

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1930.

General, Physical, and Inorganic Chemistry.

Spectra of gases lighted with strong electrical discharges. E. O. HULBURT (Physical Rev., 1930, [ii], 36, 13—15).—Hydrogen, helium, nitrogen, and oxygen were investigated under excitation by a 15,000-volt transformer or by a 0.002- or a 1-microfarad condenser, and the resulting spectra were photographed. With increasing strength of discharge the Balmer lines of hydrogen finally disappeared, and for each gas a continuous spectrum was ultimately obtained, alike for all the gases.

N. M. BLIGH.

Excitation processes in the hollow cathode discharge. R. A. SAWYER (Physical Rev., 1930, [ii], 36, 44—50; cf. Paschen, A., 1928, 97; Takahashi, A., 1929, 1350).—Theoretical. Available spectroscopic data are examined to determine the processes occurring when the negative glow in a hollow cathode discharge in a rare gas is used for the excitation of metallic spark spectra. Only those processes occur in which the metal can be excited to some term in the spark spectrum with small gain or loss of kinetic energy. Metals of high m. p., or those which sputter poorly cathodically, enter the discharge in helium in the normal state or in a low metastable state of the atom; for metals of low b. p. appreciable numbers of metallic ions enter the reactions. The conditions which determine the results are discussed.

N. M. BLIGH.

Experimental evidence for the existence of quadrupole radiation. R. FRERICHS and J. S. CAMPBELL (Physical Rev., 1930, [ii], 36, 151—152).—The transversal Zeeman effect of the forbidden green auroral line λ 5577 Å. was photographed, and the line was found to be resolved into four components, indicating that the line is quadrupole radiation, in agreement with the theory of Rubinowicz (cf. this vol., 653).

N. M. BLIGH.

Width of spectral lines excited by electron collision. U. MENNICKE (Z. Physik, 1930, 63, 584—589).—The effect of alteration of current density and excitation potential on the width of spectral lines excited by electron collision was investigated. For the mercury resonance line 2537 Å. the width did not change within a velocity range of the excitation potential up to 600 volts, and for current densities up to 5 amp./sq. cm. It is to be expected that other lines will behave similarly. The facts thus displayed were used in the construction of a primary light source for resonance radiation experiments.

A. J. MEE.

Spectra in the extreme ultra-violet. E. EKEFORS (Physikal. Z., 1930, 31, 737—738).—A vacuum grating spectrograph is described; the grating was ruled on glass with 1183 lines per mm. The use of glass gratings in the extreme ultra-violet is discussed. The spectra of calcium, aluminium between 75 and 160 Å., oxygen at 834 Å., and the *PP'* groups of C III at 1175 Å. have been experimentally determined and the results are discussed.

W. R. ANGUS.

Improved quartz spectrograph. C. LEISS (Z. Physik, 1930, 63, 287—290).—A quartz spectrograph is described in which the wave-length scale can be projected by means of an objective directly on to the plate of the spectrograph and thus photographed, thereby eliminating the present unsatisfactory method of placing the scale in direct contact with the plate before photographing it. The new method can also be applied to the quantitative observation of the fluorescence spectrum on a uranium-glass plate.

H. A. JAHN.

Influence of self-absorption on measurements of the intensities of spectral lines. R. MINKOWSKI (Z. Physik, 1930, 63, 188—197).—Theoretical. It is shown that the effect of self-absorption on the relative intensity of emission lines in gases cannot be eliminated by working at low pressures and with thin layers of the gas as is commonly supposed, since the intensity of the emission and the amount of self-absorption are related. In the case of flames and discharge tubes it is shown that the amount of self-absorption depends primarily on the width of the emission line, and the necessary relation between the strength of the line and its width for negligible effect of self-absorption is deduced. It is deduced that at the Bunsen flame temperature 5300 Å., and at the oxyhydrogen flame temperature 4400 Å., are the limits of wave-length below which the true intensity ratio cannot be obtained. The work of Füchtbauer and Wolff (this vol., 3) on the intensity ratio of the second doublet of the principal series of caesium is criticised. The difficulty of measuring the true intensity ratio with discharges at very low pressure is mentioned; the more rational way consists in measurements at higher pressures, the self-absorption being measured and corrected for.

H. A. JAHN.

Incomplete Paschen-Back effect. J. B. GREEN (Physical Rev., 1930, [ii], 36, 157—160).—Theoretical. Darwin's method for the calculation of the Zeeman effect (cf. A., 1927, 707) is applied to the marked discrepancy between the old quantum theory and

experiment for the copper ${}^2P^2D$ and the magnesium and beryllium ${}^3P^3S$ multiplets, and the calculated positions and intensities of lines are in good agreement with experiment. The distorted Zeeman patterns of ${}^3P^3D$ of magnesium and ${}^2P^2D$ of sodium are attributed to the action of the magnetic field on 3P and 2P separations.

N. M. BLIGH.

Interpretation of molecular spectra. V. Excited levels of molecules with two like nuclei (H_2 , He_2 , Li_2 , N_2^+ , N_2 . . .). F. HUND (Z. Physik, 1930, 63, 719—751).—Diatomic molecular ground levels may be specified by the Hund-Mullikan or Lennard-Jones method, but excited levels are best determined by a combination of the two. The multiplicity of terms for small nuclear distances is determined from Mullikan's scheme, and for large nuclear distances from Lennard-Jones' scheme. Rules are given for interpolating between these limits. A first approximation to the actual terms of a diatomic molecule with like nuclei is obtained from a study of an optical electron moving in a cylindrically symmetrical field superposed on the field due to the ground state of the molecular ion. The conceptions of chemical binding and of promoted electrons fall naturally into this scheme. Electron terms deduced for H_2 , He_2 , Li_2 , and N_2^+ correspond with empirical values. Nitrogen molecular levels are only partly interpreted.

A. B. D. CASSIE.

Resonance ($B-A$) band system of the hydrogen molecule. H. H. HYMAN (Physical Rev., 1930, [ii], 36, 187—206).—A vacuum spectrograph is described. The hydrogen bands in the extreme ultra-violet were photographed; frequencies and intensities, and quantum assignments of lines in 68 bands, are tabulated and discussed. The ionisation potential of H_2 is 15.34 volts. The value of B_1 is in agreement with that calculated by Birge and Jeppesen from the Raman effect (cf. this vol., 509), but that for B_0 is 0.27% lower, pointing to an irregularity in the moment of inertia of hydrogen in the $v=0$ state of the normal electronic level.

N. M. BLIGH.

Glow discharge in hydrogen. R. D. RUSK (Phil. Mag., 1930, [vii], 10, 244—248).—Measurements of the space potential in a hydrogen discharge tube were extended to the region behind the hot filament away from the anode. It is concluded from the results that not only the glow is due to resonance of neutral molecules and excited by radiation, as has been suggested, but also that electrons accelerated into the region concerned, by producing ionisation and excitation, are probably more responsible for the effect.

W. GOOD.

Intensities in the spectra of diatomic molecules in uncoupling of the electronic orbital impulses. R. DE L. KRONIG and Y. FUJIOKA (Z. Physik, 1930, 63, 168—174).—Theoretical. The intensity relations in the spectra of diatomic molecules are deduced by a perturbation method for the cases where the orbital impulse of the electrons is no longer quantised along the line joining the two nuclei owing to the rapid rotation of the molecule (cf. Weizel, A., 1929, 363). The calculations are made for the special case that

arises in the theoretical treatment of the observed He_2 bands (cf. following abstract).

H. A. JAHN.

Intensities in He_2 bands as affected by uncoupling of the orbital impulse of the electrons. Y. FUJIOKA (Z. Physik, 1930, 63, 175—187).—A quantitative investigation of the intensities in a series of bands belonging to the singlet and triplet systems of He_2 is described, and the wave-lengths and intensities of the observed transitions are tabulated. By means of the theory of Kronig and Fujioka (see preceding abstract) the relative intensities of the P , Q , and R branches of the different bands are calculated, and plotted against the rotational quantum number K . The curves obtained by consideration of the perturbation arising from the uncoupling of the electronic orbital impulses in the initial state are shown to be in good agreement with the experimental values.

H. A. JAHN.

Lithium-like spectra of carbon, nitrogen, and oxygen, C IV, N V, and O VI. B. EDLÉN and A. ERICSON (Z. Physik, 1930, 64, 64—74).—The spectra of carbon, nitrogen, and oxygen have been examined in the extreme ultra-violet, using the vacuum spark method. The series of lithium-like doublets was obtained. For the fundamental term $2^2S_{0.5}$, for the different elements, the following values were obtained: C IV, 520, 220; N V, 789, 591; O VI, 1,114, 206. These correspond with ionisation potentials of 64.19, 97.428, and 137.482 volts, respectively. The term values for the complete series for Li I, Be II, B III, C IV, N V, and O VI are compared.

A. J. MEE.

Band spectrum of ozone in the visible and photographic infra-red. O. R. WULF (Proc. Nat. Acad. Sci., 1930, 16, 507—511; cf. Colange, A., 1927, 808).—The absorption of ozone was photographed in a tube 33 m. long, using light from a carbon arc. Dark diffuse absorption strips extend from 6100 to 4300 Å. Assuming the strong peak at 9.7 μ found by Ladenburg and Lehmann (A., 1906, ii, 509) as a fundamental, the bands at 4.7 and 3.5 μ are first and second overtones. The dissociation of O_3 into normal O_2 and normal O requires 1.3 volts. A series of 10 bands in the near infra-red was found. The bands are interpreted, and the diffuseness and influence of temperature on the absorption are discussed.

N. M. BLIGH.

Red radiation of oxygen in the night sky. L. A. SOMMER (Naturwiss., 1930, 18, 752).—It has been shown on the grounds of quantum theory that the transitions of O I, $2p^3P_{210} \rightarrow 2p^1D_2$ and $2p^3P_{210} \rightarrow 2p^1S_0$, should give rise respectively to lines at approximately λ 6380 and 2970 Å. Both lines have been found by previous investigators. Examination of the red radiation in the night sky has revealed two lines at 6300 and 6363 Å. which are due respectively to the transitions $2p^3P_2 \rightarrow 2p^1D_2$ and $2p^3P_1 \rightarrow 2p^1D_2$ of O I. These lines must be interpreted as the radiation of a quadrupole moment. By the detection of this first combination between singlet and triplet terms it is possible to link up the singlet system of O I energetically with the already known system of triplets and quintuplets. The interpretation of the

green auroral lines is confirmed and their excitation potential is given as 4.17 volts. The convergence position of the Runge-Lyman bands occurs at 7.05 volts and the excitation potential of the $2p^1D_2$ term is 1.96 volts; therefore the dissociation energy of the oxygen molecule may be determined from optical data and amounts to 5.09 volts. W. R. ANGUS.

Oxygen spectrum, O I. F. PASCHEN (Naturwiss., 1930, 18, 752).—The use of a three-prism spectrometer has revealed lines in the O I spectrum at 6300 and 6364 Å. corresponding with the transitions $2p^3P_2 \rightarrow 2p^1D_2$ and $2p^3P_1 \rightarrow 2p^1D_2$, respectively, and the corresponding wave-numbers are in complete agreement with the values calculated from the data of Frerichs in the Schumann region. A diffuse line corresponding with the transition $2p^3P_0 \rightarrow 2p^1D_2$ has been observed at 6391 Å. These results agree with the values found by Sommer from observations of the red radiation in the night sky (preceding abstract). Certain stellar nebulae exhibit these lines also. W. R. ANGUS.

Zeeman effect in neon. K. MURAKAWA and T. IWAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 283—291).—The Zeeman effect in neon has been examined and the g values of seven of the twelve s , s' , d , and d' (Paschen's notation) terms, hitherto unknown, have been determined; 32 other terms were redetermined with satisfactory agreement with previous results. Those of s and p terms appear to be independent of the field intensity, but not those of d terms, and the g values for them have been extrapolated to zero field. A term scheme and photographs of the Zeeman effect from $\lambda 5080$ to $\lambda 8377$ for various intensities of field are given. The Paschen-Back effect was clear for a field of 10,000 gauss in the triplet p^3S-d^3P . C. A. SILBERRAD.

Predissociation of the phosphorus (P_2) molecule. G. HERZBERG (Nature, 1930, 126, 239—240).—Certain peculiarities of the emission band spectra of the phosphorus molecule indicate a predissociation of the P_2 molecule similar to that obtained with sulphur. L. S. THEOBALD.

Intensity relation of resonance and intercombination lines of calcium. W. BLEEKER (Z. Physik, 1930, 63, 760—761).—The intensity relation of resonance and intercombination lines was determined with the aid of filters. Reversal effects were eliminated by varying the current intensity and the salt concentration. The ratio of the intensity of the 4227 Å. resonance line to the 6573 Å. intercombination line tends towards 41:1 for infinitely small currents and concentrations. A. B. D. CASSIE.

Resonance radiation of manganese vapour. J. FRIDRICHSON (Z. Physik, 1930, 64, 43—47).—The fluorescence in saturated manganese vapour at 700—900° was examined, using the light of the manganese spark for excitation. The triplets $1S-2P$ and $1S-2P'$ of the manganese spectrum correspond with the resonance lines. With rise of temperature, and consequently less dense vapour, the triplet $1S-2P'$ becomes much more intense, whereas at a lower temperature only the triplet $1S-2P$ is found. The resonance lines found are in agreement with Catalan's

analysis of the manganese spectrum, and indicate that $1S$ is the lowest state of the manganese atom. A. J. MEE.

Spark spectrum of cobalt, Co II. J. H. FINDLAY (Physical Rev., 1930, [ii], 36, 5—12).—The analysis of Meggers (cf. A., 1928, 807) is extended with the aid of the Zeeman effect, and full results are tabulated. The former classification of the 5F and $^5D^1$ terms should be interchanged except for 5F_5 ; the new $^5F^5F^0$ and $^5F^5D^0$ multiplets show irregular intensities. The strongest lines in these multiplets are respectively $^5F_n^5F_{n-1}^0$ and $^5F_n^5D_{n-1}^0$. The former 3D terms should be d^7s^5P and the 3P , $^3D^1$, and 3F should be partly $d^7p^5P^0$ and $^5D^0$. Additional terms d^7s^3F , $d^7p^3D^0$, $^3F^0$, $^3G^0$, $^5S^0$, $^5P^0$, $^5D^0$, and the lowest terms d^8s^3F have been found. The limit of the $4s^2F_5$ series gives, with Russell's correction, an ionisation potential of 16.7 and 17.1 volts from $3d^74s$ to $3d^7$ and $3d^8$ to $3d^7$, respectively, in agreement with Russell's prediction (cf. A., 1928, 682).

N. M. BLIGH.
Variations in relative intensities in the resonance spectrum of selenium. L. NATANSON (Compt. rend., 1930, 191, 294—296).—The intensities of the components of five doublets in a resonance series of Se, molecules at 600°, excited by the mercury line 4047 Å., have been measured. With one exception attributed to strong absorption, increased pressure causes the intensity of the component of greater wave-length to increase relatively to that of lesser, similarly to, but to a smaller degree than, with sulphur (cf. Swings, this vol., 650). Other relative variations in intensities observed seem explicable only by the dependence on pressure of the probabilities of transitions between different levels of rotation as well as of vibration. Comparison of the results obtained with varying thickness of vapour indicates some analogy between the distribution of vibration states and that of velocities of thermal agitation. C. A. SILBERRAD.

Spark spectra of silver and palladium (Ag II and Pd II)—an extension. H. A. BLAIR (Physical Rev., 1930, [ii], 36, 173—186; cf. Shenstone, A., 1928, 450, 930).—An unsuccessful attempt was made to excite the $4f$ electron spectrum of Ag II in the Schüler tube with helium. New terms and about 20 new lines are tabulated. The $4d^86s$ and $5d$ configurations of Pd II were extended by about 40 terms, using the same method. A complete list of lines arising from the high levels is given. N. M. BLIGH.

Structure of the absorption bands of tellurium. A. PRZEBORSKI (Z. Physik, 1930, 63, 280—286).—The fine structure of the absorption bands of tellurium vapour is investigated, and two series of lines in the regions 5393—5406 Å. and 5357—5368 Å. have been measured and their convergence has been determined. The moment of inertia of the tellurium molecule is thereby calculated to be $J=8.63 \times 10^{-38}$ g.-cm.² and the distance between the atoms as 2.87×10^{-8} cm., in agreement with the distance calculated from X-ray investigation of solid tellurium. This distance and the value of J differ little from the values found for the iodine molecule by Kratzer and Sudholt (A., 1925, ii, 839). H. A. JAHN.

Transition probabilities in the two first doublets of the principal series of caesium. R. MINKOWSKI and W. MÜHLENBRUCH (*Z. Physik*, 1930, **63**, 198—209).—From measurements of the magnetic rotation of the plane of polarisation near the lines the ratio of the intensities of the lines in the first doublet of the caesium principal series was found to be 2.1 ± 0.2 , and in the second doublet 4.27 ± 0.12 . The ratio of the total intensity of the first doublet to that of the second was 69 ± 10 . The absolute values of the intensities for the first doublet were 0.32 ($1S-2P_{1/2}$) and 0.66 ($1S-2P_{3/2}$) and for the second doublet 0.00269 ($1S-3P_{1/2}$) and 0.0115 ($1S-3P_{3/2}$). The measurements were made at a series of temperatures from 374.2° to 592.4° Abs. in the saturated vapour in a vacuum. The optical results agree with the vapour-pressure measurements of Kröner and Hackspill made at higher temperatures, and from these results a value of $l = (18,200 - 2.86T)$ g.-cal. is deduced for the heat of vaporisation of caesium within the temperature range $455-589^\circ$ Abs.

H. A. JAHN.

Spectrum of the tungsten mercury arc. W. E. FORSYTHE and M. A. EASLEY (*Physical Rev.*, 1930, [ii], **36**, 150—151).—The behaviour of the absorption bands for the region 4000—2100 Å. when the pressure of the mercury vapour is increased by external heating in a mercury arc lamp between tungsten electrodes is described. The absorption spectrum is compared with that of mercury in a separate quartz absorption cell.

N. M. BLYGH.

Measurement of capacity for reflexion of glowing tungsten in the ultra-violet part of the spectrum. E. SPILLER (*Z. Physik*, 1930, **64**, 39—42).—The relative intensities of emission at different wave-lengths from a lamp with a tungsten filament heated to 2873° Abs. were found, using a special microphotometer. The emission departs from black body radiation. The energy distribution was measured over a wave-length range of 400—340 μ . The values of the emission coefficient for wave-lengths from 436 to 270 μ for a filament at 2100° Abs. are tabulated.

A. J. MEE.

Structure of the band from 2482.07 to 2476.06 Å. in the mercury spectrum. J. BRZOWSKA (*Z. Physik*, 1930, **63**, 577—583).—The emission spectrum of mercury in the range 2482—2449 Å. has been investigated with greater dispersion than before. Two new bands discovered at wave-lengths 2449.5 and 2458.0 Å. form a group with previously discovered bands. The bands from 2482.07 to 2476.06 Å. were fully resolved and the wave-lengths of the single lines accurately measured. The bands appear to be the null branch of a rotation band.

A. J. MEE.

Arc spectrum of mercury Hg I. F. PASCHEN (*Ann. Physik*, 1930, [v], **6**, 47—49).—The arc spectrum of mercury has been examined, but no proof of the presence of a new term $3^3P_{1,0}$, which would be required by recent work on the subject, could be found.

A. J. MEE.

Absorption and collision broadening of the mercury resonance line. M. W. ZEMANSKY (*Physical Rev.*, 1930, [ii], **36**, 219—238).—The frequency distribution of the radiation from a mercury

resonance lamp, the absorption coefficient in mercury vapour of the resonance line, and ratio of emission to absorption line breadth are investigated theoretically, and results compared with experimental data. A theoretical expression is obtained for the absorption coefficient when collision broadening is superimposed on Doppler broadening, and is evaluated for different values of the frequency, Lorentz collision breadth, and Doppler breadth. From experimental values of the absorption of mercury vapour in the presence of a number of gases the Lorentz collision breadth is found as a function of the pressure of each gas, and, when plotted against pressure, gives the effective broadening radius of each molecule, which is found to be proportional to the square root of the molecular diamagnetic susceptibility. Hence, from the Langevin theory, the effective broadening area of a molecule varies as the product of the number of outer electrons and the mean square radius of all the electronic orbits.

N. M. BLYGH.

Spectra of doubly- and trebly-ionised lead. S. SMITH (*Physical Rev.*, 1930, [ii], **36**, 1—4; cf. *A.*, 1929, 1119; Rao, *A.*, 1928, 1067).—Seventeen new lines are classified in the spectrum of Pb III arising from three new singlet terms, $6s7s^1S_0$, $6s7p^1P_1$, and $6s7d^1D_2$. Certain discrepancies between the classification of terms and that of Rao (cf. this vol., 390) are discussed. Classifications of lines in the spectrum of Pb IV (cf. Carroll, *A.*, 1926, 214; Rao, this vol., 511) are discussed.

N. M. BLYGH.

Search for the source of dielectric polarisation. R. D. BENNETT (*Physical Rev.*, 1930, [ii], **36**, 65—70; cf. Hengstenberg, this vol., 19).—A theory of the distortion of a polar cubic lattice by electric stress is derived, and the effect of the distortion on the intensity of X-ray reflexion is calculated. Measurements of change in intensity of reflected X-rays in the 4th and 5th orders for rock salt and the 5th order for sylvine indicate that the polarisation is probably not due to motion of the ions as units.

N. M. BLYGH.

Breadth of Compton modified line. J. W. M. DU MOND (*Physical Rev.*, 1930, [ii], **36**, 146—147).—Previous investigations on the Compton line from molybdenum $K\alpha_1, K\alpha_2$ scattered by beryllium (cf. *A.*, 1929, 747) are considered in relation to the work of Ross and Clark on the shifted line in the Compton effect for antimony $K\alpha_1, K\alpha_2$ scattered from beryllium and results in the two cases are shown to be consistent.

N. M. BLYGH.

X-Ray spectra and chemical combination. G. B. DEODHAR (*Nature*, 1930, **126**, 205).—The line of wave-length 5043 X (probably the $K\beta_3$ line) is emitted by certain sulphur compounds but not by pure sulphur. The sulphates of the alkali metals, of silver and mercury, the sulphides of sodium, potassium, strontium, barium, and cadmium give an intense $K\beta_3$ line, but not those of copper, silver, magnesium, zinc, mercury, lead, and molybdenum. The existence of a new type of X-ray line arising from transitions within a molecule is suggested.

L. S. THEOBALD.

Simultaneous electronic transitions in X-ray spectra. M. WOLF (*Nature*, 1930, **126**, 205).—A fine structure of the X-ray absorption edges of zinc

has been observed when zinc foil was used as absorbing screen (cf. Suckichi, *ibid.*, 125, 509).

L. S. THEOBALD.

Fine structure of the K -radiation of the lighter elements. L. Y. FAUST (Physical Rev., 1930, [ii], 36, 161—172; cf. Bazzoni and others, A., 1929, 630).—Using an improved form of Weatherby's vacuum spectrograph (cf. A., 1929, 123) and a line grating on glass, photographs were obtained of soft X -radiations from beryllium, boron, oxygen, carbon, and tungsten. On analysis with a thermo-electric densitometer these elements were found, except for oxygen and tungsten, to contain several components, the relative intensities depending on the respective exciting energies. Densitometer curves and wave-lengths are given. Wave-lengths of the $K\alpha$ lines are: for oxygen 23.7, boron 69.3, carbon 45.3 Å., and for beryllium the radiation covered 15 Å., with maxima at 107.2, 113.2, and 118.7 Å. The complex structure is considered to be partly a true fine structure, and partly a system of satellites due to interaction with associated dissimilar atoms.

N. M. BLYTH.

Absorption of X -rays in gases and vapours.

I. Gases. J. A. CROWTHER and L. H. H. ORTON (Phil. Mag., 1930, [vii], 10, 329—342).—The absorption coefficients of monochromatic copper radiation ($K\alpha$) in air, nitrogen, oxygen, carbon dioxide, ethylene, and hydrogen sulphide were measured by means of an ionisation balance method which eliminates errors due to fluctuations in intensity of the radiation and in sensitivity of the electroscope and renders slight defects in insulation of little account. The ionisation produced in the various gases was compared with that of air under the same conditions and the relative total ionisation, T , produced by the complete absorption of the radiation calculated. As a measure of the relative average energy spent in producing a pair of ions in the different gases, $1/T$ is taken and is compared with the ionisation potential, P , the comparison revealing direct proportionality of these two magnitudes except with nitrogen, for which the product PT is greater by about 15% than the mean value for the other gases investigated.

W. GOOD.

Optics of reflexion of X -rays in crystals. III. Depth of penetration, mosaic structure, line width, resolution, and blackening distribution of the spectrum. H. SEEMANN (Ann. Physik, 1930, [v], 6, 1—46).—The measurable widening of spectral lines obtained by reflexion of X -rays from crystals depends on the type of crystal, its degree of perfection, and the depth of penetration of the rays. A very well-grown specimen of rock-salt used in the camera method for the W — K lines, with a half-divergence angle of only 11", showed line widening on one side for a penetration of about 1 mm. in the first order spectrum. A still better specimen of rock-salt with still smaller divergence showed a widening of only 0.5 mm. in consequence of penetration. A calcite crystal, the camera exposure of which was excellent in sharpness, showed a line widening of about 0.1 mm. Calculation of the penetration depth for rock-salt gives to a first approximation the same value as that obtained experimentally if the rock-salt is supposed to be a regular crystallite. Errors in the use of the

different methods for obtaining spectra by the reflexion of X -rays from crystals are discussed. The camera method developed is free from these, and can be used as a criterion for the perfection of a crystal.

A. J. MEE.

Calculation of the Röntgen K terms of the lightest elements and of the rare gases from "optical" ionisation potentials. W. BRAUNBEK (Z. Physik, 1930, 63, 154—167).—The K terms in the X -ray spectra of helium, lithium, beryllium, boron, and carbon are calculated from the ionisation potentials of the corresponding series He, Li⁺, Be⁺², B⁺³, C⁺⁴ by subtraction of the outer screening terms. The ionisation potentials are calculated from the formula of Hylleraas derived from wave mechanics, whilst the screening term, *e.g.*, for lithium, is calculated approximately from classical considerations of the change of the potential energy of the L electron due to the change in the effective nuclear charge on the removal of the K electron. This potential energy is derived from the ionisation potential of a lithium atom. For the other elements the mutual action of the L electrons has to be considered. The values obtained agree with the experimental results of Södermann (A., 1929, 366). The same method is applied to the rare gases, the mutual action of the outer electrons being calculated from the inner screening constant s of Sommerfeld derived from relativistic doublet terms; s can have two values for the M level and three for the N , and it was found that the smaller values of s gave results agreeing best with the experimental values. The difficulties of extending the same method to the calculation of L and M terms are discussed.

H. A. JAHN.

Measurement of reflecting power for X -rays of long wave-length. M. A. VALOUCH (J. Phys. Radium, 1930, [vii], 1, 261—270; cf. A., 1929, 1120).—The rays emitted by a special tube are reflected by a plane mirror of the substance under investigation, and the intensities of the incident and reflected rays measured by means of a specially-constructed ionisation chamber. Curves representing reflecting power as a function of the angle of incidence are thus obtained. The classical theory gives an expression of the reflecting power as a function of the limiting angle which depends on two parameters, one of which is connected with the index of refraction and the other with the coefficient of absorption. Using the K radiation of carbon, measurements in agreement with theory have been obtained with flint glass and duralumin.

L. S. THEOBALD.

Spectroscopy of ultra-soft X -rays. I. M. SIEGBAHN and T. MAGNUSON (Z. Physik, 1930, 62, 439). K. F. SCHOTZKY (*ibid.*, 63, 864).—Polemical.

A. B. D. CASSIE.

Loss of material from the cathode of a metallic arc. R. SEELIGER and H. WULFHEKEL (Ann. Physik, 1930, [v], 6, 87—104).—Apparatus for the determination of the amount of loss of material from a cathode of a metallic arc and its dependence on current strength, thickness of cathode, length of arc, and gas pressure is described. The metals used were silver, copper, and iron. The results are discussed with reference to the physical nature of the cathode and to energy considerations.

A. J. MEE.

Definition of saturation. C. SCHAEFER and H. PESE (*Physikal. Z.*, 1930, 31, 720—737).—Different theories of saturation are discussed and the origin of probable errors is considered. The work of Seitz is discussed, together with luminosity and opacity. The conception of saturation as a sensation is also dealt with. W. R. ANGUS.

Second ionisation potential in potassium vapour. A. L. HUGHES and C. M. VAN ATTA (*Physical Rev.*, 1930, [ii], 36, 214—218; cf. Lawrence and Edlefsen, *A.*, 1929, 1356).—In order to find the possible presence of a peak or discontinuity in the curve for ionisation by electron impact corresponding with that in the photo-ionisation curve, the ionisation in potassium vapour was investigated by Hertz's method of neutralisation of space charge by positive ions. The ionisation curve indicated a second ionisation potential at 0.97 ± 0.05 volt above the first one corresponding with the series limit, *i.e.*, at $4.32 + 0.97 = 5.29$ volts. For mercury vapour, the presence of Lawrence's ultra-ionisation potentials (cf. *A.*, 1927, 85) was found, together with three new ones at 10.88, 11.40, and 12.76 volts.

N. M. BLIGH.

Method of enhancing the sensitiveness of alkali metal photo-electric cells. A. R. OLPIN (*Physical Rev.*, 1930, [ii], 36, 251—295).—Applying the fact that photo-electric emission from potassium is increased by a non-conducting hydride surface film, the cells were sensitised by introducing on to the metal surface small amounts of various inorganic dielectrics, organic compounds, or organic dyes. The increased electron emission is mainly due to increased response to red and infra-red light. Spectral response curves, showing photo-electric current against wave-length of exciting light, are similar for all cells using the same metal as cathode, and differ from the curves for pure metal by the appearance of a new selective maximum at lower frequencies, separated from the regular maximum by the frequency of a characteristic line in the vibration-rotation spectrum of the dielectric molecules. The long-wave limit shifts by an amount agreeing with the separation of the maxima. Stopping potentials were obtained for electrons, liberated by monochromatic light, from a sodium cathode before and after treatment with sulphur vapour and air. For light of wave-length range 3500—8000 Å. the electron retarding potentials were found to vary linearly with the frequency of the light, verifying Einstein's photo-electric equation for composite surfaces, and precluding an explanation on a Raman shift basis. The slope of the straight-line graph of this relationship gives 6.541×10^{-27} for Planck's constant; untreated sodium gives a similar value. The apparent stopping potentials, or voltages at which the photo-electric currents become zero, are the same before and after the sulphur and air treatment. The voltage at which the current just saturates is always greater after treatment than before, and is a measure of the change in contact potential of the cathode due to the presence of the sulphur and air. The application of the Lindemann formula for the frequency of the selective photo-electric maximum is discussed. Reference is made to apparently analogous

phenomena in photo-electricity, photography, fluorescence, and absorption. N. M. BLIGH.

Periodic system. III. Relation between ionising potentials and ionic potentials. G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1930, 52, 3076—3083; cf. *A.*, 1929, 269).—From considerations of atomic models it is shown that the ratio Δ_v/ϕ_v gives a measure of the ionic polarisability; ϕ_v is the ionic potential (volts) and $\Delta_v = \phi_v - 2V$, where V is the ionisation potential referred to the production of ions of the inert-gas type. The ionic polarisability by light or by electrons varies systematically with Δ_v/ϕ_v . This ratio for alkali ions decreases greatly in passing from lithium to caesium, corresponding with the large increase in deformability. It is computed by means of the closely linear relationships between Δ_v and ϕ_v for the alkali ions and the alkaline-earth ions that the valency electron comes within the crystal radius with ions 0.3 and 0.2 Å. larger than the caesium and barium ions, respectively.

J. G. A. GRIFFITHS.

Measurement of slow electrons by means of a point [Geiger] counter. J. HORNBOSTEL (*Ann. Physik*, 1930, [v], 6, 991—1016).—An arrangement in which the slow electrons are accelerated in a given electric field in order to pass through the foil of the Geiger counter is described, the divergence of the electron stream being prevented by subjecting it to a longitudinal magnetic field. The sensitivity of the method is thereby increased. The electron emission from a thin layer of magnesium on celluloid and of celluloid separately is analysed by an opposing electric field, and sudden changes in the velocity-intensity curve are shown to be due to electrons arising from the Auger effect. A method of analysing the electrons with a longitudinal magnetic field and a transverse electric field is described. H. A. JAHN.

Electron exchange between ionised and neutral types. H. KALLMANN and B. ROSEN (*Naturwiss.*, 1930, 18, 448—452).—The general theory of reactions between neutral and ionised molecules is discussed and experiments on the absorption of ions by gases are described. This absorption, which consists in the transference of an electron from a slowly-moving gas molecule to a relatively rapidly-moving ion, can occur only when the neutralisation energy of the ion is equal to or greater than the ionisation energy of the gas. Any ion is most strongly absorbed by the gas from which it is derived, and in addition the absorption is markedly specific. Figures are given for the relative degrees of absorption of various ions by gases. The charged nitrogen molecule is absorbed by nitrogen to a much greater extent than is the charged nitrogen atom, and doubly-charged ions such as those of argon and mercury are less strongly absorbed than ions carrying a single charge, probably because such an ion is nearly always completely discharged on collision; very rarely is only one electron exchanged between a doubly-charged ion and a neutral molecule. H. F. GILLBE.

Deflexion of electrons by passive iron. I. E. RUPP and E. SCHMID (*Naturwiss.*, 1930, 18, 459—461).—The nature of the passive coating on iron has been studied by measurement of the reflexion of a

stream of electrons from the surface at different initial velocities and angles of incidence. The passive surface is characterised by sharp maxima in the reflexion/velocity curve, which indicate the presence of a lattice spacing of 3.4 Å. By heating the passive surface to 300–400° the reflexion diagram reverts to that of the non-passive metal except that there is present a maximum corresponding with ferric oxide. Experiments with oxidised surfaces indicate that the phenomenon of passivity is confined entirely to the surface layer of atoms. H. F. GILLBE.

Velocity loss through quantum addition of slow electrons in diluted gases. H. LÖHNER (Ann. Physik, 1930, [v], 6, 50–86).—Lenard's opposing potential method is used following the procedure of Åkesson for the determination of critical potentials and collision sharing. Two forms of apparatus with quite different ray definitions were constructed. Both gave very similar gas curves in all the determinations which could be used to find critical potentials. The values of these for hydrogen, nitrogen, and carbon dioxide agree with those previously obtained by Åkesson. The value obtained for argon agrees with that arrived at by other electrical and optical determinations. From the heights of the steps in the curves for both apparatus, the probability of a velocity loss without simultaneous diversion was calculated. The form of the sharing function and its tendency to increase are discussed in connexion with the effective cross-section curve. A. J. MEE.

Electron affinity of the hydrogen atom according to wave mechanics. E. A. HYLLERAAS (Z. Physik, 1930, 63, 291–292).—In the previous paper (this vol., 518) only Kasarnovski's early negative value for E_H was quoted; it is now pointed out that the later positive value $E_H=0\pm 15$ of Kasarnovski (A., 1928, 595) is not in disagreement with the value $E_H=16$ kg.-cal./mol. found by the author. The result is also compared with the value $E=17$ kg.-cal./mol. calculated by Bethe (this vol., 132). H. A. JAHN.

Effect of small angle scattering on the electron absorption coefficient. M. C. GREEN (Physical Rev., 1930, [ii], 36, 239–247).—The scattering of electrons by gas molecules was studied indirectly by measuring electron absorption coefficients in argon, helium, hydrogen, and mercury vapour at accelerating potentials from 11 to 196 volts, using an apparatus containing a Faraday cylinder of variable aperture, the radius of which varied from one hundredth to one tenth of the path length. No consistent variation of the absorption coefficient with opening was found, although relatively large variations are predicted theoretically from an inverse square law. The results obtained are in agreement with calculations based on the Sommerfeld, or uniform scattering, law. N. M. BLIGH.

Capture of electrons by protons. H. MARK and K. WOLF (Naturwiss., 1930, 18, 753).—A method of determining by canal rays the effective cross-section of protons against electrons as a function of the relative energy is described; the upper limit for the effective cross-section has been calculated to be less than 10^{-9} cm.² It is hoped to obtain greater accuracy

by means of photographic and ionometric methods which are being developed. W. R. ANGUS.

Annihilation of electrons and protons. P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1930, 26, 361–375).—Theoretical.

Exchange phenomena in the Thomas atom. P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1930, 26, 376–385).—A theoretical justification of Thomas' atomic model is obtained. The equation deduced governing the boundary between the occupied and unoccupied phase space shows an extra term which may be considered to represent the exchange phenomena. W. GOOD.

Theory of extraction of electrons from metals by positive ions and metastable atoms. H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1930, 26, 386–401).—The theory is developed in the light of Sommerfeld's theory of metals and the analytical methods of wave mechanics. W. GOOD.

Possible electron properties. R. D. KLEEMAN (Z. Physik, 1930, 63, 859–863).—Some properties of the electron and proton, particularly the conception of inherent (Coulomb) and exchange energy, may be described without special quantum-mechanical hypotheses. A. B. D. CASSIE.

Recombination of ions in argon, nitrogen, and hydrogen. O. LUHR (Physical Rev., 1930, [ii], 36, 24–34; cf. this vol., 974).—Using the method previously described (cf. Marshall, A., 1929, 1210) the coefficient of recombination for positive ions and electrons in argon, nitrogen, and hydrogen and for positive and negative ions in hydrogen was measured. Free electrons are known to exist in the first three gases. Results are shown graphically and the probable mechanism of recombination is discussed. Absolute values of the coefficient $\times 10^6$ for air, oxygen, argon, nitrogen, and hydrogen are 1.4 ± 0.1 , 1.5 ± 0.1 ; 1.2 ± 0.1 ; 1.2 ± 0.1 , and 0.32 ± 0.05 , respectively. N. M. BLIGH.

Mobilities of ions in dry and moist air. J. ZELENY (Physical Rev., 1930, [ii], 36, 35–43). Using the method previously described (cf. A., 1929, 1122) the distribution of mobilities of aged ions in dry air has been determined, and the values for moist air have been re-measured. In dry air the positive and negative ions each consist of two main groups. The absolute values of the peak mobilities of the most numerous main group in very dry air, air dried by calcium chloride, and air containing 2 mg. of water per litre were 2.45, 2.37, and 2.08 cm./sec. for negative ions, and 1.05, 1.10, and 1.36 cm./sec. for positive ions, respectively, at 76 cm. and 20°. It is suggested that aged ions in air consist of molecular clusters the structure of which is affected by the presence of water molecules. Explanations of the results obtained are discussed. N. M. BLIGH.

Mobility of Na⁺ ions in hydrogen. L. B. LOEB (Physical Rev., 1930, [ii], 36, 152–153).—In order to determine the mobilities of a type of initially ionised carrier which would with difficulty alter its charge, the mobilities of Na⁺ ions in purified hydrogen were measured. Results indicate that the ions

within 2×10^{-5} sec. after liberation have a mobility a little more than double that of the normal ions.

N. M. BLIGH.

Interaction between excited and unexcited hydrogen atoms at large distances. E. C. KEMBLE and F. F. RIEKE (Physical Rev., 1930, [ii], 36, 153—154).—The calculations of Kemble and Zener (cf. A., 1929, 623) on the energy order of different quantum states of the hydrogen molecule is extended to internuclear distances $R=5, 6, 7, 10$ (cf. Eisen-schitz and London, this vol., 525). N. M. BLIGH.

Reflexion of hydrogen atoms from lithium fluoride. T. H. JOHNSON (J. Franklin Inst., 1930, 210, 135—152).—The method previously described (cf. *ibid.*, 1928, 206, 301) was improved so that the lithium fluoride crystal could be used for 6 hrs. before its surface became rough. Incidence was at $30^\circ, 45^\circ$, and 60° , and the crystal at temperatures of $300^\circ, 600^\circ$, and 900° Abs. When the incident beam was in the 100 azimuth, *i.e.*, with rows of alternately dissimilar ions parallel and perpendicular to the plane of incidence, the reflex patterns showed no diffraction maxima in the plane of incidence, but indicated that the rows of similar ions form a more important grating than the rows of alternately dissimilar ions. With the beam incident at 45° in the 110 azimuth, *i.e.*, with rows of similar ions parallel and perpendicular to the plane of incidence, definite diffraction bands were obtained, about one tenth as many atoms entering one of these in the first order as enter the specular beam. Similar results were obtained at normal incidence. Diffuse reflexion of atoms from lithium fluoride is due to thermal agitation (cf. Estermann and Stern, this vol., 515).

C. A. SILBERRAD.

Discrete range groups of H-particles expelled from aluminium. I. Dependence of the number and energy of the H-particles on the primary energy. H. POSE (Z. Physik, 1930, 64, 1—21).—Disintegration experiments with aluminium show that the H-particles expelled in the forward direction fall into three groups of distinct discrete ranges. Experiments were carried out to discover whether the energy of the primary particle exerted any influence on the production of H-particles in each of these groups. Two of the groups appeared only when the primary energy reached a characteristic value, but the third was produced irrespective of the energy of the primary particles. This can be explained on the new quantum theory, the first two groups being the result of resonance effects between the de Broglie waves of the α -particle and a characteristic vibration of the nucleus, and the third group being due to the simple penetration of an α -particle into the nucleus. A. J. MEE.

Absorption in hydrogen gas of hydrogen positive rays. A. C. LAW and G. MUTCH (Phil. Mag., 1930, [vii], 10, 297—306).—The beam of hydrogen positive rays was passed through the usual electric and magnetic fields and a portion of the resulting positive-ray parabola of known energy made to pass through a slit into the absorption chamber. A photographic method was used to determine the intensities of the homogeneous beam

at different points along its course in the chamber and from these the absorption was estimated. The latter was not found to be exponential, which seemed to indicate the existence of a range for the particles rather than removal of the particles from the beam by sudden stoppage or large angle scattering. The method of experiment, depending as it does on the preservation of a fairly constant velocity of the particles, was therefore capable of yielding only qualitative results. These are compared in a general way with the results of theory. W. GOOD.

Effective cross-section for the recombination of electrons with hydrogen ions. E. C. G. STUECKELBERG and P. M. MORSE (Physical Rev., 1930, [ii], 36, 16—23).—Mathematical. The computation of the cross-section for combination of electrons with a positive point charge is made in polar co-ordinates by quantum mechanics, giving the fraction of the recombination to a final state of total quantum number n arising from recombination to the sub-states of different l values. This permits a comparison of results with the experimental recombination intensities for alkali metal vapours.

N. M. BLIGH.

At. wt. tables and chemical analysis. A. THIEL (Chem.-Ztg., 1930, 54, 617—618).—Polemical against Schoorl and Bruhns. The views of these two supporters of the use of "air" at. wts. rather than "scientific" at. wts. as applied in chemical analysis to weights made in air and not in a vacuum are considered to be mutually conflicting. S. S. WOOLF.

Constitution of chromium. F. W. ASTON (Nature, 1930, 126, 200).—Using chromium hexacarbonyl, three new isotopes of chromium have been discovered. The mass numbers are 50, 52, 53, and 54, and their relative abundance is 4.9, 81.6, 10.4, and 3.1%, respectively. The packing fraction of Cr^{52} is -10 (± 3 pts. in 10,000, $O^{16}=0$). The at. wt. of chromium derived from this is 52.011 ± 0.006 .

L. S. THEOBALD.

Isotope effect in the spectrum of boron monoxide. Intensity measurements and structure of the β -bands. A. ELLIOTT (Nature, 1930, 126, 203—204).—The intensity ratios of the B^{11}O and B^{10}O bands have been determined from measurements of the intensities of the lines in four bands in the β -system of boron monoxide excited by active nitrogen. The mean values of the intensity for the four bands are 3.41, 3.28, 3.34, and 4.34, respectively, and, in this case at least, do not give a true measure of the relative abundance of the isotopes. The doublet P and R branches of approximately equal strength occur in the arc β -bands, but only the R branch occurs in the bands excited in active nitrogen. A preliminary value of 1.53 cm^{-1} for B'_0 has been obtained. L. S. THEOBALD.

Isotopes of nitrogen, mass 15, and oxygen, mass 18 and 17, and their abundances. S. M. NAUDÉ (Physical Rev., 1930, [ii], 36, 333—346).—Evidence for the existence of isotopes of nitrogen and oxygen is summarised. An apparatus is described by which the absorption spectra of the nitric oxide γ -bands, (0,0) at λ 2269, (1,0) at λ 2154, and (2,0) at λ 2052, were investigated in search of isotopes and to

verify the existence of isotopes O^{18} and O^{17} . Band heads were observed in the three bands investigated corresponding with the calculated heads for the molecules $N^{14}O^{16}$, $N^{15}O^{16}$, $N^{14}O^{18}$, and $N^{14}O^{17}$, indicating the existence of the isotope N^{15} and verifying O^{18} and O^{17} . By comparing the pressures of nitric oxide in the absorption tube at which the $(1,0)P_1 N^{14}O^{16}$ head had the same intensity as the $P_1 N^{14}O^{18}$ head the relative abundance of O^{16} and O^{18} was found to be 1075 ± 110 . From the relative intensity of the P_1 and $Q_1 N^{14}O^{16}$ heads the relative abundance of N^{14} and N^{15} was found to be 700 ± 140 . From the relative abundance of O^{16} and O^{18} , and O^{16} and O^{17} the mass of the O^{16} isotope was calculated to be 15.9980 ± 0.0002 , taking the at. wt. of the isotope mixture as 16.0000. The mass of the N^{14} isotope was calculated to be 14.0069 ± 0.0012 .

N. M. BLIGH.

Isotopes and geologic time. C. S. PIGGOT (J. Amer. Chem. Soc., 1930, 52, 3161—3164).—The calculation of geologic time from the examination of uranium minerals is discussed. The results of Aston (A., 1929, 370) show that the uncertainty due to the presence of thorium can be eliminated.

J. G. A. GRIFFITHS.

Relation between the disintegration constant of radio-elements emitting α -rays and their filiation capacity. (MME.) P. CURIE and G. FOURNIER (Compt. rend., 1930, 191, 326—329).—Combination of Fournier's formula (A., 1929, 863), the Geiger-Nuttall law, and Wolff's equation (Physikal. Z., 1921, 22, 171, 352) leads to the relationship $\log \lambda = 268 - 3.5U$, where U is the filiation capacity (*loc. cit.*) and λ the disintegration constant of a radioelement emitting α -particles in air. Experimental results give a line corresponding with $\log \lambda = 235 - 3.0U$ between $U = 75$ and 85, but the values for polonium, actinium- C' , and uranium-1 (cf. *loc. cit.*) indicate that these limits represent maximum and minimum values of $\log \lambda$, respectively, beyond which $\log \lambda$ rises with increase in U instead of falling.

J. GRANT.

Origin of the high-range α -particles of thorium- C . E. STAHEL (Z. Physik, 1930, 63, 149—153).—The recoil rays corresponding with the α -particles of abnormally high range of thorium- C have a longer range in air than the recoil rays from the other α -particles, and were separated from them by a layer of air of variable pressure. The decomposition product of these abnormal particles was thus collected separately and shown not to possess the half-life period of thorium- C'' but to be practically inactive. Contamination of the iron foil on which the product was collected was prevented by interposition of air-tight foils of celluloid 0.014μ thick. It was previously shown (this vol., 516) that the abnormal particles are not emitted from thorium- C'' , and it is hence now deduced that they arise from thorium- C' and not from thorium- C . The alternative explanation that the α -particles are emitted from thorium- C but give rise to an isotope of thorium- C'' with a different life period is discussed, and it is shown that the half-life period of this isotope could not have values between a few seconds and one day.

H. A. JAHN.

Luminescence of zinc sulphide under the action of α -, β -, and γ -rays. G. S. GESSNER (Physical Rev., 1930, [ii], 36, 207—213).—The luminescence of zinc sulphide exposed to α -rays or β - and γ -rays, or α -, β -, and γ -rays was investigated with a specially-designed brass capsule; the luminescent material and exciting agent were kept separate. Luminosities were measured by a Nutting polarisation photometer. The curves, plotted against time, showed first an increase in brightness, followed by a decrease, and a rise to a second maximum with a final gradual decrease. The decay of luminescence after removal of the exciting agent is not a single exponential. Results are not in agreement with the theory of radioactive luminosity given by Walsh (cf. A., 1927, 807).

N. M. BLIGH.

γ -Rays of potassium. F. BĚHOŮNEK (Nature, 1930, 126, 243).—The radiation emitted by potassium chloride has been examined; it consists of at least two groups of γ -rays. The absorption coefficient for the first group is of approximately the same order as in the case of the γ -rays of radium, but the second group is approximately twice as penetrating. Assuming that each β -ray of potassium is followed by one γ -ray, the intensity of the γ -rays is much lower than corresponds with a period of 10^{12} years.

L. S. THEOBALD.

Production of radium by ionium. (MME.) P. CURIE (J. Chim. phys., 1930, 27, 347—356).—Theoretical. A graphical method for determining the true quantity of radium present at any time is given.

C. W. GIBBY.

Theory of atomic disintegration. G. BECK (Z. Physik, 1930, 64, 22—33).—A mathematical investigation of two kinds of quantum process leading to agreement with the experimental work of Pose on discrete range groups of H-particles (cf. this vol., 1232).

A. J. MEE.

Atomic diameters of the rare gases. W. H. KEESOM and H. H. MOOY (Nature, 1930, 126, 243).—A correction. Using the values of the atomic diameters 2.30, 2.87, 3.10, and 3.41 Å. calculated by Rankine for neon, argon, krypton, and xenon, respectively, the ratios of the distance of nearest neighbours in the crystal lattice to the atomic diameter become 1.39, 1.34, 1.28, and 1.28, respectively. The value for krypton is lower than would be expected.

L. S. THEOBALD.

Lattice constants of the elements. W. HUME-ROTHERY (Phil. Mag., 1930, [vii], 10, 217—244).—Relations are described connecting atomic or ionic radii with the corresponding atomic structures. In any one sub-group of the periodic table, provided that the co-ordination number remains constant, the interatomic distance d is given by the relation $d/n = (1/aZ)^x$, where n is the principal quantum number of the outermost shell of electrons remaining attached to the ions, Z is the atomic number, x is a constant which is the same for groups with the same number of electrons in the outermost shell of the atomic core or ion, and a is a second constant which in some groups may be connected with the valency. The accuracy and meaning of this law are discussed and the effect of co-ordination number and crystal

structure is considered. Other relations in the periods are found. W. GOOD.

Interaction of a hydrogen and a helium atom, and of two helium atoms. G. GENTILE (Z. Physik, 1930, 63, 795—802).—Mathematical. The energy of interaction of hydrogen and helium and of two helium atoms in their respective ground states is calculated. Second-order perturbations give forces equivalent to polarisation forces (cf. this vol., 525), and these are calculable as a second order Stark effect. A. B. D. CASSIE.

Solution of the Dirac equation without specialisation of the Dirac operators. F. SAUTER (Z. Physik, 1930, 63, 803—814).—Mathematical. A. B. D. CASSIE.

The virial hypothesis. V. FOCK (Z. Physik, 1930, 63, 855—858).—Mathematical. A quantum-mechanical virial is deduced from the variation principle, and is shown to be valid for Dirac's equation. A. B. D. CASSIE.

Rate at which ions lose energy in elastic collisions. A. M. CRAVATH (Physical Rev., 1930, [ii], 36, 248—250).—Mathematical. An expression is deduced for the rate of energy loss of ions (including electrons) moving through a gas, the ions and molecules being regarded as smooth elastic spheres, with no attraction at a distance, and having Maxwellian velocity distributions corresponding with their respective absolute temperatures. N. M. BLIGH.

Electrons in metals and classification of corresponding de Broglie waves. L. BRILLOUIN (Compt. rend., 1930, 191, 292—294).—Mathematical; an extension of the results deduced previously (cf. this vol., 1082). C. A. SILBERRAD.

Analytic atomic wave functions. C. ZENER (Physical Rev., 1930, [ii], 36, 51—56; cf. Guillemin and Zener, this vol., 649).—Mathematical. The wave functions for the normal states of atoms of elements in the first row of the periodic table are written as simple analytic expressions with several parameters, the best values of which are determined by the variation method. An approximate solution is found for all the ions, positive and negative, of these atoms. N. M. BLIGH.

Atomic shielding constants. J. C. SLATER (Physical Rev., 1930, [ii], 36, 57—64).—Mathematical. The wave functions derived by Zener (cf. preceding abstract) are extended to all atoms in any stage of ionisation. These are applied to X-ray levels, sizes of atoms and ions, and diamagnetic susceptibility. N. M. BLIGH.

Calculation of energy values. C. ECKART (Physical Rev., 1930, [ii], 36, 149—150).—A modification of the Ritz method of calculating characteristic numbers, as applied to the quantum dynamical problem, is described, and results of calculations for the $2P$ and $3D$ states are given. N. M. BLIGH.

What conclusions must classical physics and chemistry draw from the principle of greatest simplicity? L. ZEHNDER (Z. Physik, 1930, 63, 706—712).—Ten postulates are given based on the principle of greatest simplicity. Classical physics

must obey these, or else be wrong in its fundamental suppositions. A. J. MEE.

Relativistic treatment of the atom with several electrons. L. GOLDSTEIN (J. Phys. Radium, 1930, [vii], 1, 271—284).—Theoretical. A development of previous views (cf. this vol., 131).

L. S. THEOBALD.
Wave-mechanical calculation of the grating energy and grating constant of lithium hydride. E. A. HYLLERAAS (Z. Physik, 1930, 63, 771—794).—The wave-mechanical theory of grating forces in a crystal composed of ions with two orbital electrons is developed. Exchange energy is shown comparable with the Coulomb energy due to interionic forces. Calculations for lithium hydride give the grating energy as 219 kg.-cal. per mol., and the grating constant as 4.42 \AA , compared with the empirical values, 217 ± 7 and 4.10 , respectively. A. B. D. CASSIE.

Colouring of alkali halide crystals by ultra-violet light. A. SMAKULA (Z. Physik, 1930, 63, 762—770).—Absorption spectra due to foreign substance colouring of the first kind are given for crystals of lithium fluoride, rubidium bromide, and potassium iodide in the range $200\text{--}800 \mu\mu$. Absolute values of the absorption coefficient are given for rubidium chloride and bromide and for potassium bromide and iodide at the ordinary temperature, and for potassium bromide at -183° . Crystals of rubidium bromide and chloride and of potassium bromide and iodide require 1.1 to 1.6 light quanta to form one colour centre when the colouring is slight. This factor is independent of the wave-length used and of the saturated colour density. A. B. D. CASSIE.

Colloidal nature of the colouring substance in coloured rock-salt. M. SAVOSTIANOVA (Z. Physik, 1930, 64, 262—278).—Mie's theory was applied to the system Na-NaCl, and the absorption and diffusion spectra for different particle sizes were calculated and compared with the experimental curves obtained for coloured rock-salt. The absorption spectra of the following kinds of coloured salts were determined by the spectrophotometer method: (a) natural blue salt, (b) additive (in liquid sodium) coloured salt, and (c) salt obtained from yellow salt by the action of heat and pressure under the influence of light. The experimental data agree with the assumption that the colours are due to particles of colloidal sodium. Besides the absorption maxima due to the presence of colloidal sodium, a further maximum was found for yellow salt in the infra-red, the explanation of which is not clear. A. J. MEE.

