxyphenylthiazole*-, m. p. 205—206°, -4-*methylamine*. The phenylthiazolemethylamine is also obtained together with *di*-(2-*phenylthiazole*-4-*methyl*)*amine* (*dihydrochloride*, m. p. 190°) by the action of ammonia on the chloromethyl derivative.

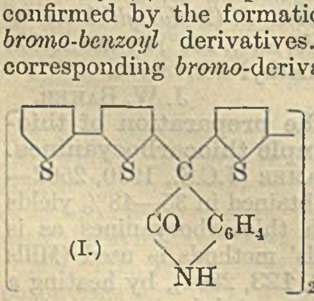
J. W. Baker.

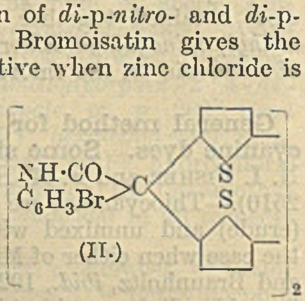
General method for the preparation of thiocyanine dyes. Some simple thiocarbocyanines. N. I. Fisher and F. M. Hamer (J.C.S., 1930, 2502—2510).—Thiocyanines are obtained in 35—48% yields (crude) and unmixed with thiocarbocyanines as is the case when either of Mills' methods is used (Mills and Braunholtz, *ibid.*, 1923, **123**, 2804), by heating a benzthiazolinium chloride containing a reactive methyl group with amyl nitrite in the presence of acetic anhydride on a water-bath. A mechanism of the reaction is tentatively suggested. Thus 1-methylbenzthiazole ethochloride is converted into 2 : 2′-*diethylthiocyanine chloride*,

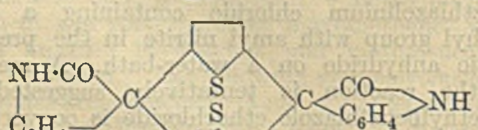


$C_6H_4\!<\!\begin{matrix} S \\ NEt \end{matrix}\!>\!C{:}CH{\cdot}C\!\lessdot\!\begin{matrix} S \\ N(EtCl) \end{matrix}\!>\!C_6H_4$, m. p. 255° (decomp.), converted by sodium bromide and potassium iodide, respectively, into the corresponding *bromide*, m. p. 298° (decomp.), and iodide. The last-named is identical with a specimen obtained by Mills' method. Similarly, the corresponding methochloride affords 2 : 2'-dimethylthiocyanine chloride, *bromide*, m. p. 287° (decomp.), and iodide, m. p. 290—292° (decomp.) (λ 4500 Å.) (Mills gives m. p. 279—280°). From 1-methyl-α-naphthathiazole ethochloride and methochloride are obtained, respectively, 2 : 2'-*diethyl-5 : 6 : 5' : 6'-dibenzthiocyanine chloride*, m. p. 264° (decomp.) (λ 4800 Å.), *bromide*, m. p. 286° (decomp.), and *iodide*, m. p. 297° (decomp.), and 2 : 2'-*dimethyl-5 : 6 : 5' : 6'-dibenzthiocyanine chloride*, m. p. 275° (decomp.), *bromide*, m. p. 309° (decomp.) (λ 4750 Å.), and *iodide*, m. p. 314° (decomp.). Only negative results were obtained with 2-methyl-β-naphthathiazole etho- and metho-chlorides. In all these derivatives the solubility decreases and the m. p. rises in the series chloride, bromide, and iodide. All are sensitisers for silver chloride emulsions, the position of the maximum being given in parentheses after the compounds concerned. Thiocyanines could not be prepared from 2 : 4-dimethylthiazole methiodide, m. p. 260° (decomp.) (lit. slow decomp. above 225°), and *ethiodide*, but by the action of ethyl orthoformate and pyridine they are converted into the corresponding *thiocarbocyanines*, m. p. 255° (decomp.) (λ 5900 Å.), and m. p. 271—294° according to the rate of heating (λ 5900 Å.), respectively, of the type  $\begin{matrix}CH\text{—}S\\ \| \\ CMe\cdot NR\end{matrix}\!\!>C{:}CH\cdot CH{:}C\!<\!\!\begin{matrix}S\text{———}CH\\ \| \\ N(RX)\cdot CMe\end{matrix}$, but in abnormally low yields. The absorption band of these thiocarbocyanines relative to that of the corresponding derivatives from 1-methylbenzthiazole is shifted much less towards the blue than would be expected. J. W. BAKER.

Thiophen series. XXI. Indophenine. W. STEINKOPF and J. ROCH (Annalen, 1930, 482, 251—264).—The condensation of dithienyl with isatin under the influence either of sulphuric acid or zinc chloride gives, not indophenine, as might be expected from Schlenk and Blum's formula (A., 1923, i, 1235), but an olive-green substance that from its ultimate analysis and mol. wt. appears to be *tris-α-dithienylbisindoxyl* (I). The presence of two isatin residues is confirmed by the formation of *di*-p-*nitro-* and *di*-p-*bromo-benzoyl* derivatives. Bromoisatin gives the corresponding *bromo*-derivative when zinc chloride is used as dehydrating agent, but with sulphuric acid a blue compound is formed, which gives analytical results agreeing with cyclo*bis-α-dithienylbisindoxyl* (II). Unlike I, it can be reduced to a soluble leuco-compound. The structure of indophenine is provisionally represented by (III), and explanations of its intense colour independent of a quinonoid structure are given. The quinonoid structure postulated by Schlenk and Blum, if established, would be the sole example of this structure in the thiophen series. Indophenine may be prepared by use of zinc chloride in place of sulphuric acid as condensing agent, and consequently oxidation is not likely to be a necessary stage in the process. The crude product, made by either method, contains 40—50% of an olive-green *substance*, which remains undissolved on reduction with hyposulphite. Its mode of isolation and approximate composition ($C_{28}H_{18}O_2N_2S_3$) point to a structure of type I. Bromoindophenine contains a small amount of a similar substance.


(I.)


(II.)


(III.)

2 : 2'-Dithienyl can be prepared in a yield of 44% by interaction of anhydrous cupric chloride and magnesium thienyl bromide in ether (Krizewski and Turner, J.C.S., 1919, **115**, 559). 5 : 5'-Dibromo- and 5 : 5'-*dimethyl*-2 : 2'-*dithienyl*, m. p. 67°, are similarly prepared. H. A. PIGGOTT.

Preparation and properties of dihydro-*m*-codeinone. C. SCHÖPF and H. PERREY (Annalen, 1930, 483, 169—175).—Bromination of dihydro-*m*-thebainone (thebainol) (A., 1927, 1209) in methyl-alcoholic solution at the ordinary temperature and treatment of the product formed with an excess of alkali hydroxide gives 1-*bromodihydro*-m-*codeinone*, m. p. 241—246°, reduced by hydrogen in presence of palladous chloride, gum arabic solution, and dilute acetic acid to *dihydro*-m-*codeinone*, m. p. 196—201°. Oximation of this at the ordinary temperature gives the corresponding *oxime*, m. p. 176—180°, but at 50° a mixture of this and *m*-thebainoneoxime is produced. Dihydro-*m*-codeinone is readily isomerised to *m*-thebainone by treatment with hydrochloric acid at 100° or by boiling with 2*N*-sodium hydroxide solution, whilst reduction with sodium amalgam and alcohol gives dihydro-*m*-thebainone. H. BURTON.

Partial syntheses in the morphine series. I. Passage from the dihydrothebainone to the dihydrocodeinone series. C. SCHÖPF and T. PFEIFER (Annalen, 1930, 483, 157—169).—Dihydrothebainone is converted by 1 mol. of bromine in acetic acid solution at about 15° into 1-*bromodihydrothebainone* (+0·5AcOEt), froths at 127° and becomes clear at 167°, m. p. (solvent-free) 167° [*hydriodide*, m. p. 215° (decomp.) after sintering and darkening at 198—200°; *hydrobromide*, m. p. 210—215° (decomp.); *oxime*, m. p. 178—180° (decomp.) after sintering from 168°]. Bromination with 2 mols. of bromine or further bromination of the above hydrobromide with methyl-alcoholic bromine at 35° affords a product (not isolated), which when treated with cold 7*N*-alkali hydroxide, passes into 1-*bromodihydrocodeinone*, m. p. 205—207° (*hydrobromide*, m. p. 217—218° after sintering at 215°), also obtained by direct bromination of dihydrocodeinone in acetic acid. Reduction of 1-bromodihydrocodeinone with zinc dust and aqueous-alcoholic ammonium chloride solution also gives 1-bromodihydrothebainone, owing to opening of the oxide ring. Similarly, 1-bromohydroxydihydrothebainone can be converted into 1-bromohydroxydihydrocodeinone, m. p. 181—184° (lit. 182°). Bromination of sinomenine with 2 mols. of bromine in acetic acid at 15—36°, evaporation of the solution below 40°/vac., and alkali treatment of the product formed yields 1-bromosinomeneine, decomp. 213° (cf. Goto and Nambo, A., 1930, 1049); an oxide ring is formed as in the above cases.

In these cases of ring (oxide) formation only one compound is produced. A strainless model can be constructed for compounds of the morphine series which shows that the hydrogen atom on C_5 which is in spatial proximity to the phenolic hydroxyl group attached to C_4 is that which is in the *trans*-position to the side-chain C_{15}–C_{16}–NMe. H. Burton.

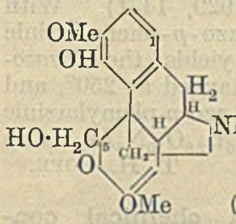
Sulphonation of alkaloids. Z. Kitasato and K. Goto (Ber., 1930, 63, [*B*], 2696—2700).—Alkaloids which contain a hydroxyl or methoxyl group in an aromatic nucleus with free *p*-position are readily sulphonated below 10° by concentrated but not by fuming sulphuric acid. The alkaloidal sulphonic acids are generally well-crystallised substances in which the sulphonyl group is united to the basic nitrogen atom to form an internal salt. *Papaverinesulphonic acid*, $C_{20}H_{21}O_7NS$, m. p. 301° (decomp.), apo*morphinesulphonic acid*, $C_{17}H_{17}O_5NS,3H_2O$, m. p. above 300°, and *sinomeninesulphonic acid*, $C_{19}H_{23}O_7NS$, m. p. 265—267°, are described. Sinomenine hydrate affords *sinomeninonesulphonic acid*, $C_{18}H_{21}O_7NS,0{\cdot}5H_2O$, m. p. 275—280° (*dioxime*, m. p. above 300°, also obtained by sulphonation of sinomenine hydrate dioxime). It is probable that the sulphonic group occupies the *p*-position to the phenolic hydroxyl, since the acids do not give the diazo-reaction. Strychnine which does not contain a hydroxyl group and brucine in which the *p*-position to the methoxyl group is not free are not sulphonated under these conditions. Derivatives of sinomenine and thebainone in which the *p*-position to the phenolic hydroxyl is not free according to the evidence of the diazo-reaction (bromosinomenine, disinomenine, dithebainone) do not afford sulphonic acids.

Although thebainone dissolves to a dark red solution in concentrated sulphuric acid it can be recovered therefrom quantitatively and unchanged by successive addition of ice and an excess of sodium carbonate.

H. Wren.

Sinomenine and disinomenine. XX. Benzeneazosinomenine. K. Goto and H. Shishido (Bull. Chem. Soc. Japan, 1930, 5, 311—314; cf. A., 1930, 1600).—The diazo-coupling reaction of phenolic alkaloids of the phenanthrene group produces a red colour visible at a dilution of 1 in 2×10^6 when the alkaloid tested has the *p*-position to the hydroxyl group unsubstituted. The following benzeneazo-compounds formed in certain cases have been isolated: *benzeneazo-sinomenine*, decomp. 253°; *-dihydrosinomenine*, m. p. 231° (decomp.); *-thebainone*, m. p. 152°. Reduction of the first-named by means of sodium hyposulphite affords 1-*aminodihydrosinomenine*, isolated as the *dihydrochloride* (+$CHCl_3$+H_2O), m. p. above 300°. R. Child.

Sinomenine and disinomenine. XXI. Reaction between sinomenine and formaldehyde. K. Goto, H. Shishido, and R. Inaba (Bull. Chem. Soc. Japan, 1930, 5, 315—320).—Interaction of sinomenine and boiling aqueous formaldehyde (40%) affords 5-*hydroxymethylsinomenine* (I), m. p. 260° (decomp.), $[\alpha]_D^{20}$ −40·71° [*oxime*, (decomp. 240—245°; *methiodide*, m. p. 223° (decomp.)], and 1 : 5-*di*(*hydroxymethyl*)-*sinomenine* (II), m. p. 242° (252°), $[\alpha]_D^{30}$ −74·39° (*oxime*, decomp. 200—215°; *methiodide*, m. p. 210°, decomp. 280—285°). I on acetolysis gives methylethylamine (cf. sinomenine itself, Goto, A., 1926, 1160) and a nitrogen-free *substance*, $C_{23}H_{22}O_8$, m. p. 192—193°, probably diacetyl-5-acetoxymethylsinomenol (4 : 6 - diacetoxy - 3 : 7 - dimethoxy - 5 - acetoxymethylphenanthrene). Catalytic reduction of I yields *dihydro-5-hydroxymethylsinomenine* (III), m. p. 244°, $[\alpha]_D^{20}$ +73·03° [*oxime*, decomp. 215—225°; *methiodide*, m. p. 205—220° (decomp.)] (not obtained from dihydrosinomenine and formaldehyde). I and III give diazo-reactions visible at dilutions up to 1 in 2×10^6; II is less sensitive (1 in 2×10^4), indicating substitution of the 1-position, *para* to a hydroxyl group. R. Child.



(I.)

Action of hydrobromic acid on certain arsinic acids. M. A. Phillips (J.C.S., 1930, 2400—2401).—Boiling hydrobromic acid (*d* 1·445) reacts with 3-nitro-4-amino-, 4-nitro-3-amino-, 3-nitro-4-methylamino-, 4-*nitro*-3-*methylamino*- (by the action of methylamine hydrochloride on 3-chloro-4-nitrophenylarsinic acid at 150—160°), and 3 : 5-dinitro-4-aminophenylarsinic acid, to give good yields of 4-, and 5-bromo-2-nitroaniline, 4- and 5-bromo-2-nitromethylaniline, and 4-bromo-2 : 6-dinitroaniline, respectively. Hydriodic acid similarly converts 3-nitro-4-aminophenylarsinic acid into 4-iodo-2-nitroaniline.

J. W. Baker.

Arsenic derivatives of cysteine. J. M. Johnson and C. Voegtlin (J. Biol. Chem., 1930, 89, 27—31).—The hydrochlorides of cysteine and of 3-amino-4-hydroxyphenylarsenious oxide, when heated together in alcoholic solution, yielded an insoluble hydrochloride from which, by treatment with sodium hydroxide, was obtained 3-*amino*-4-*hydroxyphenyl*-*di*-SS-*cysteinylarsine*, $OH{\cdot}C_6H_3(NH_2){\cdot}As[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2$, m. p. 225—227° (decomp.); arsenious chloride and cysteine · hydrochloride yielded similarly, but at the ordinary temperature, SSS-*tricysteinylarsine*, $As[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_3$, m.p. 260° (decomp.). The ready formation of these compounds is in accord with the authors' theory (A., 1925, i, 861) of the mode of protection of animals against the toxic effects of arsenious oxide derivatives by means of thiol compounds. C. R. Harington.

Arsenical azo-derivatives. IV. S. Berlingozzi and M. Liguori (Annali Chim. Appl., 1930, 20, 494—500; cf. A., 1927, 675; 1928, 434, 1146; 1929, 1471).—Condensation of diazotised *p*-aminophenylarsinic acid with resorcinol yields 1 : 3-*dihydroxybenzene*-6-*azo*-p-*phenylarsinic acid* (cf. Schmitz, A., 1914, i, 342), which remains unchanged at 250° and on further coupling with diazotised *p*-aminophenylarsinic acid gives 1 : 3-*dihydroxybenzene*-4 : 6-*bisazo*-

p-*phenylarsinic acid*, $O:As(OH)_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot AsO(OH)_2$, this also remaining solid at 250°. 1 : 3-*Dihydroxybenzene*-6-α-*naphthaleneazo*-4-*azo*-p-*phenylarsinic acid*, obtained from α-diazonaphthalene and 1 : 3-dihydroxybenzene-6-azo-*p*-phenylarsinic acid, does not melt at 250°. 1 : 3-*Dihydroxybenzene*-2 : 4 : 6-*trisazo*-p-*phenylarsinic acid*, unchanged at 250°, is obtained either from diazophenylarsinic acid and 1 : 3-dihydroxybenzene-4 : 6-bisazo-*p*-phenylarsinic acid or from diazophenylarsinic acid (3 mols.) and resorcinol (1 mol.). 1-*Amino*-3-*hydroxybenzene*-6-α-*phenylquinoline*-β-*azo*-4-*azo*-p-*phenylarsinic acid*, decomp. at about 180°, is formed from diazotised 3-amino-2-phenylquinoline and 1-amino-3-hydroxybenzene-4-azophenylarsinic acid (cf. A., 1929, 1471). With 1-amino-3-hydroxybenzene-4-azo-*p*-phenylarsinic acid, tetrazodiphenyl chloride yields the *tetrazo*-compound, $C_{36}H_{30}O_8N_{10}As_2$, unchanged at 250°, and with 1 : 3-dihydroxybenzene-4-azo-*p*-phenylarsinic acid, the *tetrazo*-compound, $C_{36}H_{28}O_{10}N_8As_2$, also unchanged at 250°. T. H. Pope.

Trypanocidal activity and chemical constitution. II. New sulphur derivatives of aromatic arsenicals (*cont.*). Derivatives of 2-thiolbenziminazole-5-arsinic acid. J. G. Everett (J.C.S., 1930, 2402—2408).—Oxidation of 2-thiolbenziminazole-5-arsinic acid (A., 1929, 709) with iodine in dilute aqueous solution affords *benziminazole-5-arsinic acid 2-disulphide* as its *monohydriodide.* The disulphide is readily converted by thiolacetamide into the *thiolacetamide*, m. p. 245° (decomp.), of the parent substance. 2-Thiolbenziminazole-5-arsinic acid reacts with chloroacetic acid and chloroacetamide in alkaline solution to give, respectively, 2-*carboxy*- and 2-*carbamyl-methylthiolbenziminazole*-5-*arsinic acid*, reduced by sodium hyposulphite to 5 : 5′-*arseno*-(2-*carboxymethylthiolbenziminazole*) and -(2-*carbamylthiolbenziminazole*), respectively. Oxidation of 2-thiolbenziminazole-5-arsinic acid with boiling alkaline potassium permanganate converts it into 2-*sulphobenziminazole*-5-*arsinic acid*, similarly reduced to 5 : 5′-*arseno*(*benziminazole*-2-*sulphonic acid*). The non-arsenated analogue *benziminazole 2-disulphide*, m. p. 198° (*monohydrochloride*, decomp. 210°), is obtained by oxidation of 2-thiolbenziminazole with iodine at 50°, whilst oxidation with alkaline potassium permanganate affords the corresponding *benziminazole*-2-*sulphonic acid*, m. p. 365° and $+0{\cdot}5H_2O$. Both the last-named and its arsenated analogue are very resistant to acid and alkaline hydrolysis. The trypanocidal activity of these derivatives against an experimental infection of *T. equiperdum* in mice has been investigated both by oral and intravenous injections. The therapeutic activity of the parent 2-thiolbenziminazole-5-arsinic acid is approached only by benziminazole-5-arsinic acid 2-disulphide, and this, owing to its ready hydrolysis, is probably present in the blood-stream and tissues as the free thiol. In the other cases replacement of the hydrogen of the thiol group causes adverse modification of the therapeutic activity in both the arsinic acid and arseno-derivatives. All these derivatives are inactive against *B. tuberculosis*. J. W. Baker.

Comparative action of iron halides on magnesium and zinc organo-compounds. G. Champetier (Bull. Soc. chim., 1930, [iv], 47, 1131—1137).—Ferric chloride and ethereal magnesium phenyl bromide give diphenyl and a black precipitate of active iron (Job and Reich, A., 1922, i, 645; 1923, i, 873). The reaction ceases when 1 mol. of ferric chloride is present for 3 mols. of magnesium phenyl bromide. When a solution of the latter is added to an ethereal solution of ferric chloride, diphenyl ferrous chloride and magnesium chloride and bromide are formed until 1 mol. of magnesium phenyl bromide has been added. On further addition the latter reacts with ferrous chloride, yielding diphenyl and metallic iron until 3 mols. have been added per mol. of ferric chloride originally present, the second stage being much closer in consequence of deposition of metallic iron on the ferrous chloride. Although no evidence of the formation of an intermediate iron organo-compound was obtained, the fact that at −40° a mixture of ferric chloride (1 mol.) and magnesium phenyl bromide (3 mols.) does not give an immediate precipitate of metallic iron is regarded as indicating its existence. These results agree with those of Bennett and Turner (A., 1921, i, 472). Ferrous chloride and iodide similarly yield only diphenyl and metallic iron with magnesium phenyl bromide, but with zinc phenyl chloride in ether in an atmosphere of nitrogen ferrous iodide yields ferrous phenyl iodide, FePhI, which on hydrolysis gives benzene. R. Brightman.

Mercuration of β-resorcylic [2 : 4-dihydroxybenzoic] acid. R. B. Sandin and J. M. Zeavin (J. Amer. Chem. Soc., 1930, **52**, 4369—4372).—β-Resorcylic acid (1 mol.) and mercuric acetate (0·5 mol.) react in hot acetic acid, forming *anhydro-5-hydroxymercuri*-β-*resorcylic acid*. With 2 mols. of the acetate in alcoholic acetic acid, *anhydro*-3-*hydroxymercuri*-5-*acetoxymercuri*-β-*resorcylic acid* is produced. Mercuration in alkaline solution (cf. Fox and Whitmore, A., 1929, 1091) affords *anhydro*-3 : 5-*dihydroxymercuri*-β-*resorcylic acid*. Quinonoid structures are suggested for these (coloured) mercurated derivatives.

H. Burton.

Formation of hetero-rings containing mercury atoms. W. Steinkopf (Ber., 1930, **63**, [*B*], 2937; cf. Vecchiotti, A., 1930, 1458).—The formation of rings of this type has been observed previously by Hilpert and Grüttner (A., 1914, i, 261, 262) and by Steinkopf and others (A., 1923, i, 125). H. Wren.