Light absorption of alkaline-earth halides in aqueous solution. H. DIAMOND and H. FROMHERZ (Z. physikal. Chem., 1930, B, 9, 289—318).—The absorption curves of aqueous solutions of pure chlorides, bromides, and iodides of magnesium, calcium, strontium, and barium, extending into the ultra-violet as far as $200 \mu\mu$, have been measured over a wide range of concentration varying from saturation to high dilutions. The weak absorption bands found by previous workers in the neighbourhood of $250 \mu\mu$ are shown to be due to traces of impurities, which are effective if present at a concentration of

only 0.001 g. per litre. With increasing concentration of solutions containing only one halogen ion a proportional displacement of chloride bands towards the ultra-violet was observed, together with a slight broadening of bromide bands, and a marked broadening of iodide bands, which, however, was not proportional to the increase in concentration. The maxima of the iodide bands are not displaced even at the highest concentrations. The iodide bands are displaced towards the ultra-violet by the addition of an excess of chloride ions, the magnitude of the effect being proportional to the chloride-ion concentration, and a similar effect is produced by an added excess of potassium fluoride or magnesium sulphate. No specific influence of the cation on the form of the absorption curve or on the degree of displacement of the iodide bands was observed, but with pure chloride solutions the ultra-violet displacement due to increase of concentration increases with the size of the cation. No evidence of the association of the ions to stoichiometric complexes was obtained.

E. S. HEDGES.

Physical properties of the fatty acids. E. L. LEDERER (Chem. Umschau, 1930, 37, 205—208).—The method of calculating the viscosity at any temperature of a fatty acid is described, and the necessary constants have been calculated for a number of the acids. The absorption by fatty acids in the ultra-violet is described and the equations and constants required for calculating the absorption at any specified wave-length are given. H. F. GILLBE.

Nitric oxide β - and γ -bands. R. SCHMID, D. VON FARKAS, and T. KÖNIG (Z. Physik, 1930, 64, 84—120).—The NO lines previously measured were classified and ordered. In this way some 3000 γ - and 1000 β -lines were arranged. The rotation and vibration constants were in some cases calculated afresh. The doublet splitting of the levels 2π , was obtained as a function of rotational and vibrational states. The potential energy curve for nitric oxide was obtained, as well as Condon's parabola.

A. J. MEE.

Nitric oxide δ -bands. R. SCHMID (Z. Physik, 1930, 64, 279—285).—In order to produce the δ -bands of nitric oxide in sufficient intensity to be photographed special means of excitation must be used. With a Tesla apparatus and other devices for special excitation it was found possible to produce the bands in the afterglow in the production of active nitrogen mixed with air. The rotation analysis of the band $\delta(0.3)$ is given, and the rotation constant of the δ -bands for the 2Σ initial level is calculated to be $B_0=1.995$ cm.⁻¹

A. J. MEE.

Extinction of fluorescence of solutions of dyes by electrolytes. A. V. BANOVA (Z. Physik, 1930, 64, 121—134).—The application of the theory of Vavilov concerning collisions of the second kind to the extinction of fluorescence in solutions of dyes by adding electrolytes does not agree fully with experimental results. This leads to the search for some other cause of extinction which is to be found in the "salting-out" effect of the electrolyte on the dye. Experimental work supports this view. Calculations of the sum of the radii of the molecule of the dye and of the ion of

the electrolyte give results in agreement with those arrived at by other methods. The extinction curves reveal a connexion between the concentration of the electrolyte, c , and the intensity ratio after and before adding the electrolyte, which can be expressed in the form $L/L_0=e^{-k\sqrt{c}}$.

A. J. MEE.

Deformation of electron shells. I. Absorption spectrum, molecular volume, and refraction of neodymium perchlorate. P. W. SELWOOD (J. Amer. Chem. Soc., 1930, 52, 3112—3120).—The densities, refractive indices, and absorption spectra of neodymium perchlorate solutions of concentrations as high as about 7*N* have been determined. Increase of concentration is associated with an increase in molecular volume and refraction, and a small shift of the absorption bands towards the red. The results agree with deductions from the Clausius-Mosotti theory of dielectrics and with the theories of Ephraim (A., 1929, 864) and Fajans on the distortion of electron shells of ions.

J. G. A. GRIFFITHS.

Infra-red filters of controllable transmission. A. H. PFUND (Physical Rev., 1930, [ii], 36, 71—76).—To eliminate higher orders when using an echelette grating in the infra-red, powders such as zinc or magnesium oxides, of suitable particle size, can be used spread uniformly with appropriate thickness over a polished speculum surface. Short wave-length radiations are reflected diffusely, and long wave-lengths are mainly transmitted. Satisfactory purity of spectrum is obtained.

N. M. BLYTH.

Effect of high pressure on the near infra-red absorption spectrum of certain liquids. J. R. COLLINS (Physical Rev., 1930, [ii], 36, 305—310).—Since a change in polymerisation of polar liquids is expected with increase of pressure, certain absorption bands of water and of methyl and amyl alcohols were studied with the liquids under pressures up to 5000 kg. and toluene up to 8000 kg./cm.² No change was found in the positions or intensities of the bands, which, being characteristic of the molecules, indicate no change in polymerisation for the pressures used. The pressure necessary to solidify toluene at 20° was found to be between 8100 and 8300 kg./cm.²

N. M. BLYTH.

Infra-red absorption of some organic liquids under high resolution. II. R. B. BARNES (Physical Rev., 1930, [ii], 36, 296—304; cf. this vol., 1090).—With an improved spectrometer giving wave-lengths accurate to $\pm 0.001 \mu$, work previously reported on the CH vibration bands in organic liquids from 3.0 to 4.0 μ has been continued and extended. Results are given for water vapour, benzene, and toluene. The CH vibration frequency close to 3.5 μ and the strong band of water near 3.0 μ indicate that almost every liquid will have pronounced absorption over the region studied, resulting in complex bands demanding high resolving power.

N. M. BLYTH.

Rotation oscillation spectrum of acetylene. I. Band analysis. K. HEDFELD and R. MECKE (Z. Physik, 1930, 64, 151—161).—In order to study the configuration and form of oscillation of simple gaseous molecules the spectrum of acetylene has been investigated. The spectrum was photographed in the

range 9000—7000 Å. with large dispersion (2.6 Å./mm.). Three absorption bands were found at wave-lengths 7887, 7956, and 8620 Å., of which the first was by far the most intense. The absorption lines were measured to 0.01 Å. The spectrum was analysed. The *P* and *R* branches were very simple, no fine structure of the lines being visible within the above limit of error. There were marked intensity changes. The simple structure of the bands leads to the conclusion that the four atoms of the molecule are arranged in a straight line, so that the method of rotation of a diatomic molecule has to be dealt with. The fact that only one line [*P*(0)] is missing in the spectrum is in agreement with the usually accepted electronic structure of acetylene and shows the analogy of the acetylene molecule HC:CH to the nitrogen molecule N:N. The moment of inertia of the molecule in the fundamental state is 23.509×10^{-40} . The nuclear distance for C—H is 1.08×10^{-8} cm., in agreement with that arrived at for the methane molecule by a study of the Raman spectrum; the value for the C:C distance is 1.19×10^{-8} cm. These figures are considerably less than those for the diamond lattice. A. J. MEE.

Rotation oscillation spectrum of acetylene.
II. Intensity measurements. W. H. J. CHILDS and R. MECKE (Z. Physik, 1930, 64, 162—172).—Accurate intensity measurements were made with the band at 7887 Å., this being a $^1\Sigma-^1\Sigma$ combination. The expected intensity changes for a combination of this type were found, the *i* factors (*i.e.*, transition probabilities) being for the *R* branch, $(J)_i = J + 1$, and for the *P* branch, $(J)_i = J$. Conclusions are reached concerning the nuclear spin of elements. The intensity ratio is 3 : 1. The odd *J* values must therefore have three times the weight, statistically, of the even *J* values. The nuclear spin of the hydrogen in the acetylene molecule must be 0.5, whilst that of the carbon is 0. Summing up the results previously obtained for nuclear spins, it is pointed out that elements having at. wts. divisible by 4 (equal, say, to $4n$), have no spin. This is true for helium, carbon, and oxygen. The elements with at. wts. equal to $4n + 1$ (hydrogen) have spins equal to 0.5. Elements with at. wts. equal to $4n + 2$ (nitrogen) have the spin 1. Elements with at. wts. equal to $4n + 3$ have the spin 1.5 (lithium). The elements sodium, chlorine, and iodine also have spins greater than 1. This rule should be useful in dealing with isotopic elements. A. J. MEE.

Rotation oscillation spectrum of acetylene.
III. Characteristic frequencies of simple symmetrical molecules. R. MECKE (Z. Physik, 1930, 64, 173—190).—The characteristic frequency of a molecule may be regarded as being made up of two parts—a valency oscillation and a deformation oscillation. A number of linear molecules are considered. Molecules of this type possess $n - 1$ valency oscillations, equal to the number of valency linkings, and $n - 2$ deformation oscillations. The symmetrical molecules of carbon dioxide, nitrous oxide, carbon disulphide, acetylene, cyanogen, and possibly also hydrogen peroxide are to be regarded as linear. The triatomic molecules possess two valency oscillations,

the size of which depends mainly on the oscillating masses, and one deformation oscillation, parallel to the axis of symmetry, but in the case of a linear arrangement of atoms, it becomes a double oscillation perpendicular to the axis of the molecule. For tetra-atomic molecules (acetylene and cyanogen) there are two C—H oscillations, one (HC):(CH), and two deformation oscillations perpendicular to the axis of the molecule. For ethylene there are four C—H oscillations, one (H₂C):(CH₂) oscillation, and five deformation oscillations, of which one, as a pure C:C oscillation, is independent of the mass of other atoms, and is found in all derivatives containing the C:C linking. The five characteristic frequencies of acetylene and the nine of ethylene are calculated.

A. J. MEE.

Raman and resonance radiation. P. DAS (Z. Physik, 1930, 63, 224—226).—The distinction between Raman and resonance lines is pointed out, and the origin of the resonance lines is explained on the basis of Rasetti's theory of the Raman effect. According to this theory, at least three energy levels (E_m, E_n, E_l) are concerned in the effect; if the two transitions $m \rightarrow l$ and $l \rightarrow n$ occur, then a frequency change ν_{mn} takes place in the scattered light. These energy changes disturb the Maxwell-Boltzmann distribution of energy for the molecules, which is restored when a certain number of molecules return first from E_n to E_l and then from E_l to E_m and thereby radiate the frequencies ν_{nl} and ν_{ml} . These last frequencies give rise to the resonance lines. It is shown that only monochromatic light gives resonance radiation, homogeneous light giving fluorescence. H. A. JAHN.

Polarisation of Raman radiation and crystal structure. F. MATOSI (Z. Physik, 1930, 64, 34—38).—It would be expected that the Raman lines from crystals with equal internal force distribution, *i.e.*, those with symmetrical oscillations, would be missing, whereas for crystals with unsymmetrical oscillations they should be strong. It should therefore be possible to arrive at conclusions respecting the structure of crystals by investigating the Raman radiation associated with them, and especially its polarisation. Experiments were made with calcite and sodium nitrate crystals in various positions, and from the results the structure of the CO₃ group was derived. To explain the results it is necessary to assume that the CO₃ group is isosceles in form. A. J. MEE.

Dispersion formula and Raman effect for the symmetrical top. M. MUSKAT (Physical Rev., 1930, [ii], 36, 363; cf. this vol., 978).—A correction. N. M. BLIGH.

Polarisation of the lines in Raman spectra. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 59—71).—The state of polarisation of Raman lines was investigated for sulphur dioxide and trioxide, carbon disulphide, ammonia, chloroform, bromoform, the trichlorides of phosphorus, arsenic, and bismuth, and the tetrachlorides of carbon, silicon, titanium, and tin. Similarity in polarisation was shown by substances having analogous structures, the influence on the polarisation being attributed to the

geometry of the various oscillations. A high degree of polarisation is usually accompanied by high intensity. Existing explanations of the polarisation phenomena in Raman spectra are briefly reviewed.

N. M. BLIGH.

Raman effect and molecular structure. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 73—95).—Theoretical. On the view that Raman lines are mainly due to transitions corresponding with fundamental vibration frequencies of molecules involved in the scattering process, an interpretation of the Raman spectra is investigated through a study of the characteristic modes of oscillation of a number of simple types of polyatomic molecules using the dynamical principles developed by Dennison (cf. A., 1926, 222). Theoretical results are correlated with existing experimental data.

N. M. BLIGH.

Raman spectrum of diamond. R. ROBERTSON and J. J. FOX (Nature, 1930, 126, 279).—With a diamond transparent at about 8μ and also at 2300 \AA ., 17 Raman lines originating from mercury lines within the range $4358\text{--}2378\text{ \AA}$. have been identified. The mean value of all differences is 1333 cm^{-1} , a value lower than that previously reported (this vol., 662) but agreeing with that of Ramaswamy (*ibid.*) and of Bhagavantam (this vol., 1091). With a quartz spectrograph, the faint, diffuse band found by these investigators is strong with a centre at about 4156 \AA .

L. S. THEOBALD.

Raman spectrum and infra-red absorption of sulphur. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 105—112).—The Raman spectrum, excited by the mercury 5461 \AA . line isolated by a didymium chloride filter, was investigated for rhombic sulphur by the powder crystal method, and for a solution of sulphur in carbon disulphide. Four prominent and two faint lines were observed for the solid, one line being attributed to the S_{16} molecule; three lines found for the solution correspond with the S_8 molecule. The infra-red measurements of Taylor and Rideal (cf. A., 1927, 925) can be explained by a combination of these fundamental frequencies. Pure carbon disulphide showed the principal line doubled, and a faint line broadened on the long wave-length side, analogous to the results of Dickinson and others for carbon dioxide (cf. A., 1929, 1215). The presence of sulphur in solution caused a slight shift of the principal line to shorter wave-length.

N. M. BLIGH.

Raman effect in crystal powders of inorganic nitrates. P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 1—12; cf. Menzies, A., 1929, 1217).—The Raman spectra of 19 inorganic nitrates in fine crystalline form were obtained, using, in some cases, a filter of didymium chloride solution to eliminate the continuous spectrum and to enhance the fainter lines. Wave-lengths and frequency shifts are tabulated. The inactive frequency of the NO_3 ion appeared as a sharp line with slight variation of position. The greatest departure from its value in solution was observed for lithium, sodium, and magnesium, and for mercury, bismuth, and thorium. It is concluded that the influence of the metal ion on the inactive frequency depends mainly on the volume

occupied by the ion in the crystal lattice. A faint component indicated a polymerised molecule in the case of lithium, mercuric, and aluminium nitrates. Lines at 7 and 14μ correspond with infra-red frequencies.

N. M. BLIGH.

Raman effect in some organic and inorganic substances. N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, 5, 13—34).—The Raman spectra were investigated for carbamide, ethyl formate, malonate, acetoacetate, monochloroacetate, and carbonate, potassium and ammonium thiocyanates, potassium cyanide and cyanate, potassium silver cyanide, acetonitrile, aniline, phenylhydrazine, hydrazine hydrate, benzaldehyde, and formaldehyde. Full data are tabulated and results are discussed in relation to chemical structure. Raman frequencies characteristic of the CN ion were found at 836 and 2080 . The difficulty due to the darkening in air under the action of light of substances such as aniline and phenylhydrazine was overcome by distillation into the observation tube in a vacuum. A theory of the continuous spectrum accompanying the Raman lines is proposed.

N. M. BLIGH.

Raman spectra of some elements and simple compounds. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 35—48).—In order to obtain correlation with known molecular structure Raman spectra were investigated, and results are tabulated for the following: liquefied chlorine, sulphur dioxide, and ammonia, diamond, phosphorus, carbon disulphide, chloroform, bromoform, phosphorus, arsenic, and bismuth trichlorides, and carbon, silicon, tin, and titanium tetrachlorides. Raman spectra of allied compounds showed a close similarity.

N. M. BLIGH.

Raman effect in trimethylethylene. (MISS) D. FRANKLIN and E. R. LAIRD (Physical Rev., 1930, [ii], 36, 147).—Raman lines corresponding with infra-red wave-lengths 3.44 ± 0.05 and $8.4 \pm 0.2\mu$, and an anti-Stokes line to 8.4μ were found. A continuous scattering with a marked denser band beginning near 4600 \AA . appears to be due to contamination with rubber, a similar effect being observed for carbon tetrachloride.

N. M. BLIGH.

Raman effect in solutions of sodium nitrate of varying concentration. (MISS) V. STERLING and E. R. LAIRD (Physical Rev., 1930, [ii], 36, 148—149; cf. Carrelli and others, A., 1929, 120).—The Raman spectrum of sodium nitrate, at 5, 10, 30%, and saturated concentrations, excited by a glass mercury arc showed a line with frequency difference $1049 \pm 6\text{ cm}^{-1}$ excited by the mercury lines 4358 , 4077 , and 4046 \AA ., equally strongly in each case. No new lines were found. The line is attributed to the NO_3 ion.

N. M. BLIGH.

Change of wave-length of light due to elastic heat waves at scattering in liquids. E. GROSS (Nature, 1930, 126, 201—202).—The light 4358 \AA . of a mercury lamp, scattered at 90° by various liquids, is partly split up into radiations of nearly the same intensity, with wave-lengths symmetrically displaced relatively to the incident light, by a value dependent on the kind of liquid but not differing greatly from 0.05 \AA . for all the liquids investigated. With highly scatter-

ing liquids, such as benzene and toluene, lines displaced by a multiple of this value have been observed. The nature of the observed splitting is discussed, and a close connexion with the elastic heat waves similar to those discussed by Debye (Ann. Physik, 1912, 39, 789) is considered to exist. Crystalline quartz gives a similar splitting of the frequency of scattered light. L. S. THEOBALD.

Influence of polymerisation and molecular association on the Raman effect. S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 49—57).—The Raman spectrum of sulphur trioxide was investigated at two temperatures. The transition from S_2O_6 to SO_3 molecules was shown by the disappearance or weakening of certain lines, and the corresponding brightening of other lines attributed to SO_3 ; the effect is reversible. The effect of molecular association on Raman spectra is discussed with reference to data for ammonia (cf. this vol., 1237). Three broad lines of widely differing intensities are found, which become of comparable intensity at low temperatures (cf. Daure, this vol., 14); another diffuse line showing no alteration in intensity is attributed to unassociated molecules. Similar results for other polar molecules are discussed. Appreciable frequency differences for the molecules as determined in the gaseous and liquid states were found. N. M. BLYTH.

Chemiluminescence of the antimony halides. S. S. BHATNAGAR and K. G. MATHUR (Z. physikal. Chem., 1930, B, 9, 229—240).—The chemiluminescence of a mixture of antimony and chlorine and the effect on it of the addition of anthracene, benzene, and the sulphides of calcium and zinc have been examined. When mercury is present, spectral lines corresponding with an energy greater than the heat of formation of any of the antimony chlorides are excited, and it seems that intermediate reactions, in this case the formation of antimony oxide by moisture, are responsible. R. CUTHILL.

Photodichroism and photoanisotropy. VII. Influence of colour of exciting light on the induced dichroism. F. WEIGERT and J. SHIDEI (Z. physikal. Chem., 1930, B, 9, 329—355).—Previous work (A., 1929, 871, 894) has been extended and repeated with more refined methods and a further study has been made of the influence of the wavelength of the exciting light on the dichroism and also the influence of the conditions of developing and the intensity of radiation. The types of curves produced can be described in terms of three principal types in the red, green, and blue, thus providing a photochemical analogy with the three-colour mixture rule observed in the sensations of the eye. A new theory of "colour-effectiveness" is evolved. E. S. HEDGES.

Photo-ionisation of salt vapours. A. TEREININ (Physical Rev., 1930, [ii], 36, 147—148; cf. A., 1928, 935; Butkov, A., 1929, 1362).—The photo-ionisation of the halides of thallium was investigated using ultra-violet light of wave-length longer than 1850 Å. The ionisation and dissociation energies and stability of the neutral and ionised molecule are discussed. A decrease in photo-sensitivity from the iodide to the chloride was observed. The possibility of photo-

ionisation appears to depend on the ionisation potential of the metallic atom falling within the range of ultra-violet frequencies used. N. M. BLYTH.

Temperature and pressure variations of the dielectric constant of some organic vapours. O. FUCHS (Z. Physik, 1930, 63, 824—848).—The apparatus described by Stuart (A., 1928, 460) has been improved to measure the temperature coefficient of the dielectric constants of substances with higher b. p. The apparatus was directly calibrated and systematic errors were investigated, especially the error due to adsorbed layers. The temperature and pressure variations of the dielectric constant were determined for ethyl ether, ethyl chloride, and methyl chloride, and the temperature variation for $C(OMe)_4$. The electric moments are: ethyl ether 1.14×10^{-18} , ethyl chloride 2.05×10^{-18} , methyl chloride 1.86×10^{-18} , and for $C(OMe)_4$ $< 0.3 \times 10^{-18}$. The infra-red molecular refraction constants have been determined, and the results are discussed. A. B. D. CASSIE.

Dielectric constants of regular crystals. S. KYROPOULOS (Z. Physik, 1930, 63, 849—854).—The dielectric constants were determined by the Stark method for regular single crystals. These included lithium fluoride, sodium fluoride, chloride, and bromide, potassium and rubidium chlorides, bromides, and iodides, and tellurium chloride and bromide. The values of these dielectric constants sometimes deviate greatly from the values for corresponding powders. The values for the single crystals show a simple correspondence with the ion radius, and the additive rule for dielectric constants appears to apply for ions of comparable radius and of small polarisability. A. B. D. CASSIE.

Influence of the solvent on the rotatory power of the acetals derived from mannitol. V. ETTTEL (Coll. Czech. Chem. Comm., 1930, 2, 457—470).—The specific rotatory power of solutions of triethylidene- and tribenzylidene-mannitol in a number of solvents have been measured, but there appears to be no simple relationship between the refractive index of the solvent and the rotatory power of the solution. H. F. GILLBE.

Influence of X-rays, according to Allison, on the magnetic rotatory polarisation and on the properties of inactive liquids. N. T. ZÉ (Compt. rend., 1930, 191, 324—325).—The experiments of Allison (A., 1929, 1220) were tested on water, carbon disulphide, and nitrobenzene, using a Coolidge X-ray tube (70 kilovolts and 6 milliamp.) and an electromagnet supplying a mean field of about 21,000 gauss, with a Cotton mercury arc as source of monochromatic light. The results recorded by Allison were not confirmed, and it is considered that if they exist their magnitude will not (under the above conditions) exceed 3 min. (cf. following abstract). J. GRANT.

[Influence of X-rays, according to Allison, on the magnetic rotatory polarisation and on the properties of inactive liquids.] A. COTTON (Compt. rend., 1930, 191, 325; cf. preceding abstract).—The rules of symmetry in physical phenomena of Curie do not forbid the supposition that X-rays may modify

the magnitude of magnetic rotation. They do not, however, allow the possibility of the creation of such a power of rotation, in a determined sense, in an inactive substance by means of a pencil of X-rays.

J. GRANT.

Dispersion of gases and vapours, and its explanation on the dispersion theory. I. Dispersion of mercury vapour in the ultra-violet. R. LADENBURG and G. WOLFSOHN (Z. Physik, 1930, 63, 616—633).—A Jamin interferometer of which the parts were made of quartz was used in the investigation. The anomalous dispersion of saturated mercury vapour at known pressure and temperature was studied in the neighbourhood of the mercury resonance line 2537 Å. The oscillator strength, f , i.e., the ratio n/N of the number of dispersion electrons to the total number of molecules per c.c., was found, and its variation with vapour pressure studied in the range 0.004—200 mm. Between 0.01 and 200 mm. f is constant and equal to 0.0255 ± 0.0005 . At pressures below 0.01 mm. there is a rise in the f value which has not been explained. From the determinations a curve could be drawn analogous to the ordinary vapour pressure-temperature curve, and of the form $p=p(T)$, where p/f represents the partial pressure of atoms in the vapour. In consequence of the constancy of f above 0.01 mm. the value of $p(T)$ is of the same form as the corresponding function for the total vapour, differing from it only by a constant factor. The heat of vaporisation of the atoms agrees to within a few per cent. with that of the total vapour. In this way the partial pressure of the molecules in the vapour can be found with fair accuracy between the pressures 0.01 and 200 mm. The constancy of f shows that the probability of transition for the mercury atom is independent of temperature and pressure in the interval under experiment, a conclusion required by the quantum theory.

A. J. MEE.

Dispersion of gases and vapours and its explanation on the dispersion theory. II. Dispersion of mercury vapour between 7500 and 2650 Å. G. WOLFSOHN (Z. Physik, 1930, 63, 634—639; cf. preceding abstract).—The apparatus used was that mentioned in the previous work. The dispersion curve, which was obtained between the wave-lengths 7500 and 2650 Å., was of the form expected on theoretical grounds, and could be represented by a formula involving three terms. The region of anomalous dispersion predicted by Herzfeld and Wolf to exist at a wave-length of 6900 Å. could not be found.

A. J. MEE.

Quantum theory of chemical valency. M. BORN (Nature, 1930, 126, 205).—The theory of the interaction of several atoms can be treated simply and without the application of the methods of the group theory (cf. Slater, this vol., 126).

L. S. THEOBALD.

Tautomerism and related phenomena in the light of the electronic theory of valency. L. KOVARSKI (Z. physikal. Chem., 1930, B, 9, 173—200).—A general qualitative electronic theory of intramolecular rearrangements has been developed by means of the new concept of "pole-transfer." It is postulated that when a duplet linking is severed

with the formation of ions the two electrons pass to the anion, but on neither ion does the charge necessarily remain on the atom at which the linking has broken; if there is present in the ion an atom or a group of higher electrovalency the charge is transferred to it. By means of this assumption, phenomena such as tautomerism and the quinonoid transformation may be embraced by a single theory. Since an octet may be regarded as equivalent to four duplets, this theory can be combined with that of Lewis and Langmuir and utilised to explain the Beckmann and Hoffmann transformations. The structure of inorganic unsaturated anhydrides, such as sulphur dioxide, is also discussed in the light of this theory.

R. CUTHILL.

Theory and systematic treatment of molecular forces. F. LONDON (Z. Physik, 1930, 63, 245—279).—Mathematical. A general review is made of the attractive forces between molecules from the point of view of the new quantum mechanics. The previous explanation of Keesom and Debye of van der Waals attractive forces in the inert gases as due to quadrupole moments is now untenable, since quantum mechanics shows that the atoms of these gases have a spherically symmetrical distribution of electrical charge. Non-polar diatomic molecules according to the quantum mechanics possess a quadrupole moment, but the value calculated for hydrogen is much too small to explain the van der Waals attraction. It is shown that the quantum-mechanical force of attraction between two hydrogen atoms due to the reciprocal perturbation of the electronic orbits (cf. Eisenschitz and London, this vol., 525) has a potential which varies inversely as the sixth power of the distance between the molecules, and would therefore at large distances completely outweigh the forces due to quadrupoles, the potential of which varies inversely as the eighth power of the distance. The theoretical calculation of this quantum-mechanical force, which is a second order perturbation effect, is too difficult to be made directly even for the simplest molecules, but it can be easily estimated from the polarisability calculated from the molecular refraction together with the values of the excitation and ionisation potentials. This is carried out for the inert gases and the values obtained for the van der Waals a are compared with the values deduced from critical data. It is thereby shown that the quantum-mechanical force can fully account for the attraction, so that the assumption of quadrupoles is not necessary. Similar calculations are made for a series of diatomic gases, and the new force is shown to be the cause of the major portion of the attraction. The values of the two other attractive forces present, viz., the force due to the direct action of the multipoles (Keesom effect) and the force due to polarisation (Debye effect), are estimated and curves drawn for hydrogen chloride and for hydrogen bromide showing the variation with distance of the three individual forces. The quantum-mechanical force (dispersion effect) is shown to be the most important.

H. A. JAHN.

Structure of the carbilamines and other compounds of bivalent carbon. D. L. HAMMICK, R. C. A. NEW, N. V. SIDGWICK, and L. E. SUTTON

(J.C.S., 1930, 1876—1887).—Direct evidence of the correctness of the formula $R-N\equiv C$ for the carbilamines was obtained from the results of measurement of the parachors and dipole moments of these substances. Chemical properties are in accordance with this structure. The co-ordinate structure, $C\equiv O$, for carbon monoxide is also discussed. W. GOOD.

Parachor of co-ordinated hydrogen in ortho-substituted phenols. N. V. SIDGWICK and N. S. BAYLISS (J.C.S., 1930, 2027—2034).—Observed values of the parachors of *o*-substituted phenols show considerable differences from those calculated. It is suggested that the anomalies are due to the formation of chelate rings and, on this basis, a decrease of 14.4 parachor units in the conversion of $=O+H-$ into $=O\rightarrow H-$ is deduced. No explanation can be given for the fact that the experimental values for *m*- and *p*-substituted phenols show no anomalies, which would be expected as a result of the recognised association in these compounds. W. GOOD.

Precision measurements of the glancing angle of reflexion from calcite for silver $K\alpha_1$ X-rays by the method of displacement. C. D. COOKSEY and D. COOKSEY (Physical Rev., 1930, [ii], 36, 85—109).—A detailed description is given of the method and apparatus used in obtaining results previously reported (cf. this vol., 526). N. M. BUGH.

Spectral lines obtained by the method of convergent X-rays. T. FUJIWARA (Mem. Coll. Sci. Kyoto, 1930, 13A, 303—306; cf. A., 1928, 1175).—A detailed study of the spectral lines produced by fine single-crystal wire is presented. C. W. GIBBY.

Dependence of the width and intensity of Debye lines and rings on the dimensions of the X-ray source, of the preparation, and of the camera. W. BUSSE (Z. Physik, 1930, 63, 227—244).—Mathematical. The effect of absorption by the preparation is considered and the distribution of intensity within the lines determined. An absolute maximum in the intensity of the line was always obtained by a source of such width that it gave rise to lines of double the natural width. For a given width of line, the greatest intensity was also obtained, in the case of small absorption, for such widths of the source and of the preparation that the lines were double the natural width, and these optimum widths of source and preparation were calculated. The most satisfactory source-focus consists of an elongated rectangle. H. A. JAHN.

Method of obtaining a single crystal of aluminium of any desired crystallographic orientation. T. SANO (Mem. Coll. Sci. Kyoto, 1930, 13A, 307—309).—An aluminium crystal of any desired orientation can be obtained by bringing another crystal into contact with molten aluminium and lowering the temperature very slowly. C. W. GIBBY.

X-Ray investigation of the alloy AuCu. K. OHSHIMA and G. SACHS (Z. Physik, 1930, 63, 210—223).—The change from a face-centred cubic lattice to a face-centred tetragonal lattice through heat treatment of the alloy AuCu is studied by X-ray reflexions from a rotating single crystal, and also by the method of Debye and Sherrer as improved by

Sachs and Weerts (this vol., 527) on finely crystalline samples. The quenched crystals exist in the cubic form and the change on tempering to the tetragonal is investigated, the experiments on the single crystal showing that the two lattices exist side by side during the change, but with the powder method the tetragonal phase could be detected only when evidence of the regular phase had disappeared. The lattice constants were determined by the powder method for the two phases, and the gradual change in the *a/c* ratio during the heat treatment observed by Gorsky was determined. The possible kinetics of the change are discussed. H. A. JAHN.

Micrography of piezo-electric quartz. P. T. KAO (Compt. rend., 1930, 191, 334—335).—Corrosion figures obtained by the action of dilute hydrofluoric acid or potassium hydroxide on the positive and negative faces (perpendicular to the electrical axis) of piezo-electric quartz crystals show in relief a crystalline structure, having the form of a parallelogram with two sides parallel to the optical axis, and a fibrous structure parallel to the same axis, respectively. Corrosion occurs more rapidly on the negative than on the positive face, and must be carefully controlled if well-defined figures are to be obtained. The faces perpendicular to the optical axis show triangles which are really the bases of microscopic pyramids. J. GRANT.

Quartz. R. WEIL (Compt. rend., 1930, 191, 380—382).—In crystals of the *S* type the birefringence normal to the axis corresponds with flat planes normal to three non-adjacent faces of the prism and inclined to one another at angles of 120° , and is always very feeble (10^{-4} to 10^{-5}). Sometimes these planes are visible to the unaided eye as fibres normal to the face of the prism. Corrosion figures produced with cold concentrated hydrofluoric acid show rectangular or lenticular orifices 3 microns long parallel to the vertical edge of the faces of the prism and in a plane normal to the b_1 faces. From these, fine capillary and often rectilinear twisted canals ("hairs") extend into the interior of the crystal, and may attain lengths of 1 cm. Crystals of the *L* type show hairs perpendicular to the faces of the rhombohedron, which appear to delimit certain regions of the crystal, hairs from one domain running parallel with those of an adjacent domain. Quartz with very few planes has very few hairs, but these are then correspondingly longer. In no case do the hairs penetrate the crystal beyond what appears to be a central nuclear region. J. GRANT.

Structure of some sodium and calcium aluminosilicates. L. PAULING (Proc. Nat. Acad. Sci., 1930, 16, 453—459; cf. A., 1929, 748).—The structures of natrolite, $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, the scapolites, or solid solutions of marialite, $Na_4Al_3Si_9O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}(SO_4, CO_3)$; davynite, $(Na, Ca)_4Al_2Si_3O_{12}(CO_3, SO_4, Cl)$, and cancrinite are described and the nature of the frameworks is deduced and illustrated by diagrams. Natrolite is pseudotetragonal, *a* : *b* : *c* = 0.97852 : 1 : 0.35362; the unit cell, *a* 18.19, *b* 18.62, *c* 6.58 Å., contains 8 mols.; the lattice is face-centred; space-group C_{2h}^{23} . The scapolites are tetragonal, *a* : *c* = 1 : 0.43925; the unit

cell, a 12.27, c 7.66 Å., contains 2 mols.; the lattice is body-centred; space-group C_{4h}^2 , C_{4v}^2 , or S_6^2 . Davynite and canerinite (cf. Gossner, this vol., 1100) are hexagonal, the unit cells, a 12.8, c 5.35 and a 12.6, c 5.18 Å., respectively, contain 2 mols.; space-group D_{6h}^1 . Cleavages of some tetrahedral framework crystals are tabulated.

N. M. BLIGH.

Crystal chemistry of the aluminosilicates. Relationship of the anorthite group to the nepheline group. W. EITEL, E. HERLINGER, and G. TRÖMEL (Naturwiss., 1930, 18, 469—474).—The following lattice constants in Å. have been determined from powder diagrams: $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$, a 9.98, c 8.44; $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$, a 10.41, c 8.70; $\text{Na}_2\text{Y}_2\text{Si}_2\text{O}_8$, a 10.79, c 8.80; $\text{CaY}_2\text{Si}_2\text{O}_8$, a 10.79, c 8.80; $\text{K}_2\text{La}_2\text{Si}_2\text{O}_8$, a 11.01, c 8.96; $\text{Na}_2\text{La}_2\text{Si}_2\text{O}_8$, a 11.01, c 8.96; $\text{CaLa}_2\text{Si}_2\text{O}_8$, a 11.01, c 8.96; $\text{Na}_2\text{Nd}_2\text{Si}_2\text{O}_8$, a 10.89, c 8.85; $\text{K}_2\text{Nd}_2\text{Si}_2\text{O}_8$, a 10.89, c 8.85; $\text{CaNd}_2\text{Si}_2\text{O}_8$, a 10.89, c 8.85. The X-ray diagrams of nepheline and kaliophilite are indicative of differences of structure, but rubidium nepheline possesses the rhombic structure of the second modification of kaliophilite. Nephelines and anorthites wherein the aluminium has been replaced by a rare-earth element have a structure closely resembling that of kaliophilite. Although homogeneous mixed crystals are formed between the rare-earth nephelines and the corresponding anorthites, this does not occur between the aluminium compounds and their rare-earth derivatives. The theoretical significance of the results is discussed and their geochemical aspect is indicated. H. F. GILLBE.

Silicate system based on crystal structure. S. VON NÁRAY-SZABÓ (Z. physikal. Chem., 1930, B, 9, 356—377).—Existing systems of classification of silicates are discussed and the characteristic features of the silicate lattices are described. A new system, applicable to all well-crystallised compounds and based on the form of the space-lattice rather than on chemical evidence, is proposed. In this classification the silicates fall into five groups: (1) orthosilicates, (2) independent chemical groups, such as Si_2O_7 , (3) unidimensional chains of silicon and oxygen atoms, (4) two-dimensional planes of silicon and oxygen atoms, (5) three-dimensional networks of silicon and oxygen atoms. Various properties of silicates, such as hardness, chemical reactivity, etc., are discussed in the light of these views.

E. S. HEDGES.

Crystal structures of the compounds Zn_2TiO_4 , Zn_2SnO_4 , Ni_2SiO_4 , and NiTiO_3 . N. W. TAYLOR (Z. physikal. Chem., 1930, B, 9, 241—264).—The compounds zinc orthotitanate, zinc orthostannate, nickel orthosilicate, and nickel metatitanate have been prepared by mixing the powdered component oxides, pressing into pastilles, and heating at or above 850°. The lattice constants, densities, and molecular volumes of these compounds have been determined and the following data are given. Zinc orthotitanate: cubic, spinel type, a 8.460 ± 0.005 Å., d 5.295; zinc orthostannate: cubic, spinel type, a 8.650 ± 0.005 Å., d 6.393; nickel orthosilicate: rhombic, olivine type, a 4.705 ± 0.005, b 10.11 ± 0.01, c 5.914 ± 0.005 Å., d 4.920 g./cm.³; nickel metatitanate: rhombohedral, corundum-ilmenite type, a 5.023 ± 0.005 Å., d 5.075. No trace of nickel metasilicate, nickel orthotitanate,

zinc metatitanate, or zinc metastannate was found. Mixtures of cupric oxide with the dioxides of silicon, titanium, and tin do not react under the conditions described.

E. S. HEDGES.

Physico-chemical investigation of amino-acids. III. G. TAKAHASHI and T. YAGINUMA (Proc. Imp. Acad. Tokyo, 1930, 6, 201—204).—Tables show the crystal constants of the α - and β -forms of the methyl, ethyl, and *n*-propyl ester hydrochlorides of *l*-leucine. Diagrams are furnished.

P. W. CLUTTERBUCK.

Crystal structure of normal paraffins. S. H. PIPER and T. MALKIN (Nature, 1930, 126, 278).—Hexacosane and tetratriacontane show two stable forms at the ordinary temperature; one form has the normal structure described by Müller (this vol., 844), but the other spacing, about 4 Å. shorter, is different from the second form of Müller. In hexacosane, this new form occurred alone when crystallised from benzene or alcohol: a fused layer showed both spacings. In tetratriacontane, crystals from benzene gave only the new spacings, whilst melted material showed only the normal form. Pure, even-numbered hydrocarbons appear to crystallise in the new form if the chain has 26 or more carbon atoms. The two spacings for hexacosane, triacontane, and tetratriacontane are 35.0 and 31.05, 40.5, and 45.3 and 40.00 Å., respectively. The appearance of the second spacing is a criterion of purity.

L. S. THEOBALD.

X-Ray investigation of the crystals of azobenzene. M. PRASAD (Phil. Mag., 1930, [vii], 10, 306—313).—The rotating crystal method was used, the radiation being copper $K\alpha$ and $K\beta$ from a Shearer tube. The dimensions of the unit cell, which contains 4 mols., were found to be a 12.65, b 15.60, c 15.60 Å.; β 114°24'.

W. GOOD.

Determination of the degree of polymerisation of some modifications of polyoxymethylene by X-ray methods. E. OTT (Z. physikal. Chem., 1930, B, 9, 378—400).—An X-ray spectrographic examination of the crystal structure of some polyoxymethylenes shows them to consist of long chains of $\cdot\text{CH}_2\cdot\text{O}$ groups, the paraformaldehyde molecule containing 32 of these groups, γ -polyoxymethylene 60, and δ -polyoxymethylene 24. The length of the unit $\cdot\text{CH}_2\cdot\text{O}$ group is 1.88—1.89 Å. An important point established is that in crystals of highly polymerised substances all the complex molecules are of the same length. Characteristic differences in the diagrams obtained from the different polymerides were observed, and the crystals are pseudo-hexagonal.

E. S. HEDGES.

Structure of organic liquids internally and on the surface. J. J. TRILLAT (Z. Physik, 1930, 64, 191—213).—The sources of error in the X-ray investigation of the structure of organic liquids are discussed, and an apparatus in which they are minimised is described. A series of determinations was carried out with different fatty acids, alcohols, and triglycerides. In all cases a very intense ring of large diameter was obtained corresponding with an identity period of 4.0—4.6 Å. The internal ring varied in diameter with the number of carbon atoms, but was observed only for the first members of the

fatty acid and alcohol series. Its intensity decreased with increasing number of carbon atoms, and disappeared almost completely for molecules containing six carbon atoms, even after a long exposure. In all cases there was also a general blackening, which changed with the number of carbon atoms. The distances calculated from the usual expression, $\lambda = 2d \sin \theta$, for the intense ring were practically constant for all substances used, except for the first members, where there was some deviation. This distance is the cross-section of the molecule which must be regarded as linear. The general blackening is supposed to be due to molecular association. The surface structure of the same series of compounds was investigated by a drop method. In certain cases a mean orientation of the molecule perpendicular to the free surface was observed. The dimensions of the molecules can be calculated approximately, and the results agree with the assumption of a perpendicular orientation of single molecules. A. J. MEE.

Diffraction of X-rays in liquids and different substances. Effects of filtration of the general radiation. Coefficients of absorption of liquid acids. J. THBAUD and J. TRILLAT (J. Phys. Radium, 1930, [vii], 4, 249—260).—When the X-ray diffraction patterns of organic substances of thickness of several mm. are measured without separating the characteristic radiation of the anticathode from the general radiation, there appears, in addition to the fundamental ring or halo, *A*, characteristic of the molecular structure of the substance, a secondary halo, *B*, which is due to selective filtration from the continuous background. With a copper anticathode and the liquid fatty acids, *B* appears when the thickness is greater than 2 mm., its intensity increasing with an increase in thickness, whilst that of *A* decreases. At a constant thickness, the breadth and diameter of *B* vary with the excitation potential; under a *P.D.* of 15 kilovolts, *B* is thin and of relatively large diameter, but at 40 kilovolts it is diffuse and smaller in diameter. *A* remains constant and is always the external halo. Data for nonoic acid are given. With an anticathode of molybdenum, *A* and *B* are intermingled. This phenomenon is general and has been observed for water, the alcohols, triglycerides, glycerol, palmitic and stearic acids, cellulose, caoutchouc, aliphatic hydrocarbons, and benzene. For the liquid fatty acids using the $K\alpha$ radiations of molybdenum and copper, the coefficients of absorption are as follow: acetic 0.73 and 7.9, heptioic 0.65, nonoic 0.5 and 4.5, stearic (fused) 0.5 and 3.72, respectively. These coefficients are additive. Precautions should be taken in structural investigations by means of X-rays to prevent the formation of secondary haloes. L. S. THEOBALD.

Structure of cellulose fibres of wood. S. PIENKOWSKI (Z. Physik, 1930, 63, 610—615).—The structure of the cellulose crystallite in woods of different nature and age was investigated by the X-ray method. This method has already shown that the crystallite of cellulose from natural fibres is partly equally oriented, and it was desired to know whether the same applies to cellulose from wood. It was found that the degree of homogeneity as regards orientation depends on the

thickness of the annual rings and the hardness of the wood. Great differences in degree of dispersion were noted for crystallites from tree parts of different thicknesses, but of the same annual layer. In agreement with the anatomical structure, exact homogeneity as regards orientation was noted for elm and ash wood in the thicker parts of the same annual ring, and for fir, pine, and poplar in the thinner parts. The drying process which takes place in the wood influences the degree of dispersion only to a small extent, making it weaker. The degree of homogeneity of the crystallites is greater the more compact is the wood, and depends apparently on the size of the cell walls parallel to the tree axis. A. J. MEE.

Sperms as living liquid crystals. F. RINNE (Nature, 1930, 126, 279).—A summary of the evidence supporting the view that sperms are also liquid crystals. L. S. THEOBALD.

Theory of superconductivity of elements. II. Basic conceptions of the origin of superconduction. Z. A. EPSTEIN (Z. Physik, 1930, 63, 640—659; cf. this vol., 986).—By an examination of thermo-kinetic theory it is possible to state what properties a superconducting element should have as distinct from ordinary conductors. Superconductors have these properties to relatively greater degree than ordinary conductors. A formula is proposed to differentiate between the two classes of the form $D \cdot \beta \cdot v^{2/3} = \text{const.}$, where *D* is the directional force and *v* the atomic volume. Various properties of superconductors and ordinary conductors are compared. A. J. MEE.

Change of resistance of gold crystals in a magnetic field at low temperatures and superconductivity. P. KAPITZA (Physikal. Z., 1930, 31, 713—720).—The interpretation of experimental results obtained by Meissner and Scheffers (this vol., 142) for the change in resistance of gold crystals at the temperatures of liquid nitrogen, liquid hydrogen, and liquid helium is discussed in the light of the author's theoretical assumptions. By applying formulæ deduced by the author, the experimental results give values in complete agreement with theoretical assumptions. Criticism by Meissner and Scheffers of the author's hypothesis of superconductivity is answered. W. R. ANGUS.

Change of electrical resistance of platinum on outgassing in a high vacuum and then absorbing hydrogen. K. WEIL (Z. Physik, 1930, 64, 237—247).—A strip of platinum was activated and outgassed by intermittent heating to redness in a high vacuum. The resistance decreased during the outgassing process, and on allowing the strip again to absorb hydrogen by placing it in the gas under a pressure of 250 mm., the resistance increased. The outgassed strip diminished in resistance by 3.5%, and on re-absorption of hydrogen it gained by 1%. On further outgassing only 1% decrease was noted. The results suggest the improbability of the existence of a stable platinum-hydrogen compound, the change in resistance depending on the amount of gas absorbed. A. J. MEE.

Hydrogenised iron of high magnetic permeability. P. P. CIOFFI (Nature, 1930, 126, 200—

201).—Initial and maximum permeabilities of 6000 and 130,000, respectively, have been obtained by heat treating iron in moist hydrogen between 1400° and 1500° for 12 hrs., and annealing at 880°, which removes any deleterious effects on the magnetic properties due to overstrain. The high permeability of hydrogenised iron is attributed, in part at least, to absorbed hydrogen, since a further treatment at a high temperature in a vacuum reduces the permeability to that obtained when ordinary iron is treated in a high vacuum. Magnetisation curves and the hysteresis loop are reproduced. L. S. THEOBALD.

Principal magnetic susceptibilities of bismuth single crystals. A. B. FOCKE (Physical Rev., 1930, [ii], 36, 319—325).—The Gouy method was used to determine the magnetic susceptibilities of bismuth single crystals grown by the method developed by Goetz (cf. this vol., 401). The specific susceptibility has a constant value -1.487×10^{-6} in all directions perpendicular to the principal crystallographic axis, and a minimum value -1.046×10^{-6} parallel to the axis; the mean is given as -1.34×10^{-6} .

N. M. BLIGH.

Discontinuous changes in length accompanying the Barkhausen effect in nickel. C. W. HEAPS and A. B. BRYAN (Physical Rev., 1930, [ii], 36, 326—332).—Using a heterodyne beat method with a modified form of an apparatus previously described (cf. A., 1929, 1217), allowing displacement measurements down to 9×10^{-9} cm., the sudden changes in length of a nickel wire subjected to a steadily changing magnetic field were measured at the instants of each Barkhausen discontinuity of magnetisation. The lengths of the wires were 1.96 and 2 cm., and the diameters 0.01 and 0.002 cm., respectively. The largest magnetostrictive jump was 4.7×10^{-7} cm., and the minimum value 3.7×10^{-7} c.c., for the volume of the element affected. A qualitative theory is discussed (cf. A., 1929, 1369), and the change in intensity of magnetisation of the volume element is shown to lie probably between 40 and 330 units. N. M. BLIGH.

Variation of the plasticity of rock-salt, silver bromide, and silver iodide with temperature. F. RINNE and W. RIEZLER (Z. Physik, 1930, 63, 752—759).—The variation of plasticity with temperature was determined with a Ludwik steel cone. The radius of curvature of the depression caused by this cone increases logarithmically with the time of application of the stress, and the parameters of the equation expressing this relation are given as functions of the temperature of the specimen. Corrections are required because of deviation of the depression from spherical form. Single crystals and compressed powders of one substance give the same results.

A. B. D. CASSIE.

Relation between the mol. wt. and the density of gold in the liquid state. A. JOUNIAUX (Bull. Soc. chim., 1930, [iv], 47, 682—686).—Cryoscopic measurements have been made of the mol. wt. of gold dissolved in various metals between 271° and 1528°. It is unimolecular between 400° and 1550°.

C. W. GIBBY.

Relation between the mol. wt. and density of magnesium in the liquid state. A. JOUNIAUX

(Bull. Soc. chim., 1930, [iv], 47, 686—690).—The mol. wt. of magnesium (which at 200° is triatomic), dissolved in other metals, falls with rising temperature up to 700°, above which the molecule is monatomic.

C. W. GIBBY.

Variation of physical constants in homologous series. A. GOSSELIN (J. Chim. phys., 1930, 27, 357—363).—Further evidence is cited in favour of a theory already put forward (cf., A., 1929, 1130).

C. W. GIBBY.

Theory of galvanomagnetic, thermomagnetic, and thermoelectric phenomena in metals. N. H. FRANK (Z. Physik, 1930, 63, 596—609).—Mathematical. The four transversal galvanomagnetic and thermomagnetic effects are calculated for adiabatic systems according to Sommerfeld's theory. The connexion between these effects is discussed from a theoretical point of view. The various thermoelectric effects in homogeneous circuits are discussed, and in particular the inversion of the Thomson effect (Benedick effect). The change of resistance of a metal in a magnetic field under adiabatic conditions vanishes to both a first and a second approximation. For isothermal conditions, however, it vanishes only to a first approximation. A. J. MEE.

Reactions in liquid hydrogen sulphide. VIII. Specific conductance of liquid hydrogen sulphide. S. D. SATWALEKAR, L. W. BUTLER, and J. A. WILKINSON (J. Amer. Chem. Soc., 1930, 52, 3045—3047).—The specific conductance of dry liquid hydrogen sulphide at -78.5° is 3.7×10^{-11} ohm $^{-1}$. The resistance is increased by the addition of small quantities of water. J. G. A. GRIFFITHS.

M. p. of tellurium dioxide. A. ŠIMEK and B. STEHLÍK [with J. ŠMÍDA] (Coll. Czech. Chem. Comm., 1930, 2, 447—456).—Pure tellurium dioxide, prepared by dissolving the purified element in nitric acid, evaporating to dryness, and igniting in a gold crucible, has m. p. 732.6° , d_4^{20} 6.02. The fused substance readily attacks glass, porcelain, quartz, and alundum, and, more slowly, platinum, but the appearance of the dark colour observed when the dioxide has been in contact with platinum at a red heat for some time is not accompanied by a change of m. p. No indication of dimorphism is given by the heating curve between the ordinary temperature and the m. p., the crystals obtained by slow crystallisation of the fused material being optically uniaxial and exhibiting double refraction. A method is described for the extrapolation of the m. p. of substances which do not exhibit a sharp step in the heating curve.

H. F. GILLBE.

Specific heat of mercury in the neighbourhood of the m. p. L. G. CARPENTER and L. G. STOODLEY (Phil. Mag., 1930, [vii], 10, 249—265).—The specific heat of very carefully purified mercury was determined over the range 198—285° Abs., which includes the m. p., 234°. The results were reduced and corrected to obtain C_p . The accuracy of the results is discussed. In the neighbourhood of 210° the C_p curve shows an increase of its positive slope and on nearing the m. p. becomes flat. At the m. p. itself the value of C_p was found to be 6.02 g.-cal., thus showing an excess over $3R$ (5.95). Two hypotheses

are considered, viz., that the anomalous rise of C_v is due to anharmonic oscillations of atoms, and that it is due to the participation of free electrons in the thermal energy of the atomic lattice. W. GOOD.

Rotational specific heat and rotational entropy of simple gases at moderate temperatures. G. B. B. M. SUTHERLAND (Proc. Camb. Phil. Soc., 1930, 26, 402—418).—The formula for the rotational specific heat of a diatomic gas is examined, the formula for the rotational energy of a molecule as given by Kramers and Pauli being first modified so as to conform to the new quantum mechanics. Formulæ for the rotational entropy of simple gases at moderate temperatures are derived. W. GOOD.

Virial law in the relativistic gas theory. V. DANILOV (Z. Physik, 1930, 63, 692—696).—Mathematical. The relativistic generalisation of the virial law is worked out for the case of an ideal gas. A. J. MEE.

Density of carbon dioxide. D. LEB. COOPER and O. MAASS (Canad. J. Res., 1930, 2, 388—395).—Modifications of the Maass and Russell method for determining densities (A., 1919, ii, 47) which permit an accuracy of about 1 in 10,000 are described. The density of carbon dioxide has been determined at two temperatures and over a pressure range of 75—25 cm. The mean value obtained for the mol. wt. of carbon dioxide at zero pressure is 44.0033 ± 0.002 , from which the at. wt. of carbon is found to be 12.0033 ± 0.002 . H. S. GARLICK.

Saturation vapour pressure of lithium. A. BOGROS (Compt. rend., 1930, 191, 322—324).—The author's modification of Knudsen's method (this vol., 829; Knudsen, A., 1909, ii, 216, 385) gave the values (in bars) of 4.2, 6.3, 7.1, 10.5, 15, and 18 at 510°, 527°, 529°, 537°, 563°, and 572°, respectively, with a maximum relative error of 15%. J. GRANT.

Vapour pressure of sodium. Low-pressure measurements with the absolute manometer. W. H. RODEBUSH and W. F. HENRY (J. Amer. Chem. Soc., 1930, 52, 3159—3161).—A modified form of the manometer of Rodebush and Coons (A., 1927, 954) is used to determine the vapour pressure of sodium at temperatures between 263° and 397°. The results are reproduced by the equation $\log p$ (mm.) = $7.551 - 5400/T$ (cf. this vol., 1104). J. G. A. GRIFFITHS.

Flow of viscous and plastic materials along an initially empty long narrow glass tube. G. W. S. BLAIR (J. Rheology, 1930, 1, 424—428).—The dynamics of flow of water and of starch paste when caused to flow along an initially empty glass tube of uniform cross-section have been investigated. E. S. HEDGES.

Fluidity of liquids. I. Relation of fluidity to temperature. S. E. SHEPPARD and R. C. HOUCK (J. Rheology, 1930, 1, 349—371).—The expression $\phi = Ae^{-K/T}$ is derived for the relation between fluidity and temperature and is shown to be valid for a large number of liquids over a wide range of temperature. The fluidity represents the statistical equilibrium between unoriented and oriented molecules or the degree of "patchy crystallisation." The constant K expresses the work or heat of disruption of the mole-

cular fields holding a molecule in these ordered patches, and is given approximately by the expression $C_v \times (M\varrho)^{2/3}$, where C_v is the specific heat, M the mol. wt., and ϱ the density. K is defined as the specific heat per unit molecular surface. As the f. p. is approached in the case of associated liquids the relation between the logarithm of fluidity and the reciprocal of absolute temperature may deviate from linearity, and values of molecular complexity may be obtained where it varies greatly with temperature, or in less favourable cases an approximate association factor can be calculated. These values are in reasonable agreement with those obtained by other methods. Evidence is adduced to show that liquid water consists mainly of $(H_2O)_6$ molecules below 30° and of $(H_2O)_3$ from 30° to 100°. E. S. HEDGES.

Determination of the fluidity of water as a reference standard. E. C. BINGHAM (J. Rheology, 1930, 1, 433—438).—The Society of Rheology recommends that the capillary-tube method is at present the most satisfactory for viscosity measurements and that 20° should be the standard temperature. The formula to be used for measurements with the capillary tube is $\eta = \pi g P R^4 t / 8 \nu (l + \Delta) - m \rho \nu / 8 \pi t (l + \Delta)$ and a list of 26 corrections to be applied is given. E. S. HEDGES.

Margules' method of measuring viscosities modified to give absolute values. H. R. LILLIE (Physical Rev., 1930, [ii], 36, 347—362; cf. B., 1929, 940, 963).—A method is described for determining absolute viscosities in a Margules rotating-cylinder type viscosimeter, without the aid of calibrating liquids of known viscosities. The viscosity of commercial castor oil was found to be 9.99 and 4.61 poises at 20° and 30°, respectively. Relative viscosities measured by this and capillary-flow methods are concordant. N. M. Blich.

Chemical constitution and association. E. C. BINGHAM and H. J. FORNWALT (J. Rheology, 1930, 1, 372—417).—The fluidities and densities of 14 mercaptans have been measured at different temperatures. The 14 curves obtained by plotting fluidity against temperature approach parallelism at high temperatures and show that fluidity decreases linearly with increase in mol. wt. and that the temperature required to give a definite fluidity to a normal compound is higher than that required for the corresponding *iso*-compound. Probably the association of normal compounds is greater than that of *iso*-compounds. Sulphur is provisionally given an atomic temperature value of 64.4. The associations of the mercaptans studied can be expressed empirically by the formula $n = 1.141 - 0.0115N_c - 0.036N_2(SH)$, where n is the association, N_c the number of carbon atoms, and the last term is the constitutional correction for the influence of the *iso*-position. The mean deviation is 0.6%. Further measurements of fluidity and density have been made with heptoic, lauric, and stearic acids and are compared with existing data for 7 other fatty acids. The associations of the 10 fatty acids can be represented by the linear equation $n = 1.75 - 0.0446N_c + 0.514(H \cdot CO_2H) + 0.185(AcOH)$, which is valid up to 17 carbon atoms, associations thereafter being considered as unity. Formic and acetic acids do not

fall on the linear part of the curve. The average deviation is 0.68%. Existing fluidity data for 11 members of the lower esters have been used to calculate the association and three accurate logarithmic formulæ have been found to fit the case. A more simple and useful, although less accurate, formula is the linear relation $n=1.315-0.04N_c$, with which the average deviation is 1.14%. When the ester is symmetrical the association is a minimum. Further measurements of a similar nature have been conducted with *n*-heptyl alcohol, diphenyl, ethyleneglycol, and ethyl lactate. The fluidities of two very viscous liquids, tolyl phosphate and ethyl abietate, have been measured. Measurements conducted with the paraffin hydrocarbons show again that normal and *iso*-compounds fall into separate groups. The investigation shows that the substances examined contain definite associating groups and that they strongly reinforce one another. Chemical constitution may be used to predict the degree of association. Among isomeric compounds the normal compound has the higher association, but this is a special case of a general law that as radicals are moved towards the centre of the molecule the association is lowered, regardless of whether the radical is an associating group or not. In all of the homologous series of compounds examined the association decreases as the mol. wt. increases.

E. S. HEDGES.

Turbulent internal friction in binary liquid mixtures. R. SPRINGER and H. ROTH (Monatsh., 1930, 56, 1—15).—The method previously described (A., 1927, 1133) has been employed to measure the turbulent internal friction in 20 binary liquid mixtures; the results are compared with those obtained by other workers using the Poiseuille method. The curves obtained with the mixtures methyl, ethyl, or propyl alcohol-water, chloral-water or ethyl alcohol, aniline-phenol agree closely with the Poiseuille figures, showing a positive curve indicating complex formation. The curves for the following mixtures show pronounced additive character: carbon disulphide with ether, toluene, acetone, ethyl alcohol, ethyl acetate, or benzene; benzene-chloroform and *m*-xylene-dimethylaniline. The mixtures benzene-propyl alcohol or ethyl alcohol, nitrobenzene-diethylaniline show additive turbulence curves, but the Poiseuille curves show a negative course. The mixtures ethyl alcohol-acetone and aniline-nitrobenzene show a negative course in both curves; the system propyl alcohol-aniline shows an S-shaped turbulence curve compared with a negative Poiseuille curve.

J. R. I. HEPBURN.

Dielectric polarisation of liquid mixtures and association. I. N. N. PAL (Phil. Mag., 1930, [vii], 10, 265—280).—Measurements of the dielectric constants of mixtures of nitrobenzene and benzene and of nitrobenzene and chloroform of various concentrations have been made by a heterodyne beat method at different temperatures. The general features of the results are tentatively accounted for by an expression derived from Debye's dipole theory and the assumption that the number of molecules is proportional to $e^{-\epsilon/KT}$, where ϵ is approximately determined by the residual electric attraction between the dipoles. W. GOOD.

F. p. of benzene-toluene, -ethyl alcohol, and -gasoline mixtures. D. TARASENKOV (J. Appl. Chem., Russia, 1930, 3, 153—155).—The following values of wt.-% of benzene and f. p., respectively, are recorded: benzene-toluene: 100, +5.5°; 89.74, -2.1°; 78.92, -9.3°; 70.04, -15.3°; 59.45, -24.1°; 50.36, -32.6°; 40.31, -42°; 29.70, -53°, 20.00, -68°; 9.85, -81°, 0, -94°. Benzene-ethyl alcohol: 89.91, +2.5°; 79.92, +1.1°; 70.00, -0.4°; 59.97, -2.6°; 49.90, -6.1°; 39.90, -11.1°; 29.96, -21.0°; 20.02, -39.5°; 9.97, -66°; 0, -114°. Benzene-petroleum (*d*¹⁵ 0.7159, Grozni): 90, +0.1°; 80, -4.5°; 70, -9.0°; 60, -14.2°; 50, -22.2°; 40, -26.5°; 30, -37.2°; 20, -43.5°; 10, -61.5°; 0, -160°.

CHEMICAL ABSTRACTS.

Silver-cadmium alloys. E. R. THEWS (Deut. Goldschmiede-Ztg., 1930, 33, 56—58; Chem. Zentr., 1930, i, 1857).

X-Ray study of the nickel-chromium system. S. SEKITO and Y. MATSUNAGA (J. Study Met., Japan, 1929, 6, 229—233).—The alloys containing 0—45% Cr are of the face-centred cubic structure, chromium dissolving in the nickel to form a solid solution. In the alloys containing 95—100% Cr the structure is body-centred cubic, the nickel dissolving in the chromium. Alloys containing 45—95% Cr consist of a mixture of these two solid solutions.

CHEMICAL ABSTRACTS.

Electrical conductivity of Cu₃Au alloys at low temperatures with and without superstructure. H. J. SEEMANN (Z. Physik, 1930, 62, 824—833).—The electrical resistance of copper-gold alloys containing approximately 25 at.-% Au has been determined at low temperatures, (1) after heating for 50 hrs. at 860° (without superstructure), and (2) with the same test-piece cooled slowly through the range 400—300° (with superstructure). Alloys without superstructure show a linear fall in resistance, but those with superstructure show a considerably greater decrease at lower temperatures. The shape of the resistance-composition curve for the alloys without superstructure indicates the formation of an intermetallic compound of the formula Cu₃Au, whereas the curve for alloys with superstructure suggests the existence of solid solutions of copper and gold. The decrease of resistance of the pure compound at low temperatures corresponds with that of the pure metal.

A. J. MEE.

Equilibrium diagram of the iron-tungsten system. S. TAKEDA (J. Study Met., Japan, 1929, 6, 298—308).—The eutectic of the ϵ - (corresponding with Fe₃W₂) and δ -phases is at 33% W; the peritectic reaction, in which the ϵ -phase is formed, occurs in alloys containing more than 43% W. The existence of a phase α , which is formed peritectically from the fused mass and tungsten (or ζ -phase), is inferred.

CHEMICAL ABSTRACTS.

Alloys of the ternary system iron-nickel-cobalt. H. KÜHLEWEIN (Physikal. Z., 1930, 31, 626—640).—A review of the properties of alloys containing iron, cobalt, and nickel. Physical data for the pure metals are recorded and the properties of the binary and ternary systems are discussed. Various electrical, mechanical, thermal, and magnetic prop-

erties are considered. The discussion of these properties is given in detail with illustrative diagrams.

W. R. ANGUS.

Solubility of silver chloride in aqueous solutions of potassium chloride. A. PINKUS and N. BERKOLAÏKO (J. Chim. phys., 1930, 27, 364—385).—The solubility of silver chloride in pure water is 1.42×10^{-5} mol./litre. On addition of potassium chloride the solubility passes through a minimum value of 8.13×10^{-7} mol./litre at 0.0196 mol./litre of potassium chloride, and rises rapidly with further increase in concentration of the latter. Activity coefficients and degrees of complex formation are calculated.

C. W. GIBBY.

Solubility of magnesium neodymium nitrate in water, nitric acid, and magnesium nitrate solutions. J. A. N. FRIEND (J.C.S., 1930, 1903—1908).—The solubility of the salt in water rises steadily to the m. p., the solid phase being $3Mg(NO_3)_2 \cdot 2Nd(NO_3)_3 \cdot 24H_2O$. Both nitric acid and magnesium nitrate reduce the solubility, the latter having the greater effect for equivalent concentrations. Indications are obtained of the possible existence of a higher hydrate at low temperatures. It is shown that on precipitation of neodymium as oxalate, adsorption of magnesium under the conditions employed is negligible.

H. I. DOWNES.

Partition law in the fractional crystallisation of radium salts. N. RIEHL and H. KÄDING (Z. physikal. Chem., 1930, 149, 180—194).—The logarithmic partition formula of Doerner and Hoskins (A., 1925, ii, 381) gives the distribution of radium between solution and precipitate more accurately when the experimental conditions correspond with the assumptions involved in the theory, viz., slow crystallisation by evaporation. The contrary results of Chlopin and his co-workers (A., 1925, ii, 438; 1927, 1133; 1928, 830; this vol., 27) and of Henderson and Kracek (A., 1927, 431) are explained by the difference in their experimental conditions. Well-developed crystals once precipitated do not show any marked subsequent change in radium content.

J. W. SMITH.

Occlusion of hydrogen by platinum-black. A. SIEVERTS and H. BRÜNING (Festschr. Heraeus, 1930, 97—114; Chem. Zentr., 1930, i, 2226—2227).—For a particular temperature and pressure the sorption of hydrogen by platinum-black depends on the previous treatment of the latter. The isobars exhibit a change of direction between 0° and -20° , becoming again rectilinear between -20° and -120° .

A. A. ELDRIDGE.

Radiometer pressure and coefficient of accommodation. M. KNUDSEN (Ann. Physik, 1930, [v], 6, 129—185).—The coefficient of accommodation of hydrogen and helium at a platinum surface has been deduced from measurements of radiometer pressure. The results for hydrogen at low pressures show that the value is the same for the internal energy as for the translational energy.

R. CUTHILL.

Specific surface area of activated carbon and silica. F. E. BARTELL and Y. FU (Coll. Symp. Ann., 1929, 7, 135—149).—Data for the adsorption by sugar charcoal and silica gel of benzene, chloro-

form, carbon disulphide, ethyl carbonate, and carbon tetrachloride are recorded. The respective specific areas were 6.3 and 4.5×10^6 cm.² With anhydrous silica gel values of the heat of wetting were: ethyl alcohol 16.64, acetone 16.83; the corresponding adhesion tensions are 3.5 and 2.77. The heat of wetting is a measure of the decrease in total surface energy; the free surface energy determines the adsorption.

CHEMICAL ABSTRACTS.

Adsorption of vapours. W. A. PATRICK (Coll. Symp. Ann., 1929, 7, 129—133).—A summary and discussion. The total internal surface of silica gel is much less than 6×10^6 cm.² Initially, the adsorbed water forms a unimolecular layer which, in tending towards a minimal surface, produces a capillary effect greatly exceeding that derived from the classical Kelvin equation.

CHEMICAL ABSTRACTS.

Adsorption of sulphide and oxide films by metallic surfaces. E. BEUTEL and A. KUTZELNIGG (Z. Elektrochem., 1930, 36, 523—528).—The colouring of metals in solutions prepared from sodium thio-sulphate and a lead, silver, or copper salt is shown to be due to the adsorption of a film of insoluble compound formed by decomposition of complex salts deposited in the nascent state. The phenomena may be regarded as a particular case of the general adsorption at an interface wherein the factor determining above all the occurrence and velocity of adsorption is the electrochemical position of the metal; for the sixteen metals examined the adsorption is slower the nobler is the metal. Diagrams obtained by using photometers show that the series of interference colours obtained on the metals are dependent on the nature both of the adsorbing metal and of the precipitating sulphide.

H. I. DOWNES.

Adsorption of fats from volatile solvents. H. N. HOLMES and C. J. B. THOR (Coll. Symp. Ann., 1929, 7, 213—222).—The results of experiments in which solutions of "oleostearin" in ether, acetaldehyde, carbon tetrachloride, light petroleum, benzene, cyclohexane, or toluene were shaken with norit, silica gel, hydrated ferric oxide, or hydrated alumina verified the prediction that the order of adsorption must be reversed when silica, instead of carbon, adsorbs fatty acids from toluene. The adsorption isotherms in general show that the order of the adhesion tension is that recorded by Bartell.

CHEMICAL ABSTRACTS.

Adsorption capacity of starch and iodine-starch. O. Y. MAGIDSON and A. G. BAITSCHKOV (J. Chem. Ind., Russia, 1929, 6, 1098—1103).—Measurements of the adsorbent power of starch and starch iodide towards iodine, alkalis, and naphthenic acids are described. The presence of various salts, especially in high concentration, considerably enhances the adsorption of potassium iodide, carbonates, and naphthenates. The substances are completely extracted by water.

CHEMICAL ABSTRACTS.

Adsorption phenomena in solutions. XX. Chemical state of the surface of active charcoal. N. SCHILOV, H. SCHATUNOVSKAJA, and K. TSCHEMUTOV (Z. physikal. Chem., 1930, 149, 211—222).—Besides the two basic oxides (oxide A and oxide B) previously reported (this vol., 991) an acidic oxide

C has been proved to exist on a carbon surface. The temperature limits of its formation from oxide *B* and also of its decomposition have been investigated. It readily adsorbs alkali. The adsorption of acid found with specimens of charcoal coated with this oxide is attributed to residual oxide *B*. Oxide *C* can be formulated as the anhydride of a carbon acid and is assumed to be an intermediate product in the oxidation of carbon dioxide and also in the equilibrium between carbon, carbon dioxide, and carbon monoxide at moderate temperatures. At higher temperatures the oxide *B* is the active intermediate compound in these reactions.

J. W. SMITH.

Methyl-violet lake. W. D. BANCROFT and J. W. ACKERMAN (J. Physical Chem., 1930, 34, 1767—1776).—The function of sodium benzoate in the formation of lakes is to adsorb the methyl-violet: the alumina adsorbs the sodium benzoate. The aluminium sulphate employed forces the dye on the mordant, and is not used to adsorb the excess of the dye. Sodium sulphate is equally satisfactory in this respect. The adsorption of the sodium benzoate and the methyl-violet by alumina increases with rise in temperature up to 90°, and then decreases. On keeping for three months, methyl-violet lakes become stronger owing to increased adsorption. Alumina is the best mordant for lakes, those of iron, tin, and zinc being less satisfactory, whilst chromium is a good mordant for darker shades.

L. S. THEOBALD.

Adsorption linking. I. H. KAUTSKY and E. GAUBATZ (Z. anorg. Chem., 1930, 191, 382—413).—The influence of the chemical constitution (*i.e.*, of the single atoms and ions) of various adsorbents with comparable surfaces on the adsorption of different gas molecules has been studied. Siloxen (*cf.* A., 1929, 257) and its mono-, tri-, and penta-bromo-derivatives were used as adsorbents. From X-ray measurements with calcium disilicide the surface per mol. of siloxen is taken to be 929,300 m.² The sp. gr. of these substances increases by a constant amount for each bromine atom introduced, and it may be assumed that all the bromine atoms are linked in the same way. Adsorption isotherms have been determined for ethane and for carbon dioxide. Ethane is more strongly adsorbed, and for both gases the adsorption (mols. gas./mol. adsorbent) increases in the order monobromosiloxen, siloxen, tribromosiloxen, pentabromosiloxen. The factors influencing adsorption are discussed and it is concluded that the degree of adsorption is determined by (*a*) the sign of the electric charge of the ions in the surface which influences the polarisability of the adsorbed gas molecule, (*b*) the constitution of the surface, *e.g.*, progressive substitution of hydrogen by bromine atoms, and (*c*) the spacial configuration of the surface. An apparatus suitable for the determination of adsorption isotherms through a wide range of pressures is described. The following values of *d* are recorded: siloxen, 1.58; mono-, tri-, and penta-bromosiloxen, 1.85, 2.39, and 2.917, respectively.

O. J. WALKER.

Adsorption of amphoteric substances by collodion membranes. G. ETTISCH, M. DOMONTOVITSCH, and P. VON MUTZENBECHER (Naturwiss., 1930, 18, 447—448).—By means of refractivity

measurements the quantity of egg-albumin adsorbed by a collodion membrane has been determined as a function of the p_H of the solution. There is a sharp peak in the p_H -adsorption curve at the isoelectric point. Analogous results are obtained with hæmoglobin, serum-albumin, and serum-paraglobulin, and also with non-colloidal solutions of glycine. A maximum adsorption of gelatin at the isoelectric point is not shown by the refractometric method, but is rendered evident by the reaction of the adsorbed layer with auric chloride or silver nitrate solution. The existence of this maximum is explained by the decrease at the isoelectric point of the affinity of the colloid for the molecules of the disperse medium and the resulting decrease in the work necessary for the removal of the protein from the solution.

H. F. GILLBE.

Thermodynamic study of surface tension, affinity, and speed of absorption. VII. R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 741—754).—The formula connecting the vapour pressure of a liquid with the curvature of its surface is generalised so as to be applicable to the partial pressure of the several components of a liquid mixture.

N. M. BLIGH.

Multimolecular films. R. S. BRADLEY (Phil. Mag., 1930, [vii], 10, 323—326).—The case of a dipole chain built up on the surface of the adsorber is theoretically investigated, regard being had to the polarisation at optical frequencies of the adsorbed molecules and the interaction between the latter and their electrical images in the surface. The latent heat of evaporation of the outside layer of molecules of a water film 3 molecules thick is evaluated, giving 8600 g.-cal. per mol., and this agrees well with Lenher's value for the case of a film 5 molecules thick, *viz.*, 9100 g.-cal.

W. GOOD.

Phase diagram for unimolecular films. C. G. LYONS and E. K. RIDEAL (Proc. Camb. Phil. Soc., 1930, 26, 419—420).—The analogy between two- and three-dimensional systems is briefly shown.

W. GOOD.

Density of ammonium nitrate solutions. F. M. A. HOEG (Z. anal. Chem., 1930, 81, 114—116).—The *d* of 20, 30, 40, 50, 60, 70, and 80% solutions of ammonium nitrate at 20°, 40°, 60°, 80°, and 100° are tabulated together with the composition and *d* of solutions saturated with the salt at these temperatures and at temperatures between 105° and 230°.

A. R. POWELL.

Fluorescence of solutions. Variation of the polarisation with the concentration and the influence of a non-fluorescent dye. (MLLE.) Y. CAUCHOIS (J. Chim. phys., 1930, 27, 336—345).—The degree of polarisation of the fluorescent light emitted by solutions of fluorescein in glycerol and in dextrose decreases with increase of concentration. The fluorescence of aqueous fluorescein solutions diminishes, and the polarisation of the light increases, if the concentration of a co-existing non-fluorescent coloured substance such as ammoniacal copper sulphate is increased.

H. F. GILLBE.

Cryoscopic study of the molecular equilibrium of resorcinol in aqueous solutions of calcium,

barium, and magnesium chlorides and ammonium and magnesium sulphates. C. R. M. TUTTLE (J. Chim. phys., 1930, 27, 307—328).—In 0.25*M*-solutions of calcium, barium, and magnesium chlorides resorcinol exists as double and single molecules at concentrations from 0.25 to 0.625, 0.25 to 0.625, and 0.25 to 0.500*M*, respectively. Equilibrium between single and triple molecules exists at resorcinol concentrations from 1.0 to 2.0*M* for all three chlorides. In 0.625*M*-solutions of the chlorides the limiting equilibrium concentrations are but slightly different. The cryoscopic constants of the three chlorides have been measured and the degrees of hydration calculated at various concentrations. In 0.25*M*-solutions of ammonium and magnesium sulphates there exists an equilibrium between single and double molecules of resorcinol at concentrations from 0.25 to 0.625 and 0.25 to 0.50*M*, respectively, and between single and triple molecules at concentrations from 1.0 to 2.0 and 1.0 to 2.375*M*, respectively; at higher sulphate concentrations the equilibria are shifted slightly. The degrees of hydration of the two sulphates at various concentrations have been determined from the cryoscopic constants; although ammonium sulphate has a smaller constant than sodium chloride, it is hydrated to approximately the same extent at equivalent concentrations. H. F. GILLBE.

Lyophile and lyophobic sols. F. J. NELLENSTEYN (Chem. Weekblad, 1930, 27, 506—507).—The accepted colloid-chemical nomenclature is criticised, and it is proposed to divide sols according to the absence or presence of insoluble nuclei. The degree of hydration in hydrophilic sols is not regarded as highly characteristic; the most important factor for stability is the surface tension at the boundary between the micelle and the medium. S. I. LEVY.

Optical analysis of some colloidal silver solutions and discussion of the results obtained. F. RIMATTEI (Rev. gén. Colloid., 1930, 8, 145—160).—The extinction coefficients of aqueous solutions of "argyrol" have been measured and the variation of the values with the wave-length of light and with the concentration of the sol has been determined. The extinction coefficient is not affected by temperature over the range investigated, but decreases slowly when the sol is kept. The spectrophotometric method can be used for determining the concentration of silver sols; for "argyrol" solutions varying in concentration from 0.6×10^{-3} to 0.00857×10^{-3} the error of the method is 1—4%. This shows an advantage over determinations made in a colorimeter (error 4—8%) and those made by matching against a standard scale of tubes (error 13%). E. S. HEDGES.

State of dispersion of cellulose in cuprammonium solvent as determined by ultracentrifuge. A. J. STAMM (J. Amer. Chem. Soc., 1930, 52, 3047—3062).—The sedimentation by ultracentrifuge of pure cotton linters α -cellulose in cuprammonium solvent (0.3—1.28% Cu, 14.8—22.0% NH_3) has been studied at 20° by the refraction method (Lamm, A., 1929, 129, 1234). The specific sedimentation velocity is practically independent of the concentrations of copper and ammonia, but decreases slightly with increasing concentration of cellulose (0.025—0.5%). The diffusion

constant is independent of the concentration of copper, decreases with decrease of ammonia, and increases markedly with decrease of cellulose, but values for fresh solutions are considerably smaller than for old solutions. The apparent ageing of the solutions is due to the oxygen of the air, which causes a greater dispersion of the cellulose particles. The results are explained on the basis of the gelation of the system. The cellulose-cuprammonium complex is mono-disperse and the mol. wt. is $55,000 \pm 7000$, which on a copper-free basis is $40,000 \pm 5000$ (cf. Herzog and Krüger, A., 1926, 903). An experiment with 0.26% viscose in 2.2% sodium hydroxide indicates that the mol. wt. of cellulose xanthate is approximately the same as for the above cellulose.

The cuprammonium solvent contained polydisperse particles (copper hydroxide?) 6.5 to $>20 \mu$ in diameter and with sedimentation velocities 10—100 times as great as that of the cellulose particles.

J. G. A. GRIFFITHS.

Differences between the state of dispersion of isolated wood cellulose and cotton cellulose in cuprammonium solvent. A. J. STAMM (J. Amer. Chem. Soc., 1930, 52, 3062—3067).—The ultracentrifuge method shows that absorbent cotton and cotton linters filter paper in cuprammonium solvent consist almost entirely of particles similar to those of cotton linters α -cellulose (cf. preceding abstract), but the first also contains a small quantity and the second a somewhat larger quantity of constituents of finer dispersion the proportion of which decreases with increasing α -cellulose content.

Sulphite pulp α -cellulose, bleached sulphite pulp, Cross and Bevan aspen wood, and white spruce celluloses all contain in various proportions material of the same mol. wt. as that of cotton cellulose together with particles of one half this mol. wt. and molecular species of still finer dispersion.

J. G. A. GRIFFITHS.

Formation of starch paste. S. V. GORBATSCHEV (Biochem. Z., 1930, 224, 91—101).—The temperature of conversion of starch from the granular into the dispersed (paste) form is followed by the iodine reaction in different media and in presence of different ions. Alkali thiocyanates, iodides, and bromides facilitate the formation of the dispersed form, whilst the sulphates and chlorides of lithium, magnesium, calcium, and aluminium act as stabilisers. Paste formation is not a specific reaction between starch and water, but may be effected with other media providing the dielectric constant is sufficiently large (glycerol). Using an aqueous medium, the effect of dissolved materials on the temperature of paste formation depends on whether they increase or diminish the adsorption of water by starch. Substances which neutralise the electric field of the hydrogen ions which are adsorbed on the surface of the starch increase the power of starch to adsorb water and thereby depress the temperature of paste formation (cf. A., 1927, 722, 1174). P. W. CLUTTERBUCK.

Heating of solutions and emulsions by electrostatic fields. W. H. MARSHALL (J. Gen. Physiol., 1930, 13, 637—646).—The rate of rise of temperature of sodium chloride solutions and water was found to

depend on the potential gradient employed as well as on the frequency. For potential gradients greater than about 70 volts per mm. the absorption increases rapidly with increase of frequency. For low potential gradients this relationship does not hold. The absorption figures for water decrease with exposure, dropping to about 40% of the original values. This decrease of absorption is not shown by the sodium chloride solutions. Emulsions of cottonseed oil in sodium oleate gave very high absorption values. This is due to their colloidal structure. G. F. MARRIAN.

Stability of colloids. H. R. KRUYT (Rev. gén. Colloid., 1930, 8, 200—209).—A summary of recent work carried out in the author's laboratory on the general problem of the stability of colloids and the relation of lyophobic to lyophilic colloids. The main conclusions are that lyophobic sols owe their stability to their electric charge, whilst lyophilic colloids depend mainly on their hydration for the stability and partly also on electric charge. In some cases, however, such as aqueous sols of gelatin and albumin, hydration alone is sufficient, since the sol persists in the isoelectric state, but in a colloid like casein, hydration alone is insufficient to keep the sol stable and the particles have to be charged by addition of acid or alkali. This constitutes a change in the direction of lyophobic properties. A reply is made to the criticisms of Lumière (A., 1929, 392). Recent work confirms the idea of discontinuous charges distributed at points on the surface of the particles, and the hydration factor of stabilisation is rendered more definite by recent experiments on coacervation and the effect of hydrated colloids on the depression of the *f. p.*

E. S. HEDGES.

Structure of colloids. A. LUMIÈRE (Rev. gén. Colloid., 1930, 8, 209—211).—A reply to the arguments of Kruyt (cf. preceding abstract). The properties of the typically hydrophobic and hydrophilic colloids copper ferrocyanide and gelatin are contrasted and it is maintained that there is as great a physico-chemical divergence as between colloids and crystalloids. It is not feasible, therefore, to treat lyophilic and lyophobic sols on the same lines. E. S. HEDGES.

Stability of organo-metallic sols. I. Influence of electrolytes and non-electrolytes on coagulation. N. A. YAJNIK, D. N. GOYLE, and C. BARN (J. Chim. phys., 1930, 27, 386—397).—The coagulation of zinc-acetone and copper-alcohol sols prepared by Bredig's method has been investigated. The order of influence of electrolytes is the same as for hydrosols. Addition of ethyl alcohol, ethyl ether, and chloroform accelerates the coagulation of the zinc-acetone sol, and ethyl ether and glycerol behave similarly with the copper-alcohol sol. The non-electrolytes exert their greatest influence at concentrations of 30—60%. C. W. GIBBY.

Coagulation of von Weimarn's Au₂ sols. II. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 1—11).—The stability of von Weimarn's gold sols towards coagulation by sodium and barium chlorides has been studied with reference to the hydrogen-ion concentration, and the effect of varying the concentrations of potassium hydroxide and of formaldehyde has been determined. The results are

presented in the form of a graph in which the co-ordinates are the amounts of reducing agent and of alkali used in preparing the sols. The graph shows that the sols fall into three regions: (1) a region of incomplete reduction, where the sols are blue or violet, (2) a stable region, where reduction is complete and the sols remain red, and (3) an unstable region, where reduction is complete, but the sols turn violet when kept. The finest red gold sols are obtained in the region 0.001—0.0035*N*-potassium hydroxide, and in this region the concentration of the formaldehyde is of little importance. The most stable gold sols are generally acidic or almost neutral. E. S. HEDGES.

Measurement of the forces operating during coagulation. A. VON BUZÁGH (Naturwiss., 1930, 18, 444—447).—The forces operating during the coagulation of a colloid have been investigated by determining the number of particles which on sedimentation adhere to a horizontal surface under specified conditions and also the force required for their displacement as derived from the minimum angle α to which the plate must be tilted to cause movement of the particles. This type of adherence is essentially an interfacial phenomenon, since there exists a maximum particle size above which it ceases to exist; there is also a lower limit governed by the inability of the particle to approach sufficiently near to the surface on account of its surrounding solvent envelope remaining undeformed by the weight of the particle. In course of time, however, the deformation of those particles nearest to the surface increases, mainly on account of thermal movements. The adherence of the smaller particles thus increases with age, whereas that of the larger particles remains unaltered, since by reason of their mass the envelope is easily deformed and the particle is less readily influenced by thermal movements. The specific adherence p may be calculated for a certain range of particle sizes from the equation $p = l(\sigma - \sigma_s) = g \sin \alpha$, where l is the length of side of the particle (assumed cubical), and σ and σ_s are the densities of the particles and of the medium, respectively. It is possible also by application of this equation to decide as to the nature of the envelope surrounding any given type of colloidal particle. Simultaneous measurements of the adherence and cataphoresis indicate that on addition of electrolyte the Freundlich potential varies on account of changes both of the charge and of the envelope thickness. In certain cases these two variables change in the same sense, and the variations of the potential and of the adherence follow a parallel course, the latter being a maximum when the former is a minimum, *i.e.*, at the isoelectric point; in such cases only is the potential an indication of the stability of the colloid. On the other hand, the stability of lyophobic colloids at the isoelectric point is due to changes in the opposite sense of the charge and the envelope thickness. H. F. GILLBE.

Swelling of cellulose, and its affinity relations with aqueous solutions. II. Acidic properties of regenerated cellulose illustrated by the absorption of sodium hydroxide and water from dilute solutions, and the consequent swelling. S. M. NEALE (J. Text. Inst., 1930, 21, T225—230).—

The value for the ionisation constant of regenerated cellulose chosen arbitrarily (this vol., 417) has been fixed more precisely, and the reality of such a constant is confirmed by confining observations to dilute solutions of sodium hydroxide (below 0.5 molal) for which precise thermodynamic measurements have been made by other workers. The value 1.84×10^{-14} at 25° is now obtained, but the adoption of this in place of the approximate figure assumed earlier is without serious effect on the quantitative relations discussed previously. The swelling/concentration curve for cellulose and dilute sodium hydroxide has been established, and its shape is in accordance with the theoretical considerations previously laid down.

B. P. RIDGE.

Osmotic pressure of gelatin solutions in equilibrium with magnesium chloride. G. S. ADAIR and E. H. CALLOW (J. Gen. Physiol., 1930, 13, 819—830).—The osmotic pressures of solutions of gelatin of different concentrations (1—10 g. per 100 c.c.), in equilibrium with 4*N*-, 6*N*-, and 9*N*-solutions of magnesium chloride have been determined. The osmotic pressure was found to increase more rapidly than the concentration of gelatin, representing a high *b* value in the equation $p(V-b)=RT$. Measurement of the membrane potentials showed that this effect could not be due to an unequal distribution of diffusible ions. Hydration of the protein molecules is insufficient to account for the high *b* term. It is suggested that inter-ionic or inter-molecular forces may cause these high osmotic pressures in concentrated solutions.

G. F. MARRIAN.

X-Ray structure of gelatin micelles. W. ABITZ, O. GERNGROSS, and K. HERRMANN (Naturwiss., 1930, 18, 754—755).—The X-ray diagram of gelatin is very complex, but moderately swollen gels on dilution give a fibre-type diagram similar to that of collagen. Careful work has shown that undiluted gels exhibit a similar, although less intense, diagram, and, further, that preliminary dilatation is not necessary to produce these effects. The splitting up of amorphous rings and the origin of dilatation diagrams are obviously cohesive processes. These results are considered together with the available chemical data, and it is suggested that in gelatin the polypeptide chains are linked by amino-acid residues by means of a van der Waals cohesion to form a crystalline substance. This assumption is used to elucidate the X-ray diagrams and to explain many of the properties of gelatin.

W. R. ANGUS.

Unequal distribution of hydrogen and hydroxyl ions in cubes of gelatin in diffusion equilibrium with an electrolyte solution. E. J. BIGWOOD (Compt. rend. Soc. Biol., 1929, 102, 600—601; Chem. Zentr., 1930, i, 1946).—When gelatin cubes, prepared with phenol-red solution, are kept at 0° in an alkaline solution of the same indicator, the thickness of the red zone around the yellow centre of the cubes is practically constant for several days and is independent of the volume of the cube.

A. A. ELDRIDGE.

Electrokinetic phenomena. II. Relation between cataphoretic and electroendosmotic mobilities. H. A. ABRAMSON (J. Gen. Physiol., 1930, 13, 657—668).—It is shown that van der

Grinten's data (cf. A., 1926, 467) relating to the electroendosmotic velocity (V_E) of a liquid past a surface, and the cataphoretic velocity (V_P) of a particle of that surface through the liquid, lead to $V_E/V_P=2.1-2.8$ instead of the recorded value 1.59. For a flat or round glass surface, and glass or quartz particles, both covered with a layer of gelatin or egg-albumin, V_E/V_P is found to be about 1.00.

G. F. MARRIAN.

Methods of the kinetic theory of gases. G. JAFFÉ (Ann. Physik, 1930, [v], 6, 195—252).—Mathematical. It is shown that Boltzmann's fundamental equation of motion for a simple gas can be transformed so as to become formally identical with the author's fundamental equation of motion of radiation in an anisotropic field of radiation (*ibid.*, 1922, [iv], 68, 583; 1923, [iv], 70, 457; Physikal. Z., 1922, 23, 500). The methods of the radiation theory are then utilised in working out the kinetic theory, and it has proved possible to bring the behaviour of gases at both moderate and low pressures within the scope of a single theory.

R. CUTHILL.

Historical note on equilibrium between methyl alcohol and its decomposition products. J. A. CHRISTIANSEN (J. Amer. Chem. Soc., 1930, 52, 3165).—Mainly a correction of statements by Lacy and others (this vol., 542).

J. G. A. GRIFFITHS.

Kinetics of the solvation of iodine and the sexatomic iodine molecule. J. GRÓH and E. TAKÁCS (Z. physikal. Chem., 1930, 149, 195—210). The addition of iodine to erucic acid in carbon tetrachloride and carbon disulphide solutions occurs less readily in the presence of ether than in the pure solvents. This is explained by assuming that in the iodine solution an equilibrium exists $3I_2 \rightleftharpoons I_6$ and that only the sexatomic iodine molecules react with the erucic acid, this reaction being expressed $E+I_6 \rightleftharpoons EI_2+2I_2$. Solvation of the I_2 molecules by ether is supposed to reduce the concentration of I_6 molecules, and in pure ether they are practically non-existent. From the change in the reaction velocity with the ether concentration the equilibrium constant of the solvation of the iodine with ether has been calculated. The velocity of decomposition of di-iodoerucic acid has also been investigated. This dissociation is dependent on the presence of a trace of iodine and therefore supports the view that these reactions occur according to the above equation and also supports the conclusion reached previously (A., 1927, 728) concerning the existence of the sexatomic iodine molecule.

J. W. SMITH.

Hydrolysis of thorium chloride. E. CHAUVENET and J. TONNET (Bull. Soc. chim., 1930, [iv], 47, 701—703).—Conductivity and calorimetric measurements made during the addition of sodium hydroxide to a solution of thorium tetrachloride indicate the existence of a "thoryl" radical ThO in the solution. Hydrolysis takes place according to the equation $ThCl_4+2H_2O=Th(OH)_2Cl_2+2HCl$.

C. W. GIBBY.

Apparent dissociation constants of arginine and of lysine; apparent heats of ionisation of certain amino-acids. C. L. A. SCHMIDT, P. L. KIRK, and W. K. APPLEMAN (J. Biol. Chem., 1930, 88, 285—293).—At 25° arginine has $K'_a, 3.32 \times 10^{-13}$,

K'_b , 1.10×10^{-5} , K'_{b_2} , 1.05×10^{-12} , isoelectric point at p_H 10.75 (at 0° the corresponding figures are 4.9×10^{-14} , 7.09×10^{-6} , 2×10^{-13} , and 11.55). Lysine has K'_{a_1} , 2.95×10^{-11} at 25° , 4.9×10^{-12} at 0° , K'_{b_1} , 0.89×10^{-5} at 25° , 7.4×10^{-6} at 0° , K'_{b_2} , 1.52×10^{-12} at 25° , 1.82×10^{-13} at 0° , isoelectric point p_H 9.74 at 25° and 10.56 at 0° . From these and similar figures are calculated the heats of ionisation of the various groups of arginine, histidine, lysine, and also of aspartic and glutamic acids.

C. R. HARRINGTON.

Conductance and activity coefficients of glutamic and aspartic acids and of their monosodium salts. W. M. HOSKINS, M. RANDALL, and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 215—239).—Measurements of the conductivity (0°) and of the depression of the f. p. are recorded. The conductivity data indicate that the free amino-acids are but little ionised, whilst the sodium salts are highly dissociated. The figures for the f.-p. depression have been subjected to thermodynamic interpretation leading to the derivation of the activity coefficients of the free amino-acids and of their salts considered as univalent electrolytes, and also of the undissociated portions of the amino-acids. The results suggest that the undissociated portions of the free acids exist in solution as neutral micelles, whilst the ionised parts of the salts exist to a small extent as ionic micelles. For the characterisation of a weak acid which forms micelles the use of the "overall" activity coefficient is to be preferred to that of the dissociation constant.

C. R. HARRINGTON.

Stability of cyanohydrins. II. Dissociation constants of cyanohydrins derived from methyl alkyl and phenyl alkyl ketones. A. LAPWORTH and R. H. F. MANSKE (J.C.S., 1930, 1976—1981; cf. A., 1928, 1245).—A number of methyl alkyl ketones and phenyl alkyl ketones have been prepared in pure condition and the dissociation constants of their cyanohydrins determined at 20° . Replacement of an α -hydrogen atom in the alkyl group usually increases the stability of the corresponding cyanohydrin; a decrease is observed in passing from methyl isopropyl ketone to methyl *tert.*-butyl ketone. Replacement of a β -hydrogen atom by methyl usually decreases the stability of the cyanohydrin. A direct influence of the substituent on the CO or C(OH)·CN groups is suggested, comprising a stabilising "steric effect" and a destabilising "electropolar effect," the former possibly being connected with the function α in van der Waals' equation.

H. I. DOWNES.

Dependence of the osmotic coefficient on the structure of the ions. II. Thermo-electric apparatus for measurement of f.-p. depression in dilute solutions of electrolytes. L. EBERT and J. LANGE (Z. physikal. Chem., 1930, 149, 389—407; cf. A., 1929, 266).—The construction and manipulation of a modified form of Randall and Vanselow's apparatus (A., 1925, ii, 33) suitable for determining f.-p. depressions in 0.001—0.1N aqueous solutions are described.

R. CUTHILL.

Activity of ions in concentrated solutions. J. PROSZT (Mitt. berg.-hütt. Abt. Hochsch. Soprow, 1929, 6 pp.; Chem. Zentr., 1930, i, 1830—1831).—Crocein-scarlet 3B is a suitable indicator for the

interval p_H -0.3 to -1 , and neutral-red for the interval p_H $+1.0$ to -0.3 . A rise in the acidity with increasing concentration of hydrochloric acid is indicated, whilst the specific conductivity curve exhibits a maximum at 5.5N. Crocein-scarlet remains red in 96% acetic acid, whilst neutral-red indicates increasing acidity (blue) with increasing concentration. The indicators are no longer dissociated in media of low dielectric constant. Many acid indicators in organic solvents of low dielectric constant and free from acid exhibit their acid colour.

A. A. ELDRIDGE.

Ionic entropy and solvation. H. ULLICH (Z. Elektrochem., 1930, 36, 487—506).—A new method for calculating the hydration numbers of monatomic ions is described. The values obtained agree with those calculated from the ionic mobilities. The connexion established between partial ionic entropy and ionic mobility permits the calculation of the one quantity from the other.

H. I. DOWNES.

Complexity of phosphorus pentoxide. I. A. SMITS [with H. W. DEINUM] (Z. physikal. Chem., 1930, 149, 337—363).—The results previously obtained for the vapour pressure of the metastable volatile form of phosphorus pentoxide (A., 1925, ii, 268; Hoeflake and Scheffer, A., 1926, 342) have been confirmed. This form represents, not a polymorphic modification, but a mixed crystal not in internal equilibrium, for by rapid heating it can be superheated far above the unary stable triple point, and moreover its vapour pressure can be considerably reduced by partial distillation. The rate at which equilibrium, represented by the stable form, is approached is slow even at 400° . By assuming the existence of two kinds of molecules forming a pseudobinary system with a eutectic, the behaviour of the system is satisfactorily explained by the author's theory of allotropy, and the equilibrium diagram has been constructed.

R. CUTHILL.

Phase-rule study of the cobalt chloride colour change. H. BASSETT and (in part) H. H. CROUCHER (J.C.S., 1930, 1784—1819).—The systems $\text{CoCl}_2\text{-HCl-H}_2\text{O}$, $\text{CoCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$, $\text{CoCl}_2\text{-HgCl}_2\text{-H}_2\text{O}$, and $\text{CoCl}_2\text{-ZnCl}_2\text{-H}_2\text{O}$ have been examined at 25° and the first also at 0° , -15° , and -20° . No compound of cobalt chloride and hydrogen chloride could be isolated, but the blue compound $\text{CoCl}_2\text{.MgCl}_2\text{.8H}_2\text{O}$ and the red compound $\text{CoCl}_2\text{.HgCl}_2\text{.4H}_2\text{O}$ are obtained. Cobalt and zinc chlorides yield five series of red solid solutions, each containing as one constituent a hydrate $\text{ZnCl}_2\text{.}n\text{H}_2\text{O}$, wherein n is respectively 3, $2\frac{1}{2}$, $1\frac{3}{4}$, $1\frac{1}{2}$, and $1\frac{1}{4}$. It appears from consideration of these complex salts that all cobalt chloride solutions contain in equilibrium the red cations: $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$, $[\text{Co}_2(\text{H}_2\text{O})_{10}]^{4+}$, $[\text{Co}_2(\text{H}_2\text{O})_6]^{4+}$, $[\text{Co}(\text{H}_2\text{O})_3]^{3+}$, and the blue anions: $[\text{CoCl}_3]^{-}$, $[\text{CoCl}_4]^{-}$; in some cases the blue non-ionised cobalt chloride is indicated. No evidence of other theoretically possible ions was obtained. The simple dehydration theory and the "variable co-ordination" theory of the colour change are not supported by the data, and the phenomena are regarded as being determined by the possibility of electron transfer between

different quantum levels. The electronic shifts responsible for the red and blue colours are considered and suggestions made. Some previous statements relative to the hydrates of zinc chloride are corrected.

H. I. DOWNES.

Equilibrium between acetone and salts. W. R. G. BELL, C. B. ROWLANDS, I. J. BAMFORD, W. G. THOMAS, and W. J. JONES (J.C.S., 1930, 1927—1931).—The solubilities of calcium chloride, iodide, and nitrate, strontium bromide, barium bromide, sodium iodide, lithium chloride and bromide, nickel bromide, cobalt chloride and bromide, and zinc bromide in absolute acetone, and the composition of the solid phases in equilibrium with the saturated solutions have been determined. For barium, lithium, and sodium bromide the solid phases are the non-solvated salts; for the remainder the solid phases are represented by acetates. Transition points at which the acetates of cobalt chloride, zinc bromide, lithium bromide, and sodium iodide are converted into the non-solvated salts, and the sesquiacetate of strontium bromide into the monoacetate have been established. The dissociation pressures of the acetates of sodium iodide, magnesium chloride, strontium bromide, calcium nitrate, cobalt chloride and bromide have been determined between 0° and -30°; the data show that $\log P$ is a rectilinear function of $1/T$. This relation permits the calculation of heats of dilution and affinities of salts for acetone.

H. I. DOWNES.

Solubility curves of mixtures and solid solutions. J. H. NORTROP and M. KUNITZ (J. Gen. Physiol., 1930, 13, 781—791).—Systems of two solid components (mixture or solid solution) in contact with a liquid phase are considered from a theoretical point of view. Assuming that such systems follow the phase rule and Raoult's law, the relative amounts and solubilities of the two solid components may be calculated from the solubility curve of the mixture or solid solution.

G. F. MARRIAN.

Equilibrium in the molten state between calcium, sodium, and their chlorides. E. RINCK (Compt. rend., 1930, 191, 404—406).—Contrary to the results of Lorenz and Winzer (A., 1929, 650, 1229), which are based on defective analysis, it is shown that the equilibrium data for $\text{Ca} + 2\text{NaCl} \rightleftharpoons 2\text{Na} + \text{CaCl}_2$ at 850—1100° conform to the requirements of the phase rule. The liquid phase contains 71% CaCl_2 and the solid phases 13% Ca and 17% Na, respectively.

J. GRANT.

Ternary system carbamide-ammonium nitrate-sodium nitrate. W. J. HOWELLS (J.C.S., 1930, 2010—2017).—The equilibrium diagram shows three main areas or saturation surfaces in the largest of which sodium nitrate is precipitated as the solid phase. The curves afford evidence of the transition of regular to rhombohedral ammonium nitrate. The transition of rhombohedral to α -rhombohedral ammonium nitrate at 83° is not observed, possibly because the latter is not readily formed in the presence of carbamide. The composition at the ternary eutectic point (37.1°) is, in mol.-%: 52.4% $\text{CO}(\text{NH}_2)_2$, 41.5% NH_4NO_3 , 6.1% NaNO_3 , and these are in the inverse order of the m. p.

H. I. DOWNES.

Equilibria in the ammonium carbamate-carbamide-water-ammonia system. H. J. KRASE and V. L. GADDY (J. Amer. Chem. Soc., 1930, 52, 3088—3093; cf. Fichter, Steiger, and Stanisch, A., 1919, i, 69).—Equilibria at 155° have been reached both from the ammonium carbamate and the carbamide sides in the presence of excess of ammonia. The conversion of carbamate ammonia into carbamide is increased from 44% to about 84% when the excess of ammonia is raised from 0 to 280%, but further additions are likely to have little effect. Carbon dioxide does not have a dehydrating action similar to ammonia.

J. G. A. GRIFFITHS.

Heat of combustion of salicylic acid. P. E. VERKADE and J. COOPS (Rec. trav. chim., 1930, 49, 864—865).—Polemical against Keffler (this vol., 702).

J. A. V. BUTLER.

Calorimetric researches. E. BERNER (Rec. trav. chim., 1930, 49, 861—863).—Some of the figures given by Keffler (this vol., 702) for the heat of combustion of salicylic acid are incorrectly quoted. It is pointed out that Keffler's results support the author's value.

J. A. V. BUTLER.

Heat of formation of molecular oxygen. L. C. COPELAND (J. Amer. Chem. Soc., 1930, 52, 2580—2581).—A provisional value afforded by direct measurement is $165,000 \pm 5000$ g.-cal.

J. G. A. GRIFFITHS.

Heat of formation of molecular oxygen. W. H. RODEBUSH and S. M. TROXEL (J. Amer. Chem. Soc., 1930, 52, 3467; cf. Copeland, preceding abstract).—When precautions are taken to eliminate spurious heat effects in the calorimeter, the heat of formation of molecular oxygen by direct determination is 131,000 g.-cal. Metastable atoms do not reach the calorimeter.

J. G. A. GRIFFITHS.

Heat of formation of zinc oxide. C. G. MAIER (J. Amer. Chem. Soc., 1930, 52, 2159—2170; cf. Parks and others, A., 1928, 22).—A calorimeter with special features and involving the use of tantalum and bakelite, which are resistant to corrosion, is described. The heats of dissolution of zinc oxide and zinc in hydrochloric acid have been redetermined (cf. Richards and Thorvaldson, A., 1922, ii, 475; Richards and Burgess, A., 1910, ii, 391). The most probable value of the heat of formation of zinc oxide at 25° is computed to be $83,270 \pm 50$ g.-cal. (15°), in good agreement with thermodynamic estimates (Millar, A., 1929, 21).

J. G. A. GRIFFITHS.

Heat of dissolution of sparingly soluble electrolytes. II. E. LANGE and Z. SHIBATA (Z. physikal. Chem., 1930, 149, 465—469).—Measurement of the heat of precipitation of silver iodide at 25° has given the value -26.71 ± 0.05 kg.-cal. per mol. AgI for the heat of dissolution. The heat of flocculation or the content of metastable modifications does not affect the result to an extent greater than the experimental error.

E. S. HEDGES.

Heats of dissolution and of formation of CuCsCl_3 . A. BOUZAT and E. CHAUVENET (Bull. Soc. chim., 1930, [iv], 47, 697—698).—The heat of dissolution in water of caesium cupric chloride, prepared by concentrating a solution of equimolecular proportions of cupric chloride and caesium

chloride in a current of hydrogen chloride, can be represented between 10° and 20° by the formula $Q = -0.65 + 0.12(t-15)$ g.-cal./mol. The heat of the reaction $\text{CuCl}_2\text{aq} + \text{CsCl} = \text{CuCsCl}_3$ is 6.96 g.-cal. and that of the reaction CuCl_2 (solid) + 2CsCl (solid) = CuCs_2Cl_4 is 6.88 g.-cal.

C. W. GIBBY.

J. Thomsen's isodynamic principle and W. Thomson's rule. J. SEBOR (Chem. Listy, 1930, 24, 322—325).—The above are valid for a number of soluble salts, but not for fluorides and sulphates.

R. TRUSZKOWSKI.

Thermal data for organic compounds. VIII. Heat capacities, entropies, and free energies of the isomeric heptanes. H. M. HUFFMAN, G. S. PARKS, and S. B. THOMAS (J. Amer. Chem. Soc., 1930, 52, 3241—3251).—The following heats of fusion are recorded (g.-cal. per g.): *n*-heptane, 33.78; β -methylhexane, 21.16; γ -ethylpentane, 22.56; $\beta\beta$ -dimethylpentane, 13.98; $\beta\delta$ -dimethylpentane, 15.97; $\gamma\gamma$ -dimethylpentane, 16.86; $\beta\beta\gamma$ -trimethylbutane, 5.25. The specific heats of the above hydrocarbons, γ -methylhexane, and $\beta\gamma$ -dimethylpentane have been measured over a wide range of temperature by the method previously described (A., 1925, ii, 491). The entropies of the hydrocarbons, calculated from the heat capacity data, agree fairly well with those obtained from the equation $S_{298} = 25.0 + 7.7n - 4.5r$ (this vol., 677). Increased branching in this series of hydrocarbons results in a free energy increase of 600 g.-cal./mol. for each side-chain.

H. BURTON.

Electrolytic resistance with alternating current. S. RAY (Z. Elektrochem., 1930, 36, 545—550).—A theoretical and mathematical treatment in which both high- and low-frequency alternations are considered.

H. I. DOWNES.

Electrical conductivity of phenol solutions. R. M. DOLBY and P. W. ROBERTSON (J.C.S., 1930, 1711—1721).—Phenolic solutions of sodium acetate, aniline hydrochloride, sodium phenoxide, picric acid, acetic acid, and hydrochloric acid at 50° show large differences in the equivalent conductivities. The conductivity of the acids increases more rapidly than required by the mass-action law, whereas the salts show the opposite behaviour. Although addition of toluene to solutions of the salts causes a decrease, addition of ethyl malonate and methyl acetate causes a considerable increase in the conductivity. Measurements of the dielectric constants, conductivities, and viscosities of phenol-ethyl malonate mixtures contribute no explanation for such an increase, which, in view of the agreement of the results with cryoscopic and molecular volume measurements (A., 1928, 947) may be due to intermolecular forces induced by internal pressures and polarities of the liquid.

H. I. DOWNES.

Mobility of a number of ions containing iron. II. Influence of substitution in co-ordinated groups. F. HÖLZL (Monatsh., 1930, 56, 79—96; cf. this vol., 862).—Further measurements of conductivity with complex ferro- and ferri-cyanides at 5° (to avoid decomposition) gave the following values for the mobility and apparent ionic radius: $[\text{Fe}(\text{CN})_6]^{4-}$, 62.5, 100; $[\text{Fe}(\text{CN})_6]^{3-}$, 61.7, 101;

$[\text{Fe}(\text{CN})_5\text{CO}]^{4-}$, 62.1, 101; $[\text{Fe}(\text{CN})_5\text{NO}_2]^{4-}$, 51.6, 122; $[\text{Fe}(\text{CN})_5\text{SO}_3]^{4-}$, 51, 123; $[\text{Fe}(\text{CN})_5\text{AsO}_2]^{4-}$, 47.4, 134; $[\text{Fe}(\text{CN})_5\text{NH}_3]^{4-}$, 45.8, 136; $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$, 41.4, 151; $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, 41.1, 152. The change in mobility with variation of temperature is not identical for different ions and this is probably connected with hydration; the respective figures at 5° and 25° for $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ are 100, 102, 142, and 100, 101, 151. The completely symmetrical ion $[\text{Fe}(\text{CN})_6]^{4-}$ has the highest mobility, which appears to be practically independent of the valency of the central atom, and to be uninfluenced by substituting a neutral group (e.g., CO) for a negative group (e.g., CN). The large effect produced by the nitroso- or amino-group is attributed to a destruction of the symmetry of the ion, producing a looser binding and increased hydration.

J. R. I. HEPBURN.

Change in the direction of migration of the alkali and other metals during electrolysis of the corresponding amalgams, in relation to the concentration. R. KREMANN, F. BAUER, A. VOGGIN, and H. SCHEIBEL (Monatsh., 1930, 56, 35—65).—An extension of earlier work on sodium amalgams (A., 1926, 801) to amalgams of potassium, lithium, barium, and bismuth. With those amalgams in which the conductivity of the mercury is diminished (viz., sodium, potassium, and barium) the metal migrates to the anode up to concentrations of 2% Na, 2.5% K, and 2.7% Ba; beyond these concentrations a reversal of the direction of migration occurs in each case towards the cathode. In lithium amalgams the migration is always towards the cathode; bismuth always migrates to the anode. The theory of Lewis, Adams, and Lanman (A., 1916, ii, 76) is not confirmed by these results. It is suggested that the migration to the anode of bismuth, with its strong metalloidal character, makes it probable that the polarity of the components of an alloy is an important factor in determining the direction of migration; with dilute amalgams of sodium, potassium, or barium, the effect suggested by Lewis may be the prominent factor, whilst at higher concentrations the difference in polarity of the components may assert itself through complex formation, giving rise to the reversal point.