Constitution of double sulphonium mercuric iodides. Optically active mercuri-tri- and -tetra-iodides and cadmium tetra- and -penta-iodides derived from *l*-phenacylmethylethylsulphonium iodide. M. P. Balfe, J. Kenyon, and H. Phillips (J.C.S., 1930, 2554—2572).—The preparation of optically active sulphonium mercuri- and cadmi-iodides, and the inter-relations of the triethyl- and phenyldiethyl-sulphonium mercuri-iodides are described. l-*Phenacylmethylethylsulphonium mercuritri-iodide* $[XHgI_3 :\ X{=}Ph \cdot CO \cdot CH_2 \cdot (Me)(Et)S^-]$, m. p. 81—82°, $[\alpha]_{5461}$ −10·7° in acetone, is obtained from mercuric iodide and aqueous potassium iodide on the *l*-sulphonium *d*-camphorsulphonate. It is converted by excess of potassium iodide or by hydrogen sulphide into the l-*mercuritetraiodide* (X_2HgI_4), m. p. 122—123°, $[\alpha]_{5461}$ $-9{\cdot}3°$ in acetone, which may be reconverted into the tri-iodide by mercuric iodide in acetone. An explanation of the racemisation of these compounds based on the reversibility of sulphonium iodide formation, $[R_3\overset{+}{S}]+\overset{-}{I}\rightleftharpoons R_2S+RI$, is advanced. Both are rapidly racemised in presence of iodide ions. The tri-iodide, which gives the stable $[HgI_3]'$ ion, is optically stable in solution, but the tetraiodide, which ionises, $X_2HgI_4\rightleftharpoons 2\overset{+}{X}+\overset{-}{HgI_3}+\overset{-}{I}$, undergoes racemisation and profound decomposition when its solution is kept and also causes racemisation of the tri-iodide. Racemisation of the tetra- but not of the tri-iodide is accelerated by methyl iodide. The failure of Pope and Neville (J.C.S., 1902, **81**, 1552) to isolate these compounds in optically active forms appears to be due to prolonged contact with ionisable halides. The "*dl*-phenacylmethylethylsulphonium tri-iodide" of these authors (*loc. cit.*; cf. Rây and Adhikary, A., 1930, 1020) appears to be the dl-*tetraiodide*, m. p. 134°; dl-*phenacylmethylethylsulphonium tri-iodide*, m. p. 82—83°, is, however, readily prepared by allowing it to react with mercuric iodide. Attempts to prepare Pope and Neville's "mercuritrichloride" led instead to dl-*phenacylmethylethylsulphonium dimercuriheptachloride* ($X_3Hg_2Cl_7$), m. p. 153° (decomp.); the l-*compound* has m. p. 153°, $[\alpha]_{5461}$ $-11{\cdot}3°$ in methyl alcohol.

dl-, m. p. 126°, and l-*Phenacylmethylethylsulphonium cadmitetraiodide* (X_2CdI_4), m. p. 132—133°, $[\alpha]_{5461}$ $-10{\cdot}2°$ in acetone, are obtained by use of cadmiun and potassium iodides in proportions corresponding with $KCdI_3$ and K_2CdI_4. By cadmium iodide in acetone they are converted into the dl-, m. p. 134—136°, and l-*cadmipentaiodide* (X_3CdI_5), m. p. 128°, $[\alpha]_{5461}$ $-9{\cdot}0°$ in acetone. Both the tetra- and penta-iodides have unstable ions, and rapidly lose their optical activity in solution.

l-Phenacylmethylethylsulphonium *d*-camphorsulphonate, $[\alpha]_{5461}$ $+59{\cdot}0°$, and picrate, $[\alpha]_{5461}$ $-13{\cdot}5°$ in acetone, slowly lose their activity in solution.

Triethylsulphonium mercuritri-iodide (I) (Smiles and Hilditch, J.C.S., 1907, **92**, 1394) is obtained from equimolecular proportions of the sulphonium iodide or its components and mercuric iodide, or from triethylsulphonium mercuritetraiodide (II) (Hofmann and Rabe, A., 1897, i, 310) by heating or the action of mercuric iodide. It is stable at 165°, but is converted into II by reagents capable of removing mercuric iodide, *e.g.*, hydrogen sulphide, potassium iodide, or triethylsulphonium iodide. Triethylsulphonium dimercuripentaiodide (III) (Smiles and Hilditch, *loc. cit.*) is obtained from 1 mol. of sulphonium iodide and 2 mols. of mercuric iodide, or from I and mercuric iodide; it is converted into I by the sulphonium iodide, and into II by a large excess of this or by 1·5 mols. of potassium iodide. *Phenyldiethylsulphonium mercuritri-iodide* (IV), m. p. 56—57°, is prepared from equimolecular proportions of phenyl ethyl sulphide, ethyl iodide, and mercuric iodide, and gives when heated, or when treated with excess of mercuric iodide, the *trimercurioctaiodide*, $[(PhSEt_2)_2Hg_3I_8]$ (V), m. p. 65—66°. The reverse change is effected by heating V with potassium mercuritri-iodide. *Phenyldiethylsulphonium mercuritetraiodide*, m. p. 114—115°, is obtained from IV or V and potassium iodide or hydrogen sulphide, and is reconverted into IV by mercuric iodide, potassium mercuritri-iodide, or by heating, with evolution of phenyl ethyl sulphide and ethyl iodide in the last case. H. A. PIGGOTT.

Mol. wt. of cocosin. B. SJÖGREN and R. SPYCHALSKI (J. Amer. Chem. Soc., 1930, **52**, 4400—4404).—Solutions of cocosin (coconut globulin) show an absorption maximum at 280 mμ and a minimum at 255 mμ at p_H 6·7; the specific volume is 0·746 at 20·2°. Determinations of the mol. wt. of the protein by the methods of sedimentation velocity and equilibrium at p_H 6·7—11·8 in phosphate buffers indicate the presence of two substances with mol. wt. of 104,000 and 208,000. The amount of the former increases with rise in p_H, probably owing to fission of the true cocosin molecule. H. BURTON.

Mol. wt. of coconut globulin. R. SPYCHALSKI (Rocz. Chem., 1930, **10**, 630—651).—Coconut globulin undergoes partial decomposition during preparation. The ultracentrifuge method indicates that two molecular species are present, of mol. wt. 208,000 (75%) and 104,000 (25%). R. TRUSZKOWSKI.

Pregl's method for the determination of carbon and hydrogen. F. HERNLER (Mikrochem., 1930, Emich Festschr., 148—151).—Details of the method are discussed. The humidity of the atmosphere in which the weighings are conducted is of importance for micro-combustion work, inaccurate results being obtained if the humidity is greater or less than 60—70%. The mean error of 16 determinations made at a humidity of 60—70% was for carbon 0·06%, and for hydrogen 0·02%. The best sequence of drying agents is soda-lime, calcium chloride, soda-asbestos, and calcium chloride. H. F. GILLBE.

Volumetric determination of methoxyl and ethoxyl groups. F. VIEBÖCK and A. SCHWAPPACH (Ber., 1930, **63**, [*B*], 2818—2823).—The substance (20—50 mg.) is heated at 140° with 5 c.c. of hydriodic acid and 0·2 g. of coarse red phosphorus and the vapours, after passage through a suspension of fine red phosphorus in water, are absorbed in 10 c.c. of a solution of potassium acetate (20 g.) in glacial or 96% acetic acid (200 c.c.) containing 6—7 drops of bromine. The process is complete after 1 hr. The contents of the absorption vessel are rinsed into an Erlenmeyer flask containing 1—1·5 g. of dissolved sodium acetate, care being exercised that solid salt does not remain attached to the sides of the flask. Formic acid is cautiously added until the colour of the bromine disappears and a drop of methyl-red remains unchanged. After addition of 0·5—1 g. of potassium iodide and sulphuric acid, the liberated iodine is titrated with 0·1*N*-sodium thiosulphate. The insensitiveness of the absorbing liquid to phosphine and hydrogen sulphide renders the purification of phosphorus unnecessary and makes the process directly applicable to materials containing sulphur. H. WREN.

Determination of picric acid. M. FRANÇOIS and L. SEGUIN (Ann. Falsif., 1930, **23**, 481—485).—The picric acid is precipitated as cuprammonium picrate, $[C_6H_2(NO_2)_3{\cdot}OH]_2,CuO,2NH_3$, by means of cuprammonium sulphate, the precipitate being dried and weighed. Phenol interferes with the precipitation and is removed by extraction with chloroform, the picric acid being first converted into its sodium salt by treatment with sodium carbonate to prevent its extraction by the solvent. Cuprammonium picrate is decomposed by hot water into ammonium picrate and copper oxide. B. W. Town.

Determination of cystine and cysteine. H. D. Baernstein (J. Biol. Chem., 1930, 89, 124—131).—The solution of cysteine (or of cystine after preliminary reduction with Devarda's alloy) in dilute hydrochloric acid is treated with excess of iodine in potassium iodide, and the excess of iodine is determined by measurement of the nitrogen evolved when it is brought into reaction with hydrazine in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The error of the method is ±4%. C. R. Harington.

Detection of tyrosine. J. A. Sánchez (Semana Méd., 1930, I, 1579—1981).—When tyrosine is treated with sodium nitrite, the nitroso-compound being then reduced with zinc and again treated with sodium nitrite, the diazo-compound gives an intense red colour with resorcinol in alkaline solution. A dilute solution of nitrosotyrosine gives a yellow colour with ammonia. Tyrosine gives with nitric acid a yellow, with sulphonylbenzenediazonium chloride a red, and with nitrobenzenediazonium chloride a violet colour; bromine gives a precipitate. After treatment with sodium hypochlorite reactions are obtained with phenylhydrazine, Fehling's solution, and Nessler's reagent. Chemical Abstracts.

Biochemistry.

Factors influencing the respiration of erythrocytes. I. Primitive avian erythrocytes. II. Mammalian reticulocytes. G. P. Wright (J. Gen. Physiol., 1930, 14, 179—199, 201—213).—I. "Primitive red cells" from fowl's blood in phenylhydrazine anæmia have an oxygen consumption 20—25 times as great as that of normal red cells. The oxygen consumption of anæmic red cells is (*a*) independent of concentrations of sodium chloride between 0·6 and 1·10%, (*b*) affected by the reaction of the medium, being at a maximum at p_{H} 7·75, (*c*) increased by 15% by 0·6% of dextrose, (*d*) unaffected by low concentrations of glycine, alanine, histidine, and *l*-aspartic acid, and (*e*) reduced by a glycine content above 5 mg. of amino-nitrogen per 100 c.c.

II. Although a greatly increased respiration is observed in reticulocytes of an anæmic rabbit, the oxygen consumption per billion reticulocytes is not appreciably changed during regeneration. Respiration attains a maximum at p_{H} about 7·75 (intracellular) and is practically independent of the tonicity of the medium. Respiration is unaffected by glycine or alanine, but a slight depression is observed in the presence of dextrose. On the basis of equal cell volume, the respiration of "primitive" avian erythrocytes is twice that of rabbit reticulocytes, which is six times as great as that of the normal avian erythrocyte. A. Cohen.

Catalytic action of methylene-blue in living cells. O. Warburg, F. Kubowitz, and W. Christian (Biochem. Z., 1930, 227, 245—271).—The consumption, in the presence of methylene-blue, of oxygen and dextrose by the red blood-cells of the rabbit has been quantitatively investigated and the results of Harrop and Barron (A., 1929, 1324) have been, in the main, confirmed. Pyruvic acid formed during the process of oxidation has been isolated as phenylhydrazone and determined by a micro-method. As regards the extent of their retarding effect on the rate of the oxidation stimulated by methylene-blue, ethyl-, propyl-, amyl-, and phenyl-urethanes, in this order, formed an ascending series. The inhibition of the action of methylene-blue by carbon monoxide was appreciable only when the concentration of the dye was low and direct inhibition by hydrogen cyanide was not proved. From these results and from others previously obtained (cf. Warburg and Kubowitz, A., 1930, 1053), as well as from consideration of the probable mechanism of the process, it is concluded that the action of methylene-blue involves a heavy metal (iron) catalysis similar to that which normally occurs in living matter. W. McCartney.

Glycolysis and phosphoric acid exchange in the blood-corpuscles of different animals. W. A. Engelhardt and M. Ljubimova (Biochem. Z., 1930, 227, 6—15).—Continuous hydrolysis of phosphoric esters normally takes place in erythrocytes and a synthesis of these esters accompanies glycolysis. The following series indicates the order of intensity of hydrolysis with cells of different animals: ox<goat<horse<dog, pig<man, guinea-pig<rabbit. This series corresponds with the organic phosphorus content for the different animals except in the case of the pig. The glycolytic power of the corpuscles is in the following order: ox<goat<dog<horse<guinea-pig, man<rabbit. This series corresponds closely with the above, the pig again forming the exception, since the corpuscles in this case have no glycolytic power. The quotient mol. of bound phosphoric acid per mol. of sugar disappeared amounts to 0·2—0·3 for goat, ox, and horse and to 0·5—1·0 for dog, man, guinea-pig, and rabbit.
P. W. Clutterbuck.

Ortho- and pyro-phosphate in aërobic and anaërobic metabolism of blood-corpuscles. W. A. Engelhardt (Biochem. Z., 1930, 227, 16—38).—Non-nucleated erythrocytes become able, in presence of methylene-blue, to utilise oxygen energetically. If the resting glycolysis is inhibited by addition of fluoride, a greater amount of phosphoric acid becomes fixed organically in presence of methylene-blue. Inhibition of respiration of nucleated erythrocytes causes a rapid increase of inorganic phosphate due, not to an increased decomposition of phosphoric ester, but to the inhibition of resynthesis which usually accompanies respiration. Aërobic resynthesis from pyrophosphate after anaërobic hydrolysis is confirmed. P. W. Clutterbuck.

Hydrolysis and esterification of phosphoric acid, and glycolysis of erythrocytes in various animals. M. N. Ljubimova (Zhur. exp. Biol. Med., 1929, **12**, 405—415).—The ability of erythrocytes to eliminate phosphoric acid increases in the series ox, goat, or horse, dog, pig, guinea-pig, man, rabbit. Pig erythrocytes do not glycolyse; otherwise the glycolytic power rises in the same order. These two functions are also related, except for the pig, to the organic phosphoric acid content of the cells.
Chemical Abstracts.

Micro-determination of velocity of sedimentation of erythrocytes. G. C. E. Burger (Arch. Néerland. Physiol., 1930, **15**, 565—584).—A pipette in which blood is diluted, citrated, and the sedimentation velocity of the erythrocytes measured, is described and by its use the effect of dilution on the velocity investigated. F. O. Howitt.

Electrokinetic phenomena. III. "Isoelectric point" of normal and sensitised mammalian erythrocytes. H. A. Abramson (J. Gen. Physiol., 1930, **14**, 163—177; cf. A., 1929, 1094).—The electrophoretic mobilities of intact human and sheep cells in 0·85% sodium chloride solution show no change of sign of charge with variation of p_H between 7·4 and 3·6. Reversal of sign is observed after sufficient time has elapsed and in the presence of normal and anti-sheep rabbit sera. It is claimed that the attainment of an isoelectric state is associated with adsorption of hæmolysis products. Sensitisation to hæmolysis by sera does not primarily affect the mobility of cells, and it is suggested that small changes of cell surface suffice to induce hæmolysis by complement.
A. Cohen.

Effect of administration of hydrochloric acid on the leucocyte count. J. Gworkówna and B. Szabuniewicz (Med. Doświad., 1930, **11**, 183—188).—0·4% Hydrochloric acid introduced into the stomach of dogs either by a stomach tube or through a gastric fistula provokes a feeble leucopænia.
R. Truszkowski.

Changes in exchange between blood and tissues following venesection. W. Ito (Tohoku J. Exp. Med., 1930, **14**, 236—253).—Of the total volume of blood rapidly removed from a normal rabbit 20% is replaced within 0·5 hr. by a fluid containing 0·1 as much protein, but about as much sodium chloride, as plasma, the exact composition depending on the amount of blood removed. The effect of poisoning by cantharidin or uranium is recorded.
Chemical Abstracts.

Hæmoglobins. Prosthetic group of hæmoglobin of *Chironomus*. A. Kirrmann (Bull. Soc. Chim. biol., 1930, **12**, 1146—1150).—Blood from the larvæ of *Chironomus* yielded hæmin which was converted into mesoporphyrin by the method of Fischer and Koegl (A., 1924, i, 1130) and then into the methyl ester. The m. p. of this ester and also that of its complex with copper established the identity of the parent substance with the mesoporphyrin obtained by Fischer and Stangler (A., 1928, 76) from mammalian blood. F. O. Howitt.

Regulation of the mineral content of body-fluids. I. *Maja squinada*, L. K. Białaszewicz (Acta Biol. Exp., Warsaw, 1930, **5**, 57—84).—The order of velocity of disappearance from the hæmolymph of the above crab of various injected salts is: $KCl > CaCl_2 > MgCl_2 > MgSO_4$. These salts are eliminated from the hæmolymph to a small extent by the antennary glands, but chiefly by sorption by the tissues. R. Truszkowski.

***Spirographis*-hæmin.** O. Warburg, E. Negelein, and E. Haas (Biochem. Z., 1930, **227**, 171—183).—The absorption spectrum of the blood of *Spirographis* (cf. A., 1926, 313) is more closely related to that of the respiratory enzyme than to that of hæmoglobin. A method for the isolation of *Spirographis*-hæmin is described. The empirical formula $C_{32}H_{32}O_5N_4FeCl(\pm 1C, \pm 1H)$ closely resembles that for the hæmin of hæmoglobin and contains one atom of oxygen more than the latter. *Spirographis*-hæmin is a dibasic acid and, in the reduced condition, absorbs 1 mol. of carbon monoxide per atom of iron in the same way as ordinary hæmin. It differs, however, from the latter in that it contains either no or at most only one double linking reducible by means of palladium and hydrogen. The absorption spectra of the carbon monoxide compounds of *Spirographis*-hæmin and of chlorocruorin were investigated. Chlorocruorin absorbs more strongly than the hæmin, the maximum absorption being for the hæmin at 410 mμ. and for chlorocruorin at 440 mμ.
P. W. Clutterbuck.

Catalytic action of the hæmins of blood and chlorophyll. O. Warburg and F. Kubowitz (Biochem. Z., 1930, **227**, 184—199).—The effect of a number of hæmins on the respiration of non-nucleated red blood-cells is investigated. The ordinary hæmin of blood, *Spirographis*-hæmin, and coprohæmin have little or no effect, pyrrohæmin is more active, whilst the hæmin of phæophorbide-*a* (A., 1912, i, 287) increases the respiration by twenty times and produces an oxidation velocity which exceeds by far that of the normal nucleated red blood-cells of birds. The oxygen utilisation which arises under the action of the hæmin is due to the oxidation of sugar or to its degradation products (lactic acid). The catalysis by phæophorbide-*a*-hæmin is a surface reaction, since it is inhibited by narcotics, the inhibition being greater the greater is the adsorption of narcotic. The catalysis is also inhibited by carbon monoxide. P. W. Clutterbuck.

Increased oxidation [of methylene-blue by hydrogen peroxide] produced by blood-pigments. K. Bingold (Biochem. Z., 1930, **227**, 457—461).—Although solutions of methylene-blue are not decolorised by hydrogen peroxide alone, decolorisation takes place when human blood which has previously been heated to 90° is added. Hæmatin and pigeon's blood act in the same way. When these substances which stimulate the oxidation are decolorised by treatment with hydrogen peroxide they lose their power to assist the decolorisation of methylene-blue by the peroxide.
W. McCartney.

Tryptophan and histidine as hæmatogenic amino-acids. G. Fontès and L. Thivolle (Compt.

rend., 1930, **191**, 1088—1090).—Subcutaneous injection of tryptophan and histidine (100 and 200 mg. per day, respectively) into dogs or rabbits fed on a normal full diet causes a marked increase in the hæmoglobin and red corpuscles of the blood, an even greater increase being caused by simultaneous daily injections of both amino-acids in the above proportion, which is that required for the synthesis of hæmatin. Since other amino-acids such as leucine, lysine, or phenylalanine have no similar action, it is concluded that the specific metabolic function of these amino-acids is the formation of blood-pigment, and the term "hæmatogenic amino-acids" is suggested for these two proteins. This view is confirmed by a decrease in hæmoglobin when rats are fed on a diet deficient in tryptophan and histidine. J. W. BAKER.

Blood-sugar. II. P. RONA and W. FABISCH (Biochem. Z., 1930, **227**, 205—220).—The agreement in results previously obtained (A., 1930, 360) in determinations of the normal human blood-sugar by the Hagedorn–Jensen and by the *B. coli* methods is confirmed. The same agreement in results is obtained with the blood of rabbits rendered hyperglycæmic with adrenaline. The determination by the two methods with the blood of diabetics showed differences which were often greater than the experimental error, but the results were not consistently larger or smaller by any one method. The blood-sugar values obtained in hypoglycæmic convulsions in rabbits by the Hagedorn–Jensen method are always greater than by the *B. coli* method. P. W. CLUTTERBUCK.

Course of blood-sugar curve after intravenous administration of sugar. O. JÜTTEMANN (Arch. exp. Path. Pharm., 1930, **156**, 253—264).—In fed rabbits the amount of dextrose which is taken up by the tissues from the blood during the first hour after intravenous administration of dextrose (10 c.c. of 20—40% solutions) is about 2·4 g., whilst in fasting animals the corresponding quantity is only about 1·1 g. In starving animals treated with ergotamine or previously submitted to thyroidectomy, the uptake of sugar by the tissues is greater than with normal animals and approaches the figure obtained with normal fed animals. Atropine has a slight effect on starved animals in the same sense.

W. O. KERMACK.

Carbohydrate complex of serum-proteins and the clinical determination of "bound sugar" in the blood. C. RIMINGTON (Nature, 1930, **126**, 882—883).—The complex obtained from the proteins of horse-serum appears to be a tri- and not a disaccharide (cf. A., 1929, 837). Each molecule of glucosamine is associated with two of mannose, giving a substance of the empirical formula $C_{18}H_{33}O_{15}N$. A similar and apparently identical trisaccharide complex has also been isolated from the mixed serum-proteins of ox blood. The preparations are optically inactive. These complexes afford a satisfactory explanation of some of the contradictory observations on the "bound sugar" of the blood.

L. S. THEOBALD.

Relation between blood-sugar and -coagulation time. F. ŠVEC (Pflüger's Archiv, 1930, **224**, 62—64; Chem. Zentr., 1930, i, 3804).—Injection of insulin diminishes the coagulability of the blood. The coagulability increases regularly with increase in the blood-sugar. A. A. ELDRIDGE.

Diffusible non-protein constituents of blood and their distribution between plasma and corpuscles. O. FOLIN and A. SVEDBERG (J. Biol. Chem., 1930, **88**, 715—728).—In normal subjects the concentration of sugar in the corpuscles is 50—60% of that in the plasma, whilst in diabetics a higher percentage is found, but in no case does it reach 80%, *i.e.*, the percentage of free water in the corpuscles (cf. Ege and Roche, Skand. Arch. Physiol., 1930, **59**, 75). The concentration of urea and creatinine in the corpuscles is approximately 80% of that in the plasma. The average concentration of uric acid in the corpuscles is about 22% of that in the plasma, whilst the amino-acid-nitrogen concentration of the corpuscles is also usually less than half of that of the plasma. When extracts of unlaked normal blood are used, the total non-protein-nitrogen of the blood is practically equal to the sum of the urea-, uric acid-, creatinine-, and amino-acid-nitrogen, so that the residual nitrogen found when extracts of laked blood are employed has disappeared. For clinical purposes it is advantageous to carry out analysis on extracts of unlaked blood. W. O. KERMACK.

Distribution of amino-acids [in blood]. V. A. MESSING (Zhur. exp. Biol. Med., 1929, **12**, 393—400). —The distribution of various amino-acids, when added to dog's blood *in vitro*, between the plasma and cells is practically constant. If the amino-acid content is not much greater than the physiological concentration the erythrocytes maintain their normal content. CHEMICAL ABSTRACTS.

Amide-nitrogen of blood. V. Theory of ammonia metabolism. S. BLISS (J. Pharm. Exp. Ther., 1930, **40**, 171—193).—Oral administration of acid to normal dogs results in an increase in the protein-amide-nitrogen of the blood, and this is associated with a high ammonia excretion by the kidneys, whilst the administration of alkali results in a decrease in the protein-amide-nitrogen associated with a decrease in the urinary ammonia. During phloridzin acidosis the amide-nitrogen of the blood increases, whilst the urinary ammonia increases. After injection of lactic acid into the femoral artery, blood from the femoral vein shows an increase of protein-amide-nitrogen, indicating that the amide synthesis proceeds partly at least in the muscles. The synthesis of amide-nitrogen is probably of importance in the metabolism of ammonia and the mechanism of the acid–base equilibrium. The theory is advanced that ammonia plays a part in the neutralisation of acid in muscle, but that for the purpose of transport in the blood to the kidneys it is detoxicated by being converted into an amide, the ammonia being regenerated in the kidneys and appearing in the urine in combination with acid as ammonium salts. W. O. KERMACK.

Determination of bilirubin in serum. S. C. LI (Z. ges. exp. Med., 1930, **70**, 452—458; Chem. Zentr., 1930, i, 3705).—Despite the use of a third series of tubes, Glass' method is not sufficiently accurate for clinical purposes. A. A. ELDRIDGE.

Determination of inorganic sulphate in serum. R. S. Hubbard (J. Biol. Chem., 1930, **88**, 663—668).—The serum-proteins are coagulated with trichloroacetic acid and removed, the sulphate is precipitated as benzidine sulphate, and the latter separated by centrifuging, dissolved in dilute hydrochloric acid, and treated with hydrogen peroxide in presence of ferric chloride. The colour developed is compared with that produced by known amounts of benzidine under similar conditions. W. O. Kermack.

Determination of phosphorus in small amounts of serum. K. Koch (Biochem. Z., 1930, **227**, 334—339).—The phosphorus content of 2—5 c.c. of serum can be determined by a slight modification of the method of Embden (A., 1921, ii, 462). W. McCartney.

Determination of the catalase content of blood. E. Bach (Biochem. Z., 1930, **227**, 221—229).—Blood immediately after removal and dilution is treated at 18° with hydrogen peroxide–buffer mixture and the undecomposed peroxide is subsequently titrated with permanganate. The catalase activity of freshly removed and diluted blood quickly decreases. Blood diluted 2500 times loses 10—20% of its activity after keeping for 20 min. and 50—60% in a few hours. Undiluted and defibrinated bloods retain unchanged the catalase content for a considerable time. During the reaction not only peroxide but also catalase is decomposed, and the velocity of decomposition increases with increasing concentration of peroxide. The decomposition of peroxide and catalase is the greater the higher is the temperature. By use of a buffer, the errors due to the acidity of the peroxide are avoided. Under the author's conditions, the unimolecular constants for different time points gave comparable results. P. W. Clutterbuck.

Action of light on blood components. A. Furniss (Brit. J. Actinother., 1930, **5**, 187—188).—A review of work on the effect of visible, ultra-violet, and infra-red rays on various constituents of blood. W. O. Kermack.

Prothrombase. Preparation and properties. J. Mellanby (Proc. Roy. Soc., 1930, B, **107**, 271—285; cf. A., 1909, ii, 158).—Experimental details are given for the preparation of prothrombase (yield of 40 mg. per 100 c.c. of plasma) by globulin-complex precipitation at p_H 5·3 from diluted oxalated mammalian blood, and reprecipitation from a calcium hydrogen carbonate extract of the complex. On activation, 1 mg. of the preparation coagulates 100 c.c. of plasma in 20 sec. Prothrombase is a non-dialysable (collodion) acid meta-protein, destroyed in suspension at 100°; in solution it is not destroyed in 5 min. at 100°, but its subsequent conversion into thrombase is retarded. The activation of prothrombase by thrombokinase is greatly accelerated by traces of calcium and strontium, and, to a far smaller extent, by barium and magnesium. A. Cohen.

Significance of the benzene nucleus in the specificity of azoproteins. M. Adant (Compt. rend. Soc. Biol., 1930, **103**, 539—540; Chem. Zentr., 1930, i, 3323).—Substitution of the aniline molecule by benzidine or α-naphthylamine causes no change in the specificity of the antibody. The diazotised antigens behave in presence of their own antibodies exactly as in that of antibodies of antigens with a different aromatic nucleus. A. A. Eldridge.

Azoprotein gelatin-aniline. M. Adant (Compt. rend. Soc. Biol., 1930, **103**, 541—543; Chem. Zentr., 1930, i, 3323; cf. preceding abstract).—Serum of rabbits treated with gelatin and diazotised aniline precipitates both gelatin and its own antigen. A. A. Eldridge.

Purinolytic enzymes of human embryos. H. Beck and R. Truszkowski (Med. Doświad., 1930, **11**, 36—44).—Xanthine-oxidase, but not uricase, was found in twenty fœtuses from the eighth to the fortieth week of pregnancy. R. Truszkowski.

Purine content and nuclear-plasmic ratio of various organs. A. Rowińska (Med. Doświad., 1930, **11**, 310—317).—The ratio of purine- to non-purine-nitrogen is a fairly constant quantity for the same organs of different species (calf, ox, horse), varying from 0·0218 for the brain to 0·1636 for the thymus gland. The mean purine contents in mg. per 100 g. are as follows: muscle 88·8 (calf), 76·5 (ox), white and red chicken muscle 98·2 and 76·6, respectively, horse brain 37·2, lung 89·4, intestine 78·0; thyroid and suprarenal glands, 126 and 116·5, respectively, pancreas 283, spleen 215·3, kidney 112·5, calf thymus 415. R. Truszkowski.

Iodine content of the thyroid gland of the sheep and ox. A. Torino and G. Ruff (Compt. rend. Soc. Biol., 1929, **102**, 871—872; Chem. Zentr., 1930, i, 3453).—Similar values were obtained; regular variations with the season were not observed. Fellenberg's method indicated only 50% of the iodine; the glands were heated with sodium carbonate, ferrous sulphate and sulphuric acid were added, and the iodine was distilled into potassium iodide solution. A. A. Eldridge.

Traces of metals in animal tissues. A. C. Chapman (Nature, 1930, **126**, 761).—Vanadium, arsenic, and antimony are added to the list of metals occurring in animal tissues. L. S. Theobald.

Elements present in animal tissues. H. M. Fox and H. Ramage (Nature, 1930, **126**, 883).—The occurrence in animal tissues of elements other than those previously mentioned (A., 1930, 1609) is pointed out from the work of previous investigators. L. S. Theobald.

Pig-stomach fat. J. S. Hepburn and W. L. Trexler (Amer. J. Pharm., 1930, **102**, 569).—The fat extracted by light petroleum from desiccated pig stomach has iodine value (Hanus) 29·9, saponification value 184·3, Hehner value 90·5, $n^{27·5}$ 1·4663, soluble acids 0·06%. H. E. F. Notton.

Phosphatides. I. Liver-phosphatide of rabbits. W. R. Witanowski (Acta Biol. Exp., Warsaw, 1930, **5**, 207—215).—The alcohol–ether extract of rabbit liver contains, per 100 g. of fresh tissue, 57·3 mg. of total choline, 4·5 mg. of free choline, 21·7 mg. of total colamine, 177 mg. of organically combined phosphorus, and 24·8 mg. of lecithin-, cephalin-, and sphingomyelin-phosphorus. The choline content of rabbit brain is 97·7 mg., of skeletal muscle 30 mg., and of heart muscle 8 mg. per 100 g. Choline and colamine are present in approximately equimolecular quantities in the liver. R. Truszkowski.

Phosphatides. I. Fatty acids of the cephalin fraction of brain. E. Klenk (Z. physiol. Chem., 1930, **192**, 217—232).—The cephalin fraction was separated into saturated and unsaturated acids. The saturated acid fraction yielded stearic and possibly palmitic acids; the unsaturated fraction after hydrogenation gave stearic and behenic acids. The unsaturated C_{22} acid contains at least four, possibly five, double linkings, and may thus be isomeric with clupanodonic acid. The proportions of the C_{18} and of the C_{22} groups in the total fatty acids are 73 and 25%, respectively. J. H. Birkinshaw.

Depressor substance in brain tissue. R. H. Major and C. J. Weber (J. Pharm. Exp. Ther., 1930, **40**, 247—252).—The depressor substance previously detected in extracts of brain (A., 1930, 104) has been obtained in protein-free solution giving a positive Sakaguchi and negative Pauly reaction. It is not identical with histamine, choline, or acetylcholine. W. O. Kermack.

Relation of the mitochondria–Golgi complex to secretion. V. Further identification of neutral-red-stained material. VI. Method for demonstrating the mitochondria–Golgi complex and other cytoplasmic inclusions. W. C. Ma (Chinese J. Physiol., 1930, **4**, 381—386, 387—389).—V. The material in the acinar cells of the pancreas, stained by neutral-red, is lipoidal in nature and is similar to the osmophilic Golgi substance.

VI. Histological technique is described for fixing and staining sections so as to demonstrate simultaneously mitochondria and Golgi material. W. O. Kermack.

Refractive index of the cerebrospinal fluid as a check on the chemical analysis. W. J. Penfold and D. H. Irving (Med. J. Austral., 1930, **1**, 772—779).—The average refractive index of normal samples was 1·335093. Calculated values based on this and on the chemical analysis agreed with observed values in more than 50% of the cases examined. Excess of urea leads to marked discrepancies. Chemical Abstracts.

Inhibitive action of the cœlomic fluid of the sea-urchin on membrane-formation and segmentation. M. Bogucki (Acta Biol. Exp., Warsaw, 1930, 5, 47—55).—The fluid is without influence on the formation of fertilisation membranes and on segmentation of fertilised eggs, except in those cases in which it contains digestive ferments. These are inactive in alkaline media such as sea-water, washing with which, therefore, entirely removes the apparent inhibitive influence of the cœlomic fluid. R. Truszkowski.

Elimination of foreign protein (egg-white) in human milk. H. H. Donnally (J. Immunol., 1930, **19**, 15—40).—Traces of egg-white were detected in the milk of three of eight fasting women after ingestion of raw egg. Chemical Abstracts.

Changes in the alkali reserve and sugar content of the bile by the action of various physiological excitants. II. Effect of acids, alkalis, and gastric juice. W. M. Karatygin and A. I. Hefter (Z. ges. exp. Med., 1930, **70**, 666—682; Chem. Zentr., 1930, i, 3573).—Introduction of 100 c.c. of 0·1% hydrochloric acid into the intestinal canal of dogs diminishes the alkali reserve and increases the bile-sugar; 5% sodium carbonate solution introduced into the duodenum has the same effect. Ingestion of meat, bread, and milk raises the alkali reserve and diminishes the bile-sugar owing to excretion of gastric juice and increasing alkalescence. A. A. Eldridge.

Salivary lipase. M. Katzenstein (Z. ges. exp. Med., 1929, **69**, 179—192; Chem. Zentr., 1930, i, 3798).—The lipase content of human saliva is high in pathological conditions with diminished salivation and low in those with increased salivation. The parotic secretion is generally richer in lipase than the total saliva. Dog's saliva also contains lipase, but the parotic secretion contains none. A. A. Eldridge.

Inhibitive action of intestinal biodialysates on the gastric secretion. J. Walawski (Med. Doświad., 1930, **11**, 348—372).—Injection into man or dogs of biodialysates into Ringer–Locke's fluid of the appendix and large intestine inhibits the secretion of gastric juice taking place under the action of histamine or secretin; this effect persists during 8 hrs. The effect is not obtained by injection of acid dialysates. The active factor is thermostable, but disappears on keeping. R. Truszkowski.

Conditions and significance of biological methylation processes. F. A. Hoppe-Seyler (Z. Biol., 1930, **90**, 433—466).—Trimethylamine oxide is present in the blood and urine of *Selachii* and in the former in sufficiently large quantities to be the chief constituent, apart from urea, responsible for the osmotic pressure. Small quantities of trimethylamine are also found in the urine. In fresh-water *Teleostii* neither trimethylamine oxide nor trimethylamine is found in the urine or other secretions, but in salt-water *Teleostii* both are present in the urine. W. O. Kermack.

Formation of urine in the frog's kidney. XIX. R. Höber (Pflüger's Archiv, 1930, **224**, 422—440; Chem. Zentr., 1930, i, 3457).—The urea content of the frog's kidney may be higher than that of the blood and urine. Experiments relating to the permeability for, and storage of, urea are described. A. A. Eldridge.

Creatinuria. I. Acidosis and creatinuria. O. Riesser and C. Brentano. **II. Relation between creatinuria and muscle-glycogen.** C. Brentano (Arch. exp. Path. Pharm., 1930, **155**, 1—20, 21—45). —I. Acidosis induced in rabbits by subcutaneous administration of ammonium chloride or ammonium phosphate does not necessarily lead to creatinuria nor to an excess of muscle-creatine, and in those cases when creatinuria follows acidosis, no proportionality exists between the degree of acidosis on the one hand and the degree of creatinuria or of the increase in muscle-creatine on the other. Alkalosis brought about by administration of sodium hydrogen carbonate subcutaneously may lead to creatinuria. Creatinuria is therefore not the direct result of acidosis. Under the influence of narcotics (urethane or morphine) marked creatinuria regularly occurs.

II. The creatinuria occurring after administration to rabbits of narcotics or during acidosis is accompanied by a fall in skeletal muscle-glycogen. When there is no creatinuria, as in certain cases of acidosis, there is no fall in muscle-glycogen. Creatinuria also occurs in other conditions when there is a fall of muscle-glycogen, as after administration of adrenaline, phloridzin, or of carbon monoxide and also during convulsions following camphor-poisoning.

W. O. KERMACK.

Uric acid in the urine of infants. R. DEBRÉ, R. GOIFFON, and S. YOSHIMATSU (Compt. rend. Soc. Biol., 1930, **102**, 994—997; Chem. Zentr., 1930, i, 3323).—When the uric acid : urea quotient is plotted against the urea concentration a hyperbolic curve is obtained. In the infant the uric acid is 1·2 g., and in the adult 0·55 g. per litre. A. A. ELDRIDGE.

Detection and determination of ammonia and amino-acids in urine. A. AGRESTINI and M. STANGANELLI (Annali Chim. Appl., 1930, **20**, 482—488).—The detection of ammonia in organic liquids by treatment with magnesium oxide or carbonate, sodium or calcium carbonate, alkali hydrogen carbonate, etc. at temperatures not above 50° is disturbed by the presence of carbamide or various amino-acids. Addition to 5—10 c.c. of the liquid of 5—10 drops of 10% potassium iodide solution, followed by a few drops of alkali hypochlorite, gives an immediate black coloration in presence of ammonium salt corresponding with 1 part of ammonia in 50,000 parts of solution. This reagent is less sensitive than Nessler's reagent, but is not affected by sulphides, mercaptans, amino-acids, carbamide, uric acid, alloxan, alloxantin, creatinine, etc., and is applicable to coloured liquids like urine. For the determination of ammonia, the Schiff–Sørensen method serves well in presence of carbamide, alloxan, etc., which do not react with formaldehyde, but not so well when amino-acids are present. The Folin method is disturbed appreciably by carbamide, alloxan, alloxantin, uric acid, and creatinine, and the use of permutit does not improve the results. The following procedure gives satisfactory results in presence of amino-acids such as alanine and glycine: 40 c.c. of the liquid are shaken with 20 c.c. of 7·5% disodium hydrogen phosphate solution for 3 min., the walls of the vessel being rubbed with a glass rod. After about 4 hrs., the liquid is filtered, 20 c.c. of the filtrate being neutralised and tested by Sørensen's method. T. H. POPE.

Iodometric determination of homogentisic acid in urine. E. METZ (Z. physiol. Chem., 1930, **193**, 46—48; cf. A., 1928, 195).—A defence of the author's method. Some of the modifications of Lieb and Lanyar (A., 1929, 593) are adopted.

J. H. BIRKINSHAW.

Anaërobic decomposition of volatile fatty acids in the human intestine. V. M. GUBIN and L. A. IVANOVA (Zhur. exp. Biol. Med., 1929, **12**, 360—364).—The fæces contain micro-organisms which produce anaërobic fermentation of the volatile fatty acids with evolution of gas. The hydrogen-ion concentration of intestinal contents depends on the anaërobic formation of volatile fatty acids and their decomposition to form methane and carbon dioxide.

CHEMICAL ABSTRACTS.

Putrefactive process and reduction of sterols in the suckling's intestine. G. BISCHOFF (Biochem. Z., 1930, **227**, 230—236).—On a milk diet considerable amounts of reduced sterols are formed in the fæces, the amount running parallel with the clinically observed intestinal putrefaction. Small amounts were also obtained in the non-putrefying stools during breast-feeding, but in this case the reduced sterol was dihydrocholesterol instead of coprosterol. In young children the coprosterol values were never so high on a pure milk as on a meat diet. Coprosterol is not resorbed in man. P. W. CLUTTERBUCK.

Artificially induced acidosis and alkalosis. G. MODRAKOWSKI and R. LENTZ (Med. Doświad., 1930, **11**, 274—287).—Acidosis produced by ingestion of ammonium chloride is accompanied in human subjects and in rabbits by acceleration of the rate of sedimentation of erythrocytes, and by concentration of the blood, expressed by increase in the concentration of plasma- and serum-proteins; at the same time the permeability of the capillaries is increased. Sodium hydrogen carbonate alkalosis provokes the opposite effects, with the exception of fibrinogen, the content of which is increased. From the point of view of respiration, this type of alkalosis is identical with acidosis, being accompanied by augmented elimination of carbon dioxide. R. TRUSZKOWSKI.

Acidosis and alkalosis. H. SIKORSKI and R. LENTZ (Med. Doświad., 1930, **11**, 318—329).—The action of the frog's heart is accelerated by reduction of the p_H of the liquid passed through it from 7·0 to 6·8. Reduction to 6·5 partly inhibits the heart-beat, as does also increase of p_H from 7·4 to 7·7.

R. TRUSZKOWSKI.

Reaction of the tissues and their buffering powers in local anæmia. N. OKUNEV (Biochem. Z., 1930, **227**, 319—325; cf. A., 1930, 942).—Experiments on the muscle of frogs suffering from experimental local anæmia showed that the anæmia causes local acidosis, which disappears, and is often succeeded by an alkaline reaction, when the normal circulation is restored or when the anæmia leads to necrosis. The buffering powers of the tissues affected by the anæmia differ from that of normal tissue, the difference apparently depending on the concentrations of hydrogen ions in the various regions. W. McCARTNEY.

Lipæmia in hæmorrhagic anæmia in rabbits. A. H. JOHANSEN (J. Biol. Chem., 1930, **88**, 669—673). —Repeated removal of blood from rabbits by venesection results in a fall of the hæmoglobin percentage to 30 and of the colloidal osmotic pressure to a little above 200 mm. of water, whilst the serum-lipins rise to about 1%. No œdema could be detected as a result of the lowered colloidal osmotic pressure.

W. O. KERMACK.

Liver enzymes in anaphylaxis. J. LASKOWSKI (Med. Doświad., 1930, **11**, 265—273).—The amylolytic and lipolytic powers of dog's liver are not affected by anaphylactic shock due to injection of horse-serum, whilst the oxidase content is reduced by 20%.

R. Truszkowski.

Hypertrophy and atrophy of muscular organs. III. Left ventricle after experimental aortic damage. H. Wassermeyer and J. Jacobi (Arch. exp. Path. Pharm., 1930, **155**, 70—90).—The normal left ventricle of the rabbit's heart contains 1·08±0·17 mg. of ammonia and 0·48±0·05 g. of glycogen per 100 g. Between 21 and 37 days after experimentally damaging the aorta, so as to produce stenosis or insufficiency, a condition of fatigue of the muscle of the left ventricle sets in, indicated by a decrease in the glycogen and an increase in ammonia content, as well as by a loss in synthetic activity. This negative phase gradually disappears, to be ultimately replaced by a condition of muscular hypertrophy. By administration of digitonin after the operation, the intensity of the negative phase may be decreased. W. O. Kermack.

Action of certain amino-acids on the isoelectric point of human serum. F. Vlès and A. de Coulon (Compt. rend., 1930, **191**, 1166—1168).—The administration of certain amino-acids to patients suffering from cancer results in a lowering of the isoelectric point of the serum. W. O. Kermack.

Oxygen content of blood from sarcoma. A. Oszacki (Bull. Acad. Polonaise, 1930, B, 391—403).—The oxygen and carbon dioxide contents of venous blood from sarcomatous tissue were compared with those of venous blood from healthy tissue of the same organ or from the anatomically corresponding vein. In the former the oxygen content was definitely higher than in the latter. F. O. Howitt.

Phosphate and chloride excretion in cases of Fröhlich's syndrome. S. M. Ling, S. T. Woo, and H. Chang (Nat. Med. J. China, 1930, **16**, 545—555).—In two cases the phosphate excretion was normal. Subcutaneous administration of "pituitrin" exerts only a transient effect in checking polyuria. Both chloride and phosphate concentrations of urine vary inversely as the volume. The pituitary does not control phosphate excretion. P. G. Marshall.

Endemic goitre in Hungary in relation to the theory of lack of iodine. J. Bodnár and J. Straub (Biochem. Z., 1930, **227**, 237—244).—The iodine content of the drinking-water of Bodahegyközség (Hungary), where goitre is particularly prevalent, is only 0—1 γ per litre. The iodine content of children's food (day) amounted to 15·8 γ. The daily urine of children affected with goitre contained 8 γ and of healthy children and adults 31—35 γ. Administration of iodine greatly benefited those affected.

P. W. Clutterbuck.

Iodine in nutrition in North China. W. H. Adolph and S. C. Chen (Chinese J. Physiol., 1930, **4**, 437—447).—Drinking-water and various foodstuffs from different localities were analysed in respect of their iodine contents. The average iodine intake per person in the non-goitrous areas is about 0·018 mg. per day, which is only slightly above the minimum iodine requirement (0·014 mg.), whilst in goitrous regions the average intake is probably considerably below this figure. W. O. Kermack.

Intensity of action of atophan and of salicylic acid on the excretion of uric acid in gout. (Rôle of kidney function in the occurrence of gout.) A. Lublin (Arch. exp. Path. Pharm., 1930, **155**, 331—353).—Salicylic acid surpassed atophan in promoting the excretion of uric acid by the kidneys in gout, but had not the favourable therapeutic effects of the latter on acute attacks of the disease.

W. O. Kermack.

Experimental hyperparathyroidism in guinea-pigs leading to osteitis fibrosa. A. Bodansky, J. E. Blair, and H. L. Jaffe (J. Biol. Chem., 1930, **88**, 629—647).—Single large doses of "parathormone" administered to young guinea-pigs cause a greater increase of blood-calcium and -phosphorus if the guinea-pigs have been fasting for 60 hrs. than when they are on their normal diet. The administration of single doses to adult fasting guinea-pigs has less effect on the blood-calcium than in the case of young fasting animals, but there is comparatively little difference between the adult fasting and the adult fed animals. After the administration of repeated small doses of "parathormone" the animals may be given progressively larger doses without any marked increase in blood-calcium. After such a series of doses, bone lesions develop resembling closely those characteristic of osteitis fibrosa in man. Similar lesions may also be produced by very large single doses. W. O. Kermack.

Serum-proteins in dogs with experimental hyper- and hypo-thyroidism. S. M. Ling and H. C. Chang (Chinese J. Physiol., 1930, **4**, 375—379).—The various fractions of the serum-proteins are not altered in quantity by thyroid feeding or by thyroidectomy. W. O. Kermack.

Precipitates of colloidal silver in inflamed tissues. H. Koller-Aeby (Kolloid-Z., 1930, **53**, 101—102).—When colloidal silver is injected intravenously it is precipitated in inflamed tissues in the form of microscopic particles. The amount of precipitation is proportional to the degree of inflammation, and the aggregation is not observed in healthy tissue. E. S. Hedges.

Liver function. III. Gaseous exchange in the destruction of liver function after administration of dextrose. M. Takuwa (Japan. Med. World, 1930, **9**, 374—394).—After administration of dextrose to man the gaseous exchange, *R.Q.*, and free blood-sugar rise and return gradually to the normal value. In hepatic disease the gaseous exchange is unchanged or falls after administration of dextrose, and the *R.Q.* maximum is late. In normal rabbits the *R.Q.* rises; in rabbits the livers of which have been destroyed it falls. Chemical Abstracts.

Urobilin substances. II. Excretion of urobilin substances in the urine and bile in various diseases. M. Oshima (Japan. J. Gastroenterol., 1930, **2**, 90—92).—The urobilin content of the urine is closely related to the liver function and is usually parallel to its concentration in the bile.

Chemical Abstracts.

Ammonia in nephrosis. A. Magnus-Levy (Z. klin. Med., 1930, **112**, 257—274; Chem. Zentr., 1930, i, 3457).—The ammonia production of the nephrotic kidney, unlike that of the nephritic kidney, is usually considerably higher than normal; the values are, however, irregular. Ammonuria in nephrosis is primary, and in diabetes secondary. In rapidly increasing œdema the ammonia rises. Urease was not definitely detected in the urine.