J. R. I. HEPBURN.

Electrolytic flow in fused silver-lead alloys. R. KREMANN, B. KORTI, and E. I. SCHWARZ (Monatsh., 56, 16—25; cf. A., 1925, ii, 679; 1926, 802).—An extension of previous work. Alloys containing 50 at.-% or 35 wt.-% Ag were electrolysed at 1000° in fireclay capillary tubes for 6 hrs. with a high current density, using steel electrodes. A stationary state is set up in the centre of the capillary; silver migrates towards the cathode, and lead towards the anode. Slight changes in the concentration of the alloy as a whole are explained by evaporation of lead. Further experiments with varying percentages of lead and silver indicate that the maximum migration effect is shown with the equiatomic alloy.

J. R. I. HEPBURN.

Electrolysis of bronzes with addition of silver. R. KREMANN and E. I. SCHWARZ (Monatsh., 1930, 56, 26—34). **Electrolysis of bronzes with addition**

of lead. R. KREMANN and W. PIWETZ (*Monatsh.*, 1930, 56, 71—78).—Complete data in connexion with an earlier paper (A., 1929, 1402) are given, with a series of photomicrographs illustrating the metallographic study of the system. J. R. I. HEPBURN.

Sodium and potassium amalgam electrodes in solutions containing sodium chloride, potassium chloride, and sodium and potassium chlorides. E. W. BIRD and R. M. HIXON (*J. Physical Chem.*, 1930, 34, 1412—1423).—A new type of flowing junction and a modified alkali amalgam electrode are described. The flow of the solutions of potassium chloride and calomel through the calomel half-cells used has no effect on their *E.M.F.* The sodium amalgam electrode gives abnormal readings in solutions of sodium chloride to which potassium chloride has been added, and the potassium electrode is similarly affected by the presence of sodium ions. The data obtained in these cases agree with those of Ringer (*Z. physiol. Chem.*, 1923, 130, 270) and Neuhausen (A., 1922, ii, 610). Constant and reproducible *P.D.* are obtained with the sodium electrode in solutions of potassium chloride, and with the potassium electrode in solutions of sodium chloride.

L. S. THEOBALD.

Voltage effect for solutions of electrolytes in acetone. F. BAUER (*Ann. Physik*, 1930, [v], 6, 253—272; cf. *Wien, A.*, 1929, 401).—The voltage effect, $\Delta\lambda$, for acetone solutions of various uni-univalent and uni-bivalent electrolytes has been measured. Up to high values of the field strength, X , the equation $\Delta\lambda = AX^2(1 - BX^2)$ (Blumentritt, *ibid.*, 512) is valid. The value of A is approximately proportional to the product of the valencies of the ions of the particular salt and increases with increasing dilution, whilst as the theory requires A is greater and B is smaller than for the corresponding aqueous solution. For potassium iodide the limiting value of $\Delta\lambda$ at high field strength has been obtained and found to correspond approximately with the conductivity at infinite dilution. R. CUTHILL.

Polarographic studies with the dropping mercury cathode. XIV. The discontinuities on the curves which are obtained with solutions of mercuric cyanide. W. KEMULA (*Coll. Czech. Chem. Comm.*, 1930, 2, 502—519).—The first discontinuity is due to the adsorption of mercuric cyanide, the second to the exhaustion of reducible matter. C. W. GIBBY.

Constitution of the aqueous pink and blue cobaltous chloride solutions. I. Electrodeposition at the dropping mercury cathode. R. BRDIČKA (*Coll. Czech. Chem. Comm.*, 1930, 2, 489—501).—The deposition of cobalt from solutions of cobalt chloride of various concentrations has been determined polarographically, using the dropping mercury cathode. In the presence of much calcium chloride the red solution becomes blue and the deposition potential more positive. Heating the solution has a similar effect on the potential, the colour changing if calcium chloride is present. Cobalt deposits reversibly only from blue solutions, the cathodic deposition potential being about 0.3 volt greater than for a pink solution with an equal cobalt

content. It is suggested that the irreversible deposition is due to slow dehydration of the pink hydrated ions, and that the reversible deposition from the blue solutions is facilitated by the ease with which the blue complexes give free cobaltous ions. C. W. GIBBY.

Formation of free hydrogen atoms during the cathodic polarisation of metals. N. KOBOSOV and N. I. NEKRASSOV (*Z. Elektrochem.*, 1930, 36, 529—544).—The emission of free hydrogen atoms from the cathode surface of platinised platinum, polished platinum, palladium, nickel, copper, tin, zinc, lead, and mercury during polarisation is demonstrated by the reducing action on a tungstic oxide suspension, and a complete parallelism is found between this emission and the overvoltage of the metal. Theoretical considerations are adduced to support this fact and to show that both factors must vary inversely with the energy of combination of the hydrogen atom with the metal. The varying capacities of the metals to accelerate the recombination of hydrogen atoms and the relation between this and overvoltage receives consequential explanation. The results are in good agreement with a relation derived from a thermodynamical treatment of the overvoltage phenomena employing the assumption that the transition of hydrogen ion to molecular hydrogen through combination with metal ion is an irreversible step. This relation connects overvoltage with the energy of combination of metal with hydrogen and the concentration of the latter, and a temperature relation for overvoltage derived from this gives good agreement with experimental values. Calculation of the dissociation energy of the hydrogen molecule from the hydrogen overvoltage value with a mercury cathode agrees well with the experimental value. The energy of combination of hydrogen with the cathode is shown to be from 10 to 50 g.-cal. over the series. It is found that addition of mercuric chloride or hydrogen sulphide when using a platinised platinum cathode increases both the overvoltage and the hydrogen emission, and that the latter is also much increased by rise of temperature when using a polished platinum cathode. H. I. DOWNES.

Unidirectional and photo-effects at the interface of cuprous oxide and deposited metal layers. E. DUHME and W. SCHOTTKY (*Naturwiss.*, 1930, 18, 735—736).—The rectifying action of the combination copper-washed cuprous oxide is due to the behaviour of a unidirectional layer of submicroscopic thickness at the interface; a unidirectional effect is also observed at the boundary of massive cuprous oxide plates and all loose or compact metals and also with graphite. The effect is more pronounced if the cuprous oxide is etched than if it is polished and has thin layers of gold deposited on it. It was expected that light in the neighbourhood of the unidirectional interface between oxide and electrode would give a photo-effect, as in the case of copper-cuprous oxide. The effect was demonstrated by using cuprous oxide plates which had been etched and on which gold or silver layers had been deposited cathodically. The photo-stream gave 5×10^{-8} Å. for light from an incandescent gas-filled lamp. The

photo-effect comes from the front of the oxide exposed to the light—a front-wall effect—in contrast with the case of copper-cuprous oxide, which shows a back-wall effect. The spectral sensitivity of the front-wall effect differs from that of the back-wall effect. In the latter case it is determined by an absorption of the thin metal layer, and in the former by the light arriving at the surface. The direction of the photo-stream is the same, electrons being liberated in the oxide which then pass through the unidirectional layer to the adjacent electrode. Only etched material shows a good effect with the deposited layers. It appears that the primarily produced photo-stream is independent of a potential applied to the cell and that the observed dependence is due for the greater part to the dependence of the resistance of the unidirectional layer on the potential. The technical applicability of the new photo-cell depends on how far the deposited metal surface remains unaltered.

J. E. MILLS.

Explosive gas reactions. I. J. BOOY (Rec. trav. chim., 1930, 49, 866—875).—Theoretical. A reaction mechanism is proposed which accounts both for the existence of explosion limits in explosive gas mixtures and for the two pressure limits of the oxidation of phosphorus.

J. A. V. BUTLER.

Speed of flame in a closed tube. Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 243—244B).—The speed of flame propagation in a horizontal closed glass tube containing mixtures in various proportions of hydrocarbon vapour and air was measured. It was much higher than in an open tube and varied rapidly with concentration. The maximum speed was with about 2.25% of hydrocarbon, the figure for complete combustion being 1.92%. This result is connected with the dissociation of carbon dioxide at high temperatures, which is nevertheless less than in an open tube. Flame photographs showed very irregular forms.

C. IRWIN.

Chain reaction theory of rate of explosion in detonating gas mixtures. B. LEWIS (J. Amer. Chem. Soc., 1930, 52, 3120—3127).—The concept of reaction chains is employed in an attempt to calculate from thermal data the velocity of propagation of gaseous explosions. It is assumed that the energy liberated in each reaction in the chain is equi-parted among all the degrees of freedom of the products and hence the velocity of the propagating molecule (i.e., the velocity of propagation of the explosion) can be calculated. For thirteen different explosive mixtures a suitable choice of reaction mechanism and propagating molecule generally leads to calculated velocities in good agreement with the experimental determinations of other observers.

J. G. A. GRIFFITHS.

Chain reactions. (A) Remarks on a paper by Lenher and Rollefson on the kinematics of carbonyl chloride. (B) Mechanism of formation and decomposition of ethylene iodide. H. J. SCHUMACHER (J. Amer. Chem. Soc., 1930, 52, 3132—3139).—A. The mechanism proposed by Lenher and Rollefson (this vol., 433) for the photo-chemical reaction between carbon monoxide and chlorine is held to be improbable and a reply is

given to their objections to the mechanism suggested by Bodenstein and others (A., 1929, 894).

B. The observed kinetics of the decomposition of ethylene iodide (Polissar, this vol., 548) are explained by the following mechanism: (1) $I_2 \rightleftharpoons 2I$, (2) $C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$, (3) $C_2H_4I \rightleftharpoons C_2H_4 + I$. The heats of activation of reactions (2) and (3) are computed to be 11,500 and 200 g.-cal., respectively. From the thermal and kinetic data the energy difference between the 5S and 3P state of the carbon atom is calculated to be 74 kg.-cal.; that between the valency linkings C-C and C:C is about 48, which is equal to the energy of the C-I linking in ethylene iodide.

J. G. A. GRIFFITHS.

Reaction regions. XX. Influence of various circumstances on the extension of explosion regions. W. P. JORISSEN, J. BOOY, and J. VAN HEININGEN (Rec. trav. chim., 1930, 49, 876—883).—The explosion limits of ternary mixtures are different for upward and downward propagation of the explosion wave. The difference at the lower explosion limit is greater with substances of small mol. wt., but at the upper explosion limit no such relation is observed.

J. A. V. BUTLER.

Ignition of hydrogen-oxygen mixtures at low pressures by heated quartz. H. N. ALYEA and F. HABER (Naturwiss., 1930, 18, 441—443).—The ignition by quartz at 500—600° of hydrogen-oxygen mixtures over a certain range of low pressures is caused by the production at the quartz-gas interface of hydroxyl, which on evaporation from the solid surface initiates the reactions $OH + H_2 = H_2O + H$ and $H + O_2 + H_2 = OH + H_2O$. The lower pressure limit of the low-temperature ignition is governed mainly by the second of these reactions, whilst when the pressure is above the upper limit, evaporation of the hydroxyl is retarded by reflexion from adjacent gas molecules.

H. F. GILLBE.

Decomposition of nitrogen peroxide at low pressures. H. J. SCHUMACHER (Proc. Nat. Acad. Sci., 1930, 16, 554).—A correction (cf. this vol., 708).

Thermal decomposition of nitrous oxide. M. VOLMER and H. KUMMEROV (Z. physikal. Chem., 1930, B, 9, 141—153).—The thermal decomposition of nitrous oxide at 640° and under pressures of 25—300 mm. has been shown to be a unimolecular reaction, and not, as other authors have affirmed, bimolecular (cf. Hinshelwood and Burk, A., 1924, ii, 751). As the pressure falls the unimolecular velocity coefficient diminishes, but this is probably due to a decrease in the number of molecular impacts transmitting energy. The mean life of the active molecule is calculated to be about 10^{-10} sec., which gives 57,500 g.-cal. per mol. for the heat of activation. If the latter is assumed to represent the energy of separation of the oxygen atom, the value of 154,500 g.-cal. is obtained for the molecular heat of dissociation of oxygen.

R. CUTHILL.

Oxidation and ignition of mixtures of pentane and air. M. PRETTRE, P. DUMANOIS, and P. LAFFITTE (Compt. rend., 1930, 191, 329—331).—Gaseous mixtures of pentane and air were passed at the rate of 6.5 litres per hr. into a glass receiver,

heated progressively by an electric furnace to 800° in about 2.5 hrs., in such a way that the effects of the products of combustion on the ignition point were not eliminated (cf. A., 1929, 271, 771). With less than 2.5 vol.-% of pentane (the quantity necessary for complete combustion) a luminescence appeared at 250–300°, and ignition occurred at 670°. With greater proportions (up to 13%) an intense blue luminescence occurred at 259–263° (depending on the composition) and ignition at 670–680°. It is concluded from changes in the nature of the luminescence in the latter case that two spontaneous ignitions may occur, at 260–300° and above 660–670°, and that in the interval (300–660°) such mixtures do not ignite but only luminesce.

J. GRANT.

Ignition and combustion of mixtures of pentane and air. M. PRETTRE, P. DUMAÑOIS, and P. LAFFITTE (Compt. rend., 1930, 191, 414–416).—Antidetonants raise the first ignition temperature observed in the authors' experiments (cf. preceding abstract) and, if sufficiently powerful or present in sufficient amount, suppress it or decrease the flame propagation velocity. Thus, 7 vol.-% of benzene or 1% of tin tetraethyl in the liquid pentane raises the temperature by 25°, and 0.4% of ethyl fluid (55% of lead tetraethyl) completely suppresses the first ignition. Prodetonants (e.g., 1 vol.-% of amyl nitrite) also raise the first ignition temperature, but increase the rate of flame propagation. J. GRANT.

Determination of the explosion pressure for acetylene saturated with water and acetone vapours. ANON. (Jahresber. VII Chem.-Tech. Reichsanst., 1928, 56–63; Chem. Zentr., 1930, i, 2037).—Water and acetone vapours depress the explosion pressure according to their tension, but the difference is the smaller the greater is the initial pressure. The explosion pressure of pure acetylene is about eleven times the initial pressure.

A. A. ELDRIDGE.

Minimum concentration of carbon tetrachloride giving non-inflammable mixtures with carbon disulphide and the effect of combustion suppressors thereon. Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 242B).—5.2 Vols. of carbon tetrachloride are required to give a non-inflammable mixture with 1 vol. of carbon disulphide. This figure is considerably reduced by adding to the carbon disulphide from 5 to 20% of ethyl bromide, tin tetramethyl, or petrol (b. p. 45–50°).

C. IRWIN.

Effect of a hydrocarbon and ethyl ether on the spontaneous ignition temperature of carbon disulphide. Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 241B).—A mixture of dimethylcyclopentane and isoheptane raises the ignition temperature of carbon disulphide markedly, whilst ethyl ether does so only slightly. Addition of 9% of the former gives a mixture which ignites spontaneously at 525°, whilst carbon disulphide with 9% of ether ignites at 240°.

C. IRWIN.

Neutral salt effect of the ferric-iodide ionic reaction. A. VON KISS and I. BOSSANYI (Z. anorg. Chem., 1930, 191, 289–308).—In dilute solution the

order of the reaction between ferric and iodide ions is unimolecular with respect to the ferric ions and bimolecular with respect to the iodide ions. The hydrolysed ferric ions do not react with measurable velocity. The process is purely ionic, and up to an ionic strength of 0.15 follows almost quantitatively the neutral salt rule of Brönsted, but sodium iodide has a specific effect. The retarding effect of ferrous and sulphate ions found by Sasaki (A., 1924, ii, 765) has been confirmed, and it is shown that hydrogen, nitrate, bromide, and chlorate ions have a feeble catalytic effect. O. J. WALKER.

Rapid reactions. Velocity and heat effects involved in neutralisation of sodium dichromate by sodium hydroxide. V. K. LAMER and C. L. READ (J. Amer. Chem. Soc., 1930, 52, 3098–3111).—The velocities of rapid chemical reactions have been investigated by a modification of the method of Hartridge and Roughton (A., 1925, ii, 47). The courses of the reactions are followed by means of thermocouples which measure the temperature change due to the heat of reaction evolved (cf. Roughton, this vol., 426). The reaction between 0.05*N*-ammonia and acetic acid is 95% complete in 0.002 sec. The velocity of neutralisation of 0.02–0.06*M*-sodium dichromate by sodium hydroxide at 25° is unaffected by the concentration of hydroxyl ions, but is a function of that of the dichromate ions. The reaction follows the unimolecular law with respect to dichromate ($k=529 \text{ min.}^{-1}$) and the heat of reaction is 15,320 g.-cal. per g.-mol. of dichromate ion. The data are best interpreted by the following series of reactions: (a) $\text{Cr}_2\text{O}_7'' + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4'$ (slow), (b) $\text{HCrO}_4' \rightleftharpoons \text{H}^+ + \text{CrO}_4''$ (rapid), and (c) $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ (rapid) (cf. Saal, A., 1928, 374). The heats of reaction involved in steps (a) and (b) have been evaluated: q_a , -13,640 g.-cal. per g.-mol. of $\text{Cr}_2\text{O}_7''$ and q_b , 780 g.-cal. per g.-mol. of HCrO_4' . J. G. A. GRIFFITHS.

Velocity of inversion of sucrose. III. Inversion by Koji-invertase. N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1930, 33, 272–274B).—The velocity coefficient of inversion of sucrose and the effect of temperature using purified Koji-invertase were determined. In general the coefficient decreases as inversion proceeds. The optimum temperature is 48–50° and the action of the enzyme is not affected by the presence of alkali salts in dilute solution or by ultra-violet rays. It is poisoned by mercuric, lead, and copper salts and to a smaller degree by formaldehyde, ethyl alcohol, etc. C. IRWIN.

Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde. H. P. TEUNISSEN (Rec. trav. chim., 1930, 49, 784–826).—When a 1% solution of hydroxymethylfurfuraldehyde in 0.5*N*-hydrochloric or -sulphuric acid is heated at 100° for 10 hrs., an equimolecular mixture of formic and lactic acids is produced; a small amount of humin is also formed. The reaction does not occur in water alone at 100°, but in presence of oxalic, sulphuric, hydrochloric, hydrobromic, or hydriodic acid the (pseudo-unimolecular) velocity coefficient increases in the above order. The coefficient also increases when more concentrated acid is used. Formic and lactic acids have no influence

on the hydrolysis, showing that the reaction is not autocatalytic. The probable course of the reaction is discussed with respect to the above example, furfuraldehyde, furfuryl alcohol, and pyromucic acid.

Formic acid was determined by the reduction of mercuric chloride, and lævulic acid by conversion into iodoform. H. BURTON.

Reaction between organic bromo-compounds and silver nitrate. H. VON EULER and A. ÖLANDER (Z. Elektrochem., 1930, 36, 506—511).—The reaction between sodium bromoacetate and silver nitrate in aqueous solution at 50° has been investigated. Three reactions occur simultaneously: (a) $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Ag} + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{AgBr}$; (b) $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Ag} + \text{CH}_2\text{Br}\cdot\text{CO}_2' = \text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2' + \text{AgBr}$; (c) $2\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Ag} = \text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Ag} + \text{AgBr}$.

The reaction velocities when followed argentometrically and acidimetrically are recorded. The reaction between ethyl bromide and silver nitrate in 10% ethylalcoholic solution at 35° proceeds simultaneously in two ways: $\text{EtBr} + \text{Ag}^+ + \text{H}_2\text{O} = \text{EtOH} + \text{AgBr} + \text{H}^+$; $\text{EtBr} + \text{AgNO}_3 + \text{H}_2\text{O} = \text{EtOH} + \text{AgBr} + \text{HNO}_3$, and the reaction velocity determined argentometrically or acidimetrically is recorded. H. I. DOWNES.

Formation of acetanilide in aqueous solution. H. VON EULER and A. ÖLANDER (Z. physikal. Chem., 1930, 149, 364—370).—The rate of formation of acetanilide from acetic acid and aniline in aqueous solution at 90° has been measured, the value 6.48×10^{-5} being obtained for the bimolecular velocity coefficient. The results indicate that the mechanism of the reaction is $\text{AcOH} + \text{PhNH}_3^+ \rightleftharpoons \text{AcNH}_2\cdot\text{Ph} + \text{H}_2\text{O}$. Measurements of the rate of the reverse reaction give 1070 for the value of the equilibrium constant $[\text{AcOH}][\text{PhNH}_3^+]/[\text{H}^+][\text{AcNHPh}]$ at 90°.

R. CUTHILL.

Decomposition of perchlorates by alkali nitrites. A. TIAN and SILVARICH (Bull. Soc. chim., 1930, [iv], 47, 698—701).—The velocity of decomposition of potassium perchlorate when heated between 444.5° and 520° is increased by adding sodium nitrite. The effect diminishes on further raising the temperature and disappears at about 600°.

C. W. GIBBY.

Theoretical significance of passivity. W. J. MÜLLER (Z. Elektrochem., 1930, 36, 550—551).—Polemical against Smits (this vol., 999).

H. I. DOWNES.

Theoretical significance of passivity. A. SMITS (Z. Elektrochem., 1930, 36, 551).—Polemical (cf. preceding abstract).

H. I. DOWNES.

Effect of movement in the system metal-nitric acid. E. ABEL (Z. angew. Chem., 1930, 43, 734).—The author reaches the same conclusion as Hedges (this vol., 549) as to the cause of the reduction of the rate of dissolution of metals in nitric acid by movement.

A. R. POWELL.

Interface potential and reactions at surfaces. I. Reduction of permanganate by charcoal. A. WASSERMANN (Z. physikal. Chem., 1930, 149, 223—239).—The actions of different charcoal preparations on potassium permanganate solution have been com-

paratively investigated. If the velocity of reduction of the potassium permanganate is a measure of the diffusion of the permanganate ion to the interface, the surface charge on the charcoal should influence the velocity of decomposition. The effect of p_{H} on the reaction velocity in the acid region confirms this assumption. Also potassium permanganate is reduced about equally readily by normal and activated sugar charcoal in alkaline solution where both charcoal surfaces are negatively charged, whereas in acid solution the positively-charged active charcoal is the more active. The fact that the velocity of reaction in alkaline solution is independent of the concentration of the alkali is explained by supposing that the carbon adsorbs hydroxyl ions only in small amounts. J. W. SMITH.

Action of mixed catalysts in the decomposition of nitrous oxide. G. M. SCHWAB and H. SCHULTES (Z. physikal. Chem., 1930, B, 9, 265—288).—The decomposition of nitrous oxide under the catalytic influence of various metallic oxides has been studied as a function of temperature and the oxides studied can be arranged in the following order of decreasing effectiveness: copper > magnesium > aluminium > zinc > titanium > chromic > ferric oxide. The activity of mixtures of the basic white oxides of magnesium, zinc, and aluminium in pairs is in each case an additive property of the components; mixtures of cupric oxide, alumina, and magnesium oxide respectively with chromic oxide have a reduced activity, but mixtures of cupric oxide with the oxides of aluminium, zinc, or magnesium exhibit an enhanced reactivity. The rate of decomposition of nitrous oxide is proportional to its concentration. A more detailed examination of the effect of cupric, magnesium, and zinc oxides and of their mixtures in pairs was made. After ignition the activity of cupric oxide is reduced without alteration of the heat of activation. Ignited mixtures of cupric and magnesium oxides show a sharp maximum activity at a certain composition, the heat of activation at this stage being less than that of either component. With mixtures of zinc and magnesium oxides the velocity of decomposition and the heat of activation vary continuously from the values of one component to those of the other. From a consideration of these results it is concluded that the varied effects of the mixtures of catalysts can be separated into structural and energetic causes. E. S. HEDGES.

Promoter action in reactions of oxidation concomitant with the catalytic decomposition of hydrogen peroxide. I. Oxidation of hydrazine. D. P. GRAHAM (J. Amer. Chem. Soc., 1930, 52, 3035—3045; cf. Bohson and Robertson, A., 1924, ii, 29; Robertson, A., 1925, ii, 690).—The decomposition of hydrogen peroxide and the concomitant oxidation of hydrazine to nitrogen in the presence of ferric and cupric sulphates are found to be comparatively free from side reactions and have been studied by means of the gases evolved. Copper sulphate alone is a much more effective catalyst for both reactions than is ferric sulphate. Promoter action is exhibited when a mixture of the two sulphates is used; in general when the concentration of one catalyst is

varied, the rate of decomposition of hydrogen peroxide and the rate of oxidation of hydrazine follow the general trends observed when the catalyst the concentration of which is being varied is used alone. In all cases, sulphuric acid has an inhibitory action. Promotion factors are computed. It is suggested that the hydrazine is oxidised by the oxygen liberated in the reaction between the catalytic intermediates (cupric or ferric acid) and hydrogen peroxide, and also by the catalytic intermediates themselves.

J. G. A. GRIFFITHS.

Effect of sodium salts of monohydroxy-acids on rate of saponification of methyl acetate by sodium hydroxide. F. L. ALLEN (Trans. Faraday Soc., 1930, 26, 527—533).—The hydrolysis of methyl acetate in 0.0125*N*-solution by sodium hydroxide at 20° is markedly retarded by sodium salicylate at a concentration of 0.1*N* or even 0.05*N*, and sodium glycollate, mandelate, lactate, β -hydroxy- β -phenylpropionate, and α -hydroxy- β -phenylpropionate at a concentration of 0.1*N* have a similar, but much less pronounced effect. The position of the hydroxyl and phenyl groups in the salt molecule bears little relation to its retarding action, which is ascribed to the formation of hydrogen ions by ionisation of the hydroxyl group. By means of this assumption the dissociation constant of the hydroxyl group can be calculated from the velocity data, the neutral salt effect apparently being small.

R. CUTHILL.

Catalysis of thermal decomposition of silver oxalate by silver sulphide. S. E. SHEPPARD and W. VANSELOW (J. Amer. Chem. Soc., 1930, 52, 3468—3470).—Silver sulphide nuclei produced on silver oxalate are very effective catalysts in the thermal decomposition of the latter and cause a marked curtailment of the induction period (cf. Macdonald and Hinshelwood, A., 1926, 134).

J. G. A. GRIFFITHS.

Potassium dichromate as catalyst in the dissolution of copper in sulphuric acid. M. M. NARKEVICH (J. Chem. Ind., Russia, 1929, 6, 1438—1439).—The acceleration, which is observed in the first period of dissolution, is not catalytic but is due to oxidation.

CHEMICAL ABSTRACTS.

Sputtered nickel films and the synthesis of ammonia. L. R. INGERSOLL (Nature, 1930, 126, 204).—By heating to 150° in hydrogen a film sputtered from a nickel cathode in an atmosphere of nitrogen, ammonia is produced. Heating in an excess of hydrogen with added nitrogen does not appear to increase the yield.

L. S. THEOBALD.

Heterogeneous catalysis and ultra-violet irradiation. A. A. BALANDIN (Z. physikal. Chem., 1930, B, 9, 319—328).—The catalytic dehydrogenation of cyclohexane and of ethyl alcohol in the presence of metallic palladium has been studied both with and without irradiation from a mercury lamp in order to determine whether the rate of decomposition is influenced by absorption of radiation having quanta greater than the heat of activation of the catalytic reaction. The results show that this reaction is not appreciably affected by the radiation.

E. S. HEDGES.

Passivity of metals. VI. Comparison between penetrating powers of anions. S. C. BRITTON and U. R. EVANS (J.C.S., 1930, 1773—1784).—The penetrating power of various ions has been determined by constructing the current-time and potential-time curves when aluminium and lead electrodes are immersed in a solution containing a film-forming salt (potassium chromate) and the desired ion, subjected to a small *E.M.F.* (2 volts). The curves obtained fluctuate generally violently at low current densities, but less so at higher values, and these fluctuations are explained by the breakdown and repair of the anode film, which adequately explains the order of reproducibility of the results. The penetrating power of the ions is in the following decreasing order (aluminium) Cl', Br', I', F', SO₄'', NO₃', HPO₄'', and (lead) NO₃', Cl', Br', I', HPO₄'', SO₄''.
J. O. CUTTER.

Explosive antimony. H. VON STEINWEHR and A. SCHULZE (Z. Physik, 1930, 63, 815—823).—This modification prepared electrolytically from antimony trichloride explodes when heated, and has a large specific electric resistance, showing electrolytic conductivity. X-Ray photographs showed it to be a mixture of antimony trichloride and amorphous antimony. The amorphous form exists only in the presence of the chloride, and on explosion returns to the ordinary metallic crystal. Energy changes during the explosion are calculated.

A. B. D. CASSIE.

Physico-chemical studies of so-called explosive antimony. IV. E. COHEN and C. C. COFFIN (Z. physikal. Chem., 1930, 149, 417—433).—The conditions of formation of explosive and non-explosive antimony in the electrolysis of aqueous solutions of antimony chloride have been studied. The most important factor is current density, increase of which favours the formation of the explosive form, whereas variation of the concentration of the solution produces a comparatively small effect. Rise of temperature favours the formation of non-explosive antimony and for each solution there is a temperature limit below which the product is explosive. The critical temperature varies with the concentration. The facts that rise of temperature and decrease of current density favour the production of the non-explosive form suggest that this modification is produced under conditions when the rate of transformation of the metastable explosive form exceeds its rate of deposition.

E. S. HEDGES.

Dissociation of carbon dioxide in the electrodeless discharge. H. HUNT [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1930, 52, 3152—3159).—Carbon dioxide at pressures less than 0.25 mm. in the electrodeless discharge is completely decomposed into oxygen and carbon monoxide, but at total pressures between 0.25 and 3 mm. the equilibrium $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ is established from either side in 2 min. This is unaffected by change of wave-length from 34 to 51 m. Distinctive afterglows are observed. The results obtained by varying the percentage composition of the mixtures are not in accord with the law of mass action. The equilibrium constant decreases with increasing equilibrium pressures. Excess of oxygen decreases the amount of decomposition to a greater

extent than does carbon monoxide, but does not increase the synthesis of carbon dioxide. Helium displaces the equilibrium in the direction of increased decomposition. In qualitative agreement only with the law of mass action, increased pressure decreases the extent of decomposition of carbon dioxide and increases the synthesis.

J. G. A. GRIFFITHS.

New group of photo-effects. F. WEIGERT (Physikal. Z., 1930, 31, 806).—Anomalous photochemical processes, such as the fading of dyes, biological photo-effects, and phototropic phenomena, are distinguished from normal photochemical processes. It is suggested that two kinds of elementary particles are responsible for the production of these effects. In the normal process an absorbing molecule is required and such a process may be termed a "photomolecular" process, whilst anomalous effects are due to a "photomicellar" process, in which the elementary particle is a complicated micelle arising from many molecules.

W. R. ANGUS.

Photochemical oxygen-carbon monoxide reaction. W. F. JACKSON and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, 52, 3471—3472).—When a mixture of oxygen and carbon monoxide at the ordinary temperature is illuminated by light which produces oxygen atoms, ozone and carbon dioxide are formed. The reaction $O + O_2 + X = O_3 + X$ proceeds at least 100 times as fast as the reaction $O + CO + X = CO_2 + X$, where X is a non-reacting molecule. At 575°, water vapour has a marked accelerating effect on the reaction (cf. Coehn and Tramm, A., 1921, ii, 476).

J. G. A. GRIFFITHS.

Photochemical dissociation of nitrogen peroxide. L. H. DAWSEY (Proc. Nat. Acad. Sci., 1930, 16, 546—552).—By means of a specially devised apparatus, which is described, the ultra-violet absorption spectra of nitrogen dioxide and nitrogen tetroxide have been photographed at the ordinary temperature and at -182° (liquid air), respectively, and compared with previous results (cf. Harris, A., 1928, 1305). The complex banded absorption attributed to nitrogen dioxide begins in the visible region, rises to a maximum at approximately 3900 Å., and then decreases to minimum intensity at approximately 3200 Å. Nitrogen dioxide absorbs radiation very feebly in the region 3200—2495 Å. With solid nitrogen tetroxide absorption begins at about 3820 Å. and increases in intensity towards the shorter wave-lengths. This long wave-length limit corresponds with 74.6 kg.-cal. for the least heat of optical activation. From known thermochemical data it is calculated that the total change in thermal energy between -182° and 25° is approximately 4.5 kg.-cal., and hence 70.2 kg.-cal. is obtained as the value of the least energy of optical activation at the higher temperature. This value corresponds with light of wave-length 4060 Å. at the ordinary temperature. The continuous character of the absorption spectrum of nitrogen tetroxide suggests that the primary photochemical decomposition in nitrogen peroxide (which consists of nitrogen dioxide and tetroxide) is due to the tetroxide constituent (cf. Urey, Dawsey, and Rice, A., 1929, 864). The threshold for complete photochemical equivalence is

calculated to be about 3800 Å. On the basis of these results the mechanism $N_2O_4 \xrightarrow{h\nu} 2NO + O_2$ (1S) is proposed to account for the primary photochemical dissociation and the continuous absorption spectrum of nitrogen tetroxide, where $h\nu = 74.6/N$ kg.-cal., corresponding with a wave-length of 3820 Å. The corresponding energy for the thermal change is 39.6 kg.-cal., whilst the energy necessary to excite an oxygen molecule in the normal 3S to the 1S state is 1.62 volts (Mulliken, A., 1928, 1165), which is equivalent to 35 kg.-cal. Thus the sum of the energy of thermal change and the energy of excitation of the oxygen molecule is 74.6 kg.-cal., in good agreement with the above value obtained from the short wave-length limit of the continuous absorption spectrum.

J. W. BAKER.

Atomic hydrogen. II. Behaviour of pentane in ultra-violet light and of its polymerisation products towards oxygen. Influence of mercury.

A. KLEMENC and F. PATAT (Z. physikal. Chem., 1930, 149, 449—464).—Both decomposition and polymerisation occur when pentane is irradiated without the presence of mercury (cf. A., 1929, 892). Under the influence of ultra-violet light the polymerisation products readily take up oxygen, carbon monoxide appearing among the gaseous products, or carbon dioxide in the presence of excess of oxygen. Further rupture of the carbon chain occurs and lighter hydrocarbons, such as methane, are formed. Carbon monoxide and hydrogen are oxidised to carbon dioxide and water, respectively, under the influence of the radiation in the absence of mercury, but under these conditions there is no formation of formaldehyde. The presence of mercury does not affect the oxidation of carbon monoxide, but exerts a marked influence on the oxidation of hydrogen and on the production of hydrogen from pentane.

E. S. HEDGES.

Use of light of short wave-length in quantitative chemical investigations. "Strong" and "weak" fluorescences and new fluorescence reactions. J. EISENBRAND (Pharm. Ztg., 1930, 75, 1033—1036).—In the examination of the fluorescence of solid substances in ultra-violet light, the small amount of visible violet light which passes through the best light filter often gives a violet colour to the compounds. This is due to reflexion and not to fluorescence. The violet light may also cause solutions to show a small Tyndall effect. When the same strength of fluorescence is obtained from a diluted solid as from a solution of the same dilution, the fluorescence from the solid is probably 1000 times as powerful as that from the solution owing to the difference in thickness of the layers used. The development of fluorescence analysis requires the provision of a wide range of specific fluorescence reactions, and also the development of methods for strengthening weak reactions (cf. A., 1929, 528; this vol., 34). A suitable method for increasing the fluorescence of a compound is the addition of salts. Thus, solutions of 8-hydroxyquinoline exhibit only weak fluorescence, but the solid derivatives with zinc, magnesium, or cadmium show brilliant fluorescence. Addition of a few drops of an alcoholic solution of 8-hydroxyquinoline to alcoholic solutions

of calcium chloride, cadmium acetate, lanthanum nitrate, lithium chloride, magnesium, strontium, or thorium nitrates, or zinc acetate gives strongly fluorescing solutions; no precipitation of metallic complex occurs. These phenomena allow the determination of the amount of 8-hydroxyquinoline in quinosol and the micro-determination of zinc to be made. 6-Hydroxyquinoline and apoquinine also show enhanced fluorescence in presence of some metallic salts.

H. BURTON.

Photochemical sensitisation in the ultra-violet.

L. FARKAS and P. HARTECK (Naturwiss., 1930, 18, 443—444).—In view of the photochemical sensitising action of ammonia on hydrogen-oxygen mixtures, that of other hydrogen compounds has been studied. Hydrogen bromide catalyses the combination of hydrogen with oxygen at 280° in the dark, and to a greater extent when the mixture is irradiated by zinc arc light; at 440° the reaction is very rapid in the dark. Hydrogen sulphide catalyses the reaction at 280° in the light, but not appreciably in the dark; at 330° the mixture readily explodes, but under certain conditions of concentration sulphur dioxide is formed rapidly in the dark, so that the reaction in the light is probably complicated by the presence of this substance, which at 350° causes rapid combination in the light, but has no influence on the dark reaction at temperatures below 480°. A mixture of hydrogen and oxygen containing a trace of nitrogen peroxide and heated to just below the ignition temperature is unaffected by light, since insufficient activated oxygen atoms are present, and no photosensitisation is observed until the nitrogen peroxide concentration is raised nearly to that which induces a rapid reaction in the dark; the action of nitrous oxide resembles that of sulphur dioxide.

H. F. GILLBE.

Precision actinometry with uranyl oxalate.

W. G. LEIGHTON and G. S. FORBES (J. Amer. Chem. Soc., 1930, 52, 3139—3152).—The quantum efficiency, γ , of the photolysis of 0.01—0.05*M*-oxalic acid in presence of 0.001—0.02*M*-uranyl sulphate has been investigated at 9.8° and 25° with monochromatic light of nine different wave-lengths between 494 and 254 $\mu\mu$, inclusive. The liquid in the actinometer must be stirred and details of the analytical procedure are recorded. The solution used in the actinometer must be 0.010*M* with respect to uranyl sulphate and 0.050*M* with respect to oxalic acid. At 25°, γ then varies from 0.60 with light of wave-length 254 $\mu\mu$ to 0.58 for 435 $\mu\mu$ and has a minimum of 0.49 at 366 $\mu\mu$. γ is diminished by the presence of sodium sulphate, sodium hydroxide, or sulphuric acid, and the temperature coefficient per 10° between 10° and 25° for light of wave-lengths 313 and 366 $\mu\mu$ is 1.03 (cf. Pierce, A., 1929, 1404). Evidence is adduced that the reaction probably proceeds by the decomposition of a complex of the type $\text{UO}_2\text{H}_2\text{C}_2\text{O}_4$ or $\text{UO}_2\text{C}_2\text{O}_4$ rather than by collisions of the second kind between activated uranyl ions and acid molecules.

J. G. A. GRIFFITHS.

Photochemical isomerisation of allocinnamic acid in presence of iodine. A. BERTHOUD and C. URECH (J. Chim. phys., 1930, 27, 291—306).—The transformation, in benzene solutions containing

iodine, of allocinnamic acid into cinnamic acid by visible radiation has been studied by observation of the change of m. p. The reaction is unimolecular and has a temperature coefficient at 25—35° of 1.3. For wave-lengths from 4580 to 5260 Å., over which range the absorption is almost complete, the reaction velocity k is independent of the iodine concentration, but for red light, which is only partly absorbed, k varies with the square root of the iodine concentration. The quantum yields at 4350 and 5600 Å. are 1.3 and 0.33, respectively. The suggested mechanism of the reaction, which accords well with the experimental data, is (1) a molecule of iodine is dissociated by the light, (2) an atom of iodine combines with a molecule of allocinnamic acid to form an unstable moniodide containing a tervalent carbon atom, (3) mutual rotation of the two doubly-linked carbon atoms takes place with the formation of an iodine derivative of cinnamic acid, (4) the iodine atoms dissociate and reform iodine molecules. The rate of formation of cinnamic acid is given by $kaI_0^{1/2}[I_2]^{1/2}$ for weak absorption and by $kaI_0^{1/2}$ for practically complete absorption, a being the initial concentration of allocinnamic acid, $[I_2]$ the mol. iodine concentration, and I_0 the radiation intensity.

H. F. GILLBE.

Determination of effect of light on dyes. P. KRAIS (Kolloid-Z., 1930, 52, 173—174).—An indicator paper suitable for measuring the amount of sunlight may be made as follows. 200 G. of white kaolin are stirred with 200 c.c. of water, and 400 c.c. of a solution containing 1 g. of Victoria-blue B per litre are added, the mixture being stirred and filtered with suction. The residue is dried in air in the dark, powdered, and sieved, and then applied to paper by means of gum arabic. On exposure to light the paper becomes pure white and not grey as in most other indicators. Directions for the quantitative use of the paper are given.

E. S. HEDGES.

Quantum yield in the photo-bromination of organic hydroxy-acids in relation to the frequency of the exciting light. J. C. GHOSH and R. M. PURKAYASTHA (Z. physikal. Chem., 1930, B, 9, 128—132).—The quantum yields in the photo-bromination of mandelic, lactic, and phenyl-lactic acids (cf. this vol., 718) increase in a continuous manner from about 3.1 to 6, 3 to 5, and 2.2 to 3.5, respectively, as the wave-length of the light diminishes from 545 to 366 $\mu\mu$.

R. CUTHILL.

Differences in mechanism of addition and substitution reactions in photo-bromination of organic compounds. J. C. GHOSH and R. M. PURKAYASTHA (Z. physikal. Chem., 1930, B, 9, 154—156).—It appears probable that in both the photo-bromination of hydroxy-acids (this vol., 718) and the photochemical addition of bromine (A., 1928, 256) continuance of the reaction chain is due to the secondary formation of bromine atoms in one of the constituent reactions. In the addition reactions it is likely that triatomic bromine molecules are formed.

R. CUTHILL.

Irradiation reaction of protein. B. RAJESKY (Strahlenther., 1929, 34, 582—586; Chem. Zentr., 1930, i, 1748—1749).—The coagulation of protein by ultra-violet light is only slightly affected by rise of

temperature, the curve being linear up to the coagulation temperature of the protein; the slight rise is attributed to the increased agglomeration of the denatured protein particles with increased molecular movement. The coagulation of protein by X-rays increases exponentially with rise of temperature.

A. A. ELDRIDGE.

Energy yield in the decomposition of chloroform by X-rays and the mechanism of this and similar X-ray reactions. G. CRONHEIM and P. GÜNTHER (Z. physikal. Chem., 1930, B, 9, 201—228; cf. A., 1928, 1340).—In the formation of hydrogen chloride from chloroform under the influence of X-rays the amount produced is proportional to the amount of energy absorbed in the form of secondary electrons, and 21 kg.-cal. are required per mol. of acid formed. Since this is small compared with the energy required to sever C-Cl and C-H linkings it is concluded that the reaction has a chain mechanism. Possibly the chloroform molecule is first shattered by a secondary electron with the formation of free chlorine atoms and a hydrogen atom which react with unchanged molecules, $\text{Cl} + \text{CHCl}_3 = \text{HCl} + \text{CCl}_3$, $\text{H} + \text{CHCl}_3 = \text{H}_2 + \text{CCl}_3$, the CCl_3 then continuing the chain by the reaction $\text{CCl}_3^* + \text{CHCl}_3 = \text{Cl} + \text{CCl}_2 \cdot \text{CHCl}_3$, and it is likely that the reactions $\text{H} + \text{CHCl}_3 = \text{HCl} + \text{CHCl}_2$, $\text{CHCl}_2^* + \text{CHCl}_3 = \text{Cl} + \text{CHCl}_2 \cdot \text{CHCl}_3$ also occur. In presence of water and oxygen, chlorine monoxide or hypochlorous acid is also formed, and the yield of hydrogen chloride is increased. It is uncertain how the water acts, but a possible mechanism for the action of oxygen is $\text{CCl}_3 + \text{O}_2 = \text{COCl} + \text{Cl}_2\text{O}$, $\text{COCl} + \text{CHCl}_3 = \text{COCl}_2 + \text{CHCl}_2$, $\text{CHCl}_2 + \text{O}_2 = \text{HClO} + \text{COCl}$, $\text{COCl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{CO}_2$. The retarding action of hydrocarbons such as petroleum on the decomposition may then depend on their interfering with the reaction of the chloroform with oxygen. In the formation of hydrogen chloride from mixtures of petroleum and carbon tetrachloride a chain of reactions is probably initiated by hydrogen atoms from the hydrocarbon as well as by chlorine atoms. In all the X-ray reactions examined it appears that the action of a secondary electron on a single molecule corresponds with the first step in the absorption of visible light in an ordinary photochemical chain reaction.

R. CUTHILL.

Mechanism of the chemical action of X-rays in aqueous solutions. O. RISSE (Strahlenther., 1929, 34, 578—581; Chem. Zentr., 1930, i, 1748).—Ultra-violet irradiation of water, whether in presence or absence of oxygen, did not lead to the formation of hydrogen peroxide unless zinc oxide was present; X- or β -irradiation of pure water leads, however, to its formation. Hydrogen peroxide is decomposed by all three radiations. The reaction depends on the dissolved oxygen; hence the presence of dissolved oxygen in irradiated solutions may cause changes dependent on the primary formation of hydrogen peroxide. The conversion of ferrous into ferric salts is an example. The mechanism of the formation of hydrogen peroxide is discussed. A. A. ELDRIDGE.

Formation of periodic structures. E. S. HEDGES (Rev. gén. Colloid., 1930, 8, 193—199).—A summary. Existing theories of Liesegang ring formation are inadequate. Periodic structures are

differentiated from periodic reactions and experiments are described in which the Liesegang phenomenon is separated into two stages, the banding occurring after the chemical reaction has been completed. Similar structures can be produced by the coagulation of colloids by electrolytes and also in the salting-out of simple salts such as sodium chloride. This particular manifestation of periodicity is considered in relation to the periodic dissolution of metals, periodic passivity, and periodic phenomena in electrolysis, both at the anode and at the cathode, and it appears that the essential condition for periodicity is the existence of a critical condition determining a change which takes place to completion every time the critical value is reached. E. S. HEDGES.

Behaviour of sodium sulphate crystals towards cold ethyl and methyl alcohols. M. A. RAKUSIN (Z. Krist., 1930, 73, 115—116; Chem. Zentr., 1930, i, 2228).—Treatment with 95% ethyl alcohol affords a powder consisting of thenardite; with methyl alcohol dehydration, but not powder formation, occurs. A. A. ELDRIDGE.

Complex fluoborates. A. TRAVERS and L. MALAPRADE (Bull. Soc. chim., 1930, [iv], 47, 788—801).—Fluoboric acid and normal fluoborates corresponding with the formula MBF_4 decompose slowly in aqueous solution, giving complex fluoborates which are readily decomposed by alkalis. When hydrofluoric and boric acids react in aqueous solution an acid is formed which is not normal fluoboric acid, but when kept is slowly transformed into an equilibrium mixture containing the latter. A complex fluoborate is formed when boric acid reacts with potassium fluoride in aqueous solution. Two new fluoborates which are decomposable by alkalis have been isolated. The compound K_2BF_5 is obtained when normal potassium fluoborate is heated at 580° . The compound $\text{K}_2\text{B}_2\text{F}_6 \cdot 1.5\text{H}_2\text{O}$ may be prepared by the following method: 50 g. of potassium hydrogen fluoride and 25 g. of boric acid are dissolved in 100 c.c. of cold water, the solution is filtered and kept for about 4 hrs., when a crystalline deposit of the substance will have formed. E. S. HEDGES.

Preparation of silver-free copper. B. PARK (J. Amer. Chem. Soc., 1930, 52, 3165—3166).—Copper, spectrographically free from silver (*i.e.*, $<0.0002\%$), is obtained by fractional electrolytic deposition on platinum electrodes from copper sulphate in 5% nitric acid. The first fractions contain the bulk of the silver. J. G. A. GRIFFITHS.

Cæsium borates. A. P. ROLLET and L. ANDRÉS (Compt. rend., 1930, 191, 375—378).—Precipitates obtained by mixing various proportions of alcoholic solutions of boric acid and cæsium oxide have approximately the same compositions as the initial mixtures for 0.25—4 mols. of boric acid to 1 mol. of cæsium oxide, but for larger proportions of the former an amorphous precipitate of composition $5\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O}$ is produced. An isothermal diagram of the system $\text{B}_2\text{O}_3 - \text{Cs}_2\text{O} - \text{H}_2\text{O}$ is shown for 18° , the following solid phases being identified by the method of residues: *cæsium pentaborate*, $5\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O} \cdot 8\text{H}_2\text{O}$, small orthorhombic crystals; *cæsium diborate*, $2\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O} \cdot 5\text{H}_2\text{O}$, large orthorhombic crystals which lose water at 80° ,

and are often contaminated with pentaborate; *caesium monoborate*, $B_2O_3 \cdot Cs_2O \cdot 7H_2O$, orthorhombic prisms, losing water at 45° . J. GRANT.

Reactions of ammonia on the system $ZnCl_2-NH_4Cl-H_2O$. R. FRIESS (J. Amer. Chem. Soc., 1930, 52, 3083—3087).—The p_H of aqueous zinc chloride-ammonium chloride solutions in the range of solubility at 20° , the concentrations of ammonia requisite to produce precipitates, and the p_H of the liquids in equilibrium with the precipitates have been determined. The precipitate has the composition $ZnCl_2 \cdot 2NH_3$ when the concentration of ammonium chloride is 15% or more, but a basic precipitate, probably $ZnCl_2 \cdot 4ZnO$, is formed when the concentration of ammonium chloride is less than 15%. The results are explained by the effect of ammonium chloride on the ionisation of the constituents of the system. J. G. A. GRIFFITHS.

Composition of deposit forming on zinc immersed in cupric sulphate solution. I. A. GALECKI and J. TOMASZEWSKI.—See B., 1930, 822.

Action of hydrogen and hydrocarbons on barium. P. REMY-GENNETÉ (Compt. rend., 1930, 191, 413—414).—Redistilled barium in contact with pure dry hydrogen at 20° and 639 mm. pressure for 2.5 months produces a fall in pressure to about 1 mm. Methane and acetylene are not adsorbed (1 month), and a method of separation of hydrogen from these gases is therefore indicated. J. GRANT.

Preparation of mercuriammonium bromides and chlorides. Crystalline dimercuriammonium bromide and chloride. M. FRANÇOIS (Bull. Soc. chim., 1930, [iv], 47, 825—833).—See this vol., 1006. E. S. HEDGES.

Reaction mechanism in the precipitation of radium preparations rich in emanation. O. ERBACHER and H. KÄDING (Z. physikal. Chem., 1930, 149, 439—448).—Radioactive preparations were made by precipitating a mixture of ferric chloride and barium radium chloride by the addition of an excess of ammonia solution containing ammonium carbonate, sulphate, or chromate. The emanating power of the precipitate was almost 100% when ammonium carbonate or sulphate was used, but only about 65% when the chromate was used. When the barium radium salt was added after precipitation of the ferric hydroxide the emanating power was unaltered in the presence of carbonate or sulphate, but was raised to about 75% in the presence of chromate. It is supposed that the sparingly soluble radium carbonate and sulphate are adsorbed at the outer surface of the ferric hydroxide gel, giving a highly emanating preparation, but the almost insoluble radium chromate is adsorbed so rapidly that a portion becomes enmeshed in inner surfaces of the gel, with reduction of the emanating power of the preparation. Similar phenomena were observed using aluminium hydroxide as the adsorbent. This conclusion is supported by the reduction of emanating power on ageing of the gel or on drying with alcohol. E. S. HEDGES.

Action of calcium hydroxide solution on aluminium. G. ASSARON (Z. anorg. Chem., 1930,

191, 333—339).—The action of calcium hydroxide solution (0.040—0.125% CaO) on aluminium has been investigated at $0-90^\circ$. Analysis and crystallographic measurements of the resulting crystalline deposits show that the following calcium aluminates are formed under appropriate conditions: $Al_2O_3 \cdot 4CaO \cdot 12H_2O$; $Al_2O_3 \cdot 3CaO \cdot 12H_2O$; and $Al_2O_3 \cdot 3CaO \cdot 6H_2O$. O. J. WALKER.

Volatility of silica in water vapour. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rev. trav. chim., 1930, 49, 857—860).—Amorphous silica, quartz, tridymite, and cristobalite were heated at 300 atm. at 395° in the presence of water for periods of 9 and 24 hrs. An appreciable loss of weight was observed in each case. The metastable forms, cristobalite and tridymite, are more volatile than quartz, but less volatile than amorphous silica. Vaporised silica combined with zinc oxide to form a crystalline zinc silicate, identical in properties with willemite. Wollastonite was obtained from lime in the same way. J. A. V. BUTLER.

Preparation of hypophosphoric acid. M. SPETER (Chem.-Ztg., 1930, 54, 599).—Priority is claimed for the author's preparation of hypophosphoric acid from red phosphorus and alkali or alkaline-earth hypochlorites (A., 1927, 1156). In using alkali hypochlorites the solution should be added gradually to the aqueous suspension of red phosphorus. E. LEWKOWITSCH.

Constitution of hyposulphurous acid. O. VON DEINES and G. ELSTNER (Z. anorg. Chem., 1930, 191, 340—381).—When solid sodium hyposulphite is heated it decomposes suddenly at about 190° . The action is exothermal and evolves 10,350 g.-cal./mol. of hyposulphite, and can be represented by the equation: $2Na_2S_2O_4 = SO_2 + Na_2SO_3 + Na_2S_2O_3$, accompanied by the secondary reactions, $SO_2 + 3Na_2SO_3 = 2Na_2SO_4 + Na_2S_2O_3$ and $SO_2 + 2Na_2SO_3 = 2Na_2SO_4 + S$. The main reaction probably takes place through the following stages: $2Na_2S_2O_4 = 2Na_2SO_3 + 2SO$; $2SO = S_2O_2$; $S_2O_2 + Na_2SO_3 = Na_2S_2O_3 + SO_2$. The decomposition of sodium hyposulphite solutions with hydrochloric acid solution at the ordinary temperature gives sulphur dioxide, oily hydrogen persulphide, and polythionic acids (cf. Meyer, A., 1903, ii, 285). With concentrated acid solution at 40° , however, no polythionic acids are formed and the main reaction is $2H_2S_2O_4 = 3SO_2 + S + 2H_2O$. The structure of the hyposulphites is discussed in detail and it is suggested that they are complex salts of the type $M_2[SO_3 \cdot SO]$. This structure accounts for the above-mentioned decomposition of solid sodium hyposulphite and agrees also with the other reactions of hyposulphites. O. J. WALKER.

Structure of the tungstic acids. A. M. MORLEY (J.C.S., 1930, 1987—1999).—Four tungstic acids have been prepared and examined. The conditions of preparation were so chosen that the products obtained may be considered typical. Each type of acid was subjected to various ageing conditions, and all products were fully analysed during such ageing processes. An X-ray study (powder method) was also made of many of the products, and other tungsten compounds for comparison (photographs reproduced).

It is concluded from the combined evidence of X-ray structure and analysis that two definite compounds, H_2WO_4 and $H_2WO_4 \cdot H_2O$, exist, but that other compounds exist which it is suggested may be condensed compounds, or compounds physically impure (*i.e.*, imperfectly or not crystalline). J. O. CUTTER.

Technical preparation of rhenium. W. FEIT.—See B., 1930, 822.