A. A. Eldridge.

Phosphatide–fat deposition in the spleen in Niemann–Pick disease compared with the lipin chemistry of Gaucher's and of Schüller–Christian's diseases. E. Epstein and K. Lorenz (Z. physiol. Chem., 1930, **192**, 145—170; cf. A., 1930, 1208).—In each of the three chief types of general lipinosis the deposits consist of complex lipin–fat mixtures, but the diseases are characterised by definite chemical differences. The Niemann–Pick phosphatide lipinosis is distinguished by ether-soluble lecithin and probably by as yet undifferentiated ether-insoluble, alcohol-soluble phosphatides. The Gaucher cerebroside lipinosis is accompanied by the presence of kerasin and probably of a related cerebroside. The presence of cholesterol and its esters marks the Schüller–Christian type. J. H. Birkinshaw.

Œdema. II. Disease conditions with change of colloid osmotic pressure. H. Horsters (Arch. exp. Path. Pharm., 1930, **155**, 248—256).—In patients with normal circulation the average colloidal osmotic pressure was equal to 371 mm. of water, whilst the total osmotic pressure was the equivalent to that of a sodium chloride solution of 0·95—1·02%. The concentration of serum-proteins was about 8·5—9·0%, so that every 1 g. of serum-protein was equivalent to a pressure of 40—45 mm. of water. The colloidal osmotic pressure was low in cases of essential or renal hypertony, acute nephritis, cardio-renal insufficiency, amyloidosis, diabetic acidosis, and diabetic coma, but was normal in uncomplicated diabetes.

W. O. Kermack.

Phosphatides. II. Choline derivatives in rabbits after extirpation of the suprarenals. W. R. Witanowski (Acta Biol. Exp., Warsaw, 1930, **5**, 217—223).—The free choline content of the arterial plasma of rabbits rises from 0·4—0·75 mg. to 1·4—3·11 mg. per 100 c.c. 7 hrs. after extirpation of the suprarenals. Simultaneously the total choline content of the liver falls from 57·3 to 48·2 mg. per 100 g. R. Truszkowski.

Chemical processes during cell division. L. Rapkine (Compt. rend., 1930, **191**, 871—874).—On fertilisation the ova of *Paracentrotus lividus*, Lk., have a content of thiol groups of 0·035%, which in 30 min. falls to 0·010%, and then rises abruptly 10—15 min. before the first division to 0·046%. Immersion of the ova in a $0\cdot00002M$-mercuric chloride in sea-water for 5 min. is sufficient to prevent further division on transference back to the normal media. If, however, they are transferred to $0\cdot001M$-cysteine or -thioglycollic acid in sea-water 70—90% of the ova divide in the normal manner. Similar solutions of alanine or cystine do not show this effect. The reduction of cystine to cysteine in the ova is due to a hydrogen donator, similar to the thermostable residue of Hopkins, which may be destroyed by treatment with mercuric chloride. The donator, as measured by the reduction of methylene-blue, is most active 20—30 min. before the division of the cell; at the same time the lactic acid content of the ova is at a maximum. An increase of the lactic acid content is observed on placing the ova in nitrogen or $0\cdot0005M$-potassium cyanide. Ova which have been treated with sea-water containing mercuric chloride contain very little lactic acid, but on transference to the cysteine solution the lactic acid content becomes normal. It is concluded that cell division may be controlled by variation of the thiol content.

T. H. Morton.

Biology of the meal worm (*Tenebrio molitor*). I. F. N. Schulz (Biochem. Z., 1930, **227**, 340—353).—Meal worms can live and, at some stages of development, can grow to maturity under conditions of great desiccation and can also exist for months in a state of suspended animation. Worms in such conditions consume greatly reduced amounts of food, but they can make use of water formed in respiration and they also insulate themselves very securely against loss of water by production of an enveloping wax-like covering. W. McCartney.

Catalase content of the Colorado potato beetle during metamorphosis. D. E. Fink (J. Agric. Res., 1930, **41**, 691—696).—On the first and second days of the prepupal stage there is a marked inhibition of catalase activity, which again rises to a maximum on the day of formation of the pupa, and thereafter again falls rapidly. P. G. Marshall.

Behaviour of κ-benzenesulphonylmethylaminoundecoic acid in the animal body. T. Hosoda (Z. physiol. Chem., 1930, **192**, 264—267).—κ-Benzenesulphonylmethylaminoundecoic acid when injected subcutaneously into a dog was oxidised to β-benzenesulphonylmethylaminopropionic acid. No evidence of γ- or δ-oxidation was found.

J. H. Birkinshaw.

Degradation of β-hydroxybutyric acid in the [animal] organism. Its connexion with carbohydrate metabolism. F. Rosenthal (Biochem. Z., 1930, **227**, 472—481).—In the mouse the degradation of β-hydroxybutyric acid takes place without an accompanying decrease in the total carbohydrate content of the animal, and such degradation also occurs even when this content is extremely low. Injection of excessive amounts of β-hydroxybutyric acid leads to a decrease in the glycogen content of the animal, but this decrease is a toxic effect and differs from the effects produced by anæsthetics such as ether and chloroform, which cause no decrease in the carbohydrate content of animals in which this is already low. No evidence of possible production of carbohydrates from fatty acids could be obtained.

W. McCartney.

Metabolism of sugars injected intravenously at a constant rate. W. Wierzuchowski [with M. Łaniewski, E. Owsiany, and W. Pieskow] (Acta Biol. Exp., Warsaw, 1930, **5**, 87—205).—Dextrose, galactose, and lævulose were injected intravenously into dogs at a rate of 2 g. per kg. per hr. The non-protein *R.Q.* during 3 hrs. of injection was for dextrose 1·01, for lævulose 1·02, and for galactose 0·82; with the simultaneous administration of insulin the corresponding values were 1·05, 1·05, and 0·94. The maximum possible oxidation of sugars at the given rate of introduction was 0·5 g. per kg. per hr. Over the whole experiment 34% of total injected dextrose underwent oxidation, 41% of lævulose, and 56% of galactose; with simultaneous injection of insulin the above values are respectively 15, 24, and 87% higher. The specific dynamic actions of these sugars are respectively 9·7, 13·8, and 17·3%. The greatest raising of heat-production is observed during the second and third hours of injection, and amounts respectively to 51, 63, and 32%. Experiments in which the influence of insulin was studied are divided into a hyperglycæmic period during which sugar and insulin were injected simultaneously, and a hypoglycæmic period during which injection was discontinued; during the former period insulin augments heat-production due to introduction of dextrose by 20·6%, of lævulose by 37·8%, and of galactose by 23·4%, the maximal increment of heat-production amounting respectively during the third hour to 57, 85, and 32%. During the hypoglycæmic period, heat-production was still increased by 30·9%. During the 4-hr. hyperglycæmic period, approximately 50% of the increase in heat-production is due to specific dynamic action, whilst for the whole 8 hrs. of the experiment the appropriate value is 36·7%. The quotient of assimilation to oxidised sugar amounts for the whole experiment for dextrose to 3·04, for lævulose to 2·48, and for galactose to 1·82; for the first 4 hrs. to 4·73 for dextrose and 3·83 for lævulose (with insulin 4·43 and 2·94, respectively). The number of calories due to the specific dynamic action of 1 mol. of dextrose, lævulose, and galactose are respectively 214, 242, and 249 g.-cal.; injection of physiological fluid under analogous conditions leads to a specific increment of only 1·87 g.-cal. The heat-production and the value of the *R.Q.* are at the height of assimilation (third hour) inversely proportional, and the value of the specific increment in heat-production is directly proportional to the concentration of the given sugar in the blood. The carbon dioxide-combining power of the blood falls by 7·3—10·5% as a result of extra production of lactic acid; with elimination of this, the alkali reserve returns to normal. The blood-lactic acid curve does not coincide with the oxygen intake curve. On the whole it appears that the specific dynamic action and the intensity of oxidation of sugar are directly proportional to the production of lactic acid. R. TRUSZKOWSKI.

Effect of acid and alkaline buffer mixtures on carbohydrate metabolism and body temperature: experimental fever. F. FISCHLER and R. SCHMID (Arch. exp. Path. Pharm., 1930, **155**, 91—113).—When an isotonic alkaline buffer mixture (carbonate or phosphate) is administered to rabbits a decrease of the reducing power of the blood is observed together with a rise of body temperature up to about 3°. In rabbits with exhausted carbohydrate reserve only a very small rise in body temperature occurs, and the reducing power remains almost constant. When isotonic acid buffer mixtures are injected a similar but smaller rise of temperature occurs together with a marked increase in the reducing power of the blood. When adrenaline or ephedrine is administered as well as the alkaline buffer mixture, a more intense and more prolonged rise of temperature is observed. When dextrose or lævulose is administered after the alkaline buffer, the temperature tends to return to normal. W. O. KERMACK.

Metabolism of the frog's isolated heart. A. J. CLARK, C. P. STEWART, and R. GADDIE (Proc. Roy. Soc. Edin., 1930, **50**, 297—303).—The carbohydrate consumption of the heart perfused with Ringer's solution containing dextrose with and without frog's serum and insulin represents only a small part of its total metabolism and its *R.Q.* is usually lower than 0·9. During the perfusion some nitrogen is excreted into the perfusing fluid, and if assumed to be a product of protein breakdown is sufficient to account for about one half of the total metabolism. No evidence could be obtained that fat is consumed by the heart. Determinations of glycogen and of the *R.Q.* of the empty heart provide no evidence that the heart builds up glycogen from protein. During the first few hours of perfusion, the heart loses more than two thirds of its glycogen. Excess of dextrose and insulin fails to bring about glycogen storage or to increase carbohydrate consumption. W. O. KERMACK.

Effect of administration of sodium hydrogen carbonate on the excretion of ketonic substances by dogs deprived of carbohydrate. F. MAIGNON and E. KNITHAKIS (Compt. rend. Soc. Biol., 1929, **101**, 870—872; Chem. Zentr., 1929, i, 3807).—Dogs with transitory acetone-substance retention exhibit increased diuresis and ketonuria on administration of sodium hydrogen carbonate. In dogs exhibiting no such retention and not having become accustomed to deprivation of carbohydrate, sodium hydrogen carbonate does not cause diminution of the production of ketonic substances. A. A. ELDRIDGE.

Metabolic activity of muscle poisoned with fluoride. F. LIPMANN (Biochem. Z., 1930, **227**, 110—115).—Frog's muscles poisoned with fluoride are able to perform work without formation of lactic acid. The rate of decomposition of phosphagen is increased and considerable esterification of hexose with phosphate and decomposition of adenylpyrophosphoric acid occur. After contraction, the muscle passes into rigor. The results correspond with those obtained by poisoning the muscle with iodoacetic acid. P. W. CLUTTERBUCK.

Activity metabolism of the muscle, poor in carbohydrate, of cold-blooded animals. S. OCHOA (Biochem. Z., 1930, **227**, 116—134).—The carbohydrate metabolism of frog's muscle, the carbohydrate content of which had been depleted by the action of insulin, is compared with the development of tension both in oxygen and nitrogen. The K_{mo_2} value for semimembranosi is about 480. The results indicate that with muscle, rendered almost carbohydrate-free, the oxidation of carbohydrate is not sufficient to account completely for the development of tension. Under anaërobic conditions the lactic acid formed corresponds with the carbohydrate present, but the K_{mL} value is considerably too large. It is not certain that the energy difference is derived from the hydrolysis of phosphagen. P. W. Clutterbuck.

Is lactacidogen (hexosephosphoric acid) decomposed in muscular contraction? K. Lohmann (Biochem. Z., 1930, **227**, 39—50).—Since there is no known method for fixing a muscle at the height of the single muscle twitch, it is difficult to decide whether any decomposition of lactacidogen occurs during contraction, but none is detectable. Lactacidogen may be a lactic acid former, but it seems doubtful that it is the immediate precursor. On the other hand, Embden's hypothesis that placing a muscle in liquid air at the height of contraction causes hydrolysis of lactacidogen is invalid. The difference in the hexosephosphoric acid contents of muscle killed before and after tetanic stimulation depends on a synthesis of ester in the stimulated muscle, the amount of difference being dependent on the duration and strength of the stimulus. P. W. Clutterbuck.

Muscular contraction without formation of lactic acid. E. Lundsgaard (Biochem. Z., 1930, **227**, 51—83).—The non-formation of lactic acid during the work of a muscle poisoned with iodoacetic acid is confirmed and the ratio of the breakdown of phosphagen to the work done in the single muscle twitch and in tetanus (K_{mp} and K_{tP}, respectively) is determined. Curarisation did not change these values for muscle poisoned with iodoacetic acid. Poisoning the muscle in this way did not affect the chronaxie, and simultaneous curarisation increased the chronaxie to the same extent as with curarisation alone. Anaërobic resynthesis of phosphagen did not occur after poisoning with iodoacetic acid. The course of esterification and the type of ester formed are investigated. Hydrolysis of pyrophosphate during performance of work and in rigor is detected.
P. W. Clutterbuck.

Effect of halogenoacetic acid poisoning on the solubility of the muscle-proteins. G. Embden and E. Metz (Z. physiol. Chem., 1930, **192**, 233—244).—Poisoning of frogs with bromoacetic and iodoacetic acids produces a lowering of the solubility of the proteins of the gastrocnemius. Electrically-produced fatigue in isolated muscle poisoned with bromoacetic acid represents a further stage in the change of colloidal state. J. H. Birkinshaw.

Reaction changes of active muscle. F. Lipmann and O. Meyerhof (Biochem. Z., 1930, **227**, 84—109).—Muscle, under anaërobic conditions, changes its reaction chiefly by hydrolysis of creatinephosphoric acid and by formation of lactic acid and to a smaller extent by formation of ammonia, by esterification, etc. These changes result, in the first phases of anaërobic fatigue, in a gradual alkalisation which later passes over to an acidification. Only the alkalisation process occurs in muscle poisoned with iodoacetic acid. Both in normal and in poisoned muscle, the changes of acid–base equilibrium, as determined chemically, agree closely with those calculated from changes of tension of carbon dioxide.
P. W. Clutterbuck.

Effect of enteral administration of biocatalysts from yeast on the course of chemical reactions in muscle and liver of exercising animals. J. A. Collazo, G. Liss, and C. Pi-Suñer Bayo (Biochem. Z., 1930, **227**, 326—333).—Administration of concentrated yeast extracts to rats which were kept well exercised produced increase of glycogen and of phosphorus and decrease of lactic acid, glutathione, and lactacidogen in the muscles. In the livers of such rats the glycogen, glutathione, and lactic acid contents are increased, whilst the phosphorus and lactacidogen contents are decreased. Examination of the livers and muscles of resting rats which received no yeast extract yielded results in harmony with the conclusions reached from observations on the exercising animals. W. McCartney.

Heat of rigor of mammalian muscle. E. C. Smith (Proc. Roy. Soc., 1930, B, **107**, 214—222).—Measurements of the *post-mortem* rise in temperature and lactic acid content of the leg muscles of normal rabbits showed that the heat production during *rigor mortis* could be entirely accounted for by the breakdown of glycogen to lactic acid and the subsequent neutralisation of the latter. The muscle of a rabbit previously injected with iodoacetic acid showed no *post-mortem* production of heat or lactic acid. On the other hand, the muscles of rabbits starved for 24—48 hrs. showed a large excess heat production which could not be accounted for by the lactic acid produced. The *post-mortem* stiffening of normal rabbit's muscle as measured by a sclerometer was parallel to the production of heat. G. F. Marrian.

Variations in permeability of muscle-cell membranes and their biological effects. W. Hołobut (Med. Doświad., 1930, **11**, 189—197).—The immersion of muscle in isotonic calcium, magnesium, or hydrogen chloride solutions leads to the suppression of its excitability, which can, however, be restored by passing a constant current through the solution, using the muscle as the cathode; with the muscle as anode, the paralysing effect of the above salts is enhanced. Lithium and potassium chlorides and sodium hydroxide act in the inverse sense; in these excitability is restored by making the muscle the anode, and depressed by making it the cathode.
R. Truszkowski.

Permeability. III. Cholesterol and lecithin in water and acid–base exchanges. J. Dahmlos and A. Solé (Biochem. Z., 1930, **227**, 401—428; cf. Spranger, A., 1930, 1054).—From examination of the blood and urine of rabbits to which lecithin, cholesterol, or ergosterol and also, in some cases, ammonium chloride or sodium hydrogen carbonate had been administered deductions are made concerning the permeability of tissues in the living organism and comparisons are made with results obtained *in vitro.*
W. McCartney.

Nitrogen content of normal and fasting white rats. S. di Frisco (Arch. Int. Physiol., 1930, **32**, 48—54; Chem. Zentr., 1930, i, 3324).—When the fat content is taken into account the nitrogen content per kg. of normal rats is surprisingly constant (3·6—4%); in hunger the values are 10% higher.
A. A. Eldridge.

Nitrogen metabolism. I. Can ammonium salts replace proteins in the diet of white rats? II. Relation between the nitrogen excreted and the nitrogen loss of fasting rats. U. Lombroso and S. di Frisco (Arch. Int. Physiol., 1930, 32, 22—39, 40—47; Chem. Zentr., 1930, i, 3324).—I. Part of the nitrogen ingested as ammonium citrate is retained.

II. The nitrogen loss is much greater than that indicated by analysis of the urine and fæces.

A. A. Eldridge.

Amino-acids of blood and tissues after injection of glycine. P. M. Re (Rev. Soc. Argentina biol., 1929, 5, 498).—After injection of glycine (0·2 g. per kg.) a rise in blood-amino-acid is followed by a fall and a secondary rise. Hyper- is followed by hypo-glycæmia. Part of the glycine injected is eliminated in the urine. Normally the amino-acid-nitrogen of the liver is greater than that of kidney or muscle. The most marked increase was observed in the kidney. Chemical Abstracts.

Biological value of the proteins of mung bean, peanut, and bean curd. J. H. C. Pian (Chinese J. Physiol., 1930, 4, 431—436).—The biological values, determined on rats, of the proteins of mung bean (*Phaseolus aureus*), Chinese peanut (*Arachis hypogœa*), and curd made from soya bean are 58, 59, and 65%, respectively, and the coefficients of digestibility (nitrogen absorbed/nitrogen intake) 86, 95, and 96%, respectively. W. O. Kermack.

Cereals and mineral metabolism. M. S. Fine (Cereal Chem., 1930, 7, 456—465).—The occurrence or non-occurrence of rickets in rats fed on 60% whole wheat or 60% oats may be controlled by adjustment of the Ca : P ratio. Better growth and food consumption were observed with wheat than with oats.

E. B. Hughes.

Mineral metabolism of dogs during inanition. S. Saks (Acta Biol. Exp., Warsaw, 1930, 5, 225—255).—The mineral excretion in the urine and fæces of dogs of about the same weight is fairly uniform during hunger for different animals, and amounts per kg. per diem over a 10-day period to 27·8 mg. P, 23 mg. S, 9·24 mg. Cl, 13·6 mg. Na, 48·3 mg. K, 7·38 mg. Ca, and 2·86 mg. Mg, with an excretion of 380 mg. N. Excretion of sodium and chlorine falls relatively with duration of inanition, whilst that of calcium rises. On the whole the rate of excretion of potassium is parallel to that of nitrogen, whilst that of magnesium is the most constant. The ratio of inorganic to organic phosphorus is the same during inanition as normally. Univalent cations are eliminated chiefly by the kidneys, as are also phosphorus and sulphur, whilst bivalent cations are chiefly excreted by the intestine. The ratio of calcium to phosphorus in the excreta during inanition is half that of the skeleton. The bases present in the excreta are not equivalent to the acids, the excretion of which rises during hunger. R. Truszkowski.

Calcium metabolism. Citrates and urinary excretion of calcium. R. Proverman and L. Brull (Bull. Soc. Chim. biol., 1930, 12, 1151—1157).—Oral or subcutaneous administration of sodium citrate lowers the serum-calcium, the urinary excretion of calcium being increased. These facts suggest that citrates play a part in the urinary elimination of calcium. F. O. Howitt.

Phosphate metabolism. I. B. Bleyer and F. Fischler (Tierernährung, 1930, 1, 88—103; Chem. Zentr., 1930, i, 2118—2119).—The importance of the phosphoric acid esters with carbohydrates in animal and vegetable systems is discussed.

L. S. Theobald.

Pharmacological action of sea-water. III—V. A. Rabbeno (Arch. Sci. biol., 1929, 14, 26—40, 41—57, 58—75; Chem. Zentr., 1930, i, 3575).—Intravenous injection of sea-water increases the excretion of chloride, the curve being S-shaped. Sea-water, but not sodium chloride solution, mitigates glycosuria by increasing the production of urine. Injection of sodium chloride solution increases the excretion of water and greatly increases that of chloride. In general, sea-water is more toxic than sodium chloride solution. The difference is attributed to a high magnesium content associated with a low calcium content. A. A. Eldridge.

Effect of the cations of Ringer's solution on the dimensions of the vessels of the frog. M. Kochmann (Biochem. Z., 1930, 227, 488—491; cf. Misske, A., 1930, 809).—The combined action of the sodium, potassium, and calcium ions of Ringer's solution produces, in general, a contraction of the vessels of the frog, but if the proportions of the ions are altered (within isotonic limits) a relatively small series of mixtures which produce dilation can be prepared. The series of mixtures which can maintain the vessels at a constant dilation for periods of several hours is also relatively small. Very small alterations in the proportions of the different cations may produce large changes in the effect on the vessels and may even suffice, in some cases, to reverse it. A solution containing 0·5612% NaCl, 0·0234% KCl, and 0·0575% $CaCl_2$ is particularly suitable for use in the investigation of pharmacological action. W. McCartney.

Metabolic reactions to acidosis produced by ammonium chloride. N. Morris and O. MacRae (Arch. Dis. Childhood, 1930, 5, 207—227).—Administration of ammonium chloride, not associated with the appearance of acidosis, was accompanied by an increase in the blood-chlorine, -calcium, and -non-protein-nitrogen and in the urinary and fæcal calcium and phosphorus, whilst the blood-carbon dioxide and -phosphorus were diminished.

Chemical Abstracts.

Early diagnosis of lead poisoning. I. Fleckel and I. Tschernov (Zentr. Gewerbehyg. Unfallverhüt., 1930, 17, 65—74; Chem. Zentr., 1930, i, 3327).—The increased reticulocyte content of the blood is an early symptom. A. A. Eldridge.

Lead poisoning; changes in the bone marrow. J. Speransky and R. Skliánskaja (Folia Hæmat., 1928, 36, 289—315; Chem. Zentr., 1930, i, 3327—3328).—Experiments with guinea-pigs are described.

A. A. Eldridge.

Mobilisation of lead under the influence of potassium iodide and sodium hydrogen carbonate. S. Schachnovskaja (Z. ges. exp. Med., 1930, 70, 513—526; Chem. Zentr., 1930, i, 3693).—

Administration of potassium iodide or sodium hydrogen carbonate to rabbits 7 months after poisoning by lead salts caused excretion of lead; the latter reagent caused a renewal of toxic symptoms.

A. A. ELDRIDGE.

Investigation into the distribution of lead in the organism on basis of a photographic (radiochemical) method. S. LOMHOLT (J. Pharm. Exp. Ther., 1930, **40**, 235—245).—A solution of lead chloride containing a very small quantity of the isotopic radium-*D* is injected subcutaneously into a suitable animal (*e.g.*, a young mouse or rat). The tissues of the animal after death are fixed in alcohol and sectioned. A section of a particular organ is allowed to remain in contact with a photographic plate with a thin gelatin coating for 1—20 days and the latter then developed. The degree of blackening of the plate gives a measure of the radium-*D* and therefore of the lead present in the section. The lead is deposited largely in the bones, to some extent in the liver and in the kidney cortex, but very little in the medulla. Only a very small amount is found in the brain. W. O. KERMACK.