Ferric hydroxide in the rusting process. G. SCHIKORR (Z. anorg. Chem., 1930, 191, 322—332).—The conditions under which the two forms of ferric hydroxide, FeO_2H , are formed in the rusting process have been investigated. The γ -hydroxide is formed when the oxidation takes place through the intermediate ferrous ferrite stage, *e.g.*, when the rusting takes place directly on the iron under water. Rust which has been formed under water at a distance from the iron consists of the α -hydroxide and is due to the direct oxidation of ferrous ions. Dehydration experiments show that slowly-formed rust corresponds closely with FeO_2H in its water content up to 160° , but that at higher temperatures the loss of water is rapid. Rust which has been formed rapidly has a considerably smaller percentage of water even at low temperatures. O. J. WALKER.

Separation on iron of carbon from carbon monoxide. III. Formation of iron oxides and iron carbides in the solid phase. U. HOFMANN and E. GROLL (Z. anorg. Chem., 1930, 191, 414—428; cf. A., 1928, 1341).—When carbon monoxide is passed not too rapidly over iron, magnetite is found in the solid phase up to 560° and ferrous oxide up to 655° . The presence of these oxides is shown by X-ray examination. Above 655° or with too rapid a gas stream no oxides are formed. At lower temperatures (275 — 320°), at which separation of carbon takes place only very slowly, formation of the carbide Fe_3C occurs. These facts, along with an examination of the equilibria in the system iron-carbon-oxygen, suggest that the reaction between iron and carbon monoxide proceeds as follows. At first iron carbide and carbon dioxide are formed. When the concentration of the latter in the gas phase is sufficiently high it oxidises the iron to oxides, which then react with carbon monoxide with further formation of carbide. The separation of carbon is due to decomposition of the carbide. In this decomposition cementite is always formed as well as iron. O. J. WALKER.

Analytical sublimation with special reference to micro-sublimation. H. HOFFMANN, jun., and W. C. JOHNSON (J. Assoc. Off. Agric. Chem., 1930, 13, 367—377).—Sublimation points of numerous substances were determined at atmospheric pressure in a vacuum in the Hortvet sublimator (B., 1923, 805). Sublimation depends on vapour pressure and is more comparable with evaporation than with boiling. Typical procedure is described and photomicrographs are given. Sublimation possesses advantages in both qualitative and quantitative analysis. A. G. POLLARD.

Optical method for the detection of substances in mixtures, residues, etc. H. WAGNER (Z. angew. Chem., 1930, 43, 686—687).—Immersion of various

transparent substances in liquids having refractive indices nearly the same as the solids causes them to appear various shades of blue when observed through the microscope by means of diffused transmitted light; thus calcium sulphate appears violet in a mixture of benzaldehyde and xylene, quartz bluish-violet in benzaldehyde and bronze-green in phenol, aluminium hydroxide light blue in toluene, and tricalcium phosphate, barium and strontium sulphates, and amphibole asbestos blue in phenylthiocarbimide. These tests serve to distinguish, *e.g.*, quartz and barium sulphate, and calcium and barium sulphates from one another when only small amounts of substance are available. A. R. POWELL.

Application of the neon lamp to photometric titrations. T. SOMIYA and S. SHIRAIISHI (J. Soc. Chem. Ind. Japan, 1930, 33, 300B).—Light from a powerful tungsten lamp passes through the solution which is being titrated, and falls on the filament of a neon lamp. The photo-electric current generated in the latter is measured, and can be used to indicate the end-point of titrations involving colour changes or precipitations. C. W. GIBBY.

Sources of error in the determination of hydrogen in gases. H. R. AMBLER.—See B., 1930, 816.

Potentiometric determination of acids and bases. F. L. HAHN (Z. angew. Chem., 1930, 43, 712—714).—The views of Jander (this vol., 51) are criticised and the potentiometric titration method for acids and bases is defended. H. I. DOWNES.

Determination of active chlorine in hypochlorite liquors. J. D. BLAKELEY, J. M. PRESTON, and F. SCHOLEFIELD.—See B., 1930, 860.

Rapid determination of free sulphur by means of silver. V. ALEKSANDROV (J. Chem. Ind., Russia, 1929, 6, 1114—1117).—The method is based on the formation of silver sulphide. If 0.3 g. of sulphur is present the minimal silver surface (wire or net) must be 28.5 cm.^2 . If the sample is solid it must be dissolved in a solvent of b. p. higher than the m. p. of sulphur. The metal is immersed at 60° , washed with toluene or ether, and dried at 50° for 15—20 min. The silver is cleaned by ignition in air, followed by washing with ammonia solution and water. CHEMICAL ABSTRACTS.

Sensitive test for ammonia. K. G. MAKRIIS (Z. anal. Chem., 1930, 81, 212—214).—A freshly prepared mixture of 20% silver nitrate solution (5 vols.) and 5% tannin solution (1 vol.) is impregnated in a suitable substrate, the presence of a trace of gaseous ammonia being indicated by a lustrous deposit of silver. The method is capable of showing the presence of 0.005 mg. of gaseous ammonia. J. O. CUTTER.

Volumetric determination of phosphoric acid. W. H. ROSS.—See B., 1930, 816.

Modified Gutzeit arsenic apparatus. A. J. LINDSEY (Analyst, 1930, 55, 503—504).—The glass apparatus affords arsenic stains of uniform size, and avoids loss of gases. A flanged tube is ground to form a plane surface with the hole of the original bore; two ears are sealed to the flange. The disc of mercuric chloride paper is secured between the ground surface

of the cap and tube, and these are held together by rubber bands. D. G. HEWER.

Separation and identification of alkali and alkaline-earth metals using isoamyl alcohol. H. YAGODA (J. Amer. Chem. Soc., 1930, 52, 3068—3076).—In the absence of sulphates and other metals, a qualitative separation of sodium, potassium, barium, magnesium, strontium, and calcium may be effected by converting the chlorides or nitrates of the metals into bromides by heating with 1 c.c. of 8*N*-hydrobromic acid until dryness is attained and then boiling the residue for 0.5 min. with 3 c.c. of isoamyl alcohol. The bromides of the first three metals are almost insoluble, and any sodium and barium in the dried residue is extracted by boiling with 1—2 c.c. of 0.2*N*-hydrobromic acid in 95% ethyl alcohol. The two metals are then precipitated as chlorides by the addition of 1 c.c. of 12*N*-hydrochloric acid. The separation of the metals with isoamyl alcohol-soluble bromides (magnesium, strontium, calcium) depends on the relatively facile decomposition of magnesium nitrate on ignition and the solubility of calcium nitrate in 16*N*-nitric acid. Relevant solubility data at 25° are recorded. J. G. A. GRIFFITHS.

Quantitative spectrum analysis of alkali metals. H. LUCAS (Physikal. Z., 1930, 31, 803—804).—In the arc spectrum of potassium and sodium the intensity relations of two lines, the higher terms of which have approximately the same excitation potential but are members of different series, are constant within the limits of experimental error. The ratio of the intensities of any two lines, the initial levels of which are different, shows a marked dependence on the experimental conditions. The necessary precautions for maintaining the constancy of the arc are dealt with. The spark spectra of sodium and potassium are characterised by a strong retrogression of the subsidiary series. The intensity relation between the principal and subsidiary series in the arc and spark spectra is 1 : 100.

W. R. ANGUS.

Determination of sodium [in water]. E. R. CALEY and C. W. FOULK.—See B., 1930, 884.

Volumetric determination of very small quantities of silver. J. GOLSE (Bull. Soc. chim., 1930, [iv], 47, 760—768).—Silver is precipitated as a compound of the formula $HgI_2 \cdot 2AgI$ by adding excess of a dilute solution of potassium iodide saturated with mercuric iodide. The iodine in the precipitate is determined volumetrically. C. W. GIBBY.

Detection of magnesium in minerals. H. LEITMEIER and F. FEIGL (Tsch. Min. Petr. Mitt., 1930, 40, 325—334).—A simple test for magnesium (A., 1929, 669) consists in warming the powdered mineral in a solution of nitrobenzeneazoresorcinol containing an excess of sodium hydroxide. In the presence of even a small amount of magnesium the powder acquires a blue colour. Silicates must be first decomposed, and if much iron is present this must be separated. L. J. SPENCER.

Iodometric determination of small amounts of zinc. H. A. PAGEL and O. C. AMES (J. Amer. Chem. Soc., 1930, 52, 3093—3098).—Minute details are given

for the iodometric determination of 3.3—33 mg. of zinc in 100 c.c. of solution. The metal is precipitated as the pyridine thiocyanate, $Zn(C_5H_5N)_2(SCN)_2$, which is then dissolved in about 125 c.c. of boiling water, 6 g. of borax are added, and the cooled liquid is poured into a volume of 0.1*N*-iodine at least 5 c.c. in excess of that required for the reaction $NCS' + 4I_2 + 8OH' = SO_4'' + 7I' + 4H_2O + ICN$. After 10—15 min., 10 c.c. of 6*N*-hydrochloric acid are added and the excess of iodine is immediately titrated slowly with thiosulphate. The quantitative relation is given by $NCS' + 3I_2 + 4H_2O = SO_4'' + 8H' + 6I' + CN'$. Chlorides and metals having insoluble pyridine thiocyanates interfere, but sulphates and nitrates are without effect. J. G. A. GRIFFITHS.

Potentiometric titrations using mercurous nitrate and sodium oxalate as titrating solutions. C. MAYR and G. BURGER (Monatsh., 1930, 56, 113—115; cf. A., 1929, 1413).—Correct results are obtained only if the sparingly soluble compound formed is crystalline. In determining phosphoric acid mercurous nitrate solution is added, precipitating mercurous phosphate; the excess is determined by potentiometric titration of an aliquot portion of the filtered solution against 0.1*N*-sodium oxalate solution. The method is not applicable to pyrophosphates, even if the salt is previously boiled with nitric acid to convert it into the ortho-acid. Nitrates of calcium, strontium, cerium, cadmium, and lead in solution are precipitated with 0.1*N*-sodium oxalate, the excess being determined by electrometric titration of an aliquot portion of the filtrate against 0.1*N*-mercurous nitrate solution. J. R. I. HEPBURN.

Separation and determination of gallium. II. Separation of gallium and aluminium from one another, and determination of these elements. S. ATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 35—47; cf. this vol., 564).—Three methods for the separation and determination of gallium and aluminium are described, the third being the most practicable. (1) An aqueous solution containing only the chlorides of the two metals is evaporated almost to dryness, and a solution of acetyl chloride in acetone (1 : 4) added with stirring. The precipitate of hydrated aluminium chloride is washed by decantation with the acetyl chloride solution. The solution is evaporated to dryness and heated repeatedly with nitric acid, evaporated again, ignited, and dissolved in hydrochloric acid, then evaporated to dryness, taken up in water, and the gallium is precipitated by adding acetic and camphoric acids, ignited, and weighed as trioxide. The filtrate is evaporated and ignited to remove organic matter, aluminium is precipitated as chloride, and, together with that precipitated at the beginning, weighed after conversion into oxide. (2) A solution containing only the chlorides is evaporated to dryness on the water-bath, the residue is dissolved in a mixture of 6*N*-hydrochloric acid and acetone (1 : 1), and the ice-cold solution saturated with hydrogen chloride. The precipitate of hydrated aluminium chloride is washed by decantation with a mixture of acetone and hydrochloric acid saturated with hydrogen chloride. Further procedure is as in (1). (3) A solution con-

taining only the chlorides is evaporated to dryness, redissolved in 6*N*-hydrochloric acid, treated with ether, and the ice-cold solution saturated with hydrogen chloride. The precipitate of aluminium chloride and the filtrate are treated as in (1) and (2).

C. W. GIBBY.

Influence of cobalt on the determination of manganese by the bismuthate method. Separation of manganese from cobalt by ammonium persulphate. T. SOMIYA (J. Soc. Chem. Ind. Japan, 1930, 33, 255—256B).—Cobalt is oxidised by sodium bismuthate and nitric acid even when the concentration of the latter is reduced to 5% and the solution ice-cooled. It is therefore not possible to determine manganese by this method without complete separation from cobalt. Ammonium persulphate will not precipitate manganese entirely free from cobalt either in ammoniacal or in neutral solution. In ammoniacal solution the precipitate is difficult to filter; in nearly neutral solution in presence of zinc it is readily filtered and contains very little cobalt, but repeated precipitation by boiling with ammonium persulphate is necessary to yield a filtrate free from manganese.

C. IRWIN.

Delicate reagent for cobalt. E. A. LUM (Pharm. J., 1930, 125, 147).—When a cobalt nitrate solution is treated with 20% ammonium thiocyanate solution and the mixture shaken with acetone or a mixture of ether and amyl alcohol a bluish-green solution is obtained. The application of this test to the analysis of group IIIB is indicated.

A. R. POWELL.

Potentiometric determination and separation of chromium, vanadium, and molybdenum in steel. W. TRZEBIATOWSKI.—See B., 1930, 821.

Separation of tungstates from arsenates, using benzidine hydrochloride. J. LUKAS and A. JÍLEK (Chem. Listy, 1930, 24, 320—322).—Tungstic acid can be quantitatively separated from arsenic acid by the addition of benzidine hydrochloride to a feebly acid solution of the two salts.

R. TRUSZKOWSKI.

Potentiometric determination of gold. E. ZINTL (Z. Elektrochem., 1930, 36, 551—552).—The high values obtained in the determination of gold with titanous chloride by Müller, Weisbrod, and Stein (A., 1928, 388) are attributed to details of their experimental procedure. A note by E. MÜLLER is appended.

H. I. DOWNES.

Use of micro-analysis in the streak test [for precious metal alloys]. R. STREBINGER and H. HOLZER.—See B., 1930, 867.

m. p. determinations. A. WINSTANLEY (Pharm. J., 1930, 125, 147).—The substance is placed at the bottom of a capillary tube 6 in. long and the upper half is then bent at right angles to the lower to form a handle by which the tube may be held against the thermometer bulb; the use of rubber bands is thus rendered unnecessary.

A. R. POWELL.

Apparatus for determination of m. p. L. M. DENNIS and R. S. SHELTON (J. Amer. Chem. Soc., 1930, 52, 3128—3132).—A bar of copper $61 \times 2.5 \times 2.5$ cm. has one end connected with a potentiometer by means of copper wire and the other end wound with an electrical heater through which the current

is adjusted so that the range of temperature of the bar between the hotter and cooler ends includes the temperature of the m. p. of the substance under examination. The finely-powdered material is spread along the bar, and a constantan wire, connected with the potentiometer, is brought into contact with the bar at the sharply-developed line between the melted and unmelted substance. In this way m. p. between the ordinary temperature and 300° are determined within 30 sec. to within 0.25°. M. p. of substances which decompose when heated are: phthalic acid, 228.5°; alloxan, 210°; barbituric acid, 250°; glycine, 297.2°; fumaric acid, 297°, and phenylboric acid, 222.5°.

J. G. A. GRIFFITHS.

Valve-operated coreless induction furnace for high-temperature research. F. ADCOCK (Trans. Faraday Soc., 1930, 26, 544—560).—The construction and manipulation of a furnace of the above type are described.

R. CUTHILL.

Electric muffle with chromium-nickel wire heaters. H. SIEBERT (Chem.-Ztg., 1930, 54, 499).—A readily replaceable heating unit composed of chromium-nickel spirals is described. Temperatures of 1000—1100° can be attained.

E. LEWKOWITSCH.

Velocity meters for gases. A. P. J. HOOGVEEN (Chem. Weekblad, 1930, 27, 508—509; cf. Nicolas, this vol., 885).—To admit of the use of a differential pressure instrument in a circuit in which the absolute pressure may vary, without requiring repeated calibrations, the instrument is provided with two gas taps, at the inlet and exit ends, respectively, and an absolute pressure manometer just before the exit tap.

S. I. LEVY.

Photo-electric density meter. F. C. TOY (J. Sci. Instr., 1930, 7, 253—256).—An instrument already described (B., 1927, 60) has been improved.

C. W. GIBBY.

Distillation apparatus. W. SWIENTOSLAWSKI (J. Chim. phys., 1930, 27, 329—335).—A modified form of Engler's distillation apparatus is described wherein a feed back of the distillate to the still may be effected by means of a by-pass drip feed from a vertical condenser; the distillation may be interrupted at any moment and the condensation temperature of the vapour determined, whilst the rate of evaporation and the degree of fractionation may be readily controlled.

H. F. GILLBE.

Adiabatic calorimeter. W. H. BARNES and O. MAASS (Canad. J. Res., 1930, 3, 70—79).—A modification of earlier adiabatic calorimeters is described (cf. Maass and Barnes, A., 1926, 668; Maass and Waldbauer, A., 1925, ii, 492). A radiation thermo-element which is capable of detecting a difference in temperature of 0.00014° between the calorimeter and the outer bath is employed. The probable error in measurements of heat capacity is 0.2% when the change in temperature of the outer bath is 2°. The specific heat of platinum, in g.-cal. per g., between +25° and -78.5° is given by the equation, $C_p = 0.013215 + 0.00010148T - 0.00000012543T^2$. The heat capacity of ice between -78.5° and -3° is recorded.

T. H. MORTON.

Aspirator for constant gas pressure. F. FRIEDRICH (Chem.-Ztg., 1930, 54, 667).—A simple improvement of the gas-holder described previously (*ibid.*, 1929, 53, 760), by which refilling of the aspirator bottle may be avoided, is depicted.

E. LEWKOWITSCH.

Thermo-spring balance. Y. OSHIMA and Y. FUKUDA (J. Soc. Chem. Ind. Japan, 1930, 33, 251—252B).—The balance consists of a quartz fibre helical spring to the lower end of which is attached an iron core carrying a sample container. The spring and core are contained in a vertical glass tube with cooling jacket and the sample container in a heating tube connected to it. A solenoid surrounds the core, and the elongation of the spring caused by the change in weight of the sample is balanced by the solenoid current. The apparatus can be used at temperatures up to 1000°.

C. IRWIN.

Light filters for the isolation of narrow spectral regions. L. A. JONES.—See B., 1930, 840.

Elliptical reflector for intensifying optically excited mercury radiation. R. N. WOLFE (Rev. Sci. Instr., 1930, 1, 471—472).—The reflector consists of a nickel elliptical cylinder, at one focus of which is placed the mercury arc and at the other the tube to be irradiated.

C. W. GIBBY.

Thin sulphur layers. D. K. BERKEY (Rev. Sci. Instr., 1930, 1, 479).—Layers of sulphur as thin as 0.0075 cm. have been obtained by the following method. Melted sulphur is poured on to a warmed piece of zinc about 1 in. square and 1/32 in. thick, and pressed out after placing a piece of cellophane over it. The cellophane is then removed and the sulphur ground down with emery cloth. A circular hole is dissolved in the zinc with dilute hydrochloric acid, the remainder being coated with protective paint. The layers crack spontaneously in a few days.

C. W. GIBBY.

Untrustworthiness of photographic emulsions on glass for recording distances and a method of minimising this defect. D. COOKSEY and C. D. COOKSEY (Physical Rev., 1930, [ii], 36, 80—84).—In order to determine the effect of development on the position of a latent image, superficial motions of double-coated emulsions were investigated, and the positions of developed images with respect to corresponding latent images were studied for singly-coated plates. The results indicate that there are stresses in undeveloped gelatin emulsions; these can be relieved before the plates are used photographically by soaking them in water and dehydrating in alcohol. This process of normalising gives increased trustworthiness for recording distances. N. M. BLIGH.

Laboratory shaking machines. E. BERL and A. SCHMIDT (Chem. Fabr., 1930, 302—304).—One type described depends on a wheel weighted on one side and driven by a motor the speed of which is so regulated that the oscillations produced by the weight are in resonance with a spring. Several variations in construction are given, and the wheel and drive may

be either vertical or horizontal with corresponding alteration in the position of the shaking bottle.

C. IRWIN.

Shaking table. F. KÖNIG (Chem. Fabr., 1930, 311).—A table is supported on six spiral springs and oscillated by the rotation of a brass disc carrying six projecting teeth which make and break a circuit from the lighting supply operating through a condenser and solenoid.

C. IRWIN.

Viscosimeter. A. KÄMPF; O. SCHRENK.—See B., 1930, 844.

Correction in viscosimetry when using capillary tubes which have trumpet-shaped openings. E. C. BINGHAM and R. R. THOMPSON (J. Rheology, 1930, 1, 418—423).—New evidence has been obtained for the validity of the customary value of *m* for capillaries which are squarely cut off at the ends. Capillary viscosimeters having trumpet-shaped openings must not be treated as if the ends of the capillary were square, for the kinetic energy correction may be greatly different. When the ends of the capillary are trumpet-shaped the kinetic energy correction cannot be neglected, but it is easy to determine what is the appropriate value of *m* for the given capillary.

E. S. HEDGES.

Ultrafilters. S. R. ZINZADZE.—See B., 1930, 844.

Cryostat for moderately low temperatures. J. BARBAUDY and A. LALANDE (Rec. trav. chim., 1930, 49, 850—856).—A cryostat for temperatures between 10° and —25° is described. The refrigerating agent is ethyl chloride. Constancy to 0.1° is attained.

J. A. V. BUTLER.

Cryostat for use at temperatures from 0° to —160°. W. E. MACGILLIVRAY and J. C. SWALLOW (J. Sci. Instr., 1930, 7, 257—260).—Pentane contained in a large silvered Dewar vessel is cooled by a continuous stream of liquid air flowing through a submerged coil at a rate sufficient to keep the temperature slightly lower than is required. Heat is supplied by a heating coil controlled by a hydrogen regulator, and the temperature may be kept constant to 0.01° down to —100° and to 0.02° down to —160°. The consumption of liquid air is comparatively low.

C. W. GIBBY.

Tables for volumetric analysis. J. LUKÁCS (Biochem. Z., 1930, 224, 151—156).—Two tables are given which serve for reading the factor of a solution from its titration value and the corrected titration value on applying a factor. P. W. CLUTTERBUCK.

Lecture demonstration of spectrograms. G. LASÈGUE and (Mlle.) T. COLLIN (Bull. Soc. chim., 1930, [iv], 47, 910—912).—The apparatus enables an enlarged image of the spectrum to be projected on to a screen simultaneously with a reference spectrum which shows the position of the principal lines of several elements.

E. S. HEDGES.

Dschâbir [Geber]. E. O. VON LIPPMANN (Chem.-Ztg., 1930, 54, 677—678).

Theodore William Richards Memorial Lecture.—(SIR) H. HARTLEY (J.C.S., 1930, 1937—1969).

Geochemistry.

Annual variation of upper atmospheric ozone. S. CHAPMAN (Phil. Mag., 1930, [vii], 10, 345—352).—The hypothesis that the temperature, T , of the upper atmosphere may be high enough to produce thermal decomposition of the ozone and so generally account for the annual fluctuations of ozone content of the atmosphere is examined. If it were certain that the annual variation of temperature is symmetrical about the solstices, then this hypothesis together with the observed annual ozone variation lead to the conclusion that the rate of production of ozone in the spring is nearly three times that in the autumn. This is considered unlikely. Agreement with observed data is, however, arrived at by assuming that the maximum of T occurs about 1 month after the summer solstice. The probability of this mode of variation of T is discussed as well as existing estimates of T between 30 and 40 kilometres.

W. GOOD.

Radium content of petroliferous waters of Baku and of Daghestan. B. NIKITIN and L. KOMLEV (Compt. rend., 1930, 191, 325—326; cf. Vernadsky, this vol., 886).—The richest group of the 72 samples of Baku well-water examined (by the emanation method) contained $3 \times 10^{-11}\%$ of radium by weight (1.6×10^{-10} in one case). Waters of similar chemical compositions from neighbouring wells of the same depth had varying radium contents, although waters from layers 600 m. deep were usually the richest. The 22 waters from Daghestan contained as a rule $1.2 \times 10^{-10}\%$ of radium (decreasing with time) and 0.03% of barium, but no proportionality between these quantities was traceable. It is calculated that in some cases 0.2 g. of dissolved radium is delivered per annum.

J. GRANT.

Clay minerals. E. T. WHERRY, C. S. ROSS, and P. F. KERR (Coll. Symp. Ann., 1929, 7, 191—193).—The main types of clay minerals (kaolins, montmorillonites, and potash-bearing clays) indicated by X-ray examination are discussed.

CHEMICAL ABSTRACTS.

Properties of chabazite. Y. TANAKA and M. NAKAMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 274—275B).—The loss of weight on ignition proceeds continuously with rise of temperature up to about 1000° , when it amounts to 22%. Chabazite has no adsorptive power even if dehydrated. Although slightly alkaline to litmus, it does not interact with neutral salts and gives no colour reaction with vitamin-A. The silica gel obtained from chabazite by treating with 5N- or 10N-hydrochloric acid at 50° showed the best adsorptive power. C. IRWIN.

Mariupolite and its related rocks. J. MOROZEWICZ (Prace Polsk. Inst. Geol., 1929, 2, 217—350; Tsch. Min. Petr. Mitt., 1930, 40, 335—436).—Mariupolite (Morozewicz, 1902) from Mariupol, Ukraine, is an extreme member of the nepheline-syenite series. It consists of albite, nepheline, and ægirine, with sometimes lepidomelane, sodalite, or cancrinite, and

accessory magnetite, beckelite, and pyrochlore. The order of intrusion of this and the associated rocks was that of increasing basicity:

	Mean d .	Mean SiO ₂ (mol.-%).
1. Upper biotite-granite	2.632	80.0
2. Diabase- and amphibole- granite	2.678	74.4
3. Alkali-syenites	2.699	70.5
4. Mariupolites	2.712	63.9
5. Foyaites	2.718	60.6
6. Wehrlite	3.359	46.2

Many chemical analyses (some of them previously published; A., 1902, ii, 668; 1905, ii, 177; 1908, ii, 201; 1909, ii, 404; 1929, 45) are given of these rocks and their constituent minerals, and the relations are discussed in detail.

L. J. SPENCER.

Sands of the Lower Austrian Marchfeld. H. WIESENEDER (Tsch. Min. Petr. Mitt., 1930, 40, 303—324).—The alluvial plain east of Vienna and north of the Danube consists of gravel with beds of sand. These sands and the Danube sands and those of the dunes are compared. Determinations have been made of the grain size, specific gravity fractions, and chemical composition. The sands consist mainly of quartz grains with some muscovite, calcite, etc., and 1% of heavy minerals (iron ores, zircon, tourmaline, etc.).

L. J. SPENCER.

Absorption and refraction of red, blue, and violet spinels of Ceylon. K. SCHLOSSMACHER (Z. Krist., 1930, 72, 447—475; Chem. Zentr., 1930, i, 1900).—The degree of dispersion, as well as the concentration, of the colouring matter affects the absorption; with violet spinels the effects of the chromic and ferrous oxides were only approximately additive. The blue spinels have a somewhat higher refractivity than red, greater density of colour affording higher values. The violet spinels give intermediate values.

A. A. ELDRIDGE.

Colloidal nature of some finely-divided natural phosphates. K. D. JACOB, W. L. HILL, and R. S. HOLMES (Coll. Symp. Ann., 1929, 7, 195—204).—Chemical and mechanical analyses of Florida and Tennessee phosphate are recorded; the colloidal fractions (11.5—63.0%) resemble soil colloids in physical properties.

CHEMICAL ABSTRACTS.

Chigrovskoye phosphorite deposit. E. B. ORLOVA (Min. Suiv. Tzvet. Met., 1929, 4, 437—445).—The average phosphoric anhydride content is 16.38% and the insoluble residue 43.64%.

CHEMICAL ABSTRACTS.

Popinskoye phosphorite deposit. M. P. FIBEG and L. A. RUSINOV (Min. Suiv. Tzvet. Met., 1929, 4, 446—452).—Concentration by selective disintegration gives a product containing 17—19% P₂O₅.

CHEMICAL ABSTRACTS.

New ideas of the genesis of petroleum. F. FISCHER (Brennstoff-Chem., 1930, 11, 354—358).—A lecture.

H. BURTON.

Organic Chemistry.

Theory of the meso-structure of organic compounds. III. Structural causes of optical activity. IV. Influence of ring formation on the molecular rotation. I. I. KOTYUKOV. V. Combined influence of radicals on optical activity. I. I. KOTYUKOV and M. N. YAKIMOV (Bull. Siberian Inst. Tech., 1928, 49, No. 4, 4 pp.; 1929, 50, No. 2, 37 pp., and 25 pp.).—If meso-linkings be assumed to exist in a number of substances new asymmetric atoms, not indicated by the classical formulæ, arise and can exhibit optical activity. All cases of optically active substances except complex inorganic compounds, the inositols, and certain diphenyl derivatives, are explainable by means of the meso-theory. Disregarding isolated exceptions, and taking into account the fact that according to the meso-formulation camphoric acid is tricyclic whilst the anhydride is dicyclic, it appears that ring formation is always associated with an increase in rotation. In 30 of 43 cases replacement of a hydroxyl by an amido-group decreased the rotation. In experiment on tartaric, malic, and lactic acids, and their R, R', and RR' derivatives, in only 13 of 48 cases could the rotations be predicted by means of an additivity formula $M_{RR'} = M + (M_{R'} - M) + (M_R - M)$.

CHEMICAL ABSTRACTS.

Decomposition of hydrocarbons in the electrodeless discharge. J. B. AUSTIN (J. Amer. Chem. Soc., 1930, 52, 3026—3027; cf. Harkins and Gans, this vol., 1171).—The spectrum of the decomposition products obtained from chlorobenzene, pentane, $\beta\beta\gamma$ -trimethylpentane, acetylene, benzene, and cyclohexane in the electrodeless discharge has been examined. In all cases, except with cyclohexane, relatively large amounts of a reddish-brown solid were obtained.

J. G. A. GRIFFITHS.

Decomposition of the paraffin hydrocarbons. G. EGLOFF, R. E. SCHAAD, and C. D. LOWRY, jun. (J. Physical Chem., 1930, 34, 1617—1740).—The literature of the decomposition of the paraffin hydrocarbons by thermal means, with and without catalysts, by electrical means, by photosensitisation, and by α -particles is extensively reviewed.

L. S. THEOBALD.

Production of hydrogen and gaseous, saturated hydrocarbons by the action of oxygen on saturated cyclic hydrocarbons containing side-chains at temperatures about 100°. G. CHAVANNE and O. MILLER (Bull. Soc. chim. Belg., 1930, 39, 287—297; cf. A., 1927, 452; this vol., 768).—Varying amounts of carbon monoxide and dioxide, hydrogen, methane, and (in some cases) homologues of methane are produced when 1:2-, 1:3-, and 1:4-dimethylcyclohexanes, 1:2- and 1:3-dimethylcyclopentanes, 1-methyl-3-*n*-butylcyclopentane, and 1:3-dimethylcyclopentanol are oxidised at 85—100° under the conditions previously described (*loc. cit.*). 1:3-Dimethylcyclopentane undergoes oxidation even at the ordinary temperature; hydrogen is produced.

H. BURTON.

Dissociation of methane at high temperatures and various pressures. F. DE RUDDER and H.

BIEDERMANN (Bull. Soc. chim., 1930, [iv], 47, 704—730).—Below 1000° the thermal decomposition of methane gives only minute quantities of ethylene and no acetylene. At 1000°/atmospheric pressure 2% of ethylene and 0.5% of acetylene can be obtained at suitable rates of flow. At higher temperatures and atmospheric pressure decomposition into carbon and hydrogen is practically complete; lower pressures are essential if any ethylene and acetylene are to be obtained. The maximum quantity of ethylene (4%) is produced at 1200°/100 mm., accompanied by 2.5% of acetylene. At 1300°/about 100 mm. 6.62% of acetylene and no ethylene are produced. At 1400° and 1500°/50 mm. no ethylene and 10.5% and 14.5%, respectively, of acetylene are produced. Quartz, Marquardt porcelain, and nickel exhibited no specific effects. Hydrogen chloride had no catalytic effect, and finely divided metallic thorium only a very slight one.

C. W. GIBBY.

Formation of ethane in the catalytic decomposition of ethyl alcohol. E. H. BOOMER and H. E. MORRIS (Canad. J. Res., 1930, 2, 384—387).—In the catalytic decomposition of alcohol by means of silica gel at 350—500°, the catalyst changes with rise of temperature from a dehydration catalyst to one possessing dehydrogenating powers, and the formation of ethane is explained as being due to the production of acetaldehyde and hydrogen by dehydrogenation, the hydrogen reacting with ethylene to form ethane.

T. T. POTTS.

Bromination of hexane. F. M. PARKER (J. Amer. Chem. Soc., 1930, 52, 3465—3466).—When hexane vapour diluted with nitrogen is passed into a mixture of bromine and water, no brominated benzene compound is produced. The reported formation of such derivatives (Blair, Ledbury, and Wheeler, A., 1924, i, 1277) is due to the presence of benzene in the hexane used.

H. BURTON.

Synthesis of higher isoparaffins. S. LANDA and R. RIEDL (Coll. Czech. Chem. Comm., 1930, 2, 520—530).—Ethyl palmitate, b. p. 185—187°/10 mm., and magnesium methyl bromide give dimethylpentadecylcarbinol, converted on distillation into β -methyl- Δ^2 -heptadecene (I), b. p. 277°/100 mm., d^{20} 0.7953 (*di*-bromide, b. p. 267—268°/28 mm.), which on oxidation with chromic acid in acetic acid yielded acetone and pentadecic acid, m. p. 51°. It is reduced by hydrogen and nickel at the ordinary pressure at 220—240° to β -methylheptadecane (II), b. p. 178.5°/15 mm., d^{25} 0.7838, n_D^{25} 1.43942.

Ethyl behenate, m. p. 48.5°, is readily prepared in good yield by hydrogenation under pressure of colza oil in presence of nickel, followed by hydrolysis of the solid product with alcoholic potassium hydroxide, conversion of the resultant acid mixture into the esters, and separation of the fraction, b. p. 255°/15 mm. With magnesium methyl bromide it yields β -methyl- Δ^2 -tricosene (III), b. p. 234—237°/10 mm., m. p. 41.5°, d^{25} 0.8047, oxidised by chromic acid in acetic acid to acetone and an acid, $C_{21}H_{42}O_2$, m. p. 73.8°, which yielded heneicosane, m. p. 40.4°, when heated with hydriodic acid at 273—277°. The substance III

is only partly hydrogenated in the presence of nickel at 180° under pressure, and the β -methyltricosane (IV), m. p. 42°, d_{20}^{42} 0.7882, is separated by dissolution of the hydrogenation product in ether and precipitation with cold alcohol.

The viscosities of I at 0—100°, of II at 10—100°, and of III and IV at 50—100°, have been determined.

A. I. VOGEL.

Nuclear synthesis of unsaturated hydrocarbons. I. Δ^{α} -Olefines. H. B. DYKSTRA, J. F. LEWIS, and C. E. BOORD (J. Amer. Chem. Soc., 1930, 52, 3396—3404).—*n*-Propyl $\alpha\beta$ -dibromoethyl, b. p. 97°/27 mm., d_{20}^{97} 1.6554, and *n*-butyl $\alpha\beta$ -dibromoethyl ethers, b. p. 115°/36 mm., d_{20}^{115} 1.5647, are obtained by the method previously described (this vol., 450). Treatment of ethyl $\alpha\beta$ -dibromoethyl and the above ethers with magnesium alkyl (R) bromides affords β -alkoxyalkyl bromides, OAlk·CHR·CH₂Br, in 34—81% yield. The following are described: β -ethoxy-*n*-butyl, b. p. 67°/34 mm., d_{20}^{67} 1.2312; β -ethoxy-*n*-amyl, b. p. 82°/34 mm., d_{20}^{82} 1.1812; β -ethoxy-*n*-hexyl, b. p. 98—99°/33 mm., d_{20}^{98} 1.1548; β -ethoxyisohexyl, b. p. 89—92°/38 mm., d_{20}^{89} 1.1578; β -ethoxyisohexyl, b. p. 106—109°/33 mm., d_{20}^{106} 1.1209; β -propoxy-*n*-propyl, b. p. 65°/32 mm., d_{20}^{65} 1.2205; β -propoxy-*n*-butyl, b. p. 66°/15 mm., d_{20}^{66} 1.1803; β -propoxy-*n*-amyl, b. p. 81—82°/13 mm., d_{20}^{81} 1.1439; β -propoxyisohexyl, b. p. 77—78°/14 mm., d_{20}^{77} 1.1349; β -propoxy-*n*-hexyl, b. p. 92—93°/14 mm., d_{20}^{92} 1.1226; β -propoxyisohexyl, b. p. 112—114°/28 mm., d_{20}^{112} 1.0872; β -propoxy- β -phenylethyl, b. p. 123°/12 mm., d_{20}^{123} 1.2518, and β -butoxyisohexyl bromides, b. p. 127—128°/27 mm., d_{20}^{127} 1.0686. Treatment of these bromides with zinc dust in 90% alcohol affords Δ^{α} -olefines,

OAlk·CHR·CH₂Br $\xrightarrow{\text{Zn}}$ CHR·CH₂ + OAlk·ZnBr. The following are prepared from the β -ethoxy-derivative in 65—90% yield: Δ^{α} -pentene, b. p. 29.5—31°, $d_{20}^{29.5}$ 0.6465 (dibromide, b. p. 84—85°/32 mm., d_{20}^{84} 1.6525); Δ^{α} -hexene, b. p. 61—64°, d_{20}^{61} 0.6784 (dibromide, b. p. 103—105°/36 mm., d_{20}^{103} 1.5632); Δ^{α} -isohexene, b. p. 52.5—54.5°, $d_{20}^{52.5}$ 0.6718 (dibromide, b. p. 96—99°/38 mm., d_{20}^{96} 1.5507), and Δ^{α} -isoheptene, b. p. 84—86°, d_{20}^{84} 0.6956 (dibromide, b. p. 110—113°/34 mm., d_{20}^{110} 1.4913). The preparation of Δ^{α} -pentene from magnesium ethyl bromide and allyl bromide, and its purification through the dibromide, are described.

When a mixture of allyl bromide and ethyl $\alpha\beta$ -dibromoethyl ether is added gradually to magnesium in ether and the resulting product treated with bromine, $\Delta^{\alpha 3}$ -pentadiene tetrabromide, m. p. 84—87°, is obtained. Treatment of this with zinc dust and alcohol gives $\Delta^{\alpha 3}$ -pentadiene, b. p. 29—30° (corr.), d_{20}^{29} 0.774.

H. BURTON.

s-Dialkyltertert.-butylethynylethanes. H. B. GILLESPIE and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 3368—3376).—Magnesium *tert.*-butylethynyl bromide and ethyl trimethylacetate yield *tert.*-butyldi-*tert.*-butylethynylcarbinol, b. p. 103—107°/7 mm., m. p. 46—47°, converted by phosphorus tribromide in light petroleum into *tert.*-butyldi-*tert.*-butylethynylmethyl bromide, b. p. 68—71°/13 mm. Treatment of this with “molecular silver” in ether affords *s*-di-*tert.*-butylethynylethane, m. p. 120—120.5°, which does not absorb oxygen when heated at 140° in *p*-dibromobenzene solution. The ethane linking is

broken only by sodium-potassium alloy (cf. A., 1929, 688) in ether; the resulting sodio-derivative gives with carbon dioxide *tert.*-butyldi-*tert.*-butylethynylacetic acid, m. p. 151.5—152.5°, also formed from the above bromide, sodium-potassium alloy, and carbon dioxide in ether.

Magnesium *tert.*-butylethynyl bromide and ethyl hexahydrobenzoate afford cyclohexyldi-*tert.*-butylethynylcarbinol, b. p. 123—128°/3 mm., d_{20}^{123} 0.8991, n_D^{20} 1.4729 (acetate, m. p. 95—96°; methyl ether, b. p. 116—121°/3.5 mm., d_{20}^{116} 0.8680, n_D^{20} 1.4640). Treatment of the crude bromide from this with “molecular silver,” sodium-potassium alloy, or 40% sodium amalgam, the corresponding chloride with 40% sodium amalgam, or the above methyl ether with sodium-potassium alloy, gives varying amounts of *s*-dicyclohexyltertert.-butylethynylethane, m. p. 149—150°, which does not undergo fission even with sodium-potassium alloy. cyclohexyldi-*tert.*-butylethynylacetic acid has m. p. 125—126°.

Dehydration of cyclohexyldi-*tert.*-butylethynylcarbinol with potassium hydrogen sulphate at 125—130° yields cyclohexyldi-*tert.*-butylmethane, b. p. 105—110°/3 mm., d_{20}^{105} 0.8578, n_D^{20} 1.4838, which with hydrogen chloride in alcohol gives an impure chloro-compound. Treatment of this with 40% sodium amalgam in ether regenerates the original hydrocarbon.

H. BURTON.

Ethylene chlorohydrin. I. G. BOZZA and L. MAMOLI (Giorn. Chim. Ind. Appl., 1930, 12, 283—292).—During the synthesis of ethylene chlorohydrin from ethylene and hypochlorous acid, direct attack of the ethylene by chlorine, and also action of the chlorine on the ready-formed chlorohydrin, become appreciable only with concentrations of chlorohydrin approaching normality. For lower concentrations, the yield of chlorohydrin remains about unity, but as the concentration is increased further the yield gradually diminishes. The velocity of the principal reaction, studied in solutions of pure hypochlorous acid, is independent of the concentration of this acid within wide limits, but is closely dependent on the surface area of the ethylene bubbles. The velocity coefficient, expressed in c.c. of ethylene absorbed per second by a surface of contact of area 1 sq. cm., with normal gas pressure is about 0.00312 under the conditions employed. This velocity is not altered by adding benzene or carbon tetrachloride or by starting with solutions already acid, but is progressively diminished by increasing proportions of sodium chloride, so that neutralisation of the acid with alkali is disadvantageous. Neutralisation with lead oxide is valueless, and if copper salts are present considerable formation of secondary products occurs. The action of chlorine on chlorohydrin solutions of medium concentration gives highly-chlorinated products very difficult to separate by distillation. To avoid marked losses owing to secondary reactions, the practical attainable limit of chlorohydrin concentration is 8—10%.

T. H. POPE.

Optically active salts of β -nitro-octane. R. L. SHRINER and J. H. YOUNG (J. Amer. Chem. Soc., 1930, 52, 3332—3340).—*d*- β -Octanol is converted by phosphorus tribromide into *l*- β -bromo-octane, b. p.

83—84°/18 mm., n_D^{20} 1.4500, α_D^{25} —33.1°, and thence by treatment with silver nitrite in benzene into *d*- β -nitro-octane, b. p. 102—105°/23 mm., d_{20}^{20} 0.9224, n_D^{20} 1.4324, α_D^{25} +15.84° in alcohol. 1- β -Nitro-octane, b. p. 100—103°/18 mm., d_{20}^{20} 0.9165, n_D^{20} 1.4292, α_D^{25} —10.8° in alcohol, is prepared similarly from *d*- β -bromo-octane, b. p. 83—84°/18 mm., n_D^{20} 1.4501, α_D^{25} +29.8°. *d*- β -Nitro-octane furnishes an optically active sodium salt when treated with 1 or 2 equivalents of sodium ethoxide; regeneration of the nitro-compounds at —10° affords a product retaining about 24% of its original activity. The product regenerated from the sodium salt of *l*- β -nitro-octane at —70° retains 71% of its original activity. Treatment of this sodium salt with bromine furnishes 1- β -bromo- β -nitro-octane, d_{20}^{20} 1.113, n_D^{20} 1.4499, α_D^{25} —2.22°. The sodium salts are considered to be mixtures of optically active and inactive forms (cf. Kuhn and Albrecht, A., 1927, 749; Branch and Deelman, *ibid.*, 852).

When *d*- β -octyl nitrite, b. p. 86—90°/18 mm., d_{20}^{20} 0.852, n_D^{20} 1.4279, α_D^{25} +8.17° in alcohol, obtained as a by-product in the preparation of the nitro-octane, is dissolved in sodium ethoxide solution, the initial rotation is α_D^{25} +3.46°. This gradually rises to α_D^{25} +6.0° owing to hydrolysis. 1- β -Octyl nitrite has b. p. 85—90°/18 mm., d_{20}^{20} 0.857, n_D^{20} 1.4218, α_D^{25} —10.8° in alcohol.

H. BURTON.

Ferric ethoxide. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1930, 191, 74—78).—A reply to Sutra (this vol., 318).

R. CUTHILL.

Addition of halogens to allyl alcohol. E. V. ZAPPI (Anal. Assoc. Quim. Argentina, 1930, 18, 43—46).—In the cold and in the dark solutions of allyl alcohol in carbon tetrachloride (0.1—1*N*) react quantitatively with solutions of chlorine in carbon tetrachloride (0.1—0.25*N*) or of bromine in carbon tetrachloride or absolute alcohol (2.5*N*), simple addition taking place.

R. K. CALLOW.

Hydroxylation of double linkings. S. SWANN, jun. (Univ. Ill. Eng. Exp. Sta. Bull., 1930, No. 204, 14 pp.).—Persulphuric acid may be used in dilute aqueous solution as a hydroxylating agent in the preparation of glycerol and *trans*-cyclohexane-1:2-diol.

CHEMICAL ABSTRACTS.

Ether and ester. II. Formation of ether from alcohol. J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 754—761).—Varying amounts of ether are formed when alcohol (96% except where stated otherwise) is heated with hydrated ferric chloride, anhydrous ferric sulphate, hydrated chromic chloride, chromic sulphate (60% alcohol), aluminium sulphate, copper sulphate (60% alcohol), copper chloride, or manganous chloride at 155—160°. When either 96% alcohol or an equimolecular mixture of ether and water is heated with ferric sulphate at 155—160°, the same equilibrium mixture is obtained; the value for the equilibrium constant is 6.1—6.2.

Varying amounts of ether are also produced when 96% alcohol is heated with sulphurous, phosphoric, arsenic, dichloroacetic, maleic, picric, or toluene-sulphonic acid at 150—160°. The yield of ether rises with increase in the strength of the acid. Hydrochloric acid is a better catalyst than sulphuric acid

under these conditions, and since ethyl chloride does not react with alcohol under the conditions used, it is unlikely that the chloride is an intermediate. The change $2\text{EtOH} \rightleftharpoons \text{Et}_2\text{O} + \text{H}_2\text{O}$ is an equilibrium reaction, catalysed in the liquid state by hydrogen (hydrated hydrogen) ions. Salts of trivalent metals are the best catalysts; the sulphate is preferred to the chloride, since, with the latter, ethyl chloride is invariably produced.

H. BURTON.

Esters of halogenated alcohols. III. Decomposition of trichloromethyl chloroformate with alcohols of different types. W. NEKRASSOV and N. MELNIKOV (J. pr. Chem., 1930, [ii], 127, 210—218; cf. this vol., 1019).—The initial product from equimolecular quantities of trichloromethyl chloroformate and an alcohol (R-OH) is the alkyl trichloromethyl carbonate (OR·CO₂CCl₃). The following are isolated: *n*-propyl, b. p. 93°/12 mm., d_4^{20} 1.359, n_D^{20} 1.4451; *iso*-butyl, b. p. 103°/14 mm., d_4^{20} 1.302, n_D^{20} 1.4446; β -chloroethyl, b. p. 110°/12 mm., d_4^{20} 1.5664, n_D^{20} 1.4748, and allyl, b. p. 89—90°/11 mm., d_4^{20} 1.4015, n_D^{20} 1.4590 (*dibromide*, b. p. 163°/11 mm., d_4^{20} 1.9532, n_D^{20} 1.5321). In some cases the alkyl trichloromethyl carbonate decomposes (partly or completely) into the alkyl chloroformate and carbonyl chloride; the alkyl chloroformate also decomposes into the alkyl chloride and carbon dioxide. Thus, benzyl alcohol gives some benzyl trichloromethyl carbonate which when distilled under ordinary pressure affords benzyl chloride. *iso*Propyl alcohol furnishes a mixture of *isopropyl* chloroformate and *isopropyl trichloromethyl carbonate*, b. p. 96°/23 mm., m. p. 29°, d_4^{20} 1.3318, n_D^{20} 1.4340, whilst *tert*-butyl alcohol, methyl-diethylcarbinol, and dimethylethylcarbinol all afford the corresponding carbonyl chloride.

H. BURTON.

Chloromethionic [chloromethanedisulphonic] acid. H. J. BACKER (Rec. trav. chim., 1930, 49, 729—734).—Decomposition of barium chloromethanedisulphonate (A., 1925, i, 359) with sulphuric acid gives *chloromethanedisulphonic acid* (+2H₂O), m. p. 96—97°. Solubility and crystallographic data are given for most of the following salts: *sodium* (+H₂O); *potassium*, anhydrous and +2H₂O; *rubidium*; *cæsium*; *thallium*; *calcium* (+H₂O), and *barium* (+4.5H₂O).

H. BURTON.

Determination of the purity of acetic anhydride. C. K. ROSENBAUM and J. H. WALTON (J. Amer. Chem. Soc., 1930, 52, 3366—3368; cf. Whitford, A., 1926, 189).—Acetic anhydride (1 g.) and anhydrous oxalic acid (1 g.) are treated with pyridine (2 c.c.), the mixture is cooled for 5 min., warmed at 50° for 10 min., and the excess of oxalic acid determined by titration with 0.1*N*-potassium permanganate. The results are calculated from the equation $\text{Ac}_2\text{O} + (\text{CO}_2\text{H})_2 = 2\text{AcOH} + \text{CO}_2 + \text{CO}$; the method is accurate to 0.1%.

H. BURTON.

Anaërobic oxidation of fatty acids. S. L. NEAVE [with A. M. BUSWELL] (J. Amer. Chem. Soc., 1930, 52, 3308—3314).—The anaërobic oxidation of calcium acetate and sodium propionate by Söhngen cultures (A., 1910, ii, 798) gives methane, carbon dioxide, and a small amount of hydrogen; olefines, carbon monoxide, or homologues of methane are not produced in determinable amounts. The yield of carbon dioxide

from the propionate is higher than that required by simple decarboxylation; the additional oxygen is provided by water. The general equation for the change is $C_nH_{2n}O_2 + (n-2)/2H_2O = (n+2)/4CO_2 + (3n-2)/4CH_4$. Side reactions of the type $AcOH + 2H_2O = 2CO_2 + 4H_2$ and $CH_3R \cdot CO_2H + NH_3 = CHR(NH_2) \cdot CO_2H + H_2$ probably occur. The gas production is temporarily stopped by the addition of glycine.

H. BURTON.

Oxidation of unsaturated compounds. II. Preparation and configuration of the γ -halogeno-derivatives of crotonic acid. III. Oxidation of γ -chlorocrotonic acid. Synthesis of *dl*-threonic acid. Proof of configuration of the *dl*- $\alpha\beta$ -dihydroxybutyric acids. IV. Oxidation of crotonic acid with hypochlorous and perbenzoic acids. V. Oxidation of conjugated systems. Oxidation of pentenoic and hexenoic acids. G. BRAUN (J. Amer. Chem. Soc., 1930, 52, 3167—3176, 3176—3185, 3185—3188, 3188—3191).—II. γ -Chloro- β -hydroxy-*n*-butyronitrile is prepared either by Lespiau's method (A., 1905, i, 406) or, more conveniently, from $\alpha\gamma$ -dichlorohydrin and aqueous sodium cyanide at 60—100°, and fractionation of the product formed. The nitrile is converted into ethyl γ -chloro- β -hydroxy-*n*-butyrate by saturating an ethereal-alcoholic solution with hydrogen chloride at -15°, and the crude ester dehydrated with phosphoric oxide whereby a mixture of unsaturated chloro-esters is produced. Hydrolysis of this with barium hydroxide in 25% alcohol below 0° gives a mixture of γ -chlorocrotonic, m. p. 83°, and probably γ -chloro- $\Delta\beta$ -butenoic acid, m. p. 10°. γ -Bromocrotonic acid, m. p. 74° (ethyl ester, b. p. 80—82°/2 mm.), is prepared similarly by way of $\alpha\gamma$ -dibromohydrin (improved method of preparation given), γ -bromo- β -hydroxy-*n*-butyronitrile, b. p. 154°/14 mm., and impure ethyl γ -bromo- β -hydroxy-*n*-butyrate, b. p. 94—96° (slight decomp.)/2 mm. γ -Iodocrotonic acid, m. p. 108°, is obtained either from the chloro- or bromo-acid and sodium iodide in acetone, or by hydrolysis of ethyl γ -iodocrotonate, b. p. 90—92° (slight decomp.)/2 mm. Reduction of $\gamma\gamma$ -dichlorocrotonic acid (improved method of preparation given) with hydrogen in presence of sodium hydroxide solution and palladised charcoal gives a mixture of products containing some γ -chlorocrotonic acid. Similar reduction of γ -chlorocrotonic acid affords *trans*-crotonic acid. Since the iodo-acid is obtained from both the chloro- and bromo-acids, it follows that all three compounds have the *trans*-configuration.

III. Oxidation of γ -chlorocrotonic acid with barium chlorate in presence of a small amount of osmic acid below 30° gives 75—78% of *dl*-threo- γ -chloro- $\alpha\beta$ -dihydroxybutyric acid, m. p. 100°. Treatment of this with silver acetate and oxidation of the product formed with nitric acid (*d* 1.21) at 55° afford *dl*-tartaric acid. The chloro-acid is converted by moist silver oxide into *dl*-threonic [$\alpha\beta\gamma$ -trihydroxybutyric] acid (46% yield), m. p. 98°, also oxidised to *dl*-tartaric acid. Reduction of the chloro-acid with hydrogen in presence of sodium hydroxide solution and palladised charcoal furnishes 70% of *dl*-threo- $\alpha\beta$ -dihydroxybutyric acid, m. p. 74—75°. The configurations previously assigned (A., 1929, 293) to *dl*-

threo- and *dl*-*erythro*- $\alpha\beta$ -dihydroxybutyric acids (racemic and meso, respectively) are thus confirmed.

IV. Treatment of an aqueous solution of crotonic acid with chlorine at 0°, neutralisation with potassium hydrogen carbonate at 0°, and evaporation in a vacuum gives an 80% yield of potassium α -chloro- β -hydroxybutyrate; the free acid is obtained from the reaction mixture only in 30% yield. When the original reaction mixture is treated with an excess of potassium hydroxide solution at 0°, potassium β -methylglycidate (86% yield) is produced; the free acid, m. p. 88.5°, is isolated in 64% yield. Acidification of the alkaline solution with 10% hydrochloric acid and heating the mixture at 98° gives *dl*-*erythro*- $\alpha\beta$ -dihydroxybutyric acid, also obtained in 97% yield by hydrolysis of the glycidic acid with water at the ordinary temperature. Crotonic acid is oxidised by perbenzoic acid in chloroform to β -methylglycidic acid (20% yield).

V. Oxidation of Δ^a -pentenoic acid with silver chlorate in presence of a small amount of osmic acid gives a *dl*- $\alpha\beta$ -dihydroxyvaleric acid (80% yield), m. p. 75° (*phenylhydrazide* + H_2O , m. p. 140.5°), whilst with perbenzoic acid in chloroform in presence of water, 75% of a *dl*- $\alpha\beta$ -dihydroxyvaleric acid, m. p. 106° (*phenylhydrazide*, m. p. 119—119.5°), results. Similar oxidations of Δ^a -hexenoic acid furnish 86 and 46%, respectively, of *dl*- $\alpha\beta$ -dihydroxy-*n*-hexoic acids, m. p. 108.5° (*phenylhydrazide* + H_2O , m. p. 141.5—142°) and 99.5° (*phenylhydrazide*, m. p. 120—121°), respectively.