Pharmacology and pharmaco-dynamics of ointments. VI. Ung. hydr. praec. alb. Ph.G. [ointment containing $NH_2\cdot Hg\cdot Cl$]. C. MONCORPS (Arch. exp. Path. Pharm., 1930, **155**, 51—69).—Only slight absorption through the skin occurs, chiefly by way of the hair follicles. The nature of the base of the ointment has little effect on the rapidity of absorption of the mercury.

W. O. KERMACK.

Toxic action of baking-powders containing alum. A. CERIOTTI (Rev. fac. cienc. quim. La Plata, 1930, **6**, 51—53).—The aluminium chloride formed in the gastric juice is not precipitated by the alkaline pancreatic juice; the absorption of aluminium may lead to displacement of iron in organs such as the pancreas. CHEMICAL ABSTRACTS.

Decomposition of amino-acids in the animal body in phosphorus poisoning. J. ARAI (Acta Schol. Med. Kyoto, 1930, **12**, 445—448).—Increased excretion of nitrogen indicates increased breakdown of protein. A slight decrease in the carbon dioxide output may indicate that the fatty acids produced by deamination of the amino-acids are not oxidised, but stored as fat. CHEMICAL ABSTRACTS.

Iron content and resistance of the organism to hydrogen cyanide and hydrogen sulphide. F. KEESER (Arch. exp. Path. Pharm., 1930, **156**, 340—345).—Three groups of rabbits were fed on rice, greens, and greens together with ferrous chloride, respectively. The hæmoglobin content of the blood, and the iron content of the tissues of the animals in the last group were increased as compared with the first. The third group showed the smaller susceptibility to the toxic effects of sodium cyanide administered orally and of sodium sulphide subcutaneously, whilst the animals of group II were more resistant than those of group I.

W. O. KERMACK.

Salicylates. XIX. Question of acidosis following the administration of salicylates. C. C. JOHNSON (J. Amer. Med. Assoc., 1930, **94**, 784—789).—Sodium or ammonium salicylate or acetylsalicylic acid, administered gastrically or hypodermically to dogs and cats, caused respiratory stimulation with depletion of the alkali reserve of the blood; the p_H was unchanged, and acetone was not found in the urine. CHEMICAL ABSTRACTS.

Influence of oxidation and tissue respiration on the toxicity of quinol on the frog's musculature. F. HINTEREGGER (Arch. exp. Path. Pharm., 1930, **155**, 354—380).—The toxic action of quinol on the frog's musculature is apparently due to the formation of quinone, and conditions such as further oxidation or strong alkali which inactivate the latter reduce the toxicity of quinol. Manganous sulphate increases the toxicity independently of p_H, presumably through its catalytic action in accelerating formation of quinone. The toxicity of quinol is not related to cell respiration. The muscles of animals treated with thyroxine, which has no action on the respiratory rate of intact frog's muscle, are abnormally sensitive to quinol, probably as the result of increased permeability of the cells. Lactic, pyruvic, and succinic acids reduce the toxicity of quinol, whilst sucrose has the opposite effect. Moderate stimulation of the muscle does not result in change of its sensitiveness to quinol, but complete exhaustion much increases it. The amount of quinol which disappears during perfusion of a limb is not affected by substances increasing cell permeability. W. O. KERMACK.

Toxic properties of ethyl phthalate. P. BLICKENSDORFER and L. TEMPLETON (J. Amer. Pharm. Assoc., 1930, **19**, 1179—1181).—Ethyl phthalate, when injected intravenously into animals in doses of 0·25 c.c. per kg., may cause death by paralysis of the respiratory centre, but administration to rabbits, by means of a stomach-tube, in doses of 3 c.c. per kg. for eight successive days caused no abnormal after-effects. It is rapidly excreted by the kidney. Doses that are insufficient to cause paralysis may cause convulsions. E. H. SHARPLES.

Effect of phloridzin intoxication on the sugar content of the aqueous humour. W. TYCHOWSKI (Med. Doświad., 1930, **11**, 331—343).—The sugar content of the aqueous humour of dogs rises during the first 20—50 min. of phloridzin intoxication and then falls. R. TRUSZKOWSKI.

Action on the frog's heart of new glucosides isolated from *Digitalis lanata*. K. W. MERZ (Arch. exp. Path. Pharm., 1930, **156**, 277—289).—The pharmacological actions of *lanata* glucoside I (*lanadigin*), II, III, and IV and the genins I, III, and IV have been investigated. The following data are given: lanadigin, $C_{41}H_{66}O_{17},4H_2O$, m.p. 245°, $[\alpha]_D^{20}+33\cdot3°$; glucoside III, $C_{36}H_{56}O_{14}$, m. p. 228—229°; glucoside IV, $C_{42}H_{66}O_{16}$, m. p. 195°, subsequently begins to melt at 225° after resolidifying, $[\alpha]_D^{20}$ about $+5\cdot5°$ in methyl alcohol.

W. O. KERMACK.

Pharmacological assay of strophanthin solutions. H. FASCHING (Arch. exp. Path. Pharm., 1930, **156**, 211—225).—A method for the assay of strophanthin employing the isolated *R. temporaria* heart is described. W. O. KERMACK.

Action of rotenone on mammals. D. E. Buckingham (Ind. Eng. Chem., 1930, **22**, 1133—1134).—Rotenone administered by mouth in doses of 4 grains to sheep or pigs produced no visible effect. Dogs were not affected by doses up to 1 grain per lb. body-weight. *Derris* extract when administered by mouth was likewise without effect. B. W. Town.

Blood-calcium and -sugar, and opium preparations. H. Zahler (Deut. med Woch., 1930, **56**, 522—523; Chem. Zentr., 1930, i, 3455).—Opium, "pantopon," morphine, and "dilaudide" in therapeutic doses cause a rise in blood-sugar, which afterwards falls to a subnormal value. With equal daily doses the effect on the blood-sugar begins to vanish. The calcium metabolism appears to be more closely associated with the sedative action of the opiate. A. A. Eldridge.

Effect of chronic injections of morphine on the nitrogen balance of dogs. N. P. Pyatnitzki and P. N. Fedorov (Zhur. exp. Biol. Med., 1929, **11**, 54—57).—The nitrogen balance of dogs is unaffected by chronic injections of 0·01—0·02 g. of morphine. Tolerance is rapidly developed. Subsequent omission of the injection produces a negative nitrogen balance. Chemical Abstracts.

Poisoning by the seeds of the thorn apple (*Datura stramonium*). A. Sartori (Chem.-Ztg., 1930, **54**, 890).—A fatal case of poisoning is recorded. Tests revealed the presence of atropine in the stomach and intestines. A. R. Powell.

Pharmacological assay of aconitine solutions. W. Brandt (Arch. exp. Path. Pharm., 1930, **156**, 203—210).—The characteristic action exerted in the frog's heart by aconitine in concentration of 1/750,000—1/1000,000 is used for the assay of aconite preparations. W. O. Kermack.

Elimination of the chlorides and citrates of bismuth and quinine. H. F. Lenormand (J. Pharm. Chim., 1930, **12**, [viii], 159—168).—Insoluble salts of bismuth, as the double chloride of bismuth and quinine, and the basic carbonate, in suspension in oil, injected intramuscularly into the dog are found in the urine for a longer period than in the case of the more soluble double citrate. The iodobismuthate, although it is similar to the double chloride in insolubility and dissociation by water, behaves similarly to the double citrate as regards elimination. Of the bismuth introduced only 46—54% was recovered in the urine over a period of 30 days. In the case of quinine the period of elimination is much shorter, but slower for the double chloride than for the double citrate. Of the quinine introduced 32—44% was recovered in the urine. W. J. Boyd.

[Pharmacology of] "sympatol." G. Kuschinsky (Arch. exp. Path. Pharm., 1930, **156**, 290—308).—The pharmacological action of "sympatol" (methyl-β-*p*-hydroxyphenyl-β-hydroxyethylamine) has been investigated. Compared to adrenaline the action of "sympatol" is more marked on the heart relative to its action on the blood-vessels, whilst the *m*-isomeride has a more marked action on the blood-vessels. W. O. Kermack.

Physiological action of 3 : 4-dihydroxyphenylaminomethylcarbinol. Raymond-Hamet (Compt. rend., 1930, **191**, 869—871).—The conclusion of Barger and Dale (A., 1910, ii, 984) that 3 : 4-dihydroxyphenylaminomethylcarbinol (arterenol) is somewhat more active than adrenaline as a hypertensive agent is confirmed. As in the case of adrenaline, this action is sensitised by cocaine, but, whilst the action of adrenaline is neutralised by yohimbine, the action of "arterenol," in this respect resembling ephedrine, is unaffected. Unlike ephedrine in large doses, however, "arterenol," even when administered in lethal quantities, does not show a hypotensive action. T. H. Morton.

Alloxan as an oxidising agent for thiol groups, as a capillary poison, and as a convulsive poison. R. Labes and H. Freisburger (Arch. exp. Path. Pharm., 1930, **156**, 226—252).—The toxic action of alloxan on the organism is correlated with (1) the tendency to form the strongly acidic alloxanic acid so that the p_H of the cells becomes unduly low, and (2) the ease with which alloxan is reduced by thiol groups (*e.g.*, cysteine). The formation of murexide in the tissues of mice injected with alloxan has been demonstrated. W. O. Kermack.

[Toxicity of] iodised and arsenated pyridine derivatives. IV. A. Binz, C. Räth, and K. Junkmann (Biochem. Z., 1930, **227**, 200—204).—The toxicities of the relatively poisonous substances, pyridine and 2-pyridone, and their less poisonous iodinated and arsenated derivatives are compared by intravenous injection into rats (cf. A., 1930, 1213). The toxicity of pyridine and 2-pyridone is of the same order. Substitution of an arsinic acid residue in position 5 or attachment of an acetic acid residue to the nitrogen atom considerably decreases the toxicity. Substitution of iodine in position 5 renders the 2-pyridone nucleus more toxic, but attachment also of an acetic acid residue to the nitrogen atom gives a much less toxic derivative. The toxicity of the same amount of iodine in "uroselectan" (sodium salt of 5-iodo-2-pyridone-*N*-acetic acid), sodium iodide, "selectan" (5-iodo-2-pyridone), "yatren," and "alival" is as 1 : 3·6 : 6·4 : 46·7 : 88. P. W. Clutterbuck.

Sources of error in forensic determination of alcohol. L. Kohberg (Deut. Z. ges. gerichtl. Med., 1930, **15**, 75—87; Chem. Zentr., 1930, i, 3470).—In diabetes the blood-alcohol is not appreciably above the normal value. Acetone must be tested for, and determined if necessary. In uræmia the blood-alcohol value is usually below the normal. Chloral, arising from chloral hydrate, affects the value; carbon monoxide does not give rise to significant error. The post-mortal action of alcohol-oxidase can, in the absence of bacterial decomposition, be neglected. The effect of non-alcoholic beverages and various fruits on the blood-alcohol cannot be ignored. A. A. Eldridge.

Detoxication in the animal organism. I. Detoxication of "avertin." H. Waelsch. II. Glutathione content of blood and toxicity. H. Waelsch and E. Weinberger (Arch. exp. Path. Pharm., 1930, **156**, 356—369, 370—376).—In white mice anæsthetised by "avertin" (tribromoethyl alcohol), thiosulphate, colldoial sulphur, cysteine, and

" detoxin " (a commercial preparation of protein nature), but not sulphite or cystine, exert a protective action against the toxic effects of the anæsthetic.

II. During " avertin " anæsthesia, the glutathione content of the blood of man and of the rabbit is decreased. The glutathione content of human blood is lowered by oral administration of sodium phenylacetate (4 g.). This may be the result of the coupling of the phenylacetic acid with glutamic acid prior to excretion. W. O. KERMACK.

Adsorption and narcotic action. H. H. KING, J. L. HALL, A. C. ANDREWS, and H. L. COLE (J. Pharm. Exp. Ther., 1930, **40**, 275—289).—The surface tension of aqueous solutions of trional, tetronal, butylchloral hydrate, sulphonal, bromal hydrate, triacetin, diacetin, chloral hydrate, ethylurethane, monoacetin, methylurethane, and ethyl methyl carbamate have been measured (1) at a water–air interface, (2) at a water–paraffin interface, and (3) at a water–paraffin solution of lecithin interface. No general relationship was found between the adsorption at the water–air interface and narcotic action of the compound measured by its liminal value except in homologous series. The adsorption curves referring to the water–paraffin solution of lecithin surface are with certain narcotics somewhat irregular, which may be the result of chemical reaction in the surface layer between the narcotic and the adsorbed lecithin. With a few exceptions capable of explanation, there is a strong relationship between the narcotic action and the adsorption at the pure paraffin–water interface, the magnitude of adsorption increasing as the liminal value decreases. A similar though not quite so definite relationship is found between narcotic action and adsorption at a water–paraffin solution of lecithin interface. W. O. KERMACK.

Toxicology of local anæsthetics. G. TAUBMANN and G. JUNG (Arch. exp. Path. Pharm., 1930, **156**, 18—25).—The toxicity of a 1% novocaine solution is approximately doubled by the addition of 2·5 mg. of adrenaline per 100 c.c. The use of freshly prepared novocaine solutions containing 0·4% of potassium sulphate and 0·0005% of adrenaline is recommended. W. O. KERMACK.

Physiology of pyrimidines. III. Intermediary metabolism of uracil. L. R. CERECEDO (J. Biol. Chem., 1930, **88**, 695—700).—Administration of *iso*barbituric acid and of *iso*dialuric acid to dogs by mouth causes an increase in the amount of urea excreted and a decrease in the inorganic sulphates. It is concluded that these compounds are partly oxidised to urea and some unknown carbon compound and partly excreted as ethereal sulphates. It is suggested that they form intermediate steps in the oxidation of uracil in the body. W. O. KERMACK.

Reduction of osmotic pressure in serum by narcotics and hypnotics. M. R. BONSMANN and B. BRUNELLI (Arch. exp. Path. Pharm., 1930, **156**, 125—130).—The colloidal osmotic pressure of the blood-serum of the dog is reduced by 78—184 mm. of water by the administration of various narcotics, *e.g.*, " luminal," ether, chloral hydrate, and " pantopon," without any corresponding fall in the concentration of serum-protein. The lowered osmotic pressure coincides with a reduced urinary flow. W. O. KERMACK.

Chloroform content in various tissues during anæsthesia and its relationship to theories of narcosis. J. L. McCOLLUM (J. Pharm. Exp. Ther., 1930, **40**, 305—325).—The solubility of chloroform in water at 37·5° is 1 g. per 100 c.c. The partition coefficient of chloroform between olive oil and water at 37·5° is 110. The chloroform content of the tissues of dogs submitted for various periods to chloroform anæsthesia has been determined as well as the lipin and water content of various tissues. Corpuscles contain more chloroform than does plasma, the excess being more than can be accounted for by their greater lipoidal content. Anæsthesia is produced when the brain cells contain about half the amount of chloroform that they can contain without the death of the animal. The passage of chloroform into the brain cells is progressive. The results do not support the Meyer–Overton theory of anæsthesia. W. O. KERMACK.

Reduction of oxidation during ether narcosis. H. FUSS and E. DERRA (Arch. exp. Path. Pharm., 1930, **156**, 64—84).—In dogs anæsthetised by the ether drop method, the oxygen content of the arterial blood is considerably below normal and the lactic acid content is increased. When the ether–air method is used the oxygen content is slightly below the normal and the lactic acid content is slightly raised. With the ether–oxygen method the oxygen content is increased and the lactic acid content is not above normal. In all cases the hæmoglobin content is increased. The increase of lactic acid in the blood during ether narcosis appears to be related to the degree of oxygen unsaturation. W. O. KERMACK.

Effect of ether anæsthesia and shock on blood-calcium. W. C. EMERSON (J. Lab. Clin. Med., 1928, **14**, 195—200).—Ether anæsthesia and asphyxia are followed by an increase (18 or 20%, respectively) in the serum-calcium; following anæsthesia with hyperventilation the serum-calcium decreases slightly. Shock has no effect on the serum-calcium. CHEMICAL ABSTRACTS.

Diuretin hyperglycæmia in cats. I. FUJI (Tohoku J. Exp. Med., 1930, **15**, 285—323).—Diuretin administered subcutaneously to cats (0·35—0·5 g. per kg.) caused immediate hyperglycæmia with two maxima; during this period food caused marked alimentary hyperglycæmia. Section of the splanchnic nerves and semilunar ganglia prevented the primary hyperglycæmia. Glycosuria appears during the second phase. The urine contains salicylic acid. CHEMICAL ABSTRACTS.

Sensitiveness of white mice to poisons after treatment with "caseosan," "sufrogel," and alcohol. H. VOLLMER (Arch. exp. Path. Pharm., 1930, **155**, 160—184).—White mice are less sensitive to the action of alcohol if " caseosan " has been administered 2—7 days previously. They are not protected against morphine, colchicine, or quinol. " Sufrogel " does not protect against alcohol. Repeated daily administration of alcohol usually results in a decrease in sensitiveness only on the fourth and fifth days, after which the sensitiveness is greater than normal. W. O. KERMACK.

Sensitiveness of white mice to poisons after treatment with substances increasing oxidation. H. VOLLMER and C. BUCHHOLZ (Arch. exp. Path. Pharm., 1930, **155**, 185—218).—Previous administration to white mice of various compounds likely to increase the rate of oxidation in the organism (thyroxine, sodium lactate, dextrose, and methylene-blue) reduces their sensitiveness to the narcotic effects of alcohol, but increases it to the toxic effects of quinol and colchicine. Their sensitiveness to morphine is not influenced by administration of thyroxine nor did sodium succinate have any action in this respect. W. O. KERMACK.

Increase of oxidation and alteration of sensitiveness to poisons of white mice by irradiation. H. VOLLMER and J. BEHR (Arch. exp. Path. Pharm., 1930, **155**, 219—247).—When white mice are irradiated with an Osram-vitalux or with a quartz–mercury lamp their sensitiveness is decreased to the toxic effects of alcohol but increased to quinol and colchichine. Their sensitiveness to morphine is unaltered. Application of the method of Lipschitz to the tissues of irradiated rats indicates an increase of the oxido-reductive mechanism.

W. O. KERMACK.

Influence of irradiation on the sensitiveness of white mice to poisons. O. RIESSER and A. HADROSSEK (Arch. exp. Path. Pharm., 1930, **155**, 139—159).—By irradiation of white mice or rats with an Osram-vitalux lamp, they are protected against narcotic doses of ethyl alcohol, the ultra-violet rays being those responsible for the action. The animals could not be protected against the narcotic action of chloral hydrate or paraldehyde by irradiation sufficient to protect against ethyl alcohol, nor could they be protected against the lethal action of acetonitrile, morphine, hydrogen sulphide, or tetanus toxin.

W. O. KERMACK.

Differential action of *X*-rays on tissue, growth, and vitality. I. II. Biological reaction in relation to "antagonism." III. Biological reaction in relation to area. IV. Biological reaction in relation to time. W. MOPPETT (Proc. Roy. Soc., 1929, B, **105**, 402—421; 1930, B, **107**, 293—301, 302—307, 308—312).—I. Histological observations of the reaction of the allantoic membrane of the embryo chick to *X*-rays are described. Atrophy and hypertrophy of a particular tissue are associated with definite wave-length bands. The maximum destruction is observed at 0·5 Å. in 1·25 hrs., whilst growth is stimulated by exposure for 0·5 hr. to the same radiation. Neutralisation of biological action (" antagonism ") occurs with mixed radiation. It is suggested, in view of the magnitude of effective wave-lengths, that biological changes are due to atomic ionisation.

II. Further experimental confirmation of " antagonism." Atrophy by normally effective diffracted *X*-rays is also prevented by prior exposure to direct radiation.

III. The threshold dose of *X*-radiation for a reaction varies as the area of tissue irradiated. This is explained by summation of stimuli from adjacent parts so that the threshold dose is inversely proportional to the square of the area when the area is small.

IV. The inverse relationship between threshold dose and time of exposure is modified by atomic changes and biological repair. Mouse skin is more resistant to *X*-rays than is the allantoic membrane.

A. COHEN.

Effect of diathermy on serum-protein concentration and fractions of human serum. H. HIRSCH (Arch. exp. Path. Pharm., 1930, **156**, 346—355).—Application of diathermy of short duration results in a decrease of the concentration of serum-protein with an increase in the globulin–albumin ratio and a decrease in the viscosity.

W. O. KERMACK.

A new enzymic oxidation (metaoxidase). I. BOAS (Biochem. Z., 1930, **227**, 135—139).—Plant juices contain an extremely thermolabile substance which gives with an alcoholic solution of benzidine and guaiacum a rose-red and a deep blue colour, respectively, the pigments being extractable with amyl alcohol, ether, and chloroform. This substance is designated *metaoxidase*, but it is not decided whether it is a new enzyme or one of the group of phenolases. It is present exclusively in plant foods and is entirely absent from animal foods (flesh, fish, milk, eggs). Market vegetables are poor, but fruits, especially stone fruits, and mushrooms are very rich in metaoxidase. Market vegetables, on the other hand, are rich in peroxidase. Whereas treatment of plant juice with 3% hydrogen peroxide for 24 hrs. does not decrease the peroxidase and oxidase action of the juice, the metaoxidase is completely destroyed. Metaoxidase is not identical with tyrosinase and is rapidly destroyed by the action of gastric juice.

P. W. CLUTTERBUCK.

Action of adenosinemonophosphoric acids and adenosinetriphosphoric acid on dehydrogenation processes induced by plant and animal enzymes. H. J. DEUTICKE (Z. physiol. Chem., 1930, **192**, 193—216).—The dehydrogenase prepared from the seeds of *Corchorus capsularis* was studied by means of the Thunberg technique. The hexosediphosphoric acid from muscle and that from yeast behaved similarly in accelerating methylene-blue reduction. The reduction in presence of boiled muscle extract is principally due to adenosinetriphosphoric acid. Muscle-adenylic acid, which is inactive alone, in low concentration accelerates reduction after addition of hexosediphosphate and especially of monophosphate, but does not affect the rate of decolorisation produced by adenosinetriphosphate. In higher concentrations it has an inhibiting effect. Inhibition is produced by yeast-adenylic acid at all concentrations. Dehydrogenase preparations from muscle are also stimulated by adenosinetriphosphoric acid and to a smaller degree by hexosediphosphoric acid. Muscle-adenylic acid alone (but not yeast-adenylic acid), inosic acid, and its corresponding pentosephosphoric acid stimulate the muscle enzyme. J. H. BIRKINSHAW.

Dehydrogenating power of cereal seeds in presence of plant acids and purines as hydrogen donators. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1930, 225, 417—425).—The dehydrogenating actions of wheat, barley, and oats were compared. Extracts of the flour showed only self-dehydrogenation and dehydrogenation of added donators in presence of boiled yeast juice. Boiled pea juice at high concentrations has an activating effect on wheat and barley extracts. With wheat, strong self-dehydrogenation occurs. Potassium malate, which hastens dehydrogenation in presence of boiled yeast juice, here acts as an inhibitor. With wheat, in presence of yeast juice, formate, malate, and purines are most active in stimulating dehydrogenation; with barley, citrate, pyruvate, malate, purines, and especially oxalate; with oats, pyruvate, oxalate, and especially malate. Phosphate inhibits the action of wheat, but favours that of barley and oat extracts.

J. H. Birkinshaw.

Active group of liver-catalase. K. Zeile and H. Hellström (Z. physiol. Chem., 1930, 192, 171—192).—Purified extracts of horse's liver showing high catalase activity contained a porphyrin–iron complex, characterised by its specific absorption bands, 629, 540, and 500 mμ. The enzymic activity was directly proportional to the amount of iron–porphyrin present in the preparation. The complex yields dissociable hydrocyanic acid and hydrogen sulphide compounds; the inhibition of the catalase action by these poisons is thus explained. The dissociation constant of the hydrocyanic acid compound, about 8×10^{-7}, confirms the value of the dissociation constant for catalase–hydrocyanic acid obtained from the kinetics of the reaction.