H. BURTON.

Partial hydrogenation of linolenic acid. K. H. BAUER and F. ERMANN (Chem. Umschau, 1930, 37, 241—249; cf. Bauer and Mitsotakis, A., 1928, 1115).—Examination of the "solid" acids obtained by the partial hydrogenation of linolenic acid (prepared from the solid hexabromide) showed that rise of temperature and speed of hydrogenation favoured the formation of solid unsaturated acids of the mono- and di-ethylenic series, whilst a low reaction temperature and slow hydrogenation increased the yield of stearic acid. The amount of diethylenic acids in the "liquid" acids was greater, and the amount of mono-ethylenic acids less, as the temperature and speed of hydrogenation were increased. The "liquid" acids were identified by ozonolysis as linolenic acid, Δ^a -linoleic and Δ^b -oleic acids. Ozonolysis of the "solid" acids of hydrogenation revealed the occurrence of stearic acid, Δ^a - and Δ^e -isoleic acids, and Δ^a -octadecadienoic acid. These results indicate that linolenic acid is hydrogenated in stages, the Δ^b - and Δ^a -linkings being hydrogenated more readily than the Δ^e -linkings; the latter appear to be capable of hydrogenation only after one of the others has been saturated, as no trace of adipic acid could be found among the oxidation products. No evidence was obtained of migration of the double linkings during hydrogenation, as postulated by Hilditch and Vidyartha (A., 1929, 423), and it is suggested that the suberic acid recovered by these workers from the products of permanganate oxidation may have been due to destructive oxidation of the primary fission products.

E. LEWKOWITSCH.

Polymerisation of methyl esters of highly unsaturated fatty acids. III. Polymerised product. IV. *cyclo*Butane ester formed by the double linking in a molecule. K. KINO (J. Soc. Chem. Ind. Japan, 1930, 33, 305—310B, 311—312B; cf. this vol. 577, 741).—III. Observations on the polymerisation of methyl esters of the highly unsaturated acids obtained from sardine oil indicates that with those containing 4 or 5 double linkings formation of a *cyclobutane* ester by intramolecular coupling of unsaturated centres occurs independently of temperature, and that dimerisation of the cyclic ester takes place subsequently. In the case of esters of trebly unsaturated acids the formation of *cyclobutane* esters is also suspected. *cyclo*Butane ring formation appears to be more facile for esters with many double linkings.

IV. Portions of the methyl ester fraction, b. p. 207—220°/4 mm., were heated in hydrogen at 285—300° for 1 hr. and 20 min., respectively. The polymerised methyl esters after repeated fractionation furnished two products: (a) (?) $C_{19}H_{31}\cdot CO_2Me$, b. p. 190—195°/4 mm., iodine value 158.9, saponification value 177.9, and (b) (?) $C_{21}H_{33}\cdot CO_2Me$, b. p. 210—215°/3 mm., iodine value 223.4, saponification value 163. The products (a) and (b) when reduced by palladium-black and hydrogen in glacial acetic acid yielded saturated solid acids (a) $C_{20}H_{36}O_2$, m. p. 70—70.5°, and (b) $C_{22}H_{40}O_2$, m. p. 78—78.2°, which were isolated by the lead salt-alcohol method. It is not yet certain that these acids are homogeneous.

C. W. SHOPPEE.

Existence of racemic compounds in solution and the application of circular dichroism to the synthesis of active compounds. A. COTTON (Trans. Faraday Soc., 1930, 26, 377—383, and Ann. Physique, 1930, [x], 13, 453—470).—A more detailed discussion of work already noted (this vol., 193).

Tautomeric forms of dimethylpyruvic acid. C. FROMAGEOT and S. PERRAUD (Biochem. Z., 1930, 223, 213—221).—Dimethylpyruvic acid obtained by distillation is the pure keto-form. When this is dissolved in water an equilibrium between enolic and ketonic forms is obtained, an *M* solution containing 0.47%, a 0.1*M* solution 0.28%, and a 0.01*M* solution only a trace of the enolic form. After addition of a small amount of alkali a third form is detectable spectrographically.

P. W. CLUTTERBUCK.

n-Valerolactone. III. Preparation. H. A. SCHUETTE and R. W. THOMAS (J. Amer. Chem. Soc., 1930, 52, 3010—3012).—Hydrogenation of lævulic acid in presence of Adams' platinum catalyst at 2.3—3 atm. during 44 hrs. gives yields of valerolactone of 52%, 48%, and 87% in ethyl alcohol, acetic acid, and ethyl ether, respectively. In the last solvent two additions of fresh portions of catalyst during the reduction increase the yield to the theoretical. In ethyl alcohol the acid reacts to some extent with the solvent.

H. E. F. NOTTON.

Detection of oxalic acid. F. W. F. ARNAUD and J. W. FLINT (Analyst, 1930, 55, 501).—Oxalic acid dissolves appreciably in ether in the presence of free mineral (hydrochloric) acid but very sparingly in its absence. If 20 c.c. of concentrated hydrochloric acid

are added to 100 c.c. of a 0.1% solution of oxalic acid three extractions with ether will remove about one fifth of the oxalic acid.

D. G. HEWER.

Polymerisation and ring formation. V. Glycol esters of oxalic acid. W. H. CAROTHERS, J. A. ARVIN, and G. L. DOROUGH (J. Amer. Chem. Soc., 1930, 52, 3292—3300).—When ethylene glycol is heated with ethyl oxalate at 180—190°, *ethyl β-hydroxyethyl oxalate*, b. p. 108—110°/0.2 mm., d_4^{20} 1.2241, n_D^{20} 1.4405, and polymeric ethylene oxalate, m. p. 153°, are produced. Distillation of the last-named substance in a vacuum gives monomeric ethylene oxalate, m. p. 143—144° (cf. Bischoff, A., 1907, i, 675), which when kept at the ordinary temperature undergoes polymerisation. The monomeric form is readily hydrolysed by 0.1*N*-alkali, and when heated at 135—140°, affords an acetone-insoluble polymeride, m. p. 172°. Extraction of a partly polymerised ester with warm acetonitrile gives soluble, m. p. 157—159°, and insoluble, m. p. 172°, forms; either of these modifications can arise spontaneously from the other by keeping at the ordinary temperature. The polymeric esters are readily hydrolysed (attempts to prepare sodium salts by the action of cold sodium hydrogen carbonate solution result in the formation of sodium oxalate) and when heated with *m*-bromobenzoic anhydride furnish *ethylene m-bromobenzoate*, m. p. 78—79°.

Propylene glycol and ethyl oxalate afford resinous material, converted by distillation at 5 mm. into monomeric *propylene oxalate*, m. p. 142°. This does not polymerise readily at the ordinary temperature, but at 140—150° it passes into a polymeride, m. p. 176—178°, insoluble in organic solvents. The trimethylene oxalate, m. p. 87—88°, of Tilitschev (A., 1927, 340) is a linear condensation polymeride (A., 1929, 1165); when heated at 250°/3—4 mm., trimethylene carbonate and stable, dimeric (14-ring) *trimethylene oxalate*, m. p. 186—187° (cf. Tilitschev, *loc. cit.*), are produced. *Hexamethylene*, m. p. 66°, and *decamethylene oxalates*, m. p. 79°, are prepared by heating ethylene oxalate with the appropriate glycol, first at atmospheric pressure and then in a high vacuum; they are both linear condensation polymerides.

H. BURTON.

Association polymerisation and properties of adipic anhydride. W. H. CAROTHERS (J. Amer. Chem. Soc., 1930, 52, 3470—3471).—Adipic anhydride, as prepared by the usual methods (cf. Farmer and Kracovski, A., 1927, 447), is a polymeride; the m. p. varies considerably with details of preparation. When heated in a vacuum partial depolymerisation occurs, and the resulting monomeric anhydride can be distilled as a colourless liquid, f. p. about 20°, which reverts spontaneously to the polymeric form. The monomeric form and aniline give adipanilic acid as the sole product, whereas the polymeride affords a mixture of adipic acid, adipanilic acid, and adipanilide. The formation of adipanilide proves that the polymeride is linear.

H. BURTON.

Applicability of the quinhydrone electrode to unsaturated acids. W. H. HATCHER and M. G. STURROCK (J. Amer. Chem. Soc., 1930, 52, 3233—3235).—The quinhydrone electrode cannot be used with

dihydroxymaleic acid; reduction of the acid to tartaric acid occurs. H. BURTON.

Sulphomaleic acid. H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1930, 49, 735—744).—Maleic anhydride (1 mol.) and sulphur trioxide (1 mol.) react at about 50°, forming *sulphomaleic acid*, isolated and purified through the *barium* salt (+7H₂O). The acid is also obtained from maleic or fumaric acid (1 mol.) and sulphur trioxide (3 mols.) (maleic anhydride is formed intermediately in each case) and in small amount from potassium acetylenedicarboxylate and potassium hydrogen sulphite (cf. A., 1928, 809). The free acid (potentiometric titration curve given) decomposes when heated without melting, decolorises permanganate slowly in the cold and rapidly in the hot, is decomposed by hydrochloric acid at 100°, and adds hydrogen sulphite, readily forming disulphosuccinic acid (*loc. cit.*). The following salts are also described: *lead* (+5H₂O); *potassium dihydrogen* (+H₂O), and *calcium* (+12H₂O; loses 9H₂O only at 200°). H. BURTON.

Metallic salts of ketones. H. H. STRAIN (J. Amer. Chem. Soc., 1930, 52, 3383—3384).—*Sodium* salts of acetone (*calcium* salt), methyl propyl ketone, acetophenone (*calcium* salt), *p*-tolyl methyl ketone, camphor, and fenchone are prepared from the ketones and sodamide in liquid ammonia. Benzophenone affords with sodamide and potassium the compounds C₁₃H₁₀O, NaNH₂ and C₁₃H₁₀O, NK₃, respectively. H. BURTON.

Separate existence and stability of dihydroxyacetone and glyceraldehyde in aqueous solution. C. NEUBERG and H. COLLATZ (Biochem. Z., 1930, 223, 494—501).—Pure dihydroxyacetone is stable in aqueous solution and does not spontaneously change either into an enolic form or into glyceraldehyde, nor is pure glyceraldehyde in aqueous solution spontaneously converted into dihydroxyacetone. Mixtures of the aqueous solutions of the two substances undergo no change on keeping. No interconversion occurs in aqueous solutions containing both substances. Glyceraldehyde does not spontaneously polymerise in aqueous solution to a hexose. *Dihydroxyacetone-2:4-dinitrophenylhydrazone*, m. p. 163—164° (corr.), *dl-glyceraldehyde-2:4-dinitrophenylhydrazone*, m. p. 167° (corr.), and the corresponding *osazone*, m. p. 265° (decomp.), are described. W. MCCARTNEY.

Alcoholysis of α -diketones in presence of hydrogen chloride. H. ADKINS, W. KUTZ, and D. D. COFFMAN (J. Amer. Chem. Soc., 1930, 52, 3212—3221).—The alcoholysis of 13 α -diketones has been studied in presence of (mainly) alcohol and hydrogen chloride at 60°. The rate is independent of the ratio diketone : alcohol, but it is a function of the amount of hydrogen chloride used. Alcoholysis of diacetylmethane proceeds to approximately the same extent with ethyl or butyl alcohol, but the rate falls appreciably with *isopropyl* or *tert.*-butyl alcohol, due to interaction of these alcohols with the hydrogen chloride. Diacetyl-mono- and -di-alkylmethanes are alcoholysed at a slower rate than diacetylmethane; the rate decreases in the following order: Bu, Pr, Et, Pr², CH₂Ph, Et₂, (CH₂Ph)₂. Benzoylacetylmethane undergoes alcoholysis more slowly than diacetyl-

methane, whilst dibenzoylmethane is practically unaffected. Substitution of the ethyl, benzyl, and *isopropyl* groups in benzoylacetylmethane causes a retardation (in the order mentioned) in alcoholysis. α -Benzoyl- α -acetylisobutane, b. p. 146—149°/10mm., d_{25}^{25} 1.043, is prepared from *isopropyl* iodide and sodiumbenzoylacetylmethane at 150°. H. BURTON.

Structure of carbohydrates and their optical rotatory power. W. N. HAWORTH (Nature, 1930, 126, 238—239).—Two recent communications of Hudson (this vol., 747) are criticised.

L. S. THEOBALD.

Structure of chloraloses. β -Xylochloralose. L. D. GOODHUE, A. WHITE, and R. M. HIXON (J. Amer. Chem. Soc., 1930, 52, 3191—3195).—Xylose and β -xylochloralose (Hanriot, A., 1910, i, 95) are converted by treatment with chloral hydrate and sulphuric acid into a mixture of *dichloralxylose*, m. p. 202°, $[\alpha]_D^{25}$ +25.2° in acetone, and probably an isomeric compound, b. p. 200°/high vac.; the former of these could not be acetylated, indicating the presence of cyclic acetal groupings. Methylation of β -xylochloralose by the method previously described (A., 1929, 429) gives *dimethyl- β -xylochloralose*, b. p. 135°/2 mm., m. p. about 53°, $[\alpha]_D^{25}$ -41.08° in chloroform, which could not be methylated further. Reduction of the dimethyl derivative with sodium amalgam and alcohol at 60° affords indefinite products. When β -glucochloralose is boiled with alcoholic potassium hydroxide, a non-reducing compound is produced; this is hydrolysed by dilute acid to dextrose.

β -Xylochloralose diacetate, m. p. 142°, $[\alpha]_D^{25}$ -7.61° in chloroform, and β -glucochloralose triacetate, m. p. 108°, $[\alpha]_D^{25}$ +22.72° in chloroform, are prepared by acetylation with acetic anhydride and pyridine. β -Glucochloralose penta-acetate, m. p. 151°, $[\alpha]_D^{25}$ +46.12° in chloroform, is formed by using acetyl and zinc chlorides; fission of the oxide ring is presumed to occur. The β -glucochloralose tetra-acetate of Hanriot (*loc. cit.*) could not be prepared. H. BURTON.

Nomenclature of ring-isomeric forms of glucose as α - or β -sugars. K. JOSEPHSON (Svensk Kem. Tidskr., 1930, 42, 12—16).—A reply to Ohle, Euler, and Lichtenstein (this vol., 69) in defence of the author's previous conclusions (A., 1929, 1278). The designation of glucofuranoses with the 1- and 2-hydroxyl groups in the *cis*- and *trans*-positions as α - and β -compounds, respectively, is analogous to that of the glucopyranoses (cf. Anderson, Charlton, and Haworth, A., 1929, 1044). The use of ring formulæ allows configuration to be shown unambiguously (cf. Drew and Haworth, A., 1926, 1125).

R. K. CALLOW.

Action of perbenzoic acid on glucal and its derivatives. C. TANAKA (Bull. Chem. Soc. Japan, 1930, 5, 214—222).—Glucal was rapidly oxidised by perbenzoic acid in chloroform solution to mannose; triacetylglucal under similar conditions required 4 days for complete oxidation and yielded 1-benzoyl-3:4:6-triacetylglucose, m. p. 141—142°, $[\alpha]_D^{25}$ +18.35° in benzene, further acetylation or benzylation, respectively, of which produced 1-benzoyl-2:3:4:6-tetra-acetylglucose, m. p. 145—146°, $[\alpha]_D^{25}$ -26.43° in chloroform, or 1:2-dibenzoyl-3:4:6-triacetyl-

glucose, m. p. 149°, $[\alpha]_D^{20}$ -15.7° in chloroform (also formed by direct benzylation of triacetylglucose).

The filtrate from the slow oxidation of water gave some 1-deoxy-3:4:6-triacetylglucose, m. p. 122°, $[\alpha]_D^{20}$ $+8.7^\circ$ in chloroform, accompanied by an isomeride, m. p. 168°, of 1-benzoyl-3:4:6-triacetylglucose. A cold chloroform solution of perbenzoic acid had practically no action on diacetyl- ψ -glucal.

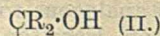
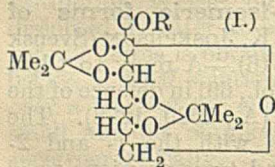
R. J. W. LE FÈVRE.

Preparation of monomethyldiethylmercaptoglucose. P. E. PAPADAKIS (J. Amer. Chem. Soc., 1930, 52, 3465).—Monomethyldiethylmercaptoglucose, m. p. 155°, is prepared from dry sodiodiethylmercaptoglucose and methyl iodide (cf. Fischer, A., 1894, i, 269).
H. BURTON.

Vicioside (vicin). H. HÉRISSEY and J. CHEYMOLE (Compt. rend., 1930, 191, 387—389).—Vicioside, obtained from the winter vetch by a method analogous to that described by Ritthausen (A., 1876, i, 936), suffers no loss in weight at 100°, and has $[\alpha]_D^{20}$ -11.93° to -12.64° , decreased by acidification with cold 4—5% sulphuric acid. Hydrolysis with 2% sulphuric acid gives a solution containing 57.7—58.5% of dextrose; hydrolysis with emulsin affords a similar solution containing 55% of dextrose, and it is concluded that the decomposition is the same in both cases. No trace of galactose was discovered (cf. Ritthausen, A., 1896, i, 696). The decomposition follows the general rule given by Bourquelot and Hérisséy (A., 1908, i, 356).
C. W. SHOPPEE.

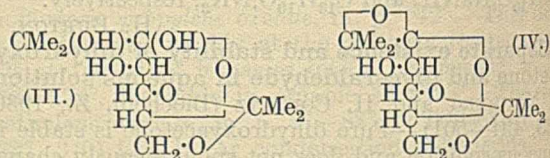
New synthesis in the sugar group. I. Preparation of 1:1-dialkylfructose derivatives. H. OHLE and O. HECHT (Annalen, 1930, 481, 233—254).

—By the action of the appropriate Grignard reagent on α -ketodisopropylidene gluconic acid (Ohle and Wolter, this vol., 744) or its methyl ester are obtained diisopropylidene-1:1-dialkylfructose derivatives (I) and diisopropylidene-1-alkylglucosone (II), the proportion of these two products formed depending on (1) the use of the acid or its ester, (2) the nature and



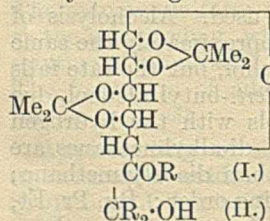
excess of the Grignard reagent used, and (3) the reaction temperature. Thus the free gluconic acid reacts with 4 mols. of magnesium methyl iodide to yield mainly β -diisopropylidene-1-methyl-d-glucosone (I; R=Me), b. p. 97.5—98.5°/0.05 mm., $d_{17.5}^{25}$ 1.163, $n_D^{17.5}$ 1.4603, $[\alpha]_D^{17}$ -40.6° in chloroform, together with a small quantity of β -diisopropylidene-1:1-dimethylfructose (II; R=Me), m. p. 88°, b. p. 101°/0.05 mm., $[\alpha]_D^{18}$ -22.9° in chloroform. The latter is also obtained by further action of magnesium methyl iodide on the former and is the sole product when methyl α -ketodisopropylidene gluconate is treated with 4 mols. of the Grignard reagent in ether. On the other hand, excess of magnesium ethyl bromide converts either the acid or its ester solely into β -diisopropylidene-1:1-diethylfructose (II; R=Et), m. p. 83—84°, b. p. 102—105°/0.1 mm., 305—310°/760 mm., $[\alpha]_D^{20}$ -19.0° in chloroform. Similarly are obtained β -diisopropylidene-1:1-di-n-propyl-, m. p. 83°, $[\alpha]_D^{20}$ -166° in chloroform, -di-n-butyl-, m. p. 64—

65°, $[\alpha]_D^{18}$ -14.1° in chloroform, -diisopropyl-, m. p. 81—82°, $[\alpha]_D^{18}$ -19.2° in chloroform, and -diisobutyl-, b. p. 125—126.5°/0.016 mm., $[\alpha]_D^{20}$ -15.3° in chloroform. Hydrolysis of these diisopropylidene-1:1-dialkylfructose derivatives with 2N-sulphuric acid occurs in two stages, the 4:5-isopropylidene group being much more readily removed to yield the intermediate β -monoisopropylidene-1:1-dialkylfructose, all of which are dextrorotatory and hence the hydrolysis—optical rotation curves all show a rapid rise to a maximum, followed by a fall as the equilibrium value of the dialkylfructose is approached. From the hydrolysis products are isolated: β -isopropylidene-1:1-dimethylfructose, m. p. 164°, $[\alpha]_D^{20}$ $+2.7^\circ$ in water, $+19.5^\circ$ in alcohol (reconverted by acetone and anhydrous copper sulphate into the parent diisopropylidene derivative), and 1:1-dimethylfructofuranose, m. p. 163° (decomp.), which has $[\alpha]_D^{18}$ -14.3° in water but exhibits mutarotation $[\alpha]_D^{18}$ $+11.0^\circ$ to -5.3° in 80% alcohol [*phenylhydrazone*, m. p. 150° (decomp.)]. The furanose structure of this sugar is proved by the following reactions. It is converted by the action of acetone and anhydrous copper sulphate at the ordinary temperature into a mixture of 4:6-isopropylidene-1:1-dimethylfructofuranose (III), b. p. 155—162°/0.1 mm., $[\alpha]_D^{18}$ $+13.3^\circ$ in chloroform, and its 1:2-anhydride (IV), b. p. 137—139°/0.15 mm., m. p. 139—140°, $[\alpha]_D^{18}$ -8.9° in chloroform, both of which possess strong reducing properties. The latter is the isopropylidene



derivative of the fructofuranose anhydride obtained by Ohle and Koller (A., 1924, i, 1168; cf. Schlubach and Flörsheim, A., 1929, 914). Similar hydrolysis of the diethyl derivative affords β -isopropylidene-1:1-diethylfructofuranose, m. p. 128°, $[\alpha]_D^{18}$ $+28.1^\circ$ in alcohol (*monobenzoyl* derivative, m. p. 128°), but the 1:1-diethylfructose could be obtained only as an impure syrup which on hydrolysis with N-potassium hydroxide affords diethyl ketone in 21% yield. β -isoPropylidene-1:1-di-n-propylfructose, m. p. 105—106°, $[\alpha]_D^{17.5}$ $+23.4^\circ$ in alcohol, is obtained similarly. J. W. BAKER.

New syntheses in the sugar group. II. 6:6-Dimethylgalactose. H. OHLE and C. DAMBERG (Annalen, 1930, 481, 255—262).—Extension of the Grignard syntheses (cf. preceding abstract) to diisopropylidene galacturonic acid, m. p. 148°, $[\alpha]_D^{18}$ -83.24° (Ohle and Berend, A., 1926, i, 150, give m. p. 157°), affords mainly diisopropylidene derivatives of 6-alkyl-6-ketogalactose (I) and smaller yields of the diisopropylidene-6:6-dialkylgalactose (II). In these cases, however, the methyl ester of the galacturonic acid cannot be prepared owing to the ease of fission of the isopropylidene groups, and the Grignard reaction must be carried out in benzene instead of in ether. Thus from the appropriate Grignard



reagent are obtained: *diisopropylidene-6-methyl-*, b. p. $120^{\circ}/1$ mm., $[\alpha]_D^{20}$ -128.5° , and *-6-ethyl-*, $[\alpha]_D^{20}$ -120.7° , *-6-keto-d-galactose*, which on further treatment with the Grignard reagent are converted into *diisopropylidene-6:6-dimethyl-*, m. p. $81-82^{\circ}$, $[\alpha]_D^{20}$ -62.3° , and *-6:6-diethyl-*, m. p. $87-88^{\circ}$, $[\alpha]_D^{20}$ -59.3° , *-d-galactose* (all rotations in chloroform). Hydrolysis of derivatives of type I affords the corresponding 6-alkyl-6-ketogalactose, which, however, is too unstable to be isolated. Hydrolysis of derivatives of type II with 2*N*-alcoholic sulphuric acid affords 6:6-dimethyl-d-galactose as a syrup [osazone, m. p. $214-215^{\circ}$ (decomp.)]. J. W. BAKER.

Oxidation of lactal. A. J. WATTERS and C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 3472-3473).—The 4-galactosidomannose of Bergmann and others (A., 1924, i, 265), obtained by the oxidation of lactal with perbenzoic acid, is a mixture of at least two sugars. H. BURTON.

Cellulose and silicates. L. MÉDARD (Rev. gén. Colloid, 1930, 8, 161-169).—The problem of the constitution of cellulose is discussed and several analogies with the corresponding problem of the silicates, particularly the zeolites, are pointed out. Classical structural formulæ have never been applicable to such compounds and in order to understand their properties the crystallographic structure is equally important. E. S. HEDGES.

Reactions relating to carbohydrates and polysaccharides. XXIX. Constitution of alkali cellulose. XXXI. Behaviour of cellulose towards solutions of aluminium salts. E. G. V. PERCIVAL, A. C. CUTHBERTSON, and H. HIBBERT (J. Amer. Chem. Soc., 1930, 52, 3257-3269, 3448-3456).—XXIX. The absorption of sodium hydroxide by cellulose has been studied over the range of concentrations 0.32-46.4% (by weight) at 25° ; the amount of alkali absorbed is determined by washing the fibre with alcohol and then employing an extrapolation method. Evidence is obtained of the formation of a compound resulting from the interaction of 1 mol. of sodium hydroxide with each anhydroglucose unit of the cellulose. Calculation of the amount of water adsorbed by the cellulose during the alkali treatment indicates that there is a maximum with 14% sodium hydroxide; this agrees with the known point of maximum swelling. Quantitative analysis of an alkali-treated cellulose (washed free from adherent alkali) indicates that it is a mixture of the forms $(C_6H_9O_5Na)_x$ and $(C_6H_{10}O_5NaOH)_x$. The suggestion is made that the equilibrium $(C_6H_{10}O_5NaOH)_x \rightleftharpoons (C_6H_9O_5Na)_x + xH_2O$ may exist. A possible explanation of the changes occurring during the treatment of cellulose with sodium hydroxide is given.

XXXI. Small but definite amounts of aluminium hydroxide are adsorbed by "ash-free" cellulose when this is shaken with solutions of aluminium sulphate, chloride, or acetate at 25° . The amount adsorbed using the sulphate increases with rise in p_H and dilution of the solution, and adsorption is greatest with the acetate. The amount of aluminium hydroxide adsorbed depends on two factors: (a) a natural and (b) an exchange adsorption. The former factor depends on the specific nature of the fibre, hydrogen-ion

concentration, dilution, and extent of hydrolysis of the solution, and the anion; the latter appears to depend on the replaceable elements (calcium and iron) in the ash. The mechanism of the hydrolysis of aluminium acetate is shown to be the same as for the chloride and sulphate. H. BURTON.

Lignin and related compounds. I. Isolation of spruce-wood lignin. H. HIBBERT and H. J. ROWLEY (Canad. J. Res., 1930, 2, 357-363).—Spruce-wood meal is dried under reduced pressure, extracted with benzene and ethyl alcohol, dried, extracted with water, and again dried. The meal is mixed with ten times its weight of ethylene glycol, heated to 110° , 2% of iodine is added, and the mixture is maintained at 110° for 6 hrs., with vigorous agitation. The filtered solids are washed with hot glycol. The filtrate and washings are added to 10 vols. of water, a flocculent solid separating which is washed and dried over phosphoric oxide. The crude lignin may be purified by dissolving in 1.0% aqueous sodium hydroxide, followed by treatment with carbon dioxide until p_H 8.8-8.9 is reached (this treatment is repeated). The main fraction of purified lignin gives on analysis C 64.65, H 6.14, O 29.21, OMe 18.79%. Methylated lignins are obtained from the purified lignin having methoxyl contents of 26-27%, repeated methylation increasing the methoxyl content to a maximum followed by a decrease. Methylated lignin treated with fuming nitric acid and acetic anhydride yields a nitrated product (C 43.15, H 3.45, N 10.65, OMe 14.1%). Purified lignin dissolved in ethylene glycol is chlorinated at 0° , yielding a product having C 45.11, H 4.14, Cl 20.77, OMe 12.22%. T. T. POTTS.

Lignin and related compounds. II. Glycol lignin and glycol ether lignin. H. HIBBERT and L. MARION (Canad. J. Res., 1930, 2, 364-375; cf. preceding abstract).—Spruce-wood meal, freed from resins as previously described, is treated at $100-103^{\circ}$ with ten times its weight of ethylene glycol containing 0.05% of hydrogen chloride. Repeated extraction shows that the pentosan:lignin ratio remains constant in the wood and in the dissolved portion. The crude glycol lignin obtained by precipitation of the filtrate with water is purified by dissolution in 1.0% sodium hydroxide, acidified with sulphuric acid, and dissolved in 95% alcohol. The alcoholic solution is boiled under reflux with fresh zinc-copper couple, filtered, and poured into water. The washed lignin is dried over phosphoric oxide. Hydrolysis with 5% sulphuric acid reduces the methoxyl content to 16.42%, and formaldehyde is recognised as a product of the hydrolysis. Glycol could not be found in the hydrolysis liquors. Wood meal treated with ethylene glycol monomethyl ether, in the same way as above, yielded a product containing 21.4% OMe. It is concluded that the higher methoxyl content of the latter product is an indication that combination takes place between the lignin and the solvent. T. T. POTTS.

Lignin and related compounds. III. Glycerol chlorohydrin lignin. H. HIBBERT and J. B. PHILLIPS (Canad. J. Res., 1930, 3, 65-69).—From spruce-wood meal, previously extracted with water and with a mixture of alcohol and benzene, glycerol lignin and lactic acid lignin may be obtained by treat-

ment with glycerol and lactic acid, respectively, under conditions similar to those employed in the production of the glycol lignins (preceding abstract). In all these cases the lignin is apparently in combination with the solvent. A similar combination has been demonstrated when the lignin is extracted with glycerol α -monochlorohydrin. Treatment of the wood meal with this substance, in the presence of 0.2—0.5% of hydrochloric acid as catalyst, for 6 hrs. at 80° yields a viscous mass from which "glycerol chlorohydrin lignin" may be isolated (5.5% Cl, 15.6% OMe). Comparison with glycol lignin indicates a mol. wt. of 309, if 1 mol. of solvent is combined in each case; cryoscopy in acetophenone gives a mol. wt. of 350. Hydrolysis with boiling 8% hydrochloric acid removes the glycerol chlorohydrin; the residue, which is substantially pure lignin as determined by the method of Klason (A., 1908, i, 717), is no longer soluble in dilute alkali, and it is suggested that, in addition to the removal of the chlorohydrin residue, the treatment has occasioned some fundamental change in the lignin molecule. Methylation of glycerol chlorohydrin lignin with methyl sulphate and alkali increases the methoxyl content to 23.2%, corresponding with an increase of methyl ether groups in a complex of mol. wt. 350 from 2 to 3. T. H. MORTON.

Action of nitrosyl bromide on amino-acids. Z. Csürös (Magyar Chem. Fol., 1929, 35, 113—119; Chem. Zentr., 1930, i, 1461).—Substitution of the amino-group by bromine takes place only with α - and β -substituted acids. The following substances are described: γ -benzamidobutyric acid, m. p. 79—80°; ϵ -benzamido-n-hexoic acid, m. p. 80°; ϵ -benzamidoamylmalonic acid, m. p. 115°; ζ -aminoheptoic acid, m. p. 186° (benzoyl derivative, m. p. 81—82°).

A. A. ELDRIDGE.

α -Methylbutenoamides. P. BRUYLANTS, L. ERNOULD, and M. DEKOKER (Bull. Acad. roy. Belg., 1930, [v], 16, 721—740).—Dehydration of methyl ethyl ketone cyanohydrin with phosphoric oxide or thionyl chloride affords a mixture of unsaturated nitriles which after fractionation, saturation of the various fractions with hydrogen chloride, and re-fractionation gives β -chloro- α -methylbutyronitrile, b. p. 64—65°/12 mm., and β -chloro- α -ethylpropionitrile, b. p. 73—74°/12 mm. The former of these is converted by boiling with quinoline into a mixture of the nitriles, b. p. 121—122°/772 mm., d_4^{20} 0.81968, n_D^{20} 1.42303, and b. p. 137—138°/772 mm., respectively, of α -methylcrotonic acid, whilst the latter furnishes α -ethylacrylonitrile, b. p. 115—116°/752 mm. The nitrile, b. p. 137—138°, is hydrolysed by cold 66% sulphuric acid to α -methylcrotonamide, m. p. 75—76° (I), whilst the form of b. p. 121—122° gives α -methylcrotonamide, m. p. 127—128° (II). α -Ethylacrylamide has m. p. 86—87° (lit. 82°). Alkaline hydrolysis of II yields only tiglic acid, also formed by the action of nitrous acid in acetic acid solution. Tiglic acid is also obtained when either α -methylcrotonitrile is hydrolysed with sulphuric acid. Prolonged treatment of methyl tiglate, b. p. 137—138°/758 mm., with concentrated ammonia at the ordinary temperature affords I, which undergoes 90% conversion into II when an acetone(?) solution is ex-

posed to ultra-violet light. These results show that the α -methylcrotonitrile, b. p. 137—138°, and I are *trans*-compounds, whilst the nitrile, b. p. 121—122°, and II are *cis*-derivatives. Langseth's rule (A., 1926, 116) applies equally well to these compounds as to the corresponding crotonic acid derivatives.

α -Ethylacrylamide is converted by exposure to ultra-violet light into a mixture of unchanged material (42%), I (7%), and II (51%). Hydrolysis of methyl ethyl ketone cyanohydrin with sulphuric acid affords a mixture of α -hydroxy- α -methylbutyric acid and its amide. H. BURTON.

Ultra-violet absorption spectra of α -methylbutenoamides. A. CASTILLE (Bull. Acad. roy. Belg., 1930, [v], 16, 811—816).—Ultra-violet absorption curves for aqueous solutions of the amides of *cis*- and *trans*- α -methylcrotonic and α -ethylacrylic acids (cf. preceding abstract) and solutions of the nitriles of the same acids in hexane are given. The absorption of the *cis*-amide and -nitrile is less than that of the *trans*-isomerides, whilst the absorption of *cis*- α -methylcrotonic acid is greater than that of the *trans*-isomeride. H. BURTON.

Ethylenethiocarbamide. C. RUIZ and L. LIBENSON (Anal. Asoc. Quím. Argentina, 1930, 18, 37—42).—As usually prepared, ethylenethiocarbamide, m. p. 194°, contains labile sulphur, accounted for by the presence of 12—18% of *N*- β -aminoethyl dithiocarbamate. Pure ethylenethiocarbamide, m. p. 199° (corr.), is prepared by heating ethylenediamine with carbon disulphide in alcohol at 100—105° for 4—5 hrs. It has no reducing properties and does not yield a precipitate with copper salts in the cold, as stated by Morgan and Burstall (A., 1928, 278).

R. K. CALLOW.

Action of halogenohydrins and ethylene oxide on thiocarbamides. J. F. OLIN and F. B. DAINES (J. Amer. Chem. Soc., 1930, 52, 3322—3327).—Thiocarbamides react with halogenohydrins and their derivatives, forming isothiocarbamides, $\text{OR} \cdot [\text{CH}_2]_n \cdot \text{SC}(\text{NR}') \cdot \text{NHR}''$; these are readily hydrolysed and when treated with amines give guanidines. Thus, ethylene chlorohydrin and thiocarbamide at 90—105° give β -hydroxyethylisothiocarbamide hydrochloride, m. p. 111°; with trimethylene chlorohydrin at 120—125°, γ -hydroxypropylisothiocarbamide hydrochloride, m. p. 130°, results. This is converted by ammonia and methylamine into guanidine and methylguanidine, respectively. Thiocarbamide and ethyl β -bromoethyl ether react at 100° in presence of a small amount of alcohol, furnishing β -ethoxyethylisothiocarbamide hydrobromide, m. p. 28—29°, hydrolysed by potassium hydroxide to β -ethoxyethyl mercaptan (phenylcarbamide derivative, m. p. 45°, also formed by heating the phenylthiocarbamide derivative, m. p. 42—43°, of β -ethoxyethyl alcohol with β -ethoxyethyl iodide at 130°), and converted by treatment with phenylcarbamide and potassium hydroxide into the compound $\text{NPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{N} \cdot \text{CO} \cdot \text{NHPh}) \cdot \text{S} \cdot \text{C}_2\text{H}_4 \cdot \text{OEt}$, m. p. 132°. This is hydrolysed by potassium hydrogen sulphide (cf. A., 1929, 1055) to the thiocarbamide $\text{CS}(\text{NH} \cdot \text{CO} \cdot \text{NHPh})_2$, m. p. 202°. Thiocarbamide and

β -bromoethyl acetate at 125° give β -acetoxyethylisothiocarbamide hydrobromide, m. p. 99° (the bisphenylcarbimide, m. p. 134°, and di-*p*-nitrobenzoyl, m. p. 189°, derivatives of the free base are described), converted by aniline into phenylguanidine. Dibenzoylphenylguanidine is obtained similarly from the dibenzoyl derivative, m. p. 149°, of methylisothiocarbamide. The β -hydroxyethyl (hydriodide, an oil) and β -acetoxyethyl (hydrobromide, m. p. 158°; *p*-nitrobenzoyl derivative, m. p. 132°; phenylcarbimide derivative, m. p. 81—82°) derivatives, m. p. 69—70°, of phenylthiocarbamide are prepared similarly.

When thiocarbamide is heated with β -chloroethyl benzoate at 130—150°, a mixture of diphenylcarbamide, phenylthiocarbimide, benzanilide, benzoic acid, and 2:3-diphenylthiazolidine, m. p. 136°, is produced. The last-named compound is formed from the phenylthiocarbimide derivative, m. p. 145°, of β -anilinoethyl benzoate.

Ethylene oxide reacts with thiocarbamide in acetone at the ordinary temperature, forming carbamide and thioethylene glycol; the latter arises by hydrolysis of the unstable β -hydroxyethylisothiocarbamide. Diphenylthiocarbamide and ethylene oxide in acetone at 50—55° yield diphenyl- β -hydroxyethylisothiocarbamide, m. p. 145° (phenylcarbimide derivative, m. p. 101°), hydrolysed by alkalis to diphenylcarbamide.

Hydrolysis of alkylisothiocarbamides with potassium hydrogen sulphide furnishes the corresponding thiocarbamides. The method is illustrated by the formation of 1:5-diphenyldithiobiuret, m. p. 149°, from the methyl derivative. Diacetylmethylisothiocarbamide, m. p. 107—108°, is, however, completely hydrolysed. The dicarbethoxy-derivative, m. p. 50—51°, of methylisothiocarbamide, prepared from the isothiocarbamide and ethyl chloroformate, is hydrolysed by potassium hydrogen sulphide to *s*-dicarbethoxythiocarbamide, m. p. 111—112°, whilst the carbethoxy-derivative, m. p. 128°, of phenylmethylisothiocarbamide undergoes fission to phenylurethane.

H. BURTON.

Constitution of cyanogen halides. I. Reactions of cyanogen chloride and iodide. II. Refractometry of cyanogen chloride and iodide. E. V. ZAPPI (Anal. Asoc. Quím. Argentina, 1930, 18, 5—11, 12—30).—See this vol., 1027, 1171.

Action of phosphine on formaldehyde. II. A. HOFFMAN (J. Amer. Chem. Soc., 1930, 52, 2995—2998).—The action of alkaline hydroxides or carbonates on tetrahydroxytetramethylphosphonium chloride (I) (cf. A., 1922, i, 8) in aqueous solution takes place in two stages, hydrogen (1 mol.) and formaldehyde (1 mol.) being liberated at each stage. Sodium hydroxide or carbonate below 80° and barium carbonate at 100° give trihydroxytrimethylphosphine oxide (tribenzoate, m. p. 111°; cf. loc. cit.), whilst the first two give at 100° dihydroxydimethylphosphinic acid, isolated as the crystalline barium salt. The chloride, I, is converted by phosphorus pentachloride in boiling carbon tetrachloride into tetrachlorotetramethylphosphonium chloride, m. p. 192—193°, which is hydrolysed by alkalis and by sodium hydrogen carbonate to trichlorotrimethylphosphine, b. p. 100°/7 mm., d_{20}^{20} 1.414. This has only slight basic properties. It is stable in

air, does not combine with hydrogen chloride, and is oxidised by nitric acid (*d* 1.2) to trichlorotrimethylphosphine oxide (+0.5H₂O), m. p. 88—89°, which with sodium benzoate at 200° gives tribenzoyloxytrimethylphosphine oxide. H. E. F. NOTTON.

Preparation of mercury dialkyls from organomagnesium halides. H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 3314—3317; cf. A., 1929, 687).—Improvements in the preparation of mercury dimethyl (71% of the theoretical yield), diethyl (80—84%), and di-*n*-butyl (80%), involving (a) the use of approximately equivalent quantities of mercuric chloride and the organomagnesium halide and (b) reduction in the time of heating, are described. Mercury diethyl, di-*n*-butyl, and diphenyl do not afford appreciable quantities of organomagnesium halides when treated with magnesium bromide or iodide. Mercury dimethyl is more stable than the diethyl or di-*n*-butyl. H. BURTON.

Determination of metal in organic compounds incapable of electrolysis. K. DOSIOS and J. PIERRI (Z. anal. Chem., 1930, 81, 214—216).—The addition of excess of bromine water to lead tetraethyl dissolved in an inert solvent (carbon tetrachloride) causes quantitative formation of lead bromide. A similar method is applied for the determination of anti-knock substances in petrol, of tin in tin tetraphenyl, and of nickel and iron in their carbonyls.

J. O. CUTTER.

Organic salts of lead triethyl hydroxide. H. GILMAN and J. D. ROBINSON (Rec. trav. chim., 1930, 49, 766—768).—The following lead triethyl salts are prepared from lead tetraethyl and the appropriate acid in presence of silica gel (cf. Browne and Reid, A., 1927, 452): salicylate, m. p. 83—91°; furoate, m. p. 153—154°; phenylacetate, m. p. 101—106°; β -furylacrylate, m. p. 119—121°; *o*-thiolbenzoate (?), m. p. 97—99°; *p*-toluenesulphonate, m. p. 167—168°, and monophosphate, not melted at 250°. Lead triethyl acetate and sodium *p*-aminobenzoate in aqueous solution give lead triethyl *p*-aminobenzoate, m. p. 84—86°. These salts are only slightly soluble in water, and they are very irritant in the dry state.

H. BURTON.

Organic gold compounds. I. Aurous chloride carbonyl; method of linking carbon to carbon. M. S. KHARASCH and H. S. ISBELL (J. Amer. Chem. Soc., 1930, 52, 2919—2927).—Aurous chloride carbonyl (20% of the theoretical) is obtained by passing a rapid stream of carbon monoxide over dry auric chloride at 110°. Contrary to the statement of Manchot and Gall (A., 1925, ii, 1182), the simultaneous passage of carbon monoxide and chlorine produces little carbonyl compound, but much carbonyl chloride. The carbonyl compound is formed quantitatively from aurous chloride and carbon monoxide in benzene at 15°, or from auric chloride in tetrachloroethylene at 130—140°. It has a mol. wt. of 223 (calc. 260) in freezing benzene and dissociates in a vacuum or in hot solvents, giving pure aurous chloride. It reacts with nitrogenous bases, but not with amides or imides, the carbonyl group being displaced by 1 mol. of base. Pyridine aurous chloride,

m. p. 92° (decomp.), and *hexamethylenetetramine aurous chloride*, decomp. from 150°, are obtained thus. With bromine it gives auric chlorodibromide and with iodine aurous iodide. With alcohols it gives metallic gold, with mercury dialkyls, gold, alkylmercuric chlorides, and bis-hydrocarbons, and with Grignard reagents, gold and a quantitative yield of the bis-hydrocarbon. The view that a gold mono-aryl is formed intermediately in the last reaction is supported by the observation that the time elapsing before gold is precipitated increases with an increase in the electronegative character of the aryl radical. Thus, magnesium benzyl and phenyl halides cause an immediate precipitation, whilst magnesium α -naphthyl bromide gives a solution from which gold is precipitated only on heating. H. E. F. NOTTON.

Oxidation of unsaturated hydrocarbons by quadrivalent lead salts. R. CRIGEE (Annalen, 1930, 481, 263—302).—The oxidation of a number of unsaturated substances, mainly hydrocarbons, by lead tetra-acetate, tetrapropionate, tetrabutyrates, and *tetrabenzoate*, m. p. 168° (decomp.) (prepared by the action of the tetra-acetate on molten benzoic acid), in the corresponding acid as solvent, occurs mainly in two ways: (1) addition of two acetoxy-groups to the double linking, or (2) the double linking is unattacked, whilst the adjacent hydrogen atom is replaced by an acetoxy-group. Thus *cyclohexene* is converted by lead tetra-acetate at 80° into a mixture of Δ^2 -*cyclohexenyl acetate*, *cyclohexane-1:2-diol diacetate* [identified after hydrolysis as the *cis*- and *trans*-diols, which are further oxidised with lead tetra-acetate to adipialdehyde (*diphenylhydrazone*, m. p. 140°, corr.)], and either Δ^2 -*cyclohexene-1:1*- or *-1:4-diol diacetate*. Indene yields *1-hydroxyindene acetate*, b. p. 118—122°/12 mm., d_4^{20} 0.981 [hydrolysed with aqueous sodium hydroxide to α -hydrindone, and with methyl-alcoholic sodium hydroxide to anhydro-bis- α -hydrindone; converted by further treatment with lead tetra-acetate into (?) *indone diacetate*, b. p. 166—172°/12 mm., d_4^{20} 1.165], *hydrindene-2:3-diol diacetate* (isolated as the glycol after reduction of the crude product with hydrogen and platinum-black in alcohol and subsequent hydrolysis), and an unsaturated ester which is probably the above indone diacetate. This in sodium or potassium hydroxide forms a pale yellow solution which is converted into a deep blue solution by addition of calcium, strontium, or barium salts. This blue solution is decolorised by shaking with air, the blue colour returning on keeping. *cyclopentadiene* with lead tetra-acetate at 30° yields a small fraction, b. p. 106—110°/12 mm., d_4^{20} 1.137, which consists mainly of the *diacetate* of Δ^3 -*cyclopentene-1:2-diol*, b. p. 110—114°/12 mm., d_4^{20} 1.152°, which is obtained on hydrolysis and is reduced to *cis-cyclopentane-1:2-diol*, and a main fraction, b. p. 119—124°/0.1 mm., d_4^{20} 1.215, which is the *monoacetate monoacetylglycollate* of Δ^3 -*cyclopentene-1:2-diol*, $\text{CH} \begin{matrix} \text{CH} \cdot \text{CH} \cdot \text{OAc} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OAc} \end{matrix}$ since on hydrolysis it affords potassium glycollate and the diol (reduced to *cis-cyclopentane-1:2-diol*). The mechanism of the formation of derivatives of this type (other examples of which are described below) is discussed fully. It is

shown that the intermediate compound cannot be of the type of 1-acetoxycyclopentadiene, since lead tetrabenzoate in benzene at 30—35° converts *cyclopentadiene* into *trans- Δ^3 -cyclopentene-1:2-diol dibenzoate*, m. p. 65.5—66° (corr.) (reduced to the *cyclopentene derivative*), further action in this case being precluded by the absence of an α -hydrogen atom, for it is this atom which is involved, as is shown by the formation of similar derivatives when lead tetrapropionate or tetrabutyrates is used (cf. below). It is concluded that although the 1:2-diol diacetate cannot subsequently be converted into the acetylglycollate by further action of lead tetra-acetate, yet it is an activated enol form, $\text{CH} \begin{matrix} \text{CH} \cdot \text{CH} \cdot \text{OAc} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{matrix}$ of this derivative which is the intermediate compound, the essential condition being the presence of such a double linking with high "addition energy." Such circumstances should arise when positive groups are attached, and, in agreement with this view, oxidation of either anethole or *isoeugenol methyl ether* with lead tetra-acetate yields, in addition to the normal additive product, compounds of the type under consideration, since on hydrolysis they yield potassium glycollate and the corresponding glycol. In the case of anethole this is further oxidised by lead tetra-acetate to anisaldehyde, whilst α - and β -methyl-*isoeugenol glycols*, m. p. 122° and 88° (corr.), are actually isolated. Oxidation of various partly reduced aromatic hydrocarbons with lead tetra-acetate has been studied, the constitution of the products being proved by hydrolysis and reduction to known compounds in each case. Thus 9:10-dihydroanthracene in benzene at 80° gives a 30% yield of anthracene; 1:4-dihydronaphthalene affords naphthalene; 1:2-dihydronaphthalene gives the diacetate, b. p. 174—178°/12 mm., hydrolysed to *trans-1:2-dihydroxytetrahydronaphthalene*, whilst tetrahydronaphthalene affords mainly 1-acetoxy-1:2:3:4-tetrahydronaphthalene. $\Delta^{1:3}$ -*cyclohexadiene* is converted into Δ^3 -*cyclohexene-1:2-diol diacetate*, and its *monoacetate monoacetylglycollate*, b. p. 132—138°/0.1 mm. Oxidation of the following aliphatic dienes was studied. Butadiene gives a mixture of oxidation and polymerisation products; $\beta\gamma$ -dimethylbutadiene gives the *diacetate*, b. p. 92—102°/12 mm., of $\beta\gamma$ -dimethyl- Δ^2 -butene- $\alpha\beta$ -diol (reduced to the saturated diol, and oxidised to α -hydroxy- $\alpha\beta$ -dimethylbutyric acid); and $\Delta^{\beta\delta}$ -hexadiene gives the *diacetate*, b. p. 67—71°/cathode vacuum, of a hexenediol the constitution of which is not determined. Oxidation of *cyclopentadiene* with lead tetrapropionate gives a 75% yield of the *monopropionate mono- α -propionypropionate* (cf. I), b. p. 125—135°/cathode vacuum, d_4^{20} 1.119 (giving ethyl propionate and ethyl *dl*-lactate on treatment with alcoholic sodium ethoxide), of Δ^3 -*cyclopentene-1:2-diol*, together with its *2-mono-propionate*, b. p. 110—115°/12 mm., d_4^{20} 1.101, and its *dipropionate*, b. p. 125—130°/12 mm., d_4^{20} 1.083. Similar oxidation of *cyclopentadiene* with lead tetrabutyrates affords the *mono-n-butyrate mono- α -n-butyryloxy-n-butyrate*, b. p. 149—154°/cathode vacuum, d_4^{20} 1.068 (converted into ethyl butyrate and ethyl α -hydroxybutyrate), of the same diol.

J. W. BAKER.

Parachors of two isomeric chlorodinitrobenzenes. D. V. SICKMAN and A. W. C. MENZIES (J. Amer. Chem. Soc., 1930, 52, 3327—3329).—Calculation of the parachor of 1-chloro-3:4-dinitrobenzene from the available data (Müller, A., 1914, ii, 188) gives a value differing greatly from that of 1-chloro-2:4-dinitrobenzene (348.2), using Jaeger's data (A., 1918, ii, 33). Re-determinations of the density and surface tension of the former compound lead to a value of 347.4 for the parachor. Both the above values are smaller than the calculated (358.3).

H. BURTON.

Reaction between *as*-diphenylethylene and a mixture of magnesium and magnesium iodide. H. GILMAN and S. A. HARRIS (Rec. trav. chim., 1930, 49, 762—765).—*as*-Diphenylethylene does not react to any appreciable extent with the binary system, Mg+MgI₂.

H. BURTON.

Tetracyclohexyldiphenylethane. S. S. ROSSANDER, L. H. BOCK, and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 2976—2981).—Dicyclohexylphenylcarbinol (Gray and Marvel, A., 1926, 43) and acetyl bromide yield dicyclohexylphenylmethyl bromide, m. p. 104—105°. The corresponding chloride gives, with 40% sodium amalgam in absence of air, red sodium dicyclohexylphenylmethyl and the chemically resistant substance C₃₈H₅₄ (I), m. p. 209—211°. The sodio-derivative with carbon dioxide gives dicyclohexylphenylacetic acid, m. p. 242—244°; with water dicyclohexylphenylmethane, b. p. 145—148°/5 mm., *d*_D²⁰ 0.9774, *n*_D²⁰ 1.5390, also prepared by hydrogenating cyclohexylcyclohexylidenephnylmethane (cf. Godchot, A., 1909, i, 19), and with dicyclohexylphenylmethyl chloride at 0° in absence of air, oily tetracyclohexyldiphenylethane. This is re-converted into the sodio-derivative by 1% sodium amalgam, gives with air dicyclohexylphenylmethyl peroxide, m. p. 186—188° (decomp.), and changes at 100° in xylene without development of colour into the hydrocarbon, I, and other products. In solution it decomposes in a few days at the ordinary temperature.

H. E. F. NOTTON.

Supposed existence of two stereoisomeric 9-phenyl-9-benzylfluorenes. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 3290—3292).—Magnesium phenyldiphenylenemethyl bromide and benzyl chloride afford 9-phenyl-9-benzylfluorene, m. p. 140.3—140.8° (corr.), also obtained from magnesium benzyl chloride and 9-bromo-9-phenylfluorene. The same compound, and not the supposed isomeride, m. p. 125—126°, is produced by using Schlenk and Bergmann's method (A., 1929, 688).

H. BURTON.

Reactivity of halogenated hydrocarbons. IV. Transformations with halogenated condensed ring system hydrocarbons. J. LOEVENICH, W. BECKER, and T. SCHRÖDER (J. pr. Chem., 1930, [ii], 127, 248—259).—The reactivity of the halogen atoms in 2- and 9-bromofluorenes, 1- and 2-chloroanthracenes, and 9-bromoanthracene towards sodium acetate, potassium phenoxide, potassium phthalimide, lead oxide, potassium carbonate, benzamide, and ethyl chloroformate is studied by the methods previously described (A., 1927, 348, 538; this vol., 200).

9-Bromofluorene resembles cyclopentyl bromide whilst 2-bromofluorene is similar to an aryl halide. 9-Bromoanthracene is more reactive than the chloro-derivatives; the difference in reactivity is, however, not so marked as with the bromofluorenes, probably because of the aromatic nature of the 9-carbon atom in the anthracene molecule. 2-Phenoxyfluorene (?), m. p. above 260°; 9-phenoxyfluorene, m. p. 152—156°, and 9-benzamidoanthracene, m. p. 240—242°, are described. Mercury 9:9'-dianthryl, m. p. above 300°, is formed as a by-product during the interaction of 9-bromoanthracene, ethyl chloroformate, and sodium amalgam.

H. BURTON.

Action of Mg+MgBr₂ on phenyldiphenylenemethyl. Formation of magnesium phenyldiphenylenemethyl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 3287—3290).—9-Bromo-9-phenylfluorene (1 mol.) and magnesium (1 atom) react in *n*-butyl ether and benzene in an atmosphere of nitrogen, yielding magnesium phenyldiphenylenemethyl bromide. When 0.5 atom of magnesium is used, a mixture of magnesium bromide and phenyldiphenylenemethyl results; addition of a further 0.5 atom of magnesium to the mixture produces the Grignard reagent, also prepared directly from the free radical, magnesium, and magnesium bromide. The Grignard reagent reacts readily with 9-bromo-9-phenylfluorene forming the free radical, which is probably an intermediate in the production of the Grignard reagent.

Contrary to the statement of Schmidt-Nickels (A., 1929, 695), 9:9-diphenylfluorene is obtained from magnesium phenyl bromide and 9-chloro-9-phenylfluorene.

H. BURTON.

Halogenation of arylamines with the hydrogen halide and hydrogen peroxide mixture. A. LEULIER and G. ARNOUX (Bull. Soc. chim., 1930, [iv], 47, 730—737).—The following have been obtained in the yield indicated by the action of hydrogen peroxide and the hydrogen halide on the acetyl or benzoyl derivative of the toluidine or xylydine: 5-bromoaceto-*o*-toluidide, m. p. 156—157° (yield 91.5%); 5-chloroaceto-*o*-toluidide, m. p. 77.2° (yield 77.2%); 6-bromobenzoyl-*o*-toluidide, m. p. 175—176° (97%); 2:6-dibromoaceto-*m*-toluidide, m. p. 117°, and 4:5-dibromoaceto-*m*-toluidide, m. p. 161—162° (72.8%); 6-bromobenzoyl-*m*-toluidide, m. p. 97—98° (100%); 5:6-dibromobenzoyl-*m*-toluidide, m. p. 105—106° (97.7%); 3-bromoaceto-*p*-toluidide, m. p. 117° (83.5%); 3-bromobenzoyl-*p*-toluidide, m. p. 147—148° (87.5%), and 6-bromoaceto-*m*-4-xylydide, m. p. 168—169° (88%). Chlorination of aceto-*m*- and -*p*-toluidides and of the benzoyl derivatives of *o*- and *m*-toluidine gave indefinite products.

R. BRIGHTMAN.

Naphthalene series. I. Methylation of α -naphthylamine. B. GOKHLÉ and F. A. MASON (J.C.S., 1930, 1757—1758).—Dimethyl- α -naphthylamine (25—50 g.) is conveniently prepared in 70% yield by methylating α -naphthylamine with methyl sulphate and sodium hydroxide solution. When α -naphthylamine sulphate is heated with methyl alcohol in a steel autoclave at 180° a mixture of dimethyl- α -naphthylamine (61%) and α -naphthol

(26%) is obtained. The naphthol arises by hydrolysis of the tertiary base. α -Naphthylamine hydrochloride and methyl alcohol at 180°/33 atm. give an 80% yield of the tertiary base (cf. Hantzsch, A., 1880, 813).

H. BURTON.

Constitution of *p*-aminoazobenzene salts. A. HANTZSCH and A. BURAWOY (Ber., 1930, 63, [B], 1760—1774).—Optical investigation of the salts of *m*-aminoazobenzene and the polyacidic salts of *p*-aminoazobenzene shows that the deeply-coloured salts of the latter bases cannot have the structure $\text{NPh}(\text{HX})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$ ascribed to them by Kehrman, since *m*-aminoazobenzene forms salts of the ammonium type, $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{X}$, in which the added acid molecule is normally united to the amino-group, quinonoid constitution being impossible. Vorländer's hypothesis that the acid molecule has no defined point of union and his arguments against the quinonoid formulation that the polyacidic salts of *p*-aminoazobenzene are appreciably lighter in colour than the monacid salts although a further quinonoid transformation is impossible cannot be maintained. Optical analogy with the di-acid salts of tetramethyl-yellow or dimethyl-yellow and the monacid salts of tetramethyl-yellow methochloride or dimethyl-yellow methochloride shows that an acid molecule is invariably attached to each amino-group. The di-acid salts of *p*-aminoazobenzene are lighter in colour than the monacid salts by reason of the diminished bathochromic action.

The quinonoid structure of the deeply-coloured *p*-aminoazobenzene salts is supported by the optical behaviour of auramine salts. The salt of *p*-dimethylaminobenzophenoneanil, $\text{NHPh}\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{X}$, absorbs more strongly than that of benzophenoneanil, whilst the absorption of the phenylauramine salt, $\text{NHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{X}$, is not materially changed on account of the introduction of a second dimethylamino-group; the auramine and anil salts have therefore the conjugated quinonoid constitution. Since the salts of *p*-aminoazobenzene and of the corresponding anils differ from one another solely by the replacement of the central nitrogen atom by the group CR and are therefore similarly constituted, the conjugated quinonoid structure must be common to both.

The spectra of the salt solutions of *p*-aminoazobenzene exhibited two markedly different bands. The short-wave ultra-violet bands of salts of the simple *p*-aminoazobenzenes are nearly identical with those of azobenzene or dimethyl-yellow methiodide; the short-wave bands of the salts of *p*-methoxydimethyl-yellow are very similar to those of *p*-methoxyazobenzene. The long-wave bands exhibit varying persistence. It follows, therefore, that equilibria between the yellow and red salts exist in the solutions of all *p*-aminoazobenzene salts and that the yellow compounds are ammonium salts. This view is confirmed by the observation that the spectra of salt solutions of azobenzene derivatives without amino-groups, which therefore cannot form ammonium salts, do not possess a second band in the ultra-violet. As

previously assumed, yellow azoid salts of the type $\text{NAr}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\text{X}$ and red quinonoid salts, $\text{NHAr}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\text{X}$, exist in the solid state. When

isomerism exists, the yellow salts can usually be transformed by pressure into the red compounds, whereby the mobile hydrogen atom is driven from the periphery to the centre of the molecule. H. WREN.

Transformation of diazoamino- into aminoazo-compounds. J. C. EARL (Ber., 1930, 63, [B], 1666; cf. this vol., 1033).—The action of very dilute alcoholic hydrochloric acid on diazoaminobenzene affords benzenediazoaminoazobenzene, m. p. 119.5°. Since the prolonged action of the reagent gives aminoazobenzene in good yield, the change may be formulated: $2\text{NHPh}\cdot\text{N}_2\cdot\text{Ph} \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ph} + \text{Ph}\cdot\text{NH}_2 \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{NHPh}\cdot\text{N}_2\cdot\text{Ph}$. The scheme is supported by the observation of Rosenhauer and Unger (A., 1928, 407) that addition of aniline increases the yield of aminoazobenzene. H. WREN.

Diazonium salts. A. HANTZSCH (Ber., 1930, 63, [B], 1786—1789).—The constitution $\text{Ar}\cdot\text{NX}\cdot\text{NHX}$ is not valid for "acid" diazonium salts, since the cryoscopic behaviour of benzenediazonium sulphate in sulphuric acid is similar to that of the sulphates of aniline bases and all other ammonium sulphates which contain only one nitrogen atom in the molecule. In the "acid" diazonium halides the added molecule of halogen hydride is not structurally united, but loosely attached to the cation. The compounds are therefore comparable with the additive products from hydrochloric acid and dimethylaniline hydrochloride and their greater stability is due to the less highly saturated condition of the central nitrogen atom.

Since diazonium salts and alcohols react with formation of hydrocarbons and aldehydes in strongly acidic solution at a rate which is independent of the concentration of the acid, only diazonium salts can be present, and the intermediate formation of *syn*-diazo-ethers is excluded. The change is considered to depend on the intermediate formation of adducts, $\text{Ar}\cdot\text{NCl}\cdot\text{N}\cdots\text{H}\cdot\text{OEt}$, which, in part, decompose with production of aryl ether, nitrogen, and hydrogen chloride, and, in part, become transformed into the non-electrolyte, $\text{Ar}\cdot\text{NCl}\cdot\text{NH}\cdot\text{OEt}$, which breaks down into ethyl hypochlorite (and thence aldehyde and acid), nitrogen, and hydrocarbon. H. WREN.

Formation of diazo-oxy-compounds. Mechanism of azo-dye coupling. H. T. BUCHEBER and C. TAMA (J. pr. Chem., 1930, [ii], 127, 39—76).— β -Naphthol-1-sulphonic acid couples in neutral or faintly alkaline solution with *p*-nitrobenzenediazonium chloride (best in equimolecular proportions in sodium hydrogen carbonate solution) to form sodium 2-*p*-nitrobenzeneazo-oxy-naphthalene-1-sulphonate (I) (decomp. 90—100°), which on acidification, or heating in aqueous solution at 70°, or in alcoholic or acetic acid solution at 50°, passes into 1-*p*-nitrobenzeneazo- β -naphthol. In strongly alkaline solution very little para-red is formed owing to fission of the diazo-oxy-compound into β -naphthol-1-sulphonate and anti-diazotate. Aqueous solutions of the diazo-oxy-compound are stabilised by the addition of solutions

of sodium hydrogen carbonate and calcium chloride, any alkali formed reacting thus: $\text{NaOH} + \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3$; $\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$. The reaction $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH} + \text{ONa}\cdot\text{N}\cdot\text{NR} \rightleftharpoons \text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}\cdot\text{NR} + \text{NaOH}$ is reversible.

A simple apparatus for measuring the rate of formation of I from its constituents is described, and the rates of formation under various conditions have been measured. The stability of the diazo-oxy-compound in the presence of aqueous sodium hydrogen carbonate, acetate, and carbonate solutions and of potassium carbonate and acetate solutions of specified concentrations was determined by adding aliquot parts of the solution after definite times to excess of hydrochloric acid (*d* 1.185), weighing the precipitated para-red, then neutralising the filtrate with sodium carbonate, and further weighing the precipitated dye produced by coupling with a hydrogen carbonate solution of R-salt.

When β -naphthol-1-sulphonic acid is coupled with *p*-nitrobenzenediazonium chloride in strongly acid solution the sparingly soluble yellowish-orange diazonium sulphonate, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\cdot\text{O}\cdot\text{N}(\text{N})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (cf. G.P. 280,371), is formed, which on dissolution in sodium carbonate or hydrogen carbonate solution and acidification yields para-red. This was hitherto assumed to be formed directly, but experimental evidence is now given showing that the diazonium sulphonate is first transformed into the diazo-oxy-compound, which isomerises into para-red.

Treatment of I (1 mol.) with 2 mols. of 30% sodium hydroxide solution yields a violet-red soluble compound, converted on keeping into a soluble yellow substance, $\text{C}_{10}\text{H}_{10}\text{O}_6\text{N}_3\text{Na}_2\text{H}_2\text{O}$, m. p. 295–300°, in 40% yield, which on boiling for 6 hrs. with hydrochloric acid loses sulphur dioxide and yields a substance, $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3\cdot 2\text{H}_2\text{O}$, m. p. 310–315°.

Diazotised benzidine couples with 2 mols. of β -naphthol-1-sulphonic acid to yield *diphenyl-4:4'-tetrazonium β -naphthol-1-sulphonate*; *3:3'-dimethoxydiphenyl-4:4'-tetrazonium β -naphthol-1-sulphonate* is obtained by using *o*-dianisidine and *m*-nitrotoluene-*p*-diazonium β -naphthol-1-sulphonate from *m*-nitro-*p*-toluidine. These give the corresponding diazo-oxy-compounds on treatment with aqueous sodium carbonate, and on further acidification the azo-compounds.

1-Chloro- β -naphthol reacts with *p*-nitrobenzenediazonium chloride in sodium hydrogen carbonate solution to give an orange-brown solution, becoming violet-red with sodium hydroxide, and yielding para-red on acidification. The latter was also similarly produced from 2:2'-dihydroxydinaphthylmethane and *p*-nitrobenzenediazonium chloride. 2-Hydroxy-1-methylnaphthalene- ω -sulphonic acid does not couple with *p*-nitrobenzenediazonium chloride.

A. I. VOGEL.

Decomposition of optically active diazo-compounds. F. E. RAY (J. Amer. Chem. Soc., 1930, 52, 3004–3010).—It has already been shown that the *cis*- and *trans*-aminolauronic esters (3-amino-1:2:2-trimethylcyclopentane-1-carboxylic esters) yield different products when treated with nitrous acid under similar conditions (cf. Skinner, A., 1923, i, 791; Noyes and Skinner, A., 1918, i, 65). The diazo-compounds, presumably formed as intermediates, are

now shown to exhibit similar differences in behaviour, thus indicating that the carbon atom to which the diazo-group is attached retains, for a time at least, its asymmetry. Methyl *cis*-diazocamphanate (Kendall and Noyes, A., 1926, 1134) is decomposed by dilute sulphuric acid to esters of hydroxy-acids (39.5%) and of unsaturated acids (60.5%) whilst the *trans*-ester at -20° with this reagent gives 68% and 27%, respectively, of the esters and 5% of the methyl ether of *cis*-camphanolic acid. These yields are similar to those obtained from the corresponding amino-esters. Furthermore, spontaneous decomposition of the *cis*-diazio-ester yields the bishydrazone of Noyes and Taveau (A., 1904, i, 807), whilst the *trans*-derivative gives a compound, m. p. 71° , of mol. wt. 320–340. H. E. F. NOTTON.

Manufacture of diaminoazoanthraquinones. I. G. FARBENIND. A.-G.—See B., 1930, 896.

Nitrosation of phenols. X. Nitrosation of *m*-iodophenol. H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 1969–1970).—The initial product of nitrosation of *m*-iodophenol is probably 3-iodo-4-nitrosophenol, decomp. about 190° , converted by treatment with acid or alkali (A., 1929, 1062; this vol., 910) into light-stable 3-iodo-*p*-benzoquinone-4-oxime (*benzoate*, m. p. 166° ; *methyl ether*, m. p. 143°). 3-Iodo-4-nitrosoanisole, obtained from 3-iodo-*p*-anisidine and Caro's acid, has m. p. 72.5° . The *syn*- and *anti*-forms of 3-iodo-*p*-benzoquinone-4-oxime previously described by Hodgson and Moore (A., 1925, i, 1408) appear to correspond with the nitrosophenol and quinoneoxime tautomerides, respectively.

H. BURTON.

Aromatic substitution. II. Action of fuming nitric acid on the 4-fluoro-2:6-dihalogenophenols and -anisoles. III. Action of fuming nitric acid on the 3-fluoro-2:4:6-trihalogenophenols and -anisoles. H. H. HODGSON and J. NIXON (J.C.S., 1930, 1868–1869, 1870–1872).—II. *p*-Fluorophenol is converted by aqueous sodium hypochlorite into 2:6-dichloro-4-fluorophenol, m. p. 42° , methylated by Haworth and Lapworth's method (J.C.S., 1923, 123, 2986) to 2:6-dichloro-4-fluoroanisole, m. p. 36° . Both these substances are converted by nitric acid (*d* 1.5) at 0° into 2:6-dichloro-*p*-benzoquinone. Treatment of a solution of *p*-fluorophenol in aqueous sodium hydroxide with iodine dissolved in aqueous potassium iodide affords 2:6-di-iodo-4-fluorophenol, m. p. 67° , methylated by methyl sulphate and sodium hydroxide solution to 2:6-di-iodo-4-fluoroanisole, m. p. 61° . The former of these is converted as above into 2:6-di-iodo-*p*-benzoquinone whilst the latter yields 6-iodo-4-fluoro-2-nitroanisole, m. p. 53° .

III. *m*-Fluorophenol is converted by bromine in aqueous potassium bromide into 2:4:6-tribromo-3-fluorophenol, m. p. 90° , and as above into 2:4:6-trichloro-, m. p. 55° , and 2:4:6-tri-iodo-3-fluorophenols, m. p. 138 – 139° . Treatment of these with nitric acid at 0° affords 2:6-dibromo-, m. p. 150° , 2:6-dichloro-, m. p. 145° , and 2:6-di-iodo-3-fluoro-*p*-benzoquinones, m. p. 195° , respectively. Similarly, 2:4:6-trichloro-3-fluoroanisole, m. p. 35° , prepared by Haworth and

Lapworth's method, gives 3-fluoro-2:4:6-trinitroanisole, m. p. 180°; 2:4:6-tribromo-3-fluoroanisole, m. p. 55°, yields 2:4:6-tribromo-3-fluoro-5-nitroanisole, m. p. 87° (cf. Kohn and Rosenfeld, A., 1926, 282), whilst 2:4:6-tri-iodo-3-fluoroanisole, m. p. 107°, furnishes 2:4-di-iodo-3-fluoro-6-nitroanisole, m. p. 102°. The last-named compound is also obtained by methylation (Haworth and Lapworth's method) of 2:4-di-iodo-3-fluoro-6-nitrophenol, m. p. 106°, prepared by treatment of 3-fluoro-6-nitrophenol with iodine in presence of alcohol and yellow mercuric oxide.

H. BURTON.

Action of freshly precipitated mercuric oxide on a suspension of 3:5-dinitrotoluene in aqueous sodium hydroxide. Novel preparation of 3:5-dinitro-*p*-cresol. H. H. HODGSON and E. W. SMITH (J.C.S., 1930, 2035—2036).—When a mixture of mercuric chloride, 3:5-dinitrotoluene, and aqueous sodium hydroxide is boiled for 10 hrs., 3:5-dinitro-*p*-cresol is produced in approximately 50% yield together with amorphous material and mercury. Mercuric oxide alone has no action on the dinitrotoluene and sodium hydroxide alone gives no simple phenolic compound. No reaction occurs when the hydroxide is replaced by carbonate. H. BURTON.

Migration of acyl groups in *o*-aminophenols. F. BELL (J.C.S., 1930, 1981—1987).—Treatment of *o*-benzylideneaminophenol with acetyl, benzoyl, α - and β -naphthoyl chlorides in pyridine at the ordinary temperature affords 2-hydroxy-acetanilide, -benzanilide, - α -naphthanilide, m. p. 194°, and - β -naphthanilide, m. p. 194°, respectively. With *p*-toluenesulphonyl chloride a mixture of 2-benzylideneaminophenyl *p*-toluenesulphonate, m. p. 98°, and 2-*p*-toluenesulphonyl-1-phenyldihydrobenzoxazole, m. p. 138°, results. Hydrolysis of the ester with boiling water gives 2-aminophenyl *p*-toluenesulphonate [formed together with 5(?)chloro-2-aminophenyl *p*-toluenesulphonate, m. p. 112° (acetyl derivative, m. p. 168°), by the reduction of the 2-nitro-ester with stannous chloride and alcoholic hydrochloric acid], whilst the oxazole is hydrolysed by alcoholic hydrogen chloride to 2-hydroxy-*p*-toluenesulphanilide (prepared also from *o*-aminophenol and *p*-toluenesulphonyl chloride in pyridine). *m*-Nitrophenyl *p*-toluenesulphonate, m. p. 112°, is reduced as above to the *m*-amino-derivative, m. p. 98° (benzylidene derivative, m. p. 90°). 4-Benzylidene- and 2-*p*-dimethylaminobenzylidene-aminophenyl *p*-toluenesulphonates have m. p. 165° and 135°, respectively. *o*-Aminophenol and β -naphthoyl chloride in pyridine give a mixture of 2-hydroxy- β -naphthanilide and 2- β -naphthoxy- β -naphthanilide, m. p. 150°. Since the above oxazole contains an asymmetric carbon atom, attempts to obtain the 2-camphorsulphonyl derivative have been made; viscous products are formed. 2-*p*-Dimethylaminobenzylideneaminophenol and *p*-toluenesulphonyl chloride afford a mixture of 2-hydroxy-*p*-toluenesulphanilide and 2-*p*-toluenesulphonyl-1-*p*-dimethylaminophenyldihydrobenzoxazole, m. p. 188°. This oxazole is converted by dilute acetic or aqueous-alcoholic *d*-camphorsulphonic acid into the *N*-*p*-toluenesulphonyl derivative, m. p. 92°, of *p*-dimethylaminobenzaldehyde-*o*-hydroxyaniline; hydration of the oxazole occurs.

Hydrolysis of various diacylated *o*-aminophenols (cf. Raiford and others, A., 1924, i, 1304; 1925, i, 809) shows that the migration of acyl groups depends on some peculiarity of the $\cdot\text{O}\cdot\text{C}\cdot\text{O}\cdot$ linking which is absent from the $\cdot\text{O}\cdot\text{SO}_2\cdot$ linking. Substituents have also a marked influence in determining migration. Thus, 2-acetoxy- α -naphthanilide, m. p. 153°, and 2- α -naphthoxyacetanilide, m. p. 139°, are both hydrolysed by sodium hydroxide solution to 2-hydroxy- α -naphthanilide, also formed by hydrolysis of 2-benzoyloxy- α -naphthanilide, m. p. 176°, or 2- α -naphthoxybenzanilide, m. p. 170°. 2-*p*-Toluenesulphoxyacetanilide, m. p. 134°, and 2-acetoxy-*p*-toluenesulphanilide, m. p. 123°, are hydrolysed to 2-hydroxyacetanilide (formed also from 2-*d*-camphorsulphoxyacetanilide, m. p. 133°, [α]_D²⁰ +60.9° in acetone) and 2-hydroxy-*p*-toluenesulphanilide (*p*-toluenesulphonyl derivative, m. p. 143°), respectively. 2-*p*-Toluenesulphoxy- α -, m. p. 125°, and - β -naphthanilides, m. p. 125°, are hydrolysed to 2-hydroxy- α - and - β -naphthanilides (also formed from 2-acetoxy- β -naphthanilide, m. p. 149°).

H. BURTON.

2:5-Dibromo-*p*-anisidine. G. BARGELLINI and A. GRIPPA (Atti R. Accad. Lincei, 1930, [vi], 11, 673—676; cf. this vol., 908).—Bromination of *p*-acetanisidide gives first 2-bromo-*p*-acetanisidide and then 2:5-dibromo-*p*-acetanisidide, m. p. 193—195°, Bures and Nedělková's statement that the action of bromine on *p*-acetanisidide gives the 3:5-dibromo-compound (A., 1929, 1437) being thus inaccurate. 2:5-Dibromo-*p*-anisidine, m. p. 92—94°, forms a picrate, m. p. 133—134°, a benzoyl derivative, m. p. 170—172°, and a piperonylidene derivative, m. p. 171—172°. 2:5-Dibromo-2':4'-dinitro-4-methoxydiphenylamine, m. p. 182—188° (decomp.), is obtained by condensation of 2:5-dibromoanisidine and chlorodinitrobenzene in presence of sodium acetate. Treatment of 2:5-dibromo-*p*-acetanisidide with hydriodic acid yields 2:5-dibromo-4-aminophenol, which gives 2:5-dibromobenzoquinone on oxidation with chromic acid (*loc. cit.*).

T. H. POPE.

3:5- and 2:6-Dibromo-*p*-anisidines. G. BARGELLINI and F. MADESANI (Atti R. Accad. Lincei, 1930, [vi], 11, 676—679; cf. preceding abstract).—Bromination of *p*-anisidine in acetic acid solution yields 3:5-dibromo-*p*-anisidine, m. p. 81—82° (cf. Wieland, A., 1910, i, 244), which forms an acetyl derivative, m. p. 225°, and a benzoyl derivative, m. p. 198°. 2:6-Dibromo-*p*-anisidine (cf. Robertson, J.C.S., 1902, 81, 1479) forms a piperonylidene derivative, m. p. 143°, and with chlorodinitrobenzene forms 3:5-dibromo-2':4'-dinitro-4-methoxydiphenylamine, m. p. 220°.

T. H. POPE.

Sulphonation of β -naphthol in presence of boric acid; β -naphthol-1:6-disulphonic acid. K. H. ENGEL (J. Amer. Chem. Soc., 1930, 52, 2835—2844).—Addition of boric acid changes the course of the reaction between β -naphthol and sulphuric acid (cf. Crossley and Simpson, B., 1926, 234), the greatest effect being produced when the proportion of boric acid reaches 0.33 mol. per mol. of naphthol. This, and the solid nature of the reaction product, suggests that formation of trinaphthyl borate precedes sulphonation. In general the effect of the catalyst is to

favour the production, or survival, of derivatives containing the 1-sulphonic acid group, and to minimise loss by destructive oxidation. Sulphuric acid (2 parts) and naphthol (1 part) at 20–28° for 4 min. give β -naphthol-1-sulphonic acid (90%) and -6-sulphonic acid (9%). In practice, it is better to continue the sulphonation for 24 hrs. at 30°, when 83% of I is formed and 74% can be isolated by precipitation with sodium chloride. In this case, β -naphthol-1:6-disulphonic acid, which forms the principal impurity, is more easily removed than the 6-sulphonic acid. When sufficient sulphuric acid to effect complete disulphonation is present, the 6-sulphonic, 8-sulphonic, and 1:6-disulphonic acids are formed in proportions varying from 2:7:81 at 0° to 20:27:53 at 85°. A further transformation of these products into the 3:6- and 6:8-disulphonic acids proceeds slowly at 35° and more rapidly at higher temperatures. For the preparation of the 1:6-disulphonic acid, naphthol (1 part) and sulphuric acid (3 parts) are heated in presence of boric acid at 45° for 30 hrs., when the ratio of products is 4:24:72 and 64% of 1:6-disulphonic acid is precipitated as the sodium salt (+3H₂O) by sodium chloride. The potassium salt (+H₂O) is obtained similarly. The 1-sulphonic acid group in the 1:6-disulphonic acid is displaced by coupling with the more reactive diazonium salts and by hydrolysis with dilute mineral acid at 85°. β -Naphthol-1-sulphonic acid is also obtained by very rapid sulphonation in absence of boric acid at 20–30°. Using more sulphuric acid and a reaction period of 24 hrs., the 1:6-disulphonic acid is obtained in yields decreasing from 74% at 2° to 23% at 25° and none at 85°. The yield of 8-sulphonic acid reaches a maximum (55%) at 25–30°, whilst that of 6-sulphonic acid increases from 3% at 0° to 74% at 85°. Boric acid also influences the course of sulphonations at 135°, increasing the yield of 1:6-disulphonic acid from 0 to 28%.

H. E. F. NOTTON.

Scission of diaryl ethers and related compounds by means of piperidine. V. Nitration of methyl, dimethyl, and polyhalogeno-derivatives of diphenyl ether. (Miss) D. L. FOX and E. E. TURNER (J.C.S., 1930, 1853–1867).—2-Chloro-2'-bromodiphenyl ether, b. p. 195–196°/10 mm., prepared by the usual method from the chloroamino-ether, is nitrated by nitric (*d* 1.5) and acetic acids to the 4:4'-dinitro-derivative, m. p. 150–151°. When nitration is effected with nitric acid at 100° some hydrogen halide is evolved (cf. this vol., 909). Introduction of a further nitro-group into diphenyl ethers substituted in the 2- and 4-positions of each nucleus with either two nitro-groups or one nitro-group and a halogen atom is not readily accomplished. The presence of methyl groups favours the introduction of more than one nitro-group. Chlorination of *p*-bromophenol in acetic acid affords 2-chloro-4-bromophenol, m. p. 50–51° (lit. 45°), the *p*-toluenesulphonate, m. p. 114–115°, of which gives with nitric acid (*d* 1.5) 2-chloro-4-bromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate, m. p. 107–108° (piperidine fission product 2-chloro-4-bromo-5-nitrophenol, m. p. 83°). Reduction of this ester with stannous chloride and hydrochloric and acetic acids, replace-

ment of the amino-groups by chlorine, and subsequent hydrolysis gives 2:5-dichloro-4-bromophenol, m. p. 71–72°, also obtained from 2:5-dichloro-4-bromoaniline, m. p. 91–92°, by Noelting and Kopp's method (A., 1905, i, 872). The last-named compound is prepared by the reduction with iron filings, 70% alcohol, and a small amount of hydrochloric acid of 1:4-dichloro-2-bromo-5-nitrobenzene, m. p. 57–58°, which is formed by nitrating 2:5-dichlorobromobenzene. 2-Chloro-4-bromophenol and 1-chloro-2:4-dinitrobenzene give a 95% yield of 2-chloro-4-bromo-2':4'-dinitrodiphenyl ether, m. p. 122–123°, which, like the 2:4-dichloro- and -dibromo-derivatives (A., 1929, 551; this vol., 907), undergoes nitration in the 5-position, yielding 2-chloro-4-bromo-5:2':4'-trinitrodiphenyl ether, m. p. 132–133° (piperidine scission products 2:4-dinitrophenylpiperidine and 2-chloro-4-bromo-5-nitrophenol). Treatment of 2:5-dichlorophenol (1 mol.) with bromine (1 mol.) in acetic acid containing sodium acetate (1 mol.) at 100° furnishes a mixture of 2:5-dichloro-4-bromo- and 2:5-dichloro-4:6-dibromo-phenol, m. p. 99–100°.

2:4:6-Trichloro-, m. p. 121–122°, 2:4:6-tribromo-, and 4-chloro-2:6-dibromo-2':4'-dinitrodiphenyl ethers, m. p. 145–146°, are all nitrated by nitric acid (*d* 1.5) at 100° to the corresponding 3:2':4'-trinitro-derivatives, m. p. 144–145°, 177–178°, and 157–159°, respectively; elimination of halogen does not occur. The trinitro-compounds show no tendency to undergo further nitration. They are decomposed by piperidine, forming 2:4-dinitrophenylpiperidine and the appropriate 2:4:6-trihalogeno-3-nitrophenol. 4-Chloro-2:6-dibromo-3-nitrophenol has m. p. 81–82°. 4-Chloro-2:6-dibromophenol, m. p. 89° (*p*-toluenesulphonate, m. p. 107–108°), is prepared by brominating *p*-chlorophenol in acetic acid. Bromination of 2:4-dichlorophenol or dichlorination of *o*-bromophenol affords 2:4-dichloro-6-bromophenol, b. p. 192°/12 mm., m. p. 68–69°, which with 1-chloro-2:4-dinitrobenzene yields 2:4-dichloro-6-bromo-2':4'-dinitrodiphenyl ether, m. p. 140–141°. Nitration of this at 100° gives a mixture (constant m. p. 149–149.5°) of 3:2':4'- and 5:2':4'-trinitro-derivatives, which were not separated but converted by piperidine into a mixture of 2:4-dichloro-6-bromo-3-, m. p. 78–79°, and -5-nitrophenols, m. p. 92–93°. These phenols are also obtained by bromination of the requisite dichloronitrophenol. Similar nitration of 2:4-dichloro-6-bromophenyl *p*-toluenesulphonate, m. p. 82–83°, yields a mixture (constant m. p. 122–125°) of 2:4-dichloro-6-bromo-3-, m. p. 122–122.5°, and -5-nitrophenyl *o*-nitro-*p*-toluenesulphonate, m. p. 134–135°, converted by piperidine into the above dichlorobromonitrophenols. These esters are also synthesised from the appropriate phenol and 2-nitro-*p*-toluenesulphonyl chloride. 2:3:4- and 2:4:5-Trichloro-6-bromophenols have m. p. 84–85° and 81–82°, respectively.

p-Cresol and 2:5-dibromonitrobenzene give 4-bromo-2-nitro-4'-methylidiphenyl ether, m. p. 109.5°, which with nitric and acetic acids yields an equimolecular compound (or mixture) of unchanged ether and 2:2'-dinitro-derivative. With nitric acid alone at

0°, a mixture of 4-bromo-2:6-dinitrophenol and a small amount of 4-bromo-2:2':3'-trinitro-4'-methyl-diphenyl ether, m. p. 166° (piperidine scission products 2:3-dinitro-*p*-cresol and 4-bromo-2-nitrophenyl-piperidine), results. 4-Bromo-2'-nitro-4'-methyl-diphenyl ether, m. p. 82°, and nitric acid give only 4-bromo-2:6-dinitrophenol. The last-named ether is converted by sulphuric acid at 100° into 2'-nitro-4'-methyl-diphenyl ether 4-sulphonic acid, m. p. 131—132°; under similar conditions the 2-nitro-isomeride is unaffected. These results are the reverse of those obtained with the analogous chloro-derivatives (this vol., 909). 2:4-Dinitro-4'-methyl-diphenyl ether, m. p. 97—98°, is nitrated to the 2:4:2'-trinitro-, m. p. 175—176°, and 2:4:2':3'-tetranitro-derivatives, m. p. 184°, whilst 2:4-dinitro-2':4'-dimethyl-diphenyl ether, m. p. 106°, affords 2:4:5'-trinitro-, m. p. 129—130° (piperidine scission products 2:4-dinitrophenyl-piperidine and 6-nitro-*m*-4-xylenol), and 2:4:3':5'-tetranitro-derivatives, m. p. 198°. Piperidine scission of the tetranitro-compound furnishes 2:4-dinitrophenyl-piperidine and 2:6-dinitro-*m*-4-xylenol, m. p. 162—163° (*p*-toluenesulphonate, m. p. 110—111°). Nitration of 6-nitro-*m*-4-xylenol with nitric acid (*d* 1.5) at the ordinary temperature gives 5:6-dinitro-*m*-4-xylenol, m. p. 119—120°, also obtained by the action of piperidine on 5:6-dinitro-*m*-4-xylol *o*-nitro-*p*-toluenesulphonate, m. p. 140—141°, formed by nitrating 5-nitro-*m*-4-xylol *p*-toluenesulphonate, m. p. 111—112°.

4-Chloro-2-nitro-2':4'-dimethyl-diphenyl ether, m. p. 77—78°, undergoes nitration, yielding the 2:5'-dinitro-, m. p. 88—89°, and 2:3':5'-trinitro-derivatives, m. p. 140°. 4-Bromo-2-nitro-2':4'-dimethyl-diphenyl ether, m. p. 89—90°, affords the 2:5'-dinitro-derivative, m. p. 98—99°, but further nitration causes elimination of halogen with the production of 2:4:5'-trinitro- and 2:4:3':5'-tetranitro-2':4'-dimethyl-diphenyl ethers. H. BURTON.

Reaction between glyoxal and resorcinol. J. MIKŠIĆ, A. REŽEK, and Z. PINTEROVIĆ (J. pr. Chem., 1930, [ii], 127, 189—194).—Glyoxal reacts with 4 mols. of resorcinol in presence of ether and phosphoric oxide, forming 16% of the theoretical yield of *s*-tetra-(2:4-dihydroxyphenyl)ethane (+0.5H₂O), m. p. (anhydrous) 235—236° (decomp.) (*octa*-acetate, m. p. 270°), also obtained in 5% yield when condensation is effected with dry hydrogen chloride. Dissolution of the hydroxy-compound in sulphuric acid gives a fluorescent solution (xanthen formation); a solution of the acetyl derivative shows no fluorescence. Xanthen formation also occurs when the hydroxy-compound is heated with zinc chloride at 150° or alone at 180° for a long time. H. BURTON.

Action of nitrous acid on resorcinol diethyl ether. H. H. HODGSON and H. CLAY (J.C.S., 1930, 1872—1875).—Nitrosation of resorcinol diethyl ether in acetic acid containing hydrogen chloride (cf. Kraus, A., 1892, 44) or sulphuric acid gives an 80—90% yield of 4-nitroso-3-ethoxyphenol; reaction does not occur in acetic acid alone. Since 4-nitrosoresorcinol diethyl ether, m. p. 104°, prepared by oxidising 4-aminoresorcinol diethyl ether with persulphuric acid, is converted into the above phenol by treatment with

cold, dilute hydrochloric or sulphuric acid (not by 5% potassium hydroxide solution), it is probable that the first product of nitrosation is the diethyl ether. The decomposition of this by mineral acid probably proceeds with a greater velocity than the nitrosation, since no 4-nitrosoresorcinol diethyl ether could be isolated. H. BURTON.

Primary additive products in indirect substitution in the benzene nucleus. (Nitration and bromination of 4:4'-dialkoxydiphenyls.) J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 769—783).—Treatment of a solution of 4:4'-dimethoxydiphenyl in cold carbon tetrachloride with an emulsion of absolute nitric acid (2 mols.) in carbon tetrachloride affords an impure, indigo-blue additive dinitrate, also formed when finely-divided 4:4'-dimethoxydiphenyl is exposed to nitric acid vapour at the ordinary temperature. The dinitrate is decomposed by water, regenerating the reactants; it reacts with phenol forming *o*-nitrophenol, and when heated at 50—100°, or dissolved in acetone, acetic acid, or acetic anhydride, affords 3:3'-dinitro-4:4'-dimethoxydiphenyl, m. p. 221°. Bromination of 4:4'-dimethoxydiphenyl in boiling acetic acid gives the 3:3'-dibromo-derivative, m. p. 167°, which on exposure to bromine vapour in the dark forms a green additive dibromide. The dibromo-compound also forms a green mononitrate, which when heated to 100° passes into 3:3'-dibromo-5-nitro-4:4'-dimethoxydiphenyl, m. p. 178°, also prepared by nitration of the dibromo-derivative in boiling carbon tetrachloride. When 4:4'-dimethoxydiphenyl is exposed to bromine vapour for 24 hrs., a tetrabromo-derivative, m. p. 139°, is produced. This is not identical with 3:5:3':5'-tetrabromo-4:4'-dimethoxydiphenyl, m. p. 209°, obtained by methylation of the 4:4'-dihydroxy-compound. 4:4'-Dihydroxy- and 4:4'-diethoxy-diphenyls also furnish coloured dinitrates, which when heated pass into the 3:3'-dinitro-derivatives. The above additive compounds are formulated as oxonium salts; their isolation supports the theory previously proposed (A., 1928, 57).

3:5:3':5'-Tetranitro-4:4'-dimethoxydiphenyl has m. p. 255° (lit. 242° and 244.6°). H. BURTON.

Mixed aromatic hydroxysulphones. II. Hydroxyphenyl-*o*-hydroxytolylsulphones. J. ZEHENTER and F. PLASS (J. pr. Chem., 1930, [ii], 127, 263—268).—When a mixture of phenol and *o*-cresol is heated with fuming sulphuric acid (8—10% SO₃) at 175—180° there are formed 4:4'-dihydroxydiphenylsulphone, di-*o*-hydroxyditolylsulphone, phenol- and *o*-cresol-sulphonic acids, and three hydroxyphenyl-*o*-hydroxytolylsulphones. These isomerides are designated α -, m. p. 246—247° [main product; diacetate, m. p. 129°; dibenzoate, m. p. 188°; tribromo-derivative, m. p. 266—267°; dinitro-derivative, m. p. 210—212°, obtained by the action of nitric acid (*d* 1.1) at 100°]; β -, m. p. 237° (diacetate, m. p. 134—135°; dibenzoate, m. p. 196°; dinitro-derivative, m. p. 214—215°; tribromo-derivative, m. p. 270—271°), and γ -, m. p. 204° (diacetate, m. p. 120°; dibenzoate, m. p. 155°). Hydrolysis of the β -diacetate or -dibenzoate affords the α -compound, which on prolonged treatment with sulphuric acid at the

ordinary temperature yields a disulphonic acid (barium salts +3 and $7\text{H}_2\text{O}$). Sulphonation of the α -derivative at 100° gives phenol- and *o*-cresol-4-sulphonic acids, indicating that the α -compound is *p*-hydroxyphenyl-4-hydroxy-*m*-tolylsulphone.

H. BURTON.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. X. Compounds of the tetra-arylbutane series. K. BRAND and W. BAUSCH. XI. Electrochemical preparation of $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- and $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- Δ^{β} -butinenes. K. BRAND, O. HORN, and W. BAUSCH (J. pr. Chem., 1930, [ii], 127, 219—239, 240—247).—X. Reduction of $\beta\beta\beta$ -tribromo- $\alpha\alpha$ -di-*p*-phenetylene with hydrogen in presence of alcoholic pyridine and palladised calcium carbonate at 45 — 50° gives about 32% of $\beta\gamma$ -dibromo- $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- Δ^{β} -butene, m. p. 184.5° (cf. Brand and Kercher, A., 1921, i, 787), together with a small amount of 4:4'-diethoxystilbene. In some of the above reduction experiments hydrogen is not absorbed, but $\beta\beta$ -dibromo- $\alpha\alpha$ -di-*p*-phenetylene is formed, probably by dehydrogenation of the alcohol and subsequent reduction of the tribromo-compound. The dibromoethane and alcoholic sodium ethoxide afford β -bromo- $\alpha\alpha$ -di-*p*-phenetylene, whilst the tribromo-compound and 10% alcoholic potassium hydroxide give $\beta\beta$ -dibromo- $\alpha\alpha$ -di-*p*-phenetylene, m. p. 118.5° . Reduction of $\beta\gamma$ -dibromo- $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- Δ^{β} -butene with zinc dust and alcohol or acetic acid yields $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- Δ^{β} -butinene, m. p. 96° (see below). Bromine is not eliminated from the above dibromobutene by catalytic reduction or treatment with copper-bronze in benzene or sodium iodide in acetone. Treatment of the dibromobutene with amyl-alcoholic sodium ethoxide affords $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\alpha\beta\gamma}$ -butatriene (A., 1927, 549) together with a small amount of 5-ethoxy-1-*p*-phenetyl-3-di-*p*-phenetylmethyleneindene (*loc. cit.*).

$\beta\beta\beta$ -Trichloro- $\alpha\alpha$ -di-*p*-chlorophenylethane is reduced similarly to the above tribromoethane, yielding either a mixture of $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- Δ^{β} -butene (I), m. p. 229° (35.6%), and a small amount of an isomeride (II), m. p. 174° , or $\beta\beta\gamma\gamma$ -tetra-*p*-chlorophenylbutane, m. p. 271.5° . The last-named compound is reduced further to I by the same process; with zinc dust and acetic acid $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- Δ^{β} -butinene, m. p. 174° , results. Treatment of I or II with amyl-alcoholic sodium ethoxide gives $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene, m. p. 288° (decomp.), together with a small amount of low melting material. Oxidation of this butatriene with chromic and acetic acids yields 4:4'-dichlorobenzophenone, whilst reduction with zinc dust and acetic acid affords a mixture of the above butinene and $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\alpha\beta\gamma}$ -butadiene, m. p. 244° (also formed when the butinene is treated with alcoholic sodium ethoxide solution). Reduction of the butatriene with sodium and amyl alcohol yields impure $\alpha\alpha\delta\delta$ -tetraphenylbutane, whilst prolonged treatment with a saturated solution of hydrogen chloride in acetic acid at 100° furnishes a mixture of 5-chloro-1-*p*-chlorophenyl-3-di-*p*-chlorophenylmethyleneindene, m. p. 222° , and an additive compound, $\text{C}_{28}\text{H}_{17}\text{Cl}_5$, m. p. 158° . Treatment of the last-named

compound with alcoholic sodium ethoxide regenerates the above butatriene, which under the influence of sunlight passes into a dimeride, m. p. 323.5° (decomp.).

XI. Electrolytic reduction of $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-*p*-phenetylene with a lead cathode and alcoholic hydrochloric acid as the cathode solution gives 4:4'-diethoxystilbene (8%) and $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- Δ^{β} -butinene (35%). Treatment of the butinene with alcoholic sodium ethoxide affords $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\alpha\beta}$ -butadiene, m. p. 202° . Similar reduction of $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-*p*-chlorophenylethane yields 4:4'-dichlorostilbene (trace) and $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- Δ^{β} -butinene (13%). This butinene and $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\alpha\beta}$ -butadiene are both oxidised by chromic and acetic acids to 4:4'-dichlorobenzophenone; the butadiene is not affected by treatment with zinc dust and acetic acid.

H. BURTON.

Pyrolysis of aryl allyl sulphides. C. D. HURD and H. GREENGARD (J. Amer. Chem. Soc., 1930, 52, 3356—3358).—When phenyl allyl sulphide, b. p. 215 — $218^\circ/750$ mm., 104 — $106^\circ/25$ mm., n_D^{20} 1.4772, obtained from sodium thiophenoxide and allyl bromide in alcohol, is refluxed for 6 hrs., about 25% of *o*-allylthiophenol, b. p. 183 — $190^\circ/17$ mm., n_D^{21} 1.6098 (lead salt), is produced together with a small amount of 2-methyl-2:3-dihydrothionaphthen, b. p. 103 — $108^\circ/8$ mm., n 1.5811. Oxidation of *o*-allylthiophenol with potassium permanganate gives *o*-sulphobenzoic acid. Similarly, *p*-tolyl allyl sulphide, b. p. 123 — $127^\circ/25$ mm., n_D^{21} 1.5711, affords some 2-allyl-*p*-thiocresol, b. p. 190 — $196^\circ/11$ mm., n_D^{21} 1.6921 [lead salt, m. p. 330° (decomp.)], oxidised to 4-sulphoisophthalic acid, sublimes at 320° .

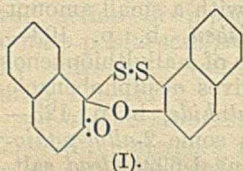
H. BURTON.

Derivatives of diphenyl sulphide and diphenyl ether. R. B. SANDIN and W. V. DRAKE (J. Amer. Chem. Soc., 1930, 52, 3353—3356).—3:4:5-Tri-iodonitrobenzene and *p*-methoxythiophenol react in presence of methyl ethyl ketone and anhydrous potassium carbonate, forming 2:6-di-iodo-4-nitro-4'-methoxydiphenyl sulphide (60% yield), m. p. 138 — 139° (all m. p. are corr.), reduced to 2:6-di-iodo-4-amino-4'-methoxydiphenyl sulphide, m. p. 172 — 173° [hydrochloride, m. p. 200° (decomp.); acetyl derivative, m. p. 230°]. 2:6-Di-iodo-4-nitro-2'-(25% yield), m. p. 149 — 150° , and -3'-methoxydiphenyl ethers (45—50%), m. p. 139 — 140° , are obtained similarly, using guaiacol and resorcinol monomethyl ether, respectively. These are reduced to 2:6-di-iodo-4-amino-2', m. p. 178 — 179° [hydrochloride, m. p. 236 — 237° (decomp.); acetyl derivative, m. p. 227 — 228° ; benzoyl derivative, m. p. 239 — 240°], and 2:6-di-iodo-4-amino-3'-methoxydiphenyl ethers, m. p. 124 — 125° [hydrochloride, m. p. 132 — 134° (decomp.); acetyl derivative, m. p. 177 — 178° ; benzoyl derivative, m. p. 201 — 202°], respectively.

H. BURTON.

β -Naphtha-1-thioquinone and dehydro-2-naphthol 1-disulphide. H. A. STEVENSON and S. SMILES (J.C.S., 1930, 1740—1745).—Treatment of a mixture of β -naphthol and sodium thiocyanate in 96% acetic acid with a solution of bromine in acetic acid (cf. Kaufmann, A., 1926, 392; 1929, 436) affords 2-naphthyl 1-thiocyanate. Reduction of this with zinc dust and acetic acid containing a small amount

of hydrochloric acid, separation of the 2-naphthylene 1-thiolcarbonate, $C_{10}H_6\langle\begin{smallmatrix} S \\ O \end{smallmatrix}\rangle CO$, m. p. 106° , formed, and oxidation of the residual solution with hydrogen peroxide affords 2-naphthol 1-disulphide. Hydrolysis of the thiolcarbonate with aqueous alcoholic sodium hydroxide affords the disulphide; with cold alcoholic sodium ethoxide, 2-naphthol-1-ethylthiolcarbonate, m. p. 127° , results. The above thiolcarbonate is also formed when a solution of 2-naphthyl 1-thiocyanate in acetic acid containing a small amount of sulphuric acid is boiled for 15 min. Reduction of 2-naphthol 1-disulphide with zinc dust and acetic-hydrochloric acids gives 1-thiol-2-naphthol, m. p. 55° , whilst treatment with bromine in carbon tetrachloride furnishes 1-bromothiolo-2-naphthol, m. p. $93-95^\circ$. Treatment of this bromothiolo with 2 mols. of β -naphthol in carbon tetrachloride affords 2-naphthol 1-sulphide; with 6-bromo-2-naphthol, 6-bromo-2:2'-dihydroxy-1:1'-dinaphthyl sulphide, m. p. 131° , results. 1-Bromo-2-naphthol and the bromothiolo react in presence of carbon tetrachloride and pyridine forming about 30% of dehydro-2-naphthol 1-sulphide (this vol., 908). Treatment of the bromothiolo with pyridine in carbon tetrachloride affords dehydro-2-



naphthol 1-disulphide (I), m. p. 171° , presumably by spontaneous polymerisation of the intermediate β -naphtha-1-thioquinone. The same disulphide is also produced by oxidation of 2-naphthol 1-disulphide with alkaline potassium ferricyanide in presence of benzene. Reduction of I with zinc dust and acetic and hydrochloric acids furnishes hydrogen sulphide and iso-2-naphthol sulphide (*loc. cit.*). Dehydro-2-naphthol 1-sulphide cannot be prepared from 1-thiol-2-naphthol and β -naphthaquinone; the normal type of nuclear additive product (G.P. 175,070) is formed.

H. BURTON.

Synthesis of cinnamyl alcohol and homologues. L. BERT and P. C. DORIER (*Compt. rend.*, 1930, **191**, 378—380).—Cinnamyl chloride (for synthesis see this vol., 1290) by treatment with fused sodium acetate in boiling glacial acetic acid yields cinnamyl acetate, b. p. $138^\circ/15$ mm., d_4^{12} 1.0603, n_D^{15} 1.555. The following substituted cinnamyl acetates are obtained similarly: o-methyl-, b. p. $147^\circ/15$ mm., d_4^{11} 1.043, n_D^{15} 1.544; p-methyl-, b. p. $149^\circ/15$ mm., $d_4^{12.5}$ 1.0153, n_D^{15} 1.541; 2:4-dimethyl-, b. p. $161^\circ/15$ mm., $d_4^{11.5}$ 1.033, n_D^{15} 1.540; 2:5-dimethyl-, b. p. $160^\circ/15$ mm., $d_4^{11.5}$ 1.018, n_D^{15} 1.541; p-isopropyl-, b. p. $164^\circ/15$ mm., d_4^{11} 0.994, n_D^{15} 1.533; 2:5-methylisopropyl-, b. p. $174^\circ/15$ mm., d_4^{11} 0.990, n_D^{15} 1.530. By hydrolysis with potassium hydroxide cinnamyl alcohol, b. p. $139^\circ/15$ mm., d_4^{25} 1.032, n_D^{15} 1.576, and the following substituted cinnamyl alcohols are obtained: o-methyl-, b. p. $149^\circ/15$ mm., d_4^{15} 1.0302, n_D^{15} 1.578; p-methyl-, b. p. $152^\circ/15$ mm., $d_4^{14.5}$ 1.005, n_D^{15} 1.565; 2:4-dimethyl-, b. p. $155^\circ/15$ mm., $d_4^{14.5}$ 1.020, n_D^{15} 1.569; 2:5-dimethyl-, b. p. $156^\circ/15$ mm., $d_4^{12.5}$ 1.004, n_D^{15} 1.564; p-isopropyl-, b. p. $161^\circ/15$ mm., d_4^{16} 0.977, n_D^{15} 1.548; 2:5-methylisopropyl-, b. p. $164^\circ/15$ mm., d_4^{15} 0.974, n_D^{15} 1.547.

C. W. SHOPPEE.

Amino-alcohols. II. Homologues and analogues of phenylpropanolamine. W. H. HARTUNG, J. C. MUNCH, W. A. DECKERT, and F. CROSSLEY (*J. Amer. Chem. Soc.*, 1930, **52**, 3317—3322).—The following aryl α -oximoalkyl ketones are prepared by the method previously described (A., 1929, 1066): phenyl α -oximopropyl, m. p. 49° ; p-tolyl α -oximopropyl, m. p. 78° ; phenyl α -oximobutyl, m. p. 69° ; phenyl α -oximinoamyl, m. p. $53-54^\circ$, and phenyl α -oximoheptyl ketones, m. p. 38.5° . These are reduced by hydrogen in presence of palladium and alcoholic hydrogen chloride to the following amino-alcohols: β -amino- α -phenylbutyl alcohol, m. p. $80.5-81^\circ$ (lit. $76-78^\circ$) (hydrochloride, m. p. 242°); β -amino- α -p-tolylbutyl alcohol, m. p. 85° (hydrochloride, m. p. 255°); β -amino- α -phenylamyl alcohol, m. p. $70-71^\circ$ (hydrochloride, m. p. 222°); β -amino- α -phenylhexyl alcohol, m. p. $72-72.5^\circ$ (lit. $65-66^\circ$) (hydrochloride, m. p. $197.5-198^\circ$), and β -amino- α -phenyloctyl alcohol, m. p. 79° (hydrochloride, m. p. 157.5°). β -Amino- α - β -diphenylethyl alcohol, m. p. 165° (hydrochloride, m. p. 235°), is prepared by similar reduction of α - or β -benziloxime. Phenyl heptyl ketone, b. p. $150-153^\circ/7$ mm. (semicarbazone, m. p. $125-125.5^\circ$), is obtained by the Friedel-Crafts reaction. Pharmacological data for the amino-alcohols are given; the toxicities of the alcohols increase with lengthening of the carbon chain.

H. BURTON.

Preparation of cyclopentane derivatives. W. R. EDWARDS, jun., and E. E. REID (*J. Amer. Chem. Soc.*, 1930, **52**, 3235—3241).—The following cyclopentylalkylcarbinols are prepared from magnesium cyclopentyl bromide and the requisite aldehyde: methyl, b. p. $85-85.5^\circ/52.5$ mm., d_4^{25} 0.9163 (3:5-dinitrobenzoate, m. p. 86° ; α -naphthylcarbimide derivative, m. p. 104°); ethyl, b. p. $97.5-98.5^\circ/52.5$ mm., d_4^{25} 0.9035, n 1.4502 (3:5-dinitrobenzoate, m. p. 83.5° ; α -naphthylcarbimide derivative, m. p. 91°); n-propyl, b. p. $114.5-115.5^\circ/52$ mm., d_4^{25} 0.8970, n 1.4510 (3:5-dinitrobenzoate, m. p. 85° ; α -naphthylcarbimide derivative, m. p. 85°); n-butyl, b. p. $114-115^\circ/23$ mm., d_4^{25} 0.8935, n 1.4548 (3:5-dinitrobenzoate, m. p. 63.5°); n-hexyl, b. p. $129.5-130.5^\circ/12-12.5$ mm., d_4^{25} 0.8848, n 1.4562. Phenylcyclopentylcarbinol has b. p. $129-131^\circ/5$ mm., d_4^{25} 1.0346. All m. p. and b. p. are corr. 2:5-Dibenzylidene- and 2:5-dianisylidene-cyclopentanones are formed as by-products when the reaction mixtures from magnesium cyclopentyl bromide and benzaldehyde and anisaldehyde, respectively, are decomposed with hydrochloric acid. These probably arise from cyclopentanone (in the cyclopentyl bromide used) which does not appear to react with the Grignard reagent.

H. BURTON.

Isomerisation of ergosterol. C. E. BILLS and F. G. McDONALD (*J. Biol. Chem.*, 1930, **88**, 337—346).—Fractional crystallisation from alcohol of the isomerides of ergosterol described by the author (this vol., 84) as also of the isoergosterol of Heilbron and Spring (*ibid.*, 210) afforded a number of (still impure) products with varying optical rotations, molecular extinction coefficients, and m. p.; the existence of numerous isomerides is thus indicated.

C. R. HARRINGTON.

ωωω-Trifluoro-*o*-toluic acid and ωωω-trifluoro-6-nitro-*m*-cresol. S. DE BROUWER (Bull. Soc. chim. Belg., 1930, 39, 298—308).—Prolonged hydrolysis of *o*-cyanobenzotrifluoride (Rouche, A., 1928, 876) with 10% sodium hydroxide solution affords ωωω-trifluoro-*o*-toluic acid, b. p. 247° (corr.)/753 mm., m. p. 108.5° [sodium (+2H₂O), lead (+2H₂O), barium (+2H₂O), calcium (+2H₂O), and silver salts; amide, m. p. 161°, prepared from the methyl ester, b. p. 207°/757 mm., 106°/20 mm., *d*¹⁸ 1.3062, and saturated ammonia solution at 110°]. The acid (*k*=2.57 × 10⁻³) is 15.7 times as strong as the *m*-isomeride and twice as strong as phthalic acid.

During the hydrolysis of the nitration product of *m*-acetamidobenzotrifluoride with 20% sodium hydroxide solution (Rouche, *loc. cit.*), some ωωω-trifluoro-6-nitro-*m*-cresol, b. p. 173°/14 mm., m. p. 78.5—79°, *k*=4.4 × 10⁻⁷ (barium salt), is produced. This is unaffected by chlorosulphonic acid at the ordinary temperature, sulphuric acid at 130—140°, or 75% hydrobromic acid in presence of silica at 140°.