J. H. Birkinshaw.

Mechanism of enzyme reactions. I. Influence of hydrogen-ion concentration on the action of liver-esterase. H. G. K. Westenbrink and H. M. Romijn. **II. Hydrolysis of a mixture of two esters by liver-esterase.** H. G. K. Westenbrink (Arch. Néerland. Physiol., 1930, 15, 529—537, 538—544).—I. The action of liver-esterase on the monoethyl esters of the homologous series of dibasic aliphatic acids (oxalic to sebacic) at various $p_{\rm H}$ values of the reaction mixture was investigated. The optimum $p_{\rm H}$ progressively increases from 5·6 to 7·3 as the series is ascended. No relation exists between the $p_{\rm H}$–activity and $p_{\rm H}$–ionisation curves for any of the acids; hence the $p_{\rm H}$–activity curves for these substrates are determined merely by their structure.

II. In the action of liver-esterase on a mixture of the monoethyl esters of sebacic and azelaic acids the enzyme is divided between the substrates and consequently the reaction velocity lies between those observed for the separate reactions. The results are contrasted with those obtained by Northrop (A., 1922, i, 693) on the hydrolysis of proteins by trypsin.

F. O. Howitt.

Susceptibility of various sugars to fermentation by rat's liver: its dependence on the state of nourishment of the animal and on the time of year. O. Rosenthal (Biochem. Z., 1930, 227, 354—384).—The fermentation of lævulose, glyceraldehyde, and dihydroxyacetone, but not that of glycogen, sucrose, maltose, lactose, galactose, mannose, dextrose, and hexosediphosphoric esters, is greatly accelerated by the presence of liver tissue from rats which have been sufficiently fed. The liver tissue from fasting rats has only a slight accelerating effect, and even amongst tissues from the other rats wide differences in accelerating power occur according to the compound concerned and to the time of year at which the rats are used. The differences in the behaviour of the various tissues are attributed to variations in their content of a fermentation activator. The rate of dismutation of methylglyoxal by the tissues is about four times as great as the maximum rate of fermentation of lævulose or of glyceraldehyde and is almost independent of the state of nourishment of the rats and of the time of year at which they are used. It is supposed that the amount of activator in the tissue is always sufficient to accelerate this dismutation, but only sometimes sufficient for acceleration of the other fermentations.

W. McCartney.

Intestinal nucleotidase. P. A. Levene and R. T. Dillon (J. Biol. Chem., 1930, 88, 753—769).—The action of intestinal nucleotidase on the following compounds has been studied at $p_{\rm H}$ 8·6—8·7: glyceryl phosphate, hexosemonophosphate from α- and from β-di*iso*propylidenefructose, Neuberg's monophosphate, hexosediphosphate and its methylglucoside, hexosemonophosphate from mono- and from di-*iso*propylideneglucose, adenylic acid, inosic acid, uridinephosphoric acid, yeast-nucleic acid, and thymus-nucleic acid. The nucleotides are hydrolysed almost as rapidly as are the sugar esters, but the nucleic acids are acted on much more slowly. Uridinephosphoric acid is more rapidly hydrolysed than is adenylic acid and the latter more rapidly than inosic acid. Thymus-nucleic acid is sometimes more resistant than yeast-nucleic acid. The rates of hydrolysis of hexosediphosphate and its methylglucoside are exactly the same. Different samples of enzyme prepared by precipitation from a solution with acetone usually hydrolysed a standard glycerophosphate solution at approximately the same rates and showed a constant parallelism in their capacity for hydrolysing both nucleotide and thymus-nucleic acid, but one sample behaved exceptionally. The use of magnesium to remove phosphate ions formed in the reaction was not advantageous.

W. O. Kermack.

Destruction, in the seed of *Soja hispida*, of one enzyme without suppression of activity of two others. R. Fosse, A. Brunel, P. de Graeve, P. E. Thomas, and J. Sarazin (Compt. rend., 1930, 191, 1025—1028).—By heating an aqueous extract of ground soya beans for 30 min. at 78°, keeping this for 24 hrs. at 0°, and centrifuging, the activity of uricase is completely destroyed, whilst that of urease and allantoinase is unimpaired. The same result is obtained by drying the beans themselves in a vacuum over calcium chloride (the water content falling from 13·1% to 6·9%), and keeping them in sealed tubes at 82° for 50 hrs.

C. W. Shoppee.

Basic processes of the Abderhalden reaction. E. Abderhalden and S. Buadze (Fermentforsch., 1930, 12, 129—179).—A general exposition and confirmation.

J. H. Birkinshaw.

Appearance of the Abderhalden reaction after parenteral administration of the pituitary preparation "praehormone," and of the ovarian

hormone "folliculin." E. Abderhalden and S. Buadze (Fermentforsch., 1930, **12**, 262—272).—After injection of prachormone or folliculin castrated animals gave the Abderhalden reaction with ovarian tissue. J. H. Birkinshaw.

Activation of cathepsin and papain. E. Waldschmidt-Leitz and A. Purr (Naturwiss., 1930, **18**, 952—953).—The action of papain on gelatin, purified by a process including treatment with potassium cyanide, in presence of citrate buffer incubated at 30°, with and without the addition of hydrocyanic acid or of a thiol compound (*e.g.* glutathione), was investigated. The presence of the activator resulted in an increased amino-nitrogen production in both cases. Hence the authors conclude that the question of whether catheptic activation (Willstätter and Bamann, A., 1929, 354) depends on a reaction of activator with enzyme or on a complex formation with inhibitory metals (Krebs, A., 1930, 957) is still unsettled. F. O. Howitt.

Determination of peptic activity: the Gates method of proteolytic titration. A. Gilman and G. R. Cowgill (J. Biol. Chem., 1930, **88**, 743—752).—The pepsin solution adjusted to a determined p_H value is allowed to act at 25° on the gelatin film of a photographic plate containing reduced silver and so arranged that as the gelatin is digested, the liberated silver particles fall to the bottom of the fluid and so do not interfere with the continuation of the reaction. After a suitable interval the opacity of the remaining gelatin film is measured in a colorimeter, comparison being made with a suspension of silver obtained by dissolving away the gelatin of a reduced film. The loss in opacity of the film is a measure of the activity of the pepsin. The method is very satisfactory and requires only small quantities (0·5 c.c.) of pepsin solution. W. O. Kermack.

[Concentration of pepsin and chemistry of its action.] B. Lustig (Biochem. Z., 1930, **227**, 385).—The differences between individual results calculated according to the method of Smorodincev and Adova (A., 1930, 1475) do not correspond with the differences in the activities of the samples of pepsin used. It is the changes which the amino- and carboxyl groups undergo and not their amount or ratio which are important for the action of pepsin.

W. McCartney.

Capability of dilute alkali hydroxide, erepsin, and trypsin-kinase for hydrolysing the CO·NH linking in polypeptides and related compounds in which the amino- and carboxyl groups are variously substituted. E. Abderhalden and E. Riesz (Fermentforsch., 1930, **12**, 180—222).—A number of widely varying substrates were prepared, usually by condensing the requisite chloride with the amino-acid: p-*cresoldisulphonyl*-dl-*leucylglycine*, m. p. 140°; m-*cresoldi*(*sulphonyl*-dl-*leucine*)*mono*(*sulphonyl*-dl-*leucylglycine*), m. p. 117—120°, from *m*-cresoltrisulphonylchloride and *dl*-leucylglycine methyl ester; m-*cresoltrisulphonyl*-dl-*leucine ethyl ester*, m. p. about 60°, yielding with *N*-sodium hydroxide m-*cresol trisulphonyl*-dl-*leucine*, m. p. (indef.) 80—120°; o-*cresoldisulphonylglycine*, m. p. 128°; m-*carboxybenzenesulphonylglycine*, m. p. 178°; m-*carboxybenzenesulphonyl*-dl-*leucine*, m. p. 187°; m-*carboxybenzenesulphonyl*-dl-*leucylglycine*, m. p. 190°; *di*(*ethanesulphonyl*-dl-*leucyl*)*diketopiperazine*, m. p. 140°, from ethanesulphonyl chloride and *dl*-leucylglycine; a *compound*, $C_{11}H_{20}O_5N_2S$, m. p. 117°, from β-bromoethanesulphonyl chloride and leucylglycine methyl ester; *benzoylglycylaspartic acid*, m. p. 191°; o-*nitrophenylthiolglycine ethyl ester*, m. p. 83°; o-*nitrophenylthiol*-dl-*leucine ethyl ester*, m. p. 90°; o-*nitro*-p-*chlorophenylthiol*-dl-*leucine ethyl ester*, m. p. 99°; o-*nitro*-p-*chlorophenylthiol*-dl-*leucylglycine*, m. p. 128—130° (*methyl* ester, m. p. 97—100°); *dichlorodinitrophenylthiol oxide*, sinters at 115°, decomp. at high temp.; o-*nitro*-p-*chlorophenylthiol*-dl-*leucine*, m. p. 126°; *phenyl*-dl-*leucylglycine*, m. p. 139°; *dinitrophenyl*-dl-*leucylglycine*, m. p. 150—152°; 2:4-*dinitrophenylcystine*, m. p. 156°, from 1-chloro-2:4-dinitrobenzene and cysteine hydrochloride; p-*aminobenzoyl*-dl-*leucylglycine*, m. p. above 250°, from *p*-aminobenzoyl chloride, m. p. 31°, which readily forms p-*aminobenzoyl*-p-*aminobenzoic acid*, m. p. above 300° (decomp.); p-*aminobenzoyl*-dl-*leucylglycine methyl ester*, m. p. 60°; o-*chlorobenzoyl*-dl-*leucylglycine*, m. p. 208—210°; o-*nitrobenzoyl*-dl-*leucylglycine*, m. p. 231°; o-*nitrobenzoyl*-dl-*leucine*, m. p. 145°, yielding on reduction o-*aminobenzoyl*-dl-*leucine anhydride*, m. p. 255°; o-*nitrobenzoylglycine*, m. p. 190°, yielding on reduction o-*aminobenzoylglycine anhydride*, m. p. 320° (decomp.); dl-α-*bromo*iso*hexoyl*-o-*aminobenzoic acid*, m. p. 110°, yielding on amination *leucyl*-o-*aminobenzoic anhydride*, m. p. 185° (*hydrochloride*, decomp. 215—220°), which on methylation gives a *monomethylimide*, m. p. 105°; α-*hydroxy*iso*hexoyl*-o-*aminobenzoic acid*, m. p. 146°; *chloroacetyl*-dl-*leucyl*-o-*aminobenzoic acid*, m. p. 176°; *chloroacetyl*-o-*aminobenzoic acid*, m. p. 185°; *glycyl*-o-*aminobenzoic acid*, m. p. 215—220° (decomp.); dl-α-*bromo*iso*hexoyl*-p-*aminobenzoic acid*, m. p. 173°; dl-*leucyl*-p-*aminobenzoic acid*, m. p. 220° (by-product, α-*hydroxy*iso*hexoyl*-p-*aminobenzoic acid*, m. p. 193—195°); *chloroacetyl*-dl-*leucyl*-p-*aminobenzoic acid*, m. p. 217°; *toluenesulphonchloroacetamide*, m. p. 88—89°; N-*glycyltoluenesulphonamide*, m. p. 207°; N-α-*bromo*iso*hexoylglycyl*-p-*toluenesulphonamide*, m. p. 137°; m-*carboxybenzenesulphonchloroacetamide*, m. p. 212° (decomp.), giving N-dl-α-*bromo*iso*hexoylglycyl*-m-*carboxybenzenesulphonamide*, m. p. 174°; dichlorodiacetimide; diglycineimide; N-*chloroacetylbenzamide*, m. p. 157°; chloroacetylcarbamide; dl-*leucyltaurine*, m. p. 285°.

Various factors such as valency, position of entry of the substituent, strength of the acidity or basicity of the substituent, and polysubstitution exert an effect on the ease of hydrolysis of the CO·NH linking by dilute alkali hydroxide. J. H. Birkinshaw.

Removal of halogen by dilute alkali from stereoisomeric halogenoacylamino-acids and their behaviour towards erepsin and trypsin-kinase. E. Abderhalden and F. Schweitzer (Fermentforsch., 1930, **12**, 231—243).—*dl*-Norvaline was separated into optically active components by formylation and crystallisation of the brucine salt. l-*Norvaline*, m. p. 300° (uncorr.), $[\alpha]_D^{22}$ −5·08°, with bromoacetyl bromide furnished *bromoacetyl*-l-*nor*-

valine, m. p. 92°, $[\alpha]_{D}^{20}$ +9·20°. Likewise there were prepared *bromoacetyl*-d-*norvaline*, m. p. 95°, $[\alpha]_{D}^{20}$ −8·6°; l-α-*bromopropionyl*-l-*norvaline*, m. p. 110°, $[\alpha]_{D}^{20}$ −9·0°; l-α-*bromopropionyl*-d-*norvaline*, m. p. 105°, $[\alpha]_{D}^{20}$ −18°; d-α-*bromopropionyl*-d-*norvaline*, $[\alpha]_{D}^{22}$ +8·5°; d-α-*bromopropionyl*-l-*norvaline*, $[\alpha]_{D}^{22}$ +15°; *racemate A* of *dl*-α-bromopropionyl-*dl*-leucine, m. p. 149—150° (corr.); *racemate B*, m. p. 118—119°; *racemate A* of dl-α-*bromo*iso*hexoyl*-dl-*valine*, m. p. 173—174° (uncorr., decomp.); *racemate B*, m. p. 125—126°. Dilute alkali hydroxide removes bromine much more rapidly from *d*-α-bromopropionyl-*d*-norvaline and from *l*-α-bromopropionyl-*l*-norvaline than from the *l*-*d*- and *d*-*l*-compounds. Racemate A (cf. A., 1930, 816) behaves like the first pair and racemate B like the second pair of compounds. Of the racemates from *dl*-α-bromopropionyl-*dl*-leucine, A is hydrolysed more slowly than B. Trypsin-kinase hydrolyses A more rapidly than B. Of the racemates from α-bromo*iso*hexoylvaline the halogen is removed more rapidly from A than from B. Trypsin-kinase did not attack either racemate. Erepsin hydrolysed none of the substrates. J. H. Birkinshaw.

Homogeneity of erepsin. E. Abderhalden and E. von Ehrenwall (Fermentforsch., 1930, **12**, 223—230).—Erepsin completely free from trypsin hydrolyses chloroacetyl-*d*-alanine and chloroacetyl-*dl*-leucine, but not chloroacetyl-*l*-tyrosine. Trypsin-kinase hydrolyses chloroacetyl-*l*-tyrosine and chloroacetyl-*dl*-leucine, but not *chloroacetyl*-d-*alanine*. Trypsin-kinase solutions which originally did not hydrolyse leucylglycine gain this power on keeping. J. H. Birkinshaw.

Oxidation–reduction. Brewers' yeast. R. Fabre and H. Simonnet (Compt. rend., 1930, **191**, 1075—1077).—The conclusion previously reached (A., 1930, 949) that reducing sulphur compounds are extracted from rabbits' liver by Ringer's solution only after the tissue has been killed is confirmed by a similar investigation with brewers' yeast. A centrifuged aqueous extract of fresh yeast gives no reaction with ammoniacal nitroprusside, but a strong positive reaction is obtained when the extraction is carried out in an atmosphere of chloroform. Desiccation of the yeast over phosphoric oxide in a vacuum causes a progressive increase in the amount of reducing sulphur compounds extracted by water. The aqueous extract of desiccated yeast reduces cystine. J. W. Baker.

Porphyrin of component *c* of cytochrome: relationship to other porphyrins. R. Hill and D. Keilin (Proc. Roy. Soc., 1930, **B**, **107**, 286—292).—Methods of preparing two different porphyrins from the *c* component of cytochrome from bakers' yeast are described. Treatment of the *c* component with hydrogen bromide and acetic acid yields hæmatoporphyrin identical in solubility and absorption spectrum with ordinary hæmatoporphyrin. Both are convertible into protoporphyrin, and the facts support the view that cytochrome is derived from protohæmatin in yeast cells. Under the action of hydrogen chloride and sulphur dioxide, the *c* component yields "*porphyrin*-c," insoluble in ether, acetic acid, or chloroform. This shows absorption bands at 6230, 5975, 5675, 5354, and 5000 Å. in pyridine, whilst the bands for a solution in *N*-hydrochloric acid are at 5970 and 5520 Å. Its copper compound in pyridine shows absorption at 5648 and 5298 Å., and the pyridine-hæmochromogen prepared from it is indistinguishable in absorption spectra from the *c* component in aqueous pyridine, exhibiting bands at 5498 and 5212 Å. A. Cohen.

Arbitrarily influenced asymmetric cleavage of *dl*-borneolphosphoric acid by yeast- and taka-phosphatase. M. Kuroya (Biochem. Z., 1930, **225**, 452—463).—The borneol eliminated from *dl*-borneolphosphoric acid by yeast- or taka-phosphatase was lævorotatory for a 50% fission and dextrorotatory for a higher degree of hydrolysis. Addition of strychnine in the taka-phosphatase hydrolysis lowered the activity of the borneol produced and only lævorotation was observed. With yeast-phosphatase the alkaloid also lowered the rotation of the borneol obtained, and in the case of advanced hydrolysis reversed the rotation as compared with the alkaloid-free substrate. J. H. Birkinshaw.

Detection and intensity of mitogenetic radiation. I. H. Schreiber and W. Friedrich (Biochem. Z., 1930, **227**, 386—400).—Attempts to detect mitogenetic radiation from germinating yeast cultures (*Saccharomyces ellipsoideus*) by a modification of the method of Elster and Geitel (Physikal. Z., 1916, **17**, 268) were unsuccessful. Since the sensitivity of the apparatus used was known, some conclusions could be reached as to the behaviour which the radiation, if it occurs at all, must exhibit. W. McCartney.

Effect of ionised air on rate of respiration of fungi. S. R. van A. de Boer (Ann. Bot., 1930, **44**, 989—999).—No effect was observed with *Phycomyces Blakesleeanus* and *Polyporus destructor*. F. O. Howitt.

Resorption of ammoniacal and nitrate-nitrogen by *Aspergillus oryzæ*. T. Sakamura (Planta, [Z. wiss. Biol.], 1930, **11**, 765—813).—In culture solutions containing ammonium salts and nitrates *A. oryzæ* may assimilate either form of nitrogen preferentially or both simultaneously. When ammonia absorption predominates the c_{H} of the culture solution increases and the growth of the fungus is retarded, but when nitrate assimilation is high the reaction of the nutrient remains practically constant, growth is luxuriant, and the total nitrogen absorbed is high. The form of nitrogen chiefly utilised varies with cultural conditions and to a large extent with the nature of the carbohydrate present. The ease of nitrate absorption in the presence of sugars decreases in the order lævulose>sucrose>dextrose. In ammoniophilic cultures the addition of phosphates tends to limit acidification and causes improved growth. A. G. Pollard.

Variations in the fatty acids of *Aspergillus niger* as a function of the mineral composition of the culture medium. C. Pontillon (Compt. rend., 1930, **191**, 1148—1151).—*A. niger* has been grown on various liquid media differing in their mineral composition and p_{H}, and analysed at various periods of growth in respect of fatty acids. In slightly alkaline media, the quantity of fatty acids formed is approximately equal to that obtained in the neutral medium, but in acid medium it is decreased. The mol. wt. of the fatty acids is approximately independent of the p_H and is minimal at the time of fructification. The iodine value of the fatty acids is about 30 in a neutral medium and is greater in an acid medium. It is still more raised in an alkaline medium and is minimum immediately before sporulation. In a medium kept approximately neutral it is somewhat high and relatively constant. W. O. Kermack.

Acidoproteolytic bacteria in pasteurised milk. C. Gorini (Compt. rend., 1930, 191, 885—886).—Thermophilic acidoproteolytic bacteria of the type *subtilis* are responsible for the premature coagulation of milk pasteurised for 30 min. at 53°. It is possible for spores of these organisms to survive pasteurisation at 80—85°. T. H. Morton.

Cultural characteristics and metabolism of the organism producing red spots in English cheese. J. G. Davis and A. T. R. Mattick (Zentr. Bakt. Par., 1930, 80, 30—33; Chem. Zentr., 1930, i, 2113).—The red spots are practically pure cultures of a bacterium, $0{\cdot}85\times2\,\mu$, the characteristics of which are described. A living pigmented culture is quickly decolorised in air, but not after death caused by drying or by treatment with alcohol, whereby the pigment is fixed. The pigment is insoluble in water, ether, benzene, chloroform, glycerol, dilute acid, and alkali. Boiling with concentrated acid, but not alcoholic alkali, decomposes it; concentrated sulphuric acid gives a deep blue colour. The pigment appears to play no part in the metabolism of the organism.

L. S. Theobald.

Growth of anaërobic micro-organisms and the potential of the culture medium. H. Plotz and J. Geloso (Ann. Inst. Pasteur, 1930, 45, 613—640).—*P. D.* are measured by two electrical methods using the calomel electrode, anaërobiosis being best produced by evacuation of the apparatus. A colorimetric method is also employed. A definite potential is always finally established, corresponding with r_H $5{\cdot}5\pm0{\cdot}5$, irrespective of the nature of the organism employed. The curves obtained for bouillon containing platinum-black are similar to those obtained for bacterial cultures. Rapid growth takes place provided that the potential corresponds with a value of r_H 0—14. P. G. Marshall.

Specificity of the tuberculin type of sensitiveness produced with the different protein substances of egg-white. L. Dienes (J. Immunol., 1930, 18, 279—283). Chemical Abstracts.

Antigenic substances of the tubercle bacillus. V. Antigenic substances of the synthetic culture medium. L. Dienes and E. W. Schoenheit (J. Immunol., 1930, 18, 285—314).—In filtrates of cultures grown on Long's synthetic medium two distinct antigenic substances, separable by acid precipitation, are present together with the carbohydrate-precipitable substance.

Chemical Abstracts.

Separation of antibodies from serum-proteins. M. Frankel and L. Olitzki (Nature, 1930, 126, 723—724).—Active antibodies free from proteins have been obtained from diphtheria antitoxin and antityphoid serum by Willstätter's method of adsorption on kaolin and specific elution with solutions of glycine containing 2% of sodium chloride.

L. S. Theobald.

Action of dyes on bacteria. M. Kawai (Zentr. Bakt. Par., 1930, I, 115, 241—271; Chem. Zentr., 1930, i, 3319).—There is a connexion between the chemical structure of dyes and their growth-inhibiting power. The inhibitive effect of basic dyes, particularly of triaminotriphenylmethane, is increased by alkyl groups. Dyes containing chlorine, and their double metallic salts, have a strong effect, whilst those containing sulpho-, nitro-, carboxyl, and hydroxyl groups have little effect. Dyes favour the development of abnormal bacterial forms.

A. A. Eldridge.

Effect of small additions of acid for increasing the germicidal action of E.C. [electrolytic chlorogen] on bacterial spores. C. S. R. Ayyar (Agric. J. India, 1930, 25, 213—219).—The addition of 0·035 g. of citric acid to a 0·2% solution of the disinfectant increases its efficiency to the point of destroying resistant spores after 30 min. contact (cf. A., 1930, 645). E. Holmes.

Bacteriophage, a central biological problem. C. J. Schnuurmann (Kolloid-Z., 1930, 53, 231—239).—A discussion. E. S. Hedges.

Kinetics of bacterium-bacteriophage reaction. A. P. Krueger and J. H. Northrop (J. Gen. Physiol., 1930, 14, 223—254).—An analytical study of a system containing antistaphylococcus bacteriophage (P) acting on *S. aureus* (B), using methods already described (cf. A., 1930, 960). It is shown that, following a short lag, during which rapid adsorption of P by B occurs, there is logarithmic increase of B and P, the latter proceeding more rapidly. Phage formation is dependent on bacterial growth, and lysis, which is also logarithmic, begins when $\log [P]/[B]=2{\cdot}1$. Equations deduced to determine the commencement of lysis under standard conditions are experimentally confirmed. A. Cohen.

Fat metabolism of the liver. I. Effect of hormones on the fat content of the liver. II. Effect of biogenic amines. Z. Oshima (Z. ges. exp. Med., 1929, 64, 694—706, 707—713; Chem. Zentr., 1930, i, 3801).—The increase in the fatty acid content of the liver of rabbits after subcutaneous injection rose in the order thyroxine, menoformone, pituitrin. The increase is due chiefly to saturated acids. Choline has little, and tyramine a marked, effect; histamine causes a small reduction in the fatty acid content.

A. A. Eldridge.

Water content of various tissues of animals treated with powdered mammary gland. C. I. Parhon, M. Cahane, and A. Blinov (Bull. Acad. Sci. Roumaine, 1930, 13, 165—167).—In guinea-pigs treated daily with mammary gland powder there is a very slight increase in the water content of the brain and of liver, whilst other organs suffer a diminution.

F. O. Howitt.

The unitary versus the multiple hormone theory of posterior pituitary principles. J. J. Abel (J. Pharm. Exp. Ther., 1930, 40, 139—170).—New methods are described for the preparation of an active substance from fresh pituitary gland or from commercial pituitary powders in the form of a colourless dry powder which in respect of its oxytocic, pressor, and melanophore-expanding activities is 50—60 times as powerful as the international standard preparation. Some preparations are even more active, but the ratios of the pressor, oxytocic, and melanophore-expanding activities remain approximately constant. After boiling with 0·25% acetic acid, however, the material may be separated into fractions in which one or other activity is particularly marked, whereas such fractionation appears to be impossible before boiling. It is therefore considered probable that the initial preparations contain a unitary principle, the molecules of which carry at least four groups respectively responsible for the four characteristic activities, and that treatment with hot dilute acid results in the separation from the unstable molecule of the groups exerting the specific activities. The crude unitary principle as isolated contains at least 50% of inactive protein and also a crystalline base of unknown composition, m. p. about 179°. It is probable that the commercial product pitressin, as primarily isolated, is the unitary product minus the oxytocic group, so that it has approximately equal activities in international units in respect of its pressor, melanophore-expanding, and anti-diuretic functions. A further scission into its individual components may take place during sterilisation.

W. O. KERMACK.

Assay for the testicular hormone by the comb-growth reaction. T. F. GALLAGHER and F. C. KOCH (J. Pharm. Exp. Ther., 1930, 40, 327—339).—The variability in the responses of brown Leghorn capons to injections of testicular hormone is not specially related to age and weight of the bird nor to the initial size and shape of the combs. The best results are obtained by determining the minimal dose injected on five successive days causing a growth of 3—7 mm. in the height and length of the comb. A bird unit is defined as the amount of the hormone which when injected daily for 5 days yields an average of 5 mm. increase in length and height of the combs of at least five brown Leghorn capons.

W. O. KERMACK.

Influence of nutrition on blood-sugar regulation. IV. Reversal of the effect of food by removal of the thyroid. E. GEIGER (Arch. exp. Path. Pharm., 1930, 156, 333—339).—In normal rabbits the fasting blood-sugar level is higher after feeding on green food than after oats, and the rise in blood-sugar after oral administration of dextrose, according to Staub's method, is also greater. After thyroidectomy the higher values are obtained with oat feeding. The effect of green feeding is therefore exerted through an action on the thyroid gland.

W. O. KERMACK.

Calcium content of skeletal muscles after thyroparathyroidectomy and "parathormone" injection. F. Y. HSU and C. TSAI (Chinese J. Physiol., 1930, 4, 423—429).—The normal calcium content of the muscles of dogs varies from 6·4 to 12·2 mg. per 100 g. of fresh tissue, the average values for temporal, diaphragm, and gastrocnemius muscle being 9·5, 9·4, and 8·5 mg., respectively. After thyroparathyroidectomy the calcium content of the muscle is below normal, whilst the results obtained after administration of "parathormone" to normal animals were inconstant, but in no case was a decrease observed. The results do not support the view that muscle is the immediate source of the calcium mobilised by the parathyroid hormone.

W. O. KERMACK.

Plasma-calcium-raising principle of bovine parathyroid glands. I. Preparation and properties of the product. W. R. TWEEDY (J. Biol. Chem., 1930, 88, 649—657).—Potent preparations of parathyroid hormone in dry form in quantities of 1—3 mg. per gland may be separated from hot hydrochloric acid extracts by removal of inert material with acetone, followed by trichloroacetic acid precipitation of the active fraction, and removal of inert lipoid material from this fraction by chloroform extraction. The product dissolved in dried phenol retains its activity when heated at 70° for 7 hrs., but is partly inactivated at 150° for 1 hr. and completely inactivated at 175° for ½ hr. in an atmosphere of nitrogen. Complete inactivation results when the active material is suspended in 0·5% hydrochloric acid in absolute alcohol and heated for 20 min. at 70°, or when it is suspended for 1 hr. in absolute alcohol saturated with gaseous hydrogen chloride at 10°.

W. O. KERMACK.

Medullary substance of the adrenals in the biochemistry of the organism. S. A. SCHTSCHERBAKOV, V. S. SIMNITZKI, and V. R. DMITRIEV (Pflüger's Arch. Physiol., 1930, 224, 328—336; Chem. Zentr., 1930, i, 3452).—Experiments on the electrical stimulation of the splanchnic nerve show that adrenaline is a true hormone, having an important effect on the carbohydrate economy of the cells.

A. A. ELDRIDGE.

Influence of adrenaline on immediate variations of the alkaline reserve. Rôle of apnœa. Comparative action of formaldehyde and of acetylcholine. J. GAUTRELET, D. BENNATI, E. HERZFELD, and L. VALLAGNOSC (Bull. Soc. Chim. biol., 1930, 12, 1100—1145).—The alkaline reserve and reaction of the blood immediately after injection of adrenaline were investigated in chloralosed dogs. There is a well-marked increase in alkaline reserve within three minutes of intravenous injection, the p_H undergoing a parallel rise. Vagotomy greatly reduces these effects and the apnœa is eliminated. Practically no change occurs in the alkaline reserve during the apnœa due to formaldehyde or acetylcholine, whilst administration of adrenaline in amounts insufficient to cause apnœa results in an increase in the alkaline reserve. The action of adrenaline during paralysis of the sympathetic system by atropine or of the parasympathetic by yohimbine and by ergotamine and the changes in the alkaline reserve following peripheral stimulation of the splanchnics were also studied.

F. O. HOWITT.

Influence of adrenaline on the blood-sugar content in connexion with reticular-endothelial blockage. H. GNOIŃSKI (Med. Doświad., 1930, 11, 117—123).—Intravenous injection of colloidal silver raises the blood-sugar level by 30%, at the expense of hepatic glycogen, whilst adrenaline causes an increase of 70%; injected simultaneously, an increase of only 43% is observed, this time at the expense chiefly of muscle-glycogen. The inhibitive effect of colloidal silver on the action of adrenaline persists for at least 8 hrs. R. Truszkowski.

Rôle of suprarenal glands in hyperglycæmia caused by injection of colloidal silver. P. Demant (Med. Doświad., 1930, **11**, 81—87).—Injection of colloidal silver into suprarenalectomised dogs does not provoke the hyperglycæmia observed under such conditions in normal animals, nor are the calcium or sodium chloride contents of the blood affected by the injection. Colloidal silver acts by exciting the sympathetic through the reticular-endothelial system, thereby provoking the activity of the chromogenic substance of the suprarenal glands, which in turn leads to hyperglycæmia. R. Truszkowski.

Action of insulin, adrenaline, and morphine on the distribution of sugar in the organism during digestion in angiostomised dogs. N. P. Kochneva (Arkh. biol. nauk, 1930, **30**, 45—56).—In the first 2 hrs. after subcutaneous injection of adrenaline together with or after injection of carbohydrate alimentary hyperglycæmia is not observed, whilst after intravenous or subcutaneous injection of insulin the absorption from the alimentary tract continues and the blood-sugar does not reach high values only because of the retention of sugar by the kidneys. During the absorption of protein from the intestine, blood-sugar is equally distributed in different parts of the body; administration of insulin leads to renal retention of sugar. Subcutaneous injection of morphine as well as of adrenaline during digestion of carbohydrate arrests the absorption of carbohydrate from the intestine. The injection of morphine and adrenaline, as well as carbohydrate, into fasting animals leads to retention of sugar by the lungs.

Chemical Abstracts.

Metabolic-physiological action of insulin in phloridzin diabetes. W. Möbius (Pflüger's Archiv, 1930, **224**, 511—526; Chem. Zentr., 1930, i, 3454).—Disappearance of ketonuria, retardation of fat infiltration of the liver, and diminution of glycosuria are outstanding indications. A. A. Eldridge.

Influence of the blood on the activity of insulin. A. A. Schmidt and R. L. Saatchian (Zhur. exp. Biol. Med., 1929, **11**, 37—40).—When added to defibrinated blood insulin loses little of its activity. The insulin remains entirely in the serum. The rapid disappearance of insulin when injected intravenously is due to its absorption by the tissues.

Chemical Abstracts.

Effect of some tissues of the animal organism on the activity of insulin. A. A. Schmidt and R. L. Saatchian (Zhur. exp. Biol. Med., 1929, **11**, 42—53).—Rabbit's muscle tissue inactivates insulin very little; increasingly greater effect is exhibited by spleen, kidney, and liver tissue. The inactivation is probably due to the action of proteolytic enzymes.

Chemical Abstracts.

Difference of activity of technical insulin and of crystalline preparations in relation to primary insulin hyperglycæmia. M. Bürger and H. Kramer (Arch. exp. Path. Pharm., 1930, **156**, 1—17).—The hyperglycæmic action of commercial insulin, exhibited within 20 min. of intravenous administration to rabbits and other animals, is possessed in varying degree by each of 14 different samples of insulin. It is not a property of crystalline insulin and is still possessed by an insulin solution after it has been heated so as to become inactive in respect of its hypoglycæmic activity. It is therefore due to the presence in commercial insulin preparations of some other product apparently originating in the pancreas. W. O. Kermack.

Callicrein, a pancreatic hormone. H. Kraut (Chem.-Ztg., 1930, **54**, 849—851).—A summary of work previously abstracted (A., 1926, 1168; 1928, 798, 1057; 1930, 1069, 1624). R. K. Callow.

Quantitative differentiation of vitamins-*A* and -*D*. II. H. C. Sherman and H. K. Stiebeling (J. Biol. Chem., 1930, **88**, 683—693; cf. A., 1927, 702).—The best conditions for the determination of vitamins-*A* and -*D* when rats are used as test animals are discussed. The vitamin-*A* content of a substance is best estimated by finding the amount required to produce limited growth (3—4 g. per week) on a diet otherwise adequate, whilst the vitamin-*D* content may best be assayed by finding the amount required to produce a degree of calcification midway between the maximum and minimum obtainable respectively with abundance and in the practically complete absence of vitamin-*D*. W. O. Kermack.

Growth-promoting action of carotenoids. N. Rydbom (Biochem. Z., 1930, **227**, 482—487).—Normal growth is promoted in rats by intramuscular injection, every second day, of 0·06 mg. of carotene.

W. McCartney.

Biochemical investigations on rubrene. M. Javillier and L. Emerique (Compt. rend., 1930, **191**, 882—884).—Administration of rubrene (2·4—5 mg. per kg. daily) is without effect on rats suffering from vitamin-*A* deficiency. Larger doses of rubrene are without toxic action; 75% is excreted unchanged, and of that absorbed none can be detected spectrometrically in any tissue. T. H. Morton.

Composite nature of vitamin-*B*. M. Skarzyńska-Gutowska (Med. Doświad., 1930, **11**, 176—182).—Pigeons develop polyneuritis, with loss of weight, when fed on polished rice with the addition of either the colloidal or the crystalloidal constituents of vitamin-*B* extracts; the administration of both fractions together has a protective influence.

R. Truszkowski.

[Derangement of the resorption due to lack of vitamin-*B*.] G. Gál (Biochem. Z., 1930, **227**, 492; cf. A., 1930, 1625).—Acknowledgment of prior work of Never (Pflüger's Archiv, 1930, 787) is made. W. McCartney.

Activator *Z* and its relation to the growth factor of yeast, bios, and to the vitamins-*B*. T. Philipson (Z. physiol. Chem., 1930, **193**, 15—45).—Activator *Z* is not precipitated by the method of Kinnersley and Peters for the purification of the antineuritic factor, but the carbon treatment indicated that it could be separated into two components. The Lucas and Eastcott method gave a separation of the growth factor (bios) from the activator *Z*. The activator is soluble to the extent of 3000 *Z* units per litre in 95% alcohol. Various methods of separation were compared; the best was Chick's mercury precipitation method.

The factor *Z* was separated into two components by treatment with basic lead acetate. The two fractions are separately less active than is the original mixture. The full activity of the filtrate is restored by the addition of the portion of activator present in the precipitate, or in many cases by the addition of inositol. The evidence is not sufficient to affirm that inositol is the active component of the precipitate.

J. H. Birkinshaw.

Influence of vitamin-*D* on growth and protein metabolism. F. Goebel (Med. Doświad., 1930, **11**, 124—151).—Non-irradiated ergosterol has little effect on animals maintained on a vitamin-*D*-deficient diet, and kept in the dark, an increase in weight of 28% being observed in 2 weeks. When the rats are kept in the light, they gain 50% under the same conditions, as compared with 65% for normal control rats. The gain in weight of thyroidectomised rats during 4 weeks is 68%, and on a diet containing "vitasterol" 82%, as compared with 150% for normal animals. The rate of growth after removal of the thymus is unaffected by the administration of "vitasterol." Nitrogen retention is augmented by 6—20% by administration of 0·05—10·0 mg. of "vitasterol" daily to young rabbits; no ill effects are observed as a result of such large doses. In the case of "vitasterol"-fed rats nitrogen retention is 24% higher than that of those receiving a normal diet; the nitrogen contents of the liver, spleen, kidneys, and muscles are respectively 20, 44, 33, and 39% higher than are those of control rats, whilst for rabbits the corresponding figures are 22, 11·7, 5·2, and 11·1%. R. Truszkowski.

Antirachitic substances. X. Relation of the *iso*ergosterols to vitamin-*D*. W. M. Cox and C. E. Bills (J. Biol. Chem., 1930, **88**, 709—713).—When ergosterol is irradiated in alcoholic solution until the antirachitic activity has begun to decline a band at 248 mμ ($\varepsilon = 16{,}000$) begins to appear. This band closely resembles that characteristic of the various *iso*ergosterols, but the substance responsible for it differs from the known *iso*ergosterols in not being precipitable by digitonin. W. O. Kermack.

Further observations on the toxic effects of irradiated ergosterol. J. C. Hoyle (J. Pharm. Exp. Ther., 1930, **40**, 351—372).—When ergosterol dissolved in alcohol is irradiated two substances are formed which may produce toxic effects when administered in excess. One of these is vitamin-*D*; the second is an unknown substance which, less readily destroyed by over-irradiation than is vitamin-*D*, is chiefly responsible for the arterial lesions produced by over-dosage with ergosterol irradiated in alcohol. This substance is not readily formed when ergosterol is irradiated in oil. Excess of vitamin-*D* may result in the formation of urinary calculi and also retardation of growth. Bread and milk together protect animals against the arteriosclerosis following overdosage with ergosterol irradiated in alcohol, but bread or milk alone, or a synthetic diet modified to resemble bread and milk in composition or one poor in calcium and phosphorus, has no protective effect.

W. O. Kermack.

Action of irradiated ergosterol and the parathyroid hormone on tissue-phosphatases. W. Heymann (Biochem. Z., 1930, **227**, 1—5).—The influence of irradiated ergosterol, of irradiation by the sun, and of parathyroid hormone on the glycero- and hexosedi-phosphatase content of various organs of the rat is investigated *in vitro*. Whereas "vigantol" is without effect, irradiation with ultra-violet light in 6 of 15 experiments caused an inhibition of these enzymes. Both enzymes (of bone) are inhibited *in vitro* by parathyroid hormone. P. W. Clutterbuck.

A new nutrition factor. A. Bakke, V. Aschehoug, and C. Zbinden (Compt. rend., 1930, **191**, 1157—1159).—The addition of wheat germ to the diets of black rats causes their coats to turn silver-grey. A disease of the eye, resembling but not identical with xerophthalmia, and a derangement of the reproductive functions are also associated with the effect. The action is neutralised by whole wheat, which brings about a rapid return of the original black coat. W. O. Kermack.

Accumulation of electrolytes in plant cells. Suggested mechanism. G. E. Briggs (Proc. Roy. Soc., 1930, **B**, **107**, 248—269).—The problem of the mechanism by which cations and anions accumulate in the interior of plant cells in greater concentration than that in which they are present in the surrounding medium is treated theoretically. The suggestion is made that alternating phases in which the cell membrane is permeable to cations and then to anions would explain this accumulation.

G. F. Marrian.

Accumulation of electrolytes. II. Nature of accumulation in *Valonia*. W. J. V. Osterhout. **III. Behaviour of sodium, potassium, and ammonium in *Valonia*.** A. G. Jacques and W. J. V. Osterhout (J. Gen. Physiol., 1930, **14**, 285—300, 301—314; cf. A., 1930, 1483).—II. The concentration of potassium chloride in cell sap of *V. macrophysa* is about forty times as great as that in sea-water. It is suggested that accumulation is due to entrance of potassium hydroxide (and sodium hydroxide to a smaller extent) by virtue of a higher external thermodynamic potential. A salt is formed with a weak acid produced by the cell, and potassium chloride is produced by hydrogen chloride entering from the sea-water. Electrolyte penetration is considered to be molecular.

III. The rise in concentration of sodium and fall in that of potassium in cells of *V. macrophysa* placed in sea-water containing ammonium chloride are explained by their diffusion in accordance with the gradients of their respective thermodynamic potentials. The accumulation of ammonium chloride in cell sap is explained in a manner similar to that for potassium chloride. A. Cohen.

Kinetics of penetration. III. Equations for the exchange of ions. W. J. V. Osterhout (J. Gen. Physiol., 1930, **14**, 277—284).—Mathematical. Equations are given determining the rate of exchange of ions of the same sign between the interior of a living cell and external solution under standard conditions. A. Cohen.

Kinetics of oxygen uptake and of carbon dioxide output of pea-meal. A. Fodor, L. Frankenthal, and S. Kuk (Biochem. Z., 1930, 225, 409—416; cf. A., 1930, 964).—Addition of potassium formate to the meal as donator changes the oxygen uptake only slightly, but in presence of phosphate the carbon dioxide production by well-germinated peas sinks to about half the former value. With only slightly germinated material and in absence of phosphate, the effect on the carbon dioxide production is small. The carbon dioxide production is increased, but the oxygen uptake is unchanged in the presence of an acceptor (*e.g.*, acetaldehyde) with the donator. Potassium cyanide inhibits both processes. These effects are explained on the hypothesis that methylglyoxal (hydrate) is dehydrogenated and pyruvic acid is decarboxylated. J. H. Birkinshaw.

Seasonal change in the catalase content of conifer leaves. J. Doyle and P. O'Connor (Ann. Bot., 1930, **44**, 907—915).—Suspensions formed by grinding the leaves with water and calcium carbonate were examined manometrically for catalase content at different seasons of the year. The results confirmed the earlier finding of Doyle and Clinch (A., 1928, 1408) that the catalase content rises in winter and remains unchanged during that season. The theory of Burge (A., 1926, 541) of a close relationship between catalase content and general metabolism was not confirmed. Abnormal temperature effect was also studied. F. O. Howitt.

The rôle and significance of quinic acid in higher plants. A. Kiesel (Planta [Z. wiss. Biol.], 1930, **12**, 131—143).—Seasonal variations in the quinic acid contents of leaves of various trees are recorded. Quinic acid is probably an assimilation product, not directly derived from carbohydrates. A. G. Pollard.

Iodine-phenol for histological detection of starch. J. Kisser (Mikrochem., Emich Festschr., 1930, 175—179).—The difficulty of detecting small quantities of starch in, *e.g.*, chloroplasts is noted. A mixture of 8 parts of iodine–phenol, 4 parts of iodine–alcohol, and 1 part of water is satisfactory, in that it does not readily form an emulsion with water, and if the alcohol is replaced by glycerol the mixture is still less disturbed by the presence of water, and the refractive index of the phenol is not reduced to too great an extent. H. F. Gillbe.

Transformation of carbohydrates in the banana. I. Formation of starch. H. Belval (Chinese J. Physiol., 1930, 4, 365—372).—The leaves and fruit of the banana have been analysed in respect of their water and carbohydrate contents. In the limb of the leaves sucrose predominates, but in the nerve and especially in the petiole its place is taken by reducing sugars, presumably due to its hydrolysis as it proceeds towards the fruit. In the base of the peduncle the reducing sugars predominate, but in the upper part these tend to disappear, whilst in the very young fruit they are practically absent, being presumably converted into insoluble carbohydrates. W. O. Kermack.

Biochemical studies on the bamboo. III, V. Chemical development of shoots. D. Kamija and K. Nishioka. **IV. Chemical development of sheaths.** T. Tashima. **VII. Seasonal variation in the chemical composition of the Madake (*Phyllostachys quilioi*, F.M.).** T. Nagasawa (Chikashige Anniv. Vol., 1930, 149—159, 161—165, 167—173, 183—193).—III, V. The nodes contain total reducing sugars (pentose+hexose), cellulose, lignin, and pentosan to the extent of 12·16, 18·6, 0·7, and 23·7%, respectively. The ash content varies as the water content, and the water-soluble ash is related to the content of reducing sugars. The internode gas contains nitrogen, oxygen, and carbon dioxide, the oxygen content varying inversely with that of carbon dioxide in every stage of life. The respiration curve of the culm is similar to that of the hexosan content (not the hexose content). In slabs of internode taken from the base of the shoots, the largest amount of non-protein-nitrogen and fatty acids is found in the inside slabs along with the least amount of carbohydrate. The different slabs of the youngest internodes do not vary greatly in composition.

IV. The sheaths of the youngest portions of the shoots are richer in total nitrogen and hexoses but poorer in protein and polysaccharides than the oldest portions. The total ash content varies from 0·72 in the youngest to 0·42% in the oldest portions. The ash is rich in silica, alumina, and iron, but poor in phosphorus.

VII. The seasonal variation of hexoses and polysaccharides runs parallel with that of ash and water. Total nitrogen decreases and fat increases with age. P. G. Marshall.

Function of the mannitol in olives. R. Nuccorini [with M. Aronovskis] (Annali Chim. Appl., 1930, **20**, 535—546).—The mannitol contained in olives is formed by reduction of lævulose and contributes to the formation of oleanolic acid, from which the fatty acids of the glycerides are derived. T. H. Pope.

Physiology of the nitrogen exchange in higher plants with special reference to nitrate accumulation. W. Dittrich (Planta [Z. wiss. Biol.], 1930, **12**, 69—119).—Plants may be classified according to their capacity for accumulating nitrates in the tissues. The nitrate content of plants increases with age and varies daily with light intensity and transpiration. Leaves and roots exhibit a preferential reducing power for nitrates as compared with the stems. The sap of nitrate-accumulating plants has a lower reducing power than that of plants poor in nitrate. Nitrate-accumulating plants utilise the reserve nitrate if grown in nutrients containing carbohydrates only. The nitrate storage of sugar beet occurs in the central regions only. Optimum reducing power of the expressed plant sap is associated with p_{H} about 7·6. Nitrate-accumulating plants have more alkaline sap than others. The fate of nitrates in plant-tissues is largely controlled by the p_{H} value of the sap, and the reduction process is ascribed to enzymic activity. A. G. Pollard.