H. BURTON.

Walden inversion. XIV. Influence of substituent groups on optical rotation in α-phenylaliphatic acids. P. A. LEVENE, L. A. MIKESKA, and K. PASSOTH (J. Biol. Chem., 1930, 88, 27—59).—The order of effect of substituent groups on optical rotation in the α-methyl-aliphatic acid series (this vol., 63) does not hold good for the corresponding α-phenyl series, in which the descending order is ·CO₂H, ·CHOH, ·CH₂Hal, ·CN; thus in the nitriles, substitution of methyl by phenyl actually reverses the direction of rotation. The *l*-nitriles obtained from *d*-α-phenylpropionic and *d*-α-phenylbutyric acids yield *l*- and *d*-amines, respectively, which apparently represents a change of reversal of rotation accompanying substitution of ethyl for methyl. *d*-α-Phenyl-*n*-valeric acid (itself related to *d*-α-phenyl-*n*-butyric and *d*-α-phenylpropionic acids) when hydrogenated gives *l*-α-cyclohexyl-*n*-valeric acid, from which the unexpected result follows that the latter is configuratively related to *d*-α-cyclohexyl-*n*-butyric and *d*-α-cyclohexylpropionic acids. In all series conversion of the *d*-carbinol into the halide has been accompanied by change of rotation towards the left, which confirms the conclusions of Levene and Mikeska (A., 1928, 170).

d-α-Phenylpropionic acid was resolved with the aid of quinine to give the *l*-acid, [α]_D²⁵ -59.7° in ether; this was converted successively into the *l*-chloride, [α]_D²⁵ -68.8° in ether, *l*-amide, m. p. 92°, [α]_D²⁵ -26.3° in 75% alcohol, *d*-α-phenylpropionitrile, b. p. 109°/8 mm., [α]_D²⁵ +12.7° in ether, *d*-β-phenyl-*n*-propylamine, b. p. 90°/12 mm., [α]_D²⁵ +12.4° in ether (hydrobromide, [α]_D²⁵ +16.4° in water). The latter amine gave, with nitrosyl chloride, *d*-α-chloro-β-phenylpropane, b. p. 52—54°/1 mm., [α]_D²⁵ +0.33° in ether, and *l*-β-phenyl-*n*-propyl alcohol, [α]_D²⁵ -16.3° in ether (isolated through the hydrogen phthalate, [α]_D²⁵ -16.5° in ether). The above chloro-compound yielded *d*-α-thiol-β-phenylpropane, b. p. 70—71°/1.5 mm., [α]_D²⁵ +9.3° in ether, whilst *d*-α-phenylpropionyl chloride, [α]_D²⁵ +44.9° in ether, afforded *d*-α-phenylthiopropionic acid, b. p. 136—138°/3 mm., [α]_D²⁵ +61.6° in ether. *dl*-α-Phenyl-*n*-butyric acid was converted through the cinchonidine salt into the *d*-acid, [α]_D²⁵ +81.0° in ether (sodium

salt, [α]_D²⁵ +8.2° in water; ethyl ester, b. p. 80—85°/3 mm., [α]_D²⁵ +72.2° in ether). From the *d*-acid were derived successively the *d*-chloride, [α]_D²⁵ +89.0° in ether, *d*-amide, [α]_D²⁵ +19.9° in 75% alcohol, *l*-α-phenylbutyronitrile, b. p. 56—57°/4.1 mm., [α]_D²⁵ -27.6° in ether, and *d*-β-phenyl-*n*-butylamine, b. p. 74°/2.6 mm., [α]_D²⁵ +9.7° in ether (hydrobromide, [α]_D²⁵ -2.1° in water). The amine yielded, with nitrosyl chloride, *d*-α-chloro-β-phenyl-*n*-butane (87% pure), b. p. 62—64°/1 mm., [α]_D²⁵ +11.2° in ether, and, with nitrous acid, *d*-β-phenyl-*n*-butyl alcohol, b. p. 95—96°/4 mm., [α]_D²⁵ +30.0° in ether; the chloro-compound afforded *d*-α-thiol-β-phenyl-*n*-butane, b. p. 81°/1.3 mm., [α]_D²⁵ +7.0° in ether (with the corresponding disulphide, b. p. 178—180°/1.5 mm., [α]_D²⁵ -31.1° in ether), which was oxidised to *l*-β-phenyl-*n*-butane-α-sulphonic acid (impure), [α]_D²⁵ -32.7° in water (barium salt, [α]_D²⁵ -27.6° in water); *l*-β-phenyl-*n*-butyryl chloride, [α]_D²⁵ -23.7° in ether, gave *l*-β-phenylthio-*n*-butyric acid, b. p. 124—125°/13 mm., [α]_D²⁵ -35.2° in ether. *l*-α-Phenylpropionic acid, [α]_D²⁵ -54.6° in ether, was reduced with hydrogen and platinum to *l*-α-cyclohexylpropionic acid, [α]_D²⁵ -12.5° in ether (sodium salt, [α]_D²⁵ -1.9° in water), from which were prepared the *l*-chloride, b. p. 54°/12 mm., [α]_D²⁵ -7.6° in ether, *l*-amide, m. p. 138—139°, [α]_D²⁵ -9.9° in 75% alcohol, *l*-α-cyclohexylpropionitrile, b. p. 80°/3 mm., [α]_D²⁵ -13.3° in ether, and β-cyclohexyl-*n*-propylamine, b. p. 65—66°/2 mm., which was optically inactive. *d*-α-Phenyl-*n*-butyric acid, [α]_D²⁵ +79.8° in ether, yielded *d*-α-cyclohexyl-*n*-butyric acid, [α]_D²⁵ +2.4° in ether, and *l*-α-phenyl-*n*-valeric acid, [α]_D²⁵ -16.3° in ether (from the *dl*-acid through the cinchonidine salt), gave *d*-α-cyclohexyl-*n*-valeric acid, [α]_D²⁵ +2.2° in ether. *d*-αβ-Diphenylpropionic acid, [α]_D²⁵ +36.6° in ether (from the *dl*-acid through the quinine salt), was converted successively into the *d*-chloride, [α]_D²⁵ +43.0° in ether, *d*-amide, m. p. 134°, [α]_D²⁵ +41.2° in 95% alcohol (partly racemised), and *l*-nitrile, [α]_D²⁵ -7.9° in alcohol. The inactive nitrile was reduced to αβ-diphenylpropylamine, which was resolved with the aid of tartaric acid to give the *l*-amine, [α]_D²⁵ +40.1° in ether; a preparation with [α]_D²⁵ +27.1° in ether gave, with nitrous oxide, *d*-αβ-diphenylpropanol, [α]_D²⁵ +18.6° in ether, and with nitrosyl chloride *d*-α-chloro-βγ-diphenylpropane, b. p. 130—132°/0.3 mm., [α]_D²⁵ +12.2° in ether; the latter yielded *l*-α-thiol-βγ-diphenylpropane, b. p. 123—127°/0.3 mm., [α]_D²⁵ +13.3° in ether, which was oxidised to *d*-βγ-diphenylpropane-sulphonic acid, [α]_D²⁵ +11.2° in water (barium salt, [α]_D²⁵ +11.5° in water).

C. R. HARRINGTON.

Optical resolution of 2:4-dinitro-2'-methyl-diphenyl-6-carboxylic acid. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1930, 1758—1765).—When equimolecular quantities of ethyl 2-chloro-3:5-dinitrobenzoate and iodobenzene are heated with copper-bronze at 220—240°, ethyl 2:4-dinitrodiphenyl-6-carboxylate, m. p. 84—85°, is produced as the sole product. The free acid, m. p. 193—194°, obtained only by hydrolysis of the ester with sulphuric and acetic acids, is converted by sulphuric acid at 100° into 2:4-dinitrofluorenone. *m*-Iodotoluene, ethyl 2-chloro-3:5-dinitrobenzoate, and copper-bronze at 220—230° give the ethyl ester, m. p. 120—121°, of

2:4-dinitro-3'-methyl-diphenyl-6-carboxylic acid, m. p. 118—119°. The above acids could not be resolved by brucine. When they are incompletely esterified with *l*-menthol, the unesterified acid is optically inactive. Ethyl 2:4-dinitro-2'-methyl-diphenyl-6-carboxylate, m. p. 95—96°, is hydrolysed as above to the free acid (I), m. p. 156—157°, which is resolved by brucine (using the fractional crystallisation method) into *d*- and *l*-isomerides, m. p. 158—159°, $[\alpha]_{5791} \pm 18.7^\circ$ in alcohol. Crystallisation of these from benzene gives optically active acids ($[\alpha]_{5791} \pm 7.8^\circ$ in alcohol) containing 0.5 mol. of benzene of crystallisation, which is not removed by repeated evaporation of alcoholic solutions. The acid remaining unesterified during partial esterification of I with *l*-menthol at 140° has $[\alpha]_{5791} + 2.8^\circ$ in acetone. Esterification of 2-chloro-3:5-dinitrobenzoic acid with *l*-menthol at 150° affords *l*-menthyl 2-chloro-3:5-dinitrobenzoate, m. p. 113—114°, $[\alpha]_{5791} - 53.6^\circ$ in acetone, which with *o*-iodotoluene and copper-bronze gives an ester, hydrolysed to 2:4-dinitro-2'-methyl-diphenyl-6-carboxylic acid, $[\alpha]_{5791} + 4.4^\circ$ in acetone; with iodo-benzene, only a very small amount of product results.

The above facts suggest that it is unnecessary to replace the theory explaining the resolution of 2-phenylnaphthylene-1:3-diamine (A., 1929, 1061) by a purely stereochemical one. H. BURTON.

Activated silica gel in the esterification of salicylic acid and of β -naphthol. R. CHELBERG and G. B. HEISIG (J. Amer. Chem. Soc., 1930, 52, 3023).—Commercial "silica gel" activated by treatment with air at 150°, unlike the product of Korolev (A., 1928, 637), failed to catalyse the reaction between methyl alcohol and salicylic acid or β -naphthol.

H. E. F. NOTTON.

Mutarotation of optically active esters of α -keto-acids. A. MCKENZIE and A. G. MITCHELL (Biochem. Z., 1930, 224, 242—252).—The authors' previous paper (A., 1929, 877) is extended. Both cinchonine and cinchonidine give crystalline derivatives with phenylglyoxylic acid; *cinchonidine phenylglyoxylate* has m. p. 176—177°, $[\alpha]_{5461} - 88^\circ$; *cinchonine phenylglyoxylate*, m. p. 258°, $[\alpha]_{5461} + 148.5^\circ$. Evidence of the existence in these products of two optically isomeric forms could not be obtained. The rates of mutarotation of the *d*- and *l*-bornyl pyruvates are the same after careful fractionation of these esters in a vacuum, the previous quicker mutarotation of the *d*-ester being due to the presence of a trace of some catalyst. The acceleration of mutarotation by hydrochloric acid and by pyridine of *l*-menthyl phenylglyoxylate and *d*- and *l*-bornyl pyruvate is followed. When two drops of 1.47*N*-ethyl-alcoholic potassium hydroxide are added to an alcoholic solution of *l*-menthyl phenylglyoxylate, an acceleration of mutarotation first occurs, followed by a gradual exchange of the menthyl for the ethyl radical.

P. W. CLUTTERBUCK.

Unsaturated 1:4-diketones. V. Configurations of unsaturated dibromo-1:4-diketones and -ketonic acids. Synthesis and structure of *cis*- and *trans*- $\alpha\beta$ -dibromo- β -benzoylacrylic acids and derivatives. VI. Synthesis and configurations of unsaturated 1:4-diketones and

ketonic acids, and the stereochemical mechanism of the addition of bromine. R. E. LUTZ (J. Amer. Chem. Soc., 1930, 52, 3405—3422, 3423, 3436).—V. Dibromomaleic anhydride and benzene in presence of aluminium chloride give *cis*- $\alpha\beta$ -dibromo- β -benzoylacrylic acid, m. p. 92° (all m. p and b. p. are corr. except where stated otherwise), esterified by methyl-alcoholic hydrogen chloride to the *methyl* ester, m. p. 71.5°. Hydrolysis of the ester with alcoholic sodium ethoxide at the ordinary temperature regenerates the acid, but with aqueous sodium hydroxide benzoic acid results. The dibromo-acid is stable towards reagents which usually effect isomerisation, it is reduced by zinc dust and acetic acid to β -benzoyl-propionic acid, and gives with phosphorus pentachloride the ψ -chloride, $\text{CPhCl}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}$, m. p. 82.5° which is hydrolysed only slowly by water. This chloride reacts with benzene in presence of aluminium chloride forming 2-bromo-1:1-diphenylindene-3-carboxylic acid, m. p. 242—243° (decomp.), oxidised by alkaline potassium permanganate to diphenylphthalide. The indene is also formed in small amount from benzene and dibromomaleic chloride. The ψ -chloride, m. p. 76°, from *cis*- $\alpha\beta$ -dibromo- β -2:4:6-trimethylbenzoylacrylic acid, m. p. 157°, obtained by the Friedel-Crafts reaction with dibromomaleic anhydride and mesitylene, reacts with mesitylene in presence of aluminium chloride and carbon disulphide, forming a small amount of a compound, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{Br}$, m. p. 240—242° (uncorr.).

Treatment of dibromofumaryl chloride with 1 equivalent of methyl alcohol in benzene gives the *chloride*, b. p. 83—86°/3.5 mm., of methyl hydrogen dibromofumarate (the *dimethyl* ester has b. p. 113—114°/5 mm., m. p. 41.5°), which gives with benzene and aluminium chloride the *methyl* ester, m. p. 80.5°, of *trans*- $\alpha\beta$ -dibromo- β -benzoylacrylic acid, m. p. 108° [normal acid *chloride*, b. p. 164° (uncorr.)/7 mm., m. p. 37°]. The *methyl* ester, m. p. 115.5—116°, of *trans*- $\alpha\beta$ -dibromo- β -2:4:6-trimethylbenzoylacrylic acid, m. p. 139° (acid *chloride*, m. p. 73—73.5°), is prepared similarly, using mesitylene diluted with carbon disulphide. The Friedel-Crafts reaction with dibromofumaryl or *trans*- $\alpha\beta$ -dibromo- β -benzoylacrylyl chloride and benzene affords the less fusible (*trans*) form of $\alpha\beta$ -dibromo- $\alpha\beta$ -dibenzoyl-ethylene (Conant and Lutz, A., 1925, i, 681), also obtained as the main product from dibenzoyl-ethylene and bromine in boiling chloroform. *cis*- $\alpha\beta$ -Dibromo- $\alpha\beta$ -dibenzoyl-ethylene (*loc. cit.*) is not rearranged into the *trans*-isomeride by treatment with aluminium chloride in benzene. *trans*- $\alpha\beta$ -Dibromo- $\alpha\beta$ -di-2:4:6-trimethylbenzoyl-ethylene, m. p. 198.5°, and *trans*- $\alpha\beta$ -dibromo- α -benzoyl- β -2:4:6-trimethylbenzoyl-ethylene, m. p. 102.5°, are prepared from mesitylene and dibromofumaryl and *trans*- $\alpha\beta$ -dibromo- β -benzoylacrylyl chloride, respectively, in presence of aluminium chloride and carbon disulphide.

VI. The *chloride*, b. p. 69.5°/14 mm., m. p. 16°, of methyl hydrogen fumarate, m. p. 144.5°, is converted as above into the methyl ester of *trans*- β -benzoylacrylic acid. The unstable *chloride* from this acid gives with benzene and aluminium chloride *trans*- $\alpha\beta$ -dibenzoyl-ethylene; the *cis*-form is isomerised under the same conditions. *Methyl trans*- β -2:4:6-tri-

methylbenzoylacrylate, m. p. 53°, is also described; when the free acid is esterified with methyl-alcoholic hydrogen chloride *methyl α-chloro-β-2 : 4 : 6-trimethylbenzoylpropionate*, m. p. 78°, is produced. *trans-αβ-Di-2 : 4 : 6-trimethylbenzoylethylene* is obtained together with a small amount of an acid, m. p. 217° (uncorr.), when *trans-β-2 : 4 : 6-trimethylbenzoylacrylyl chloride* reacts with mesitylene in presence of benzene and aluminium chloride.

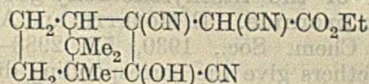
The normal $\alpha\beta$ -dibromo- β -benzoylpropionic acid, m. p. 150° (decomp.) (cf. Bougault, A., 1909, i, 102), obtained as the main product when bromine is added to *trans-β-benzoylacrylic acid* in acetic acid, is converted into the chloride and thence by the Friedel-Crafts reaction with benzene into *meso-αβ-dibromo-αβ-dibenzoylthane* (cf. A., 1927, 565). *iso-αβ-Dibromo-β-benzoylpropionic acid*, m. p. 150° (decomp.) (cf. Bogert and Ritter, A., 1925, i, 816), gives by the same series of reactions *dl-αβ-dibromo-αβ-dibenzoylthane*. These results show that under certain controlled conditions the addition of bromine to the dibenzoylthylenes is *trans*; addition to dibenzoylacetylene is *cis*. A third *bromo-β-benzoylacrylic acid*, m. p. 105°, is formed together with the known β -bromo-derivative when $\alpha\beta$ -dibromo- β -benzoylpropionic acid is treated with sodium acetate and carbonate in acetone containing a small amount of methyl alcohol.

The Friedel-Crafts reaction with diphenyl ether and fumaryl chloride yields *trans-αβ-di-p-phenoxybenzoyl-ethylene*, m. p. 170.5–171°, reduced by zinc and acetic acid to *αβ-di-p-phenoxybenzoylthane*, m. p. 160°. A small amount of *dl-αβ-dibromo-αβ-di-p-toluoylthane*, m. p. 138°, is obtained with much *meso*-form when *trans-αβ-di-p-toluoylthane* is treated with bromine in acetic acid. The Friedel-Crafts reaction with benzene and *trans-β-2 : 4 : 6-trimethylbenzoylacrylyl chloride* affords *trans-α-benzoyl-β-2 : 4 : 6-trimethylbenzoylethylene*, m. p. 61.5°, whilst benzene and maleic chloride furnish a small amount of *trans-γ-hydroxy-γγ-diphenyl-Δ-butenic acid*, m. p. 224° (decomp.). *αβ-Di-α-naphthoylthane* has m. p. 130–131°.

H. BURTON.

Condensation of benzoin and benzil with ethyl cyanoacetate. J. A. McRAE and A. L. KUEHNER (J. Amer. Chem. Soc., 1930, 52, 3377–3382).—Benzoin condenses with ethyl cyanoacetate in presence of alcoholic sodium ethoxide, forming α -cyano- γ -hydroxy- $\beta\gamma$ -diphenylcrotonolactone, m. p. 141°, and not $\alpha\delta$ -dicyano- $\beta\gamma$ -diphenyl- $\Delta\beta$ -butene- $\alpha\delta$ -dicarboxylic acid as stated by Haworth (J.C.S., 1909, 95, 480). The lactone is hydrolysed by slightly diluted sulphuric acid and at 130–140° to β -benzoyl- β -phenylpropionic acid, and converted by boiling nitric acid into α -cyano- β -benzoyl- β -m-nitrophenylacrylic acid, m. p. 218–220° (decomp.) after softening at 212°, which is oxidised by potassium permanganate in aqueous acetone to 3-nitrobenzil. Oxidation of the lactone with dilute nitric acid gives α -cyano- β -benzoylcinnamic acid ($+0.5C_6H_6$), m. p. 116–117° after softening at 112°, m. p. (benzene-free) 135–136°, also obtained by hydrolysis of *ethyl α-cyano-β-benzoylcinnamate*, m. p. 141°, which is prepared from benzil and ethyl cyanoacetate in presence of alcohol and a small amount of piperidine. The last-named ester and the above

lactone do not add hydrogen cyanide, but ethyl camphorylidencyanoacetate (Forster and Withers, J.C.S., 1912, 101, 1327) does so, yielding *ethyl 2 : 3-*



dicyano-2-hydroxy-1 : 7 : 7-trimethyldicyclo-(1 : 2 : 2)-heptane-3-cyanoacetate (I), m. p. 202–204°, $[\alpha]_D^{20} +115.1^\circ$. Benzoin methyl ether and ethyl cyanoacetate do not condense.

H. BURTON.

Reaction of sodium phenoxide with α -chloro- β -hydroxypropionic acid. C. F. KOEHLER (J. Amer. Chem. Soc., 1930, 52, 3364–3366).—The formation of α -hydroxy- β -phenoxy- (main product) and β -hydroxy- α -phenoxy-propionic acids from α -chloro- β -hydroxypropionic acid and sodium phenoxide is confirmed (cf. this vol., 1038).

H. BURTON.

Physical identity of enantiomerides. A. N. CAMPBELL and F. C. GARROW (Trans. Faraday Soc., 1930, 26, 560–564; cf. A., 1929, 1370).—Slight differences in m. p., solubility in water, rotatory dispersion, and numerical value of the rotatory power between *d*- and *l*-mandelic acids have been detected.

R. CUTHILL.

Anthracene-1-carboxylic and -1 : 5-dicarboxylic acids and their derivatives. E. A. COULSON (J.C.S., 1930, 1931–1936).—1 : 5-Dicyanoanthraquinone, obtained in 83% yield when 1 : 5-dichloroanthraquinone, phenylacetonitrile, and cuprous cyanide are heated at 230° (bath), is hydrolysed with slightly diluted sulphuric acid to the 1 : 5-dicarboxylic acid. Reduction of this with zinc dust and ammonia gives *anthracene-1 : 5-dicarboxylic acid*, m. p. above 360°, converted by way of the chloride (formed only by the action of phosphorus pentachloride at 150°) into the ethyl ester, m. p. 185°, which with magnesium methyl iodide yields 1 : 5-*di-α-hydroxyisopropylanthracene*, m. p. 182.5°; no reaction occurs with magnesium benzyl chloride. This diol is dehydrated by dissolution in boiling acetic acid to 1 : 5-diisopropenylanthracene, m. p. 121°; oxidised by chromic oxide in acetic acid to 1 : 5-diacetylanthraquinone, m. p. 317° after darkening above 280°. *Methyl anthracene-1-carboxylate*, m. p. 108°, forms resinous products with the above Grignard reagents. When treated with bromine in cold carbon disulphide it gives the unstable 9 : 10-dibromo-9 : 10-dihydro-derivative, which when crystallised from acetic acid passes into *methyl 10(or 9)-bromoanthracene-1-carboxylate*, m. p. 130°, and on treatment with pyridine furnishes unstable 1-carbomethoxy-9 : 10-dihydroanthranil-9 : 10-dipyridinium dibromide, m. p. 180°. This passes readily by loss of pyridine hydrobromide into 1-carbomethoxyanthranil-10(or 9)-pyridinium bromide, m. p. 271° (decomp.) (*dichromate*, m. p. 192°, from the bromide and aqueous potassium dichromate). Bromination of ethyl anthracene-1 : 5-dicarboxylate in boiling acetic acid gives a small amount of *ethyl 9-bromoanthracene-1 : 5-dicarboxylate*, m. p. 117°; prolonged action of chlorine in carbon tetrachloride furnishes impure, unstable 9 : 10-dichloride, m. p. 125°. *Ethyl anthraquinone-1 : 5-dicarboxylate* has m. p. 155°. The above anthracene-carboxylic esters and the diol show

brilliant purple fluorescence when illuminated by the carbon arc.

H. BURTON.

Scission of the methylenedioxy-group with aluminium bromide. E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1930, 52, 2988—2994).—Methylene ethers give the corresponding dihydroxy-derivatives when treated with aluminium bromide in nitrobenzene at 0° or 15° and subsequently with water. The highest yields are obtained when sufficient of the bromide is used to allow of the intermediate formation of a compound of the type $R \begin{matrix} \diagup O(AlBr_3) \\ \diagdown O(AlBr_3) \end{matrix} CH_2$.

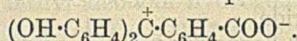
Methoxyl and ester groups are stable under these conditions and the ethylene ethers of pyrocatechol and protocatechuic acid are not attacked even at 130°. Dihydroxy-derivatives have been obtained, in the yields given in parentheses, from piperonaldehyde (82% of the theoretical), piperonylic acid (92%), methyl piperonylate (58%), acetopiperone (48%), and 4-nitropiperocatechol methylene ether (65%). *i*-Tetrahydroberberine is converted into the base, $C_{17}H_{13}N(OH)_2(OMe)_2$ (Späth and Mosettig, A., 1926, 965). 6-Nitropiperonaldehyde (Ekeley and Klemme, A., 1928, 1375), sodium phenylacetate, and zinc chloride in acetic anhydride give 2-nitro-4:5-methylenedioxy- α -phenylcinnamic acid, m. p. 193—195°, reduced by ferrous hydroxide and ammonia to the 2-amino-derivative, yellow, m. p. 201—203° (decomp.) (pink modification, yellow at 100°). This with nitrous acid and finely divided copper gives 2:3-methylenedioxy-phenanthrene-9-carboxylic acid (I), m. p. 259—260° (methyl ester, m. p. 151—151.5°), from which by the new method 2:3-dihydroxyphenanthrene-9-carboxylic acid (97%), decomp. 280°, is obtained. When distilled under reduced pressure, this gives 2:3-dihydroxy-phenanthrene, m. p. 158.5—159°. Decarboxylation of I gives 2:3-methylenedioxyphenanthrene, m. p. 93—94° (picrate, m. p. 151—152°), which, like safrole, isosafrole, piperonyl alcohol, and its benzoate, fails to give a crystalline product after treatment with aluminium bromide and water. H. E. F. NOTTON.

Constitution of phenolphthalein. II. Fading of phenolphthalein in alkaline solution. H. LUND (J.C.S., 1930, 1844—1852).—The velocity coefficients of the reversible reaction $C_{20}H_{12}O_4'' + OH' \xrightleftharpoons[k_{-1}]{k_1} C_{20}H_{13}O_5'''$, assumed to occur during the fading of phenolphthalein in alkaline solution, have been determined at 18° by spectrophotometric measurements. It is assumed that the concentration of the bivalent ion is proportional to the colour intensity, *i.e.*, the extinction. In aqueous sodium hydroxide solution k_1 increases more rapidly than the hydroxyl-ion concentration (cf. Biddle and Porter, A., 1915, ii, 539); in presence of 2*N*-sodium chloride k_1 is proportional to the hydroxyl-ion concentration and the absolute values are more than twice those in aqueous solution. The value of k_1 increases from 0.0015 in aqueous solution to 0.0043 in *N*-sodium chloride for 0.01*N*-sodium hydroxide, whereas k_{-1} increases only from 0.00065 to 0.00090. It is predicted that the forward reaction is rather sensitive to the presence of salts, whilst the reverse change is nearly independent of electrolytes.

Dimethylanilinephenolphthalein in an excess of

alkali fades considerably faster than phenolphthalein; the reverse reaction is slower. The salt effect is evaluated as being approximately half that for phenolphthalein. The above salt effects are in agreement with Brønsted's theory.

Various anomalies in the behaviour of phenolphthalein are explained by assuming that it has the character of an amphoteric ion,



H. BURTON.

Pyrocatecholsulphonephthalein. C. B. WOOD (J. Amer. Chem. Soc., 1930, 52, 3463—3464).—The colours obtained with pyrocatecholsulphonephthalein (cf. Moir, A., 1920, ii, 628) and solutions of varying p_a show a marked tendency to change, in some cases even after a few minutes. It is essential that the phthalein be prepared at a relatively low temperature; at 130—160° insoluble products result. H. BURTON.

Synthesis of cinnamaldehyde and its homologues. L. BERT and P. C. DORIER (Compt. rend., 1930, 191, 332—333).— γ -Chloroallylbenzene (A., 1925, i, 803) is converted by heating with potassium hydroxide (3 mols.) and an alcohol into a cinnamyl alkyl ether, from which cinnamyl chloride is formed by heating with concentrated hydrochloric acid under pressure. The cinnamyl chloride yields cinnamaldehyde when heated with hexamethylenetetramine in aqueous alcohol. The following homologues prepared by these methods are described: *cinnamyl chlorides*: *o*-methyl-, b. p. 123°/9.5 mm., d_4^{25} 1.071, n_D^{25} 1.575; *p*-methyl-, b. p. 132°/13 mm., d_4^{25} 1.0465, n_D^{25} 1.571; 2:4-dimethyl-, b. p. 135°/13 mm., d_4^{25} 1.110, n_D^{25} 1.566; 2:5-dimethyl-, b. p. 141°/17 mm., d_4^{25} 1.042, n_D^{25} 1.570; *p*-isopropyl-, b. p. 150°/13 mm., d_4^{25} 1.007, n_D^{25} 1.551; 2-methyl-5-isopropyl-, b. p. 154°/13 mm., d_4^{25} 1.002, n_D^{25} 1.550; *cinnamaldehydes*: *o*-methyl-, b. p. 137°/16 mm., d_4^{25} 0.9855, n_D^{25} 1.5623 (*semicarbazone*, m. p. 217°); *p*-methyl-, b. p. 147°/16 mm., d_4^{25} 0.967, n_D^{25} 1.547 (*semicarbazone*, m. p. 243°); 2:4-dimethyl-, b. p. 147°/15 mm., d_4^{25} 1.005, n_D^{25} 1.540 (*semicarbazone*, m. p. 231°); 2:5-dimethyl-, b. p. 151°/11 mm., d_4^{25} 0.9577, n_D^{25} 1.534 (*semicarbazone*, m. p. 256°); *p*-isopropyl-, b. p. 156°/17 mm., d_4^{25} 0.952, n_D^{25} 1.537 (*semicarbazone*, m. p. 219°); 2-methyl-5-isopropyl-, b. p. 162°/11—15 mm. (All b. p. are corrected, and m. p. by Maquenne block.)

R. K. CALLOW.

Ring enlargement with diazomethane in the hydroaromatic series. E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1930, 52, 3456—3463).—Treatment of cyclohexanone with ethereal methyl-alcoholic diazomethane first at 0° and then at the ordinary temperature gives cycloheptanone (main product), cyclooctanone, and the oxide, $C_5H_{10} > C \begin{matrix} \diagup O \\ \diagdown CH_2 \end{matrix}$. The oxide (not obtained pure) is isomerised by distillation over a small amount of zinc chloride into hexahydrobenzaldehyde, and gives with piperidine at 95—100°, 1-hydroxy-1-piperidinomethyl-cyclohexane (?) (*hydrochloride*, m. p. 194.5—195°). cyclopentanone is converted similarly into cycloheptanone (main product) and -octanone. The ketones do not react with diazomethane in absence of the methyl alcohol. H. BURTON.

Action of aluminium chloride on arylaliphatic, aliphatic, and hydroaromatic ketones in presence of tertiary aromatic amines. C. COURTOT and V. OUPEROFF (Compt. rend., 1930, 191, 416—418; cf. this vol., 1184).—Acetophenone and aluminium chloride in the presence of dimethylaniline yield 50% of triphenylbenzene, styryl methyl ketone gives non-basic resins, whilst phenyl styryl ketone at 30—40° affords a double compound with dimethylaniline (cf. A., 1923, i, 683), which undergoes fission at 91—92° to give leuco-malachite-green; α -indanone gives exclusively anhydrobisindanone and truxene. Acetone, with aluminium chloride and dimethylaniline at 10°, yields the ketol, $C_9H_{16}O_2$, which is probably the precursor of phorone (cf. Grignard and Fluchaire, A., 1928, 396); propione (diethyl ketone) at 40—50° gives 20% of dipropione alcohol identical with that obtained by Grignard and Fluchaire. Of the hydroaromatic ketones examined, only cyclohexanone reacts at 40—50° to give 1:1-tetramethyldiaminodiphenyl-cyclohexane, m. p. 158°; at 10—20° cyclohexylene-2-cyclohexanone is formed exclusively. cycloPentane at 15° yields no isolable product, but at 0° furnishes anhydrobiscyclopentanone; cycloheptanone yields cycloheptylenecycloheptanone, but camphor is unaffected.

C. W. SHOPPEE.

Cleavage of carbonyl compounds by alkalis.

I. Trihalogenomethyl ketones of the mesitylene series. R. C. FUSON and J. T. WALKER (J. Amer. Chem. Soc., 1930, 52, 3269—3275).—The fission of ketones by alkali is presumed to involve the addition of hydroxyl ion to the carbonyl carbon atom. If the substituents on the adjacent carbon atom are sufficiently "negative," dissociation then occurs. The 2:4:6-trimethylphenyl trihalogenomethyl ketones have been prepared and found to be stable towards alkali; this is attributed to inhibition of addition reaction at the carbonyl group through the presence of two *ortho*-substituents.

Treatment of acetomesitylene with sodium hypobromite solution at the ordinary temperature affords $\omega\omega\omega$ -tribromo-2:4:6-trimethylacetophenone (I), m. p. 68.5—69°, which with nitric acid (*d* 1.6) at 0° gives the 3:5-dinitro-derivative, m. p. 114.6—115.1° (corr.), also obtained from 3:5-dinitroacetomesitylene, m. p. 139.6—140.6° (corr.), and sodium hypobromite. Similar treatment of 2:4:6-trimethylphenacyl bromide also furnishes I, which when boiled with alcoholic silver nitrate and the mixture then decomposed with sodium hydroxide solution gives β -isodurylic acid. $\omega\omega\omega$ -Trichloro-2:4:6-trimethylacetophenone, b. p. 130—140°/5 mm., and its 3:5-dinitro-derivative, m. p. 100.1—100.6° (corr.), are prepared by analogous methods using sodium hypochlorite. H. BURTON.

Synthesis by means of magnesium amyl halides. **II. Reduction of benzophenone.** W. C. DAVIES, R. S. DIXON, and W. J. JONES (J.C.S., 1930, 1916—1921).—Treatment of magnesium *n*-amyl, *dl*- β -methylbutyl, or *iso*amyl bromide with benzophenone in ether gives benzhydrol (main product), benzpinacol, and the appropriate decane. The formation of these products is explained by the following changes (cf. Gomberg and Bachmann, A., 1927, 245, 1190; Blicke and Powers, this vol., 85; Gilman

and Brown, *ibid.*, 778): $R_2CO + C_nH_{2n+1} \cdot MgX \rightarrow \cdot C_nH_{2n+1} + \cdot CR_2 \cdot O \cdot MgX$ (I); $2 \cdot CR_2 \cdot O \cdot MgX \rightleftharpoons (CR_2 \cdot O \cdot MgX)_2 \rightarrow \begin{matrix} CR_2 \cdot O \\ | \\ CR_2 \cdot O \end{matrix} > Mg + MgX_2$;
 $2 \cdot C_nH_{2n+1} \rightarrow C_{2n}H_{4n+2}$; $C_nH_{2n+1} + \cdot CR_2 \cdot O \cdot MgX \rightarrow C_nH_{2n} + CHR_2 \cdot O \cdot MgX$. In the above reactions a deep red coloration is first produced, probably due to the formation of the ketyl I. H. BURTON.

Attempts to resolve derivatives of fluorene. ***p*-Aminobenzophenonehydrazone.** C. W. BENNETT and W. A. NOYES (J. Amer. Chem. Soc., 1930, 52, 3437—3440).—Reduction of 2-aminofluorenonehydrazone with zinc dust and acetic acid gives the *monoacetyl* derivative, m. p. 219°, of 2:9-diaminofluorene, which could not be resolved by means of *d*-camphorsulphonic acid, *d*- α -aminophenylacetic acid, or *d*-hydroxymethylencamphor. Nitration of 9-acetamidofluorene with nitric and sulphuric acids affords probably 1:8-dinitro-9-acetamidofluorene, m. p. 236—238° (cf. Schmidt and Stützel, A., 1910, i, 29).

p-Aminoacetophenonehydrazone, m. p. 139—140° (corresponding *azine*, m. p. 225°), is oxidised by mercuric oxide or mercury acetamide in various solvents forming a purple solution of the corresponding diazo compound; this decomposes readily to the above *azine*. H. BURTON.

Electrolytic reduction of ketones. **II. Formation of hydrocarbons.** G. SHIMA (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 315—322).—Optimum yields (60—90%) of hydrocarbons are obtained when ketones are reduced electrolytically in a modified form of the apparatus previously described (A., 1929, 521) using an amalgamated zinc cathode, a mixture of 70—85% sulphuric acid and alcohol as the cathode solution, a current strength of 15 amp., and a temperature of 65—75°. Thus, benzoin affords mainly dibenzyl together with small amounts of stilbene and deoxybenzoin (*p*-nitrophenylhydrazone, m. p. 163°); dibenzyl is also produced from benzil or deoxybenzoin. Benzophenone, *p*-methoxybenzophenone, phenyl *p*-tolyl, phenyl *p*-cymyl, and phenyl α -naphthyl ketones all give the corresponding methanes. The yield of benzyl-*o*-xylene, m. p. 33—34° (from phenyl *o*-xylyl ketone), is much smaller than those of benzyl-*m*- and -*p*-xylenes. H. BURTON.

Reduction of benzoin with sodium amalgam and alcohol. A. WEISSBERGER and H. BACH (J. pr. Chem., 1930, [ii], 127, 260—262).—Reduction of benzoin with 4% sodium amalgam and aqueous alcohol at 50° in an atmosphere of nitrogen gives much improved yields of hydro- and *isohydro*-benzoin. The small amount of by-product formed during the reduction (cf. Breuer and Zincke, A., 1880, 116) is probably benzoinpinacol, m. p. 249—250° (corr.) (lit. 233°), since when this is heated alone or with alcoholic potassium hydroxide, a mixture of benzoin and probably hydrobenzoin is obtained. H. BURTON.

Reactions of quinol and constitution of quinhydrone. T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 3204—3206).—Treatment of quinol with sodium iodate in cold, aqueous solution affords an almost quantitative yield of quinhydrone.

The yield is not so good in presence of acetic acid, whilst in presence of sodium hydroxide a brown dye results. Varying amounts of quinhydrone are also produced when quinol is oxidised with potassium permanganate and acetic acid, alkaline potassium ferricyanide, potassium persulphate, and potassium bromate. When quinol is treated with a hot solution of sodium iodate, a 40% yield of *p*-benzoquinone is produced.

Addition of dioxan to a saturated solution of quinol in ether precipitates an additive compound, probably $O_2C_6H_4 \cdot O \cdot OH \cdot C_6H_4 \cdot OH$, m. p. (sealed tube) 93—100°, the existence of which supports the analogous oxonium formula for quinhydrone (Richter, A., 1911, i, 136).
H. BURTON.

New synthesis in the 1:2-naphthanthraquinone series. H. WALDMANN (J. pr. Chem., 1930, [ii], 127, 195—200).—1:2-Naphthanthraquinones are prepared by ring closure of 1-benzoyl-2-naphthoic acids, which are obtained by the Friedel-Crafts reaction with benzene derivatives and naphthalene-1:2-dicarboxylic anhydride.

[With U. WEISS].—1:2-Dicyanonaphthalene is formed in 50% yield when small amounts of sodium 1-chloronaphthalene-2-sulphonate and dry potassium ferrocyanide are distilled in a current of carbon dioxide. Hydrolysis of the dinitrile with aqueous-alcoholic potassium hydroxide at 150° gives naphthalene-1:2-dicarboxylic acid, the anhydride of which reacts with benzene in presence of aluminium chloride, forming 1-benzoyl-2-naphthoic acid, m. p. 219—220°. Fusion of this with potassium hydroxide at 300° affords benzoic and β -naphthoic acids. Ring closure of the keto-acid is accomplished by phosphorus pentachloride at 120°, whereby 1:2-naphthanthraquinone, m. p. 168°, results. With sulphuric acid, ring closure is accompanied by sulphonation. The Friedel-Crafts reaction with naphthalene-1:2-dicarboxylic anhydride and chlorobenzene yields 1-*p*-chlorobenzoyl-2-naphthoic acid, m. p. 249° (potassium hydroxide fusion product, β -naphthoic acid), which when heated with phosphoric oxide gives 6-chloro-1:2-naphthanthraquinone, m. p. 222°. The chloro-compound gives a red vat with alkaline sodium hyposulphite.
H. BURTON.

Derivatives of naphthanthraquinone. H. WALDMANN (J. pr. Chem., 1930, [ii], 127, 201—209).—Various halogeno- and amino-naphthanthraquinones and condensation products of 6(or 7)-bromo-1:2-naphthanthraquinone with 1-amino- and 1:5-diamino-anthraquinones are described.

[With G. STESKAL].—4-Bromophthalic anhydride and naphthalene react in presence of benzene and aluminium chloride, forming 4(or 5)-bromo-2-naphthoylbenzoic acid, m. p. 208°, which when warmed with sulphuric acid at 58—60° gives (6 or 7)-bromo-1:2-naphthanthraquinone, m. p. 228°, together with a small amount of sulphonated product. Prolonged interaction of this bromo-derivative with 1-amino- and 1:5-diamino-anthraquinone in presence of naphthalene, sodium acetate, and copper chloride affords 6-(1-anthraquinonylamino)-1:2-naphthanthraquinone and 1:5-di-(6-naphthanthraquinonylamino)anthraquinone, respectively. These secondary amines dye

cotton with a red shade from an alkaline vat. Prolonged treatment of the bromo-derivative with concentrated ammonia and copper chloride at 190° yields 6(or 7)-amino-1:2-naphthanthraquinone, m. p. 240°, 3-Amino-1:2-, m. p. 254°, and 1:6(or 7)-diamino-2:3-naphthanthraquinones, m. p. 307°, are prepared similarly from 3-chloro-1:2-, m. p. 207.5° (Heller, A., 1912, i, 357), and 6(or 7)-chloro-1-hydroxy-2:3-naphthanthraquinones, respectively. The Friedel-Crafts reaction with 4-chlorophthalic anhydride and 1-chloronaphthalene gives 4(or 5)-chloro-2'-chloro-naphthoylbenzoic acid, m. p. 199°, converted by treatment with sulphuric acid at 65—75° into 3:6(or 7)-dichloro-1:2-naphthanthraquinone, m. p. 155°. Treatment of 4(or 5)-chloro-2-naphthoylbenzoic acid (G.P. 234,917) with sulphuric acid at 58—60° furnishes a chloronaphthanthraquinonesulphonic acid, which with sodium chlorate and dilute hydrochloric acid affords a dichloro-1:2-naphthanthraquinone, m. p. 204°. When 3:4:5:6-tetrachloro-2-naphthoylbenzoic acid is heated with phosphoric oxide and kieselguhr at 250°, 5:6:7:8-tetrachloro-1:2-naphthanthraquinone, m. p. 253°, results. The last-named substance is formed in small amount, together with a substance, m. p. 150°, when the keto-acid is heated in a current of carbon dioxide.
H. BURTON.

Bilirubin. II. Coloured oxidation stages of bilirubin and their behaviour with changes in hydrogen-ion concentration. III. Effect of radiated energy on bilirubin. IV. Solubility of bilirubin and of its coloured oxidation products, and their treatment with reducing and condensing agents. V. Properties of the bile pigments. VI. Detection and determination of bilirubin and of the coloured oxidation products. W. KERPPOLA and E. LEIKOLA (Skand. Arch. Physiol., 1929, 55, 70—77, 78—86, 87—90, 258—259, 260—265; Chem. Zentr., 1929, i, 1571—1572).—II. The colour of bilirubin varies with the p_H of the solution. On treating a solution in chloroform with increasing amounts of hydrochloric acid and sodium nitrite, the colour changes from reddish-yellow, through shades of violet, to ochre-yellow; finally, the solution is decolorised. The p_H values corresponding with each colour have been determined.

III. The colour of air-dried bilirubin and of a solution in glycerol is unchanged by exposure to ultra-violet light for many hours. In chloroform, the solution is decolorised in a few minutes. The same changes occur in all liquids, but the velocities are different. Daylight acts most strongly in alkaline solution. X-Rays and the radiations from radium act more slowly. The colours vary with the p_H of the solution.

IV. The effect of reducing and condensing agents on the colour of the oxidation products of bilirubin is tabulated.

V. In strongly alkaline solution, bilirubin reduces phosphotungstic acid to the blue pentoxide. Bilirubin and biliverdin both migrate to the anode.

VI. A critical discussion of the usual methods of determination.
L. S. THEOBALD.

Partial dehydrogenation of α - and β -amyrin. W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1930,

88, 137—152).— β -Amyrin benzoate, when heated with sulphur at 220—230°, yielded a *compound*, $C_{37}H_{48}O_2S$, m. p. 224—225°, $[\alpha]_D^{25} +96^\circ$ in pyridine, which was hydrolysed to a *compound*, $C_{30}H_{44}OS$, m. p. 200—201°, $[\alpha]_D^{25} +88^\circ$ in pyridine (also obtained directly by heating β -amyrin with sulphur at 200—210°). The above dehydroamyrin benzoate by oxidation with permanganate and hydrolysis with potassium hydroxide gave a *lactone*, $C_{30}H_{44}O_4$, m. p. 299—300° (decomp.), $[\alpha]_D^{25} -14^\circ$ in pyridine, and a *ketone*, $C_{30}H_{46}O_3$, m. p. 274—275°, $[\alpha]_D^{25} -127^\circ$ in pyridine. The lactone afforded an *acetate*, m. p. 269—271°, and a *benzoate*, m. p. 292—293° (also isolated from the crude oxidation product), and was hydrolysed with difficulty to the *acid*, m. p. 237—238°, $[\alpha]_D^{25} +96^\circ$ in pyridine. The ketone [*oxime*, m. p. 234—236° (decomp.); *acetate*, m. p. 231—232°; *benzoate* (also from above oxidation product), m. p. 261—262°, $[\alpha]_D^{25} -77^\circ$ in pyridine] was reduced with zinc and hydrochloric acid to a *compound*, $C_{30}H_{48}O_2$, m. p. 155—160° (impure), and was hydrogenated to a mixture of isomerides having the approximate empirical composition of amyrin. *Dehydro- α -amyrin benzoate*, $C_{33}H_{52}O_2$, m. p. 171—172°, $[\alpha]_D^{25} +304^\circ$ in pyridine, was obtained by heating α -amyrin benzoate with sulphur at 220—230° or by benzoylating the product which resulted from heating α -amyrin with sulphur at 200—210°, and was hydrolysed with alcoholic potassium hydroxide to *dehydro- α -amyrin*, $C_{30}H_{48}O$, m. p. 162—163°, $[\alpha]_D^{25} +358^\circ$ in pyridine; this was oxidised with chromic acid to *dehydro- α -amyrone*, $C_{30}H_{46}O$, m. p. 133—134°, $[\alpha]_D^{25} +412^\circ$ in pyridine [*oxime*, m. p. 233—235°]. C. R. HARRINGTON.

Saponins. V. Partial dehydrogenation of hederagenin. W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1930, 88, 153—161).—Hederagenin methyl ester and methyl hedraganate, $C_{31}H_{50}O_2$ (A., 1926, 1250), have both been hydrolysed by heating with 10% alcoholic potassium hydroxide at 120—130°, yielding in the latter case *hedraganic acid*, m. p. 242—243°. Methyl hedraganate gave, when heated with sulphur at 215—220°, a *compound*, $C_{31}H_{44}O_2S$, m. p. 137—138°, in which the sulphur and the ester group were both stable towards boiling alkali; oxidation of this compound with permanganate afforded a *lactone ester*, $C_{31}H_{44}O_5$, m. p. 274—275°, $[\alpha]_D^{25} -16^\circ$ in pyridine, and a *keto-ester*, $C_{31}H_{46}O_4$, m. p. 202—204°, $[\alpha]_D^{25} -184^\circ$ in pyridine [*oxime*, m. p. 236—237°]. Treatment of the lactone ester with dilute sodium hydroxide yielded the *lactone acid*, m. p. 255—256°, whilst hydrolysis with 10% potassium hydroxide also eliminated carbon dioxide giving the *acid*, $C_{29}H_{44}O_4$, m. p. 209—210°. Neither the lactone ester nor the keto-ester could be acylated. The keto-ester was hydrolysed with dilute sodium hydroxide to the *acid*, m. p. 184—185° (decomp.), and, with 10% potassium hydroxide, lost carbon dioxide to give a neutral *compound*, $C_{29}H_{42}O_2$, m. p. 262—264°. The degradation is evidently closely analogous to that of β -amyrin (cf. preceding abstract). The increased lability of the ester group in the products obtained by oxidative removal of sulphur from the compound $C_{31}H_{44}O_2S$ suggests that the sulphur in the latter is attached to that carbon atom which forms the lactone

and the carbonyl groups of the respective oxidation products. C. R. HARRINGTON.

Optical activity and the polarity of substituent groups. XIV. Influence of substituent poles and dipoles on the rotatory power of menthyl acetate. H. G. RULE, R. H. THOMPSON, and (in part) A. ROBERTSON (J.C.S., 1930, 1887—1894).—The values previously obtained (A., 1925, ii, 1120) for the rotatory powers of *l*-menthyl esters of mono-substituted acetic acids are discussed in conjunction with the dipolar character of the substituents. Introduction of an electronegative substituent is regarded as creating a positive field, and an electro-positive substituent a negative field, in that part of the molecule to which it is attached. The magnitude of the negative rotatory power of a *l*-menthyl acetate rises with increasing strength of the positive field exerted at the asymmetric atom by the substituent; conversely, a negative field will lead to a diminished rotatory power. These deductions are illustrated by the following observations. The rotatory power of sodium *l*-menthyl malonate (superimposed negative field caused by ionisation) is lower than that of the hydrogen ester. The value for *l*-menthyl dimethylaminoacetate, b. p. 132°/9 mm., $d_{40}^{20} 0.9357$, $[M]_{5461}^{20} -185.5^\circ$, -201° in alcohol, is slightly lower than that for *l*-menthyl acetate, but increases for the *hydrochloride*, m. p. 169°, $[M]_{5461}^{20} -207^\circ$ in alcohol, and the *methiodide*, m. p. above 250°, $[M]_{5461}^{20} -208^\circ$ in alcohol. A similar relationship exists for *l*-menthyl diethylaminoacetate, b. p. 142.5—143°/9 mm., its *hydrochloride*, m. p. 127° (lit. 108°), and *methiodide*, m. p. 161—162° (lit. 157°). *l*-Menthyl chloroacetate and aqueous-alcoholic sodium sulphite give *l*-menthyl sulphoacetate (+2H₂O), $[M]_{5461}^{20} -210^\circ$ in water, the rotatory power of which is somewhat high. This relatively high value may be partly due to the powerful electronegative character of the sulpho-group, which contains two semipolar double linkings arranged with their positive poles directed towards the menthyl group. H. BURTON.

Optical activity and the polarity of substituent groups. XV. Phenyl-substituted esters and ethers of *l*-menthol and β -octyl alcohol. H. G. RULE and J. BAIN (J.C.S., 1930, 1894—1903).—The *l*-menthyl and β -octyl ethers of mono-, di-, and tri-phenylcarbinol, and the β -octyl esters of mono-, di-, and tri-phenylacetic acid have been prepared and their rotatory powers determined for light of four different wave-lengths. Comparison with the analogous non-phenylated compounds shows that the rotatory power increases with successive introduction of two phenyl groups and then decreases with a third phenyl group. With the exception of *l*-menthyl triphenylmethyl ether, this decrease is so pronounced that an inversion of sign results. The variations in rotatory powers of the phenylated acetic acids do not correspond with alterations in the strengths of the acids; molar conductivity determinations with aqueous-alcoholic solutions of the acids at 20° show that triphenylacetic acid is the strongest of the series. The statements in the literature (Elbs and Toller, A., 1886, 352; Schmidlin and Hodgson, A., 1908, i, 170) describing it as an extremely weak

acid are, therefore, incorrect. The diminished rotatory powers of compounds containing the triphenylmethyl group are assumed to be due to the close proximity of this group and the active complex. The abnormally low rotatory power of *l*-menthyl δ -phenylvalerate (Rupe and Münter, A., 1909, i, 928) is probably due to the proximity of the phenyl and menthyl groups, owing to the normal bending of the carbon chain.

The following ethers are prepared from the requisite chloride and alcohol: *l*-menthyl triphenylmethyl, m. p. 136°; *triphenylmethyl* 1- β -octyl, b. p. 178°/0.3 mm., d_4^{16} 1.026; *d*-bornyl triphenylmethyl, m. p. 116°; *l*-menthyl diphenylmethyl, m. p. 67°; *diphenylmethyl* 1- β -octyl, b. p. 202°/10 mm., d_4^{17} 0.9675; *benzyl* 1- β -octyl, b. p. 154°/18 mm., d_4^{20} 0.8974. 1- β -Octyl phenylacetate, b. p. 174°/12 mm., d_4^{20} 0.9578, *d*- β -octyl diphenylacetate, b. p. 221°/17 mm., d_4^{15} 0.9974, and *d*- β -octyl triphenylacetate, b. p. 206°/0.03 mm., are obtained by the acid chloride method.

H. BURTON.

Preparation of thymol from piperitone. S. KIMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 301B).—Pure *l*-piperitone may be extracted from eucalyptus oil by treatment with a concentrated solution of resorcinol or sodium salicylate followed by steam-distillation.

The oxidation of piperitone with ferric chloride in acetic acid solution using manganese salts as catalyst gives a maximal yield of 48–53% of thymol during 5–6 hrs. heating with gentle boiling. The concentration of acetic acid had no influence at above 20%, and the yield of thymol at first increased with increasing amount of ferric chloride, but decreased with a large excess.

C. W. SHOPPEE.

Reduction of piperitone with aluminium amalgam. S. KIMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 301–302B).—*l*-Piperitone is reduced by aluminium amalgam to a ketone, $C_{20}H_{34}O_2$, m. p. 125–126°, but sodium amalgam affords the ketone $C_{20}H_{34}O_2$, m. p. 166–167°, also obtained together with the isomeride, m. p. 135–136°, from *dl*-piperitone by reduction with aluminium amalgam; the isomerides, m. p. 166–167° and 135–136°, are identical with the ketones previously obtained by Smith and Penfold (1921) by reduction of piperitone with sodium or sodium amalgam. The use of aluminium amalgam appears to avert racemisation.

C. W. SHOPPEE.

Oxidation of *d*- Δ^3 -carene and α -pinene with benzoyl hydrogen peroxide and peracetic acid. B. A. ARBUSOV and B. M. MICHAÏLOV (J. pr. Chem., 1930, [ii], 127, 1–15).—Partly an account of work previously reviewed (this vol., 1044). The following is new. Oxidation of *d*- Δ^3 -carene with peracetic acid in acetic acid solution gives mainly the acetate, b. p. 134–141°/11 mm. (probably a mixture), of *d*- Δ^3 -carene β -glycol. When the oxidation is carried out in ether the chief product is *d*- Δ^3 -carene oxide, b. p. 75.5–77°/10 mm., identical with that previously described (*loc. cit.*); a very small amount of glycol acetate is produced. These results do not agree with Böeseken's views (A., 1928, 734) of the mode of action of peracetic acid. It is, however, pointed out that,

unlike Böeseken, the authors have used peracetic acid free from sulphuric acid.

α -Pinene is oxidised by peracetic acid in ether to the oxide (88.6% of the theoretical); in chloroform, a mixture of the oxide (main product), glycol acetate, and high-boiling material results. Similar high-boiling products are formed when α -pinene oxide is treated with acetic acid. Prolonged treatment of *d*- Δ^3 -carene oxide with acetic acid