Determination of seed quality from enzyme content. M. I. Lischkevitsch (Fermentforsch., 1930, **12**, 244—261).—Barley and wheat from northerly regions had a higher catalase, amylase, and protease content than grain from lower latitudes. The difference in wheat was not so sharply defined, but the catalase content was much higher than that of barley. In peas and soya beans the geographical factor had no effect. Castor oil and hemp seeds from northern areas had a stronger lipolytic action than seeds from southern districts. J. H. Birkinshaw.

Oil and lipase-like enzyme in Para rubber seed. Y. Iwamoto (J. Soc. Chem. Ind., Japan, 1930, **33**, 409—411b).—Malayan rubber seeds yielded ether-extracted oils having acid values from 7·2 to 110·9 according to the condition of the seed. An oil extracted by light petroleum from fresh seeds had d_4^{15} 0·9234, n^{20} 1·4757, acid value 7·12, iodine value 138·8, f. p. 2°, saponif. value 189·2, Reichert–Meissl value 2·28, acetyl value 2·41, unsaponif. matter 1·62, insoluble hexabromide (fatty acids) 15·48%, solid acids (lead salt–ether method) 17·81% (m. p. 62°), liquid acids 79·99%. Linolenic, linoleic, and oleic acids were present, and the solid acids appeared to consist of stearic (70%) and palmitic acid (30%). Cold-pressing yielded 28·5% of a pale yellow sweet oil (acid value 19·7) and a second hot-pressing a further 16·7% of a brown oil. The kernels contained a lipolytic enzyme. E. Lewkowitsch.

Soluble enzymes secreted by hymenomycetes. Anti-oxygenic function of quinones. L. Lutz (Compt. rend., 1930, **191**, 880—882).—The oxidation of guaiacol and α-naphthol in cultures of *Corticium quercinum*, *Coriolus versicolor*, and *Pleurotus ostreatus*, which contain both oxidases and reductases, is prevented by the addition of benzoquinone, or less effectively by thymoquinone. In cultures of *C. quercinum* the reduction of methylene-blue is accelerated by the presence of benzoquinone. The mechanism suggested is the cyclic reduction and re-oxidation of the benzoquinone. T. H. Morton.

Carboxylic tannins. L. Reichel (Naturwiss., 1930, **18**, 952).—In order to extract carboxylic tannins in a non-polymerised form they must be isolated as salts. Vacuum-distillation of extracts at reactions equal to those of the original sources (investigated for leaves of *Quercus*, *Rosa canina*, and *Tilia*) resulted in residues which contained only small amounts of condensation products. Crystalline acetyl derivatives were obtained from oak- and lime-tannins; that from the oak had two carboxyl groups and the acetylation indicated 10—12 hydroxyl groups, corresponding with a formula of $C_{24}H_{28}O_{18}$ or $C_{28}H_{34}O_{20}$ for the tannin. Acid hydrolysis of the acetylation product resulted in the formation of ellagic acid and phlobaphen, but no sugar was detected.

F. O. Howitt.

Presence of tannins in flowers. S. Ionesco (Compt. rend., 1930, **191**, 867—868).—The presence of tannins has been demonstrated in the flowers of a large number of shrubs, trees, and herbaceous plants. The flowers, after decolorisation with 96% alcohol or acetone, show colour reactions typical of the tannins. The flowers may be divided into two groups according as they give, with iron salts, a green coloration due to catechu tannins, or a blue coloration due to tannins containing a digallic acid residue. To the first class belong the trees and shrubs, *Æsculus hippocastanum*, *Liriodendron tulipifera*, *Philadelphus coronarius*, *Pirus communis*, *Symphoricarpus racemosus*, and *Syringa vulgaris*; to the second the trees and shrubs, *Acer platanoides*, *Rhus cotinus*, and *Rosa canina*, and the herbaceous plants, *Fragaria vesca*, *Geum urbanum*, *Helianthemum glaucum*, *H. guttatum*, *H. lavandulifolium*, *Lysimachia nummularia*, *Pæonia romanica*, *Potentilla argentea*, and *P. recta*.

T. H. Morton.

Quercetin in *Magnoliaceæ* and its distribution in the plant kingdom. T. Weevers (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 778—785).—Quercetin may be isolated from the flowers of *Magnolia Yulan*, var. *Soulangiana*, but not from the leaves or stems; it is not present in the blooms of *M. stellata*. Quercetin is not the colouring matter responsible for the brown coloration observed in these flowers on freezing or on oxidation with hydrogen peroxide. During the development of *M. Yulan* from the bud to the flower, a period of marked anthocyanin production, the amount of quercetin present does not decrease, but rather shows a slight increase.

T. H. Morton.

Preparation and properties of franguloside (frangulin) from black alder bark. M. Bridel and C. Charaux (Compt. rend., 1930, **191**, 1151—1153).—Franguloside exists in the bark in a combined form, from which it may be set free by the action of an enzyme present in the bark. A yield of 2·5% may be obtained after hydrolysis by the enzyme, the small yields previously recorded representing only that portion of franguloside accidentally set free by the manipulations employed. Franguloside, $C_{21}H_{20}O_9,H_2O$, has m. p. 246° on rapid heating, m. p. 249° after changing colour at 197° on slow heating, $[\alpha]_D - 134·40°$ in 80% acetic acid. W. O. Kermack.

Capsanthin. L. Cholnoky (Magyar Chem. Fol., 1930, **36**, 11—16, 17—25; Chem. Zentr., 1930, i, 3560).—The ground pericarp (2 kg.) is percolated with light petroleum (2 litres), the extract diluted with 1 litre of ether, and left over-night in contact with 30% methyl-alcoholic potash (200 c.c.). The crystals which separate are dissolved in 2 litres of ether, the solution being repeatedly washed with water and dried with sodium sulphate. After evaporation to 500 c.c., 1·5 litres of light petroleum are added, the yield of colouring matter precipitated being 3·9 g. The product is recrystallised from methyl alcohol.

A. A. Eldridge.

***Psyllium* seed.** J. S. Hepburn and T. L. Laughlin (Amer. J. Pharm., 1930, **102**, 565—568).—One sample contained moisture 8·5%, crude fat 6·4%, insoluble ash 2·9%, soluble ash 0·2%, crude protein 17·8%, crude fibre 11·5%, nitrogen-free extractives 52·6%, pentosans 9·8%, and galactans 0·3%. The blackish-brown, acid gum extracted by hot water contained pentosan 16·4% and galactan 0·02%. It is free from starch, does not reduce Fehling's solution, and is precipitated by lead acetate or alcohol, but not by borax, ferric chloride, or copper sulphate. H. E. F. NOTTON.

Pigment of the water-melon. L. ZECHMEISTER and P. TUZSON (Ber., 1930, 63, [*B*], 2881—2883).—The fruit of *Cucumis citrullus* contains extremely little lipoid material. Xanthophyll and esterified carotenoids are absent. The pigment consists of a mixture of lycopene and carotene, separated from one another by means of their differing solubilities in light petroleum. For South Hungarian material the ratio of lycopene to carotene varies between 8 : 1 and 10 : 1. H. WREN.

Presence in edible plants of allantoin, allantoic acid, allantoinase, and uricase. R. FOSSE, A. BRUNEL, P. DE GRAEVE, P. E. THOMAS, and J. SARAZIN (Compt. rend., 1930, **191**, 1153—1155).—Allantoin is present in a large number of edible plants, including many grains, legumes, and vegetables. Allantoic acid, allantoinase, and uricase are not so widely distributed, but are not infrequently also present.
W. O. KERMACK.

Paraffins of tobacco. M. E. KURILO (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 35—42).—After treatment with cold alcohol to remove resins, the product extracted from cigarette tobacco by hot ether, light petroleum, benzene, or alcohol consists of a mixture of saturated hydrocarbons of m. p. 58—70°. Fractionation of the mixture yielded heptacosane, m. p. 59—59·5°, and hentriacontane, m. p. 67·5—68°. The constituents of tobacco described by Kissling as waxes (" Handbuch der Tabakkunde ") are most probably mixtures of hydrocarbons. The paraffin contents of cigarette tobaccos of different types are very nearly constant.
T. H. POPE.

Nicotine metabolism in the tobacco plant. G. S. ILJIN (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 81—85).—When isolated tobacco seedlings are placed in toluene vapour, profound decomposition of the nitrogenous material takes place. The amino-acids and amides decreased markedly in amount and a larger amount of ammonia was formed, liberation of carbon dioxide continuing during the whole period of the experiment but diminishing in intensity towards the end. If sufficient oxygen is supplied, the nicotine completely disappears, this process occurring more slowly if the supply of oxygen is restricted. Under these conditions, nicotine is not formed as a result of initial hydrolysis of the protein material but requires profound decomposition of the nitrogenous substances to ammonia which, by condensation with non-nitrogenous carbon compounds, gives rise to the nicotine molecule. It is probable that nicotine is a reserve form of nitrogen and that it participates in the general cycle of biological processes of the organism, its physiological function being analogous to that of asparagine. T. H. POPE.

Microanalytical tobacco determinations. III. Determination of those constituents of the ash which influence smouldering. J. BODNÁR and L. BARTA. **IV. Determination of nicotine.** J. BODNÁR and V. L. NAGY (Biochem. Z., 1930, 227, 429—451, 452—456; cf. B., 1928, 546; A., 1929, 729).—III. The capacity of tobacco to smoulder satisfactorily when being smoked depends to a large extent on the amount and composition of the ash which it yields. Micro-methods can be applied to the determination of potassium, calcium, chloride, phosphate, and sulphate in the ash from 0·5 g. of tobacco.

IV. The residue left when 10·0 c.c. of the supernatant ether–light petroleum solution is evaporated to dryness is dissolved in water (10·0 c.c.) and titrated with 0·01*N*-hydrochloric acid, methyl-red being used as indicator. W. MCCARTNEY.

Power of liberating iodine from iodides possessed by the *Phæophyceæ*. H. KYLIN (Z. physiol. Chem., 1930, 191, 200—210).—No special iodine liberator was found in extracts of *Laminaria digitata*. When the fresh leaves were placed in contact with paper containing starch and slightly acidified with aqueous acetic acid an iodine reaction was detected. In the surface cells of *Laminaria* there appears to be an iodide-oxidase, but " iodine volatilisation " happens in nature only when, owing to some change in osmotic equilibrium, iodide diffuses to the outer wall of the surface cells.
J. H. BIRKINSHAW.

Liberation of iodine from the iodiferous parts of *Bonnemaisonia asparagoides* by ultra-violet irradiation. R. LAMI (Compt. rend., 1930, **191**, 863—865).—When the iodiferous parts of *B. asparagoides* are irradiated with ultra-violet light, iodine diffuses out into the surrounding water. It is suggested that this is due rather to direct liberation of loosely bound iodine than to its liberation by acid diffusing from the vacuoles, following necrosis caused by the irradiation. T. H. MORTON.

Influence of inorganic ions on the properties of seeds. I. Crystal-polyamphion theory of gels and the crystal-polyamphion-emulsoid theory of biological phenomena. V. KURBATOV. **II. Changes in p_H and p_{Cl} during the soaking of seeds in solutions of different ionic composition.** S. A. GLÜCKMANN (Protoplasma, 1930, 9, 34—65, 66—96).—I. A theoretical discussion.

II. Seeds soaked in aqueous solutions tend to bring the p_H value of the liquid to a definite point, viz., 7·0 in water, a lower value in solutions of univalent salts, and still lower with bivalent salts. The p_H value of solutions in contact with seeds changes sharply in a few hours and subsequently remains constant, being independent of temperature or the extent of swelling of the seeds. During soaking chloride ions are leached from seeds at a rate varying with the nature of the salts in solution, being greatest for salt solutions of univalent metals, followed in order by bi- and tervalent metals. The rates of swelling of the seeds in various solutions were in the order water>univalent>bivalent>tervalent salts. Effects of soaking are irreversible and may be directly continued in subsequent soakings. The increased rate of germination following soaking in water is retarded by the use of salt solutions to an amount increasing with the concentrations and with the valency of the metal. The yield of plants was not affected by the soaking of the seed. A. G. POLLARD.

Calcium oxalate crystals in the seed coat of *Fumaria officinalis*, L. J. GREGER (Planta [Z. wiss. Biol.], 1930, **12**, 49—52).—Contrary to general opinion, monoclinic crystals of calcium oxalate are formed in the outer integument of the seed coat of *F. officinalis* in the early stages of development and are subsequently absorbed. A. G. POLLARD.

Precipitation of calcium oxalate in plant cells. A. NIETHAMMER (Planta [Z. wiss. Biol.], 1930, **12**, 53—59).—Calcium oxalate crystals are formed in fruit cells and are reabsorbed as the fruit ripens. The formation of calcium oxalate is not merely the deposition of unutilisable material, but represents a temporary storage of reserve material in excess of the metabolic requirements of the plant. A. G. POLLARD.

Biochemistry and histochemistry of fruits and seeds. II. A. NIETHAMMER (Biochem. Z., 1930, **227**, 462—471; cf. A., 1930, 964).—In unripe fruits and seeds deposits of calcium oxalate, which in most cases disappear as ripening proceeds, are often found. The acetaldehyde content of most fruits increases with increasing ripeness, the increases in the case of dry seeds and fruits being maintained only until the germinating power has reached its maximum. W. MCCARTNEY.

Determination of the acid–base balance in the ash of plants. D. E. FREAR (J. Biol. Chem., 1930, **88**, 675—681).—The finely-powdered plant material (2 g.) is wetted with 10 c.c. of water and mixed with 25 c.c. of 25% magnesium nitrate solution. After drying the mixture is ignited first at 250° and then at 500°. The ash is mixed with 10 c.c. of water and 60 c.c. of *N*-nitric acid and kept for 3 hrs. just below the b. p. The excess of nitric acid is titrated with standard alkali. A blank test is made using 1 g. of sugar in the place of plant material. W. O. KERMACK.

Sugar content [of plants] and the action of potassium. J. SZOLNOKI (Wein u. Rebe, 1930, **11** 583—584; Chem. Zentr., 1930, i, 3449).—The effect of potassium on the formation and storage of sugar is regarded as being photo-electric in character. A. A. ELDRIDGE.

Mechanism of the separation of silica gels in plant cells. H. PFEIFFER (Protoplasma, 1930, **9**, 120—127; Chem. Zentr., 1930, i, 3447).—Dehydration of adsorbed hydrosols is indicated. A. A. ELDRIDGE.

Stempell's detection of mitogenetic radiation by means of Liesegang rings. G. VAN ITERSON, jun., and W. H. VAN DER HEIDE (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 702—706).—The claim of Stempell (Biol. Zentr., 1930, **50**, 248) that there exists a residual mitogenetic radiation (cf. Siebert, A., 1930, 966), proceeding from minced onion roots, capable of passing through quartz or uviol glass and of causing distortion in growing Liesegang rings, is not confirmed. T. H. MORTON.

Parasitic behaviour of *Pseudomonas tabaci* (Wolf and Foster) causing "wildfire" in tobacco. K. BÖNING (Z. Parasitenk. [Z. wiss. Biol.], 1930, **2**, 645—755).—The sensitiveness of tobacco plants to "wildfire" is largely dependent on nutritional factors. The greatest sensitiveness results from insufficient supplies of potash and excessive nitrogen. Phosphate deficiency increases the sensitiveness to infection, but generous phosphatic manuring has no very marked beneficial effect. Liming did not affect the incidence of disease to any appreciable extent. A. G. POLLARD.

Rust diseases of cereals. III. Copper adsorption of oat-smut spores (*Ustilago avenæ* [Pers.], Jens). A. TERÉNYI (Z. physiol. Chem., 1930, **192**, 274—280; cf. A., 1930, 648).—Oat-smut spores adsorb up to 50% more copper from copper sulphate, acetate, and cuprammonium sulphate solutions than wheat-smut spores, but are less sensitive, since they require 3% of adsorbed copper to prevent germination as against 0·5% for the wheat fungus. Oat-smut spores treated for 15 min. with copper solution are again capable of germination on extraction with 0·5% hydrochloric acid; if the copper treatment is continued for 24 hrs. the hydrochloric acid does not restore the germinating power, since the copper has penetrated to the interior of the spores. Cuprammonium sulphate renders the spores of both species incapable of germination. J. H. BIRKINSHAW.

Resistance to poisons of desiccated plant tissues. W. W. ALLEN (Ann. Bot., 1930, **44**, 1001—1009).—Moss (*Mnium hornum*), when thoroughly desiccated by drying in air, can withstand several hours' immersion in absolute alcohol, acetone, ether, or xylene, being able to grow when transferred directly to water and then planted. Such treatment with chloroform or dilute alcohol, however, proved fatal. F. O. HOWITT.

Fine structure of wood tracheids according to the examination of fossil woods. E. OPFERMANN and G. RUTZ (Papier-Fabr., 1930, **28**, 780—786).—Lignite (fossil wood) is discussed with reference to its importance in the theory of coal formation. The fibrous constituents of lignite have been isolated and investigated microscopically. Tracheids of coniferous woods were present to the exclusion of deciduous woods. Many of the tracheids presented a similar appearance to that of swollen ramie fibre. Swelling by means of cuprammonium caused the tracheids to assume a spiral formation similar to that shown by cotton under the same conditions, the middle lamella of the wood acting similarly to the cuticle of cotton. T. T. POTTS.

Structure of lignite. F. LUFT (Papier-Fabr., 1930, **28**, 787—791).—*X*-Ray spectrographic analysis of the fossil wood tracheids referred to in the preceding abstract shows that interference figures similar to those of native cellulose, and not of the ordinary woods, are obtained. The spiral structure of the middle lamella, shown to be an early condition of the tracheids, appears to be absent in the tracheids as examined. The lamella appears to consist primarily of a number of parallel layers, and a similar condition is shown to be naturally present in the spurs of *Opuntia papyracantha*. T. T. POTTS.

Technique of microchemical reactions. G. C. VAN WALSEM (Z. wiss. Mikros., 1930, **47**, 81—82; Chem. Zentr., 1930, i, 3703—3704).—The staining and microscopical examination of urinary sediments are described. A. A. ELDRIDGE.

Staining of fat [for microscopical analysis]. W. Gross (Z. wiss. Mikros., 1930, 47, 64—68; Chem. Zentr., 1930, i, 3704).

Determination of uric acid in urine by means of its absorption spectrum. J. Eisenbrand (Arch. Pharm., 1930, **268**, 520—536).—In solutions of p_H 5—6, uric acid shows a very intense absorption band at 289 mμ (ε=11,800) and is responsible for more than half the total absorption of urine at this wavelength. An expression is given by which the concentration of uric acid solutions may be derived from absorption data, and no other substance absorbing in this region is precipitable from urine by ammonium chloride. Precipitation followed by optical determination offers, however, no advantage over the original method of Hopkins, since the chief faults of the latter lie in the difficulty of filtering the precipitate, which consists almost entirely of uric acid, and not, as has been supposed, of ammonium urate, and in the uncertainty as to the amount of uric acid remaining in the filtrate (cf. Jung, A., 1922, i, 1070). An improved method is based on the fact that the absorption spectrum of uric acid changes considerably with the p_H, the greatest change in intensity being observed at about 300 mμ. Two equal quantities of 2—5 c.c. of urine with 10 c.c. of 0·1N-hydrochloric acid and 0·1N-sodium hydroxide, respectively, are each diluted to 100 c.c. and the intensities of absorption (E_1 and E_2, respectively) for the line Hg_{303} are compared by means of Scheibe's spectrophotometer. The concentration of uric acid in mg. per 100 c.c. is given by $2{\cdot}58(E_2-E_1)$, the absorptions being calculated for 1 c.c. of undiluted urine. The differences between the results obtained by this method and by Hopkins' method (without correction for the filtrate) vary between 20·6 mg. and 3·1 mg. per 100 c.c. This apparent variation in solubility is not attributed to p_H variations, but to the formation in certain cases of colloidal solutions of uric acid, which may easily be obtained at p_H 4—5, even in the absence of organic protectives. The new determination can be completed in 30 min., or, using photo-electric apparatus, in 6 min.

H. E. F. Notton.

Determination of uric acid in urine. D. Ganassini (Arch. Ist. Biochim. Ital., 1930, 2, 505—508).—To obviate a possible slight loss of uric acid and also the use of potassium iodide and silver nitrate, the Salkowski–Ludwig reagent employed in the author's method (A., 1914, ii, 823) may be replaced by zinc sulphate solution, followed by a slight excess of sodium carbonate, the uric acid being thus precipitated as basic zinc urate. This is dissolved in dilute hydrochloric acid and the zinc precipitated as phosphate by adding disodium hydrogen phosphate; the uric acid dissolves as neutral sodium urate and is determined in the filtrate by titration with 0·1N-iodine, indigo-carmine being used as indicator.

T. H. Pope.

Colorimetric determination of the p_H of urine. V. C. Myers and E. Muntwyler (J. Lab. Clin. Med., 1930, **15**, 752—755). Chemical Abstracts.

Glass light filter for Folin's new micro-determination of blood-sugar. H. Tauber (J. Lab. Clin. Med., 1930, **15**, 766—767).—A yellow glass filter is employed. Chemical Abstracts.

Tests for madar juice (*Calotropis gigantea*) and for snake venom. D. N. Chatterji (Analyst, 1930, **55**, 683—684).—The crude chemical characteristics of extracts of the juice are described. Snake venom is detected by its toxicity to frogs.

D. G. Hewer.

Gravimetric methods in biochemistry. II. Determination of potassium, using the torsion balance. L. Jendrassik and P. Petrás (Biochem. Z., 1930, **226**, 381—386).—For the determination of potassium in urine and in liquids of similar potassium content the metal is precipitated as cobaltinitrite, which is weighed on a torsion balance. Ammonia must be removed from urine before precipitation and if much protein is present it should be removed first by precipitation with lead acetate. W. McCartney.

Determination of iron in biological material. R. Hill (Proc. Roy. Soc., 1930, B, **107**, 205—214).—2 : 2′-Dipyridyl gives with ferrous salts, or with ferric salts in the presence of a reducing agent, a red colour over the p_H range 3·5—8·5. The presence of other metals, unless in great excess, does not influence the colour. The colour is adsorbed by insoluble proteins, but not by vegetable fibres. Adsorption by proteins, however, is small in the presence of sulphur dioxide and sodium acetate, or of 30% ethyl alcohol. Iron can be determined in biological material without preliminary ashing in the following way. 2 : 2′-Dipyridyl is added to a suspension of the substance in acetate buffer in the presence of sulphur dioxide and sodium hyposulphite. The mixture is filtered and the coloured filtrate is matched against a series of iron–2 : 2-dipyridyl standards. The iron in baker's yeast and egg-yolk was shown to be in the ferric state. 2 : 2′-Dipyridyl inhibits the catalytic action of iron but not of copper on the oxidation of cysteine.

G. F. Marrian.

Colorimetric determination of small amounts of arsenic in biological material. E. H. Maechling and F. B. Flinn (J. Lab. Clin. Med., 1930, **15**, 779—782).—The solution containing arsenic is treated with an acidified solution of ammonium molybdate which has previously been reduced by means of hydrazine sulphate. Chemical Abstracts.

Determination of iodine in organic products. G. Pfeiffer (Biochem. Z., 1930, **228**, 146—153).—Further details and modifications of the author's method are given, the combustion being now carried out in a heated quartz tube in presence of a platinum catalyst (cf. A., 1928, 928; 1929, 110, 1204).

P. W. Clutterbuck.

Can the formula of Arrhenius be used in biology? J. Bělehrádek (Protoplasma, 1928, 5, 310—318).—It is concluded that Arrhenius' law cannot be applied to heterogeneous systems. Changes in μ for biological reactions with changes in temperature are attributed to changes in the viscosity of the protoplasm. Chemical Abstracts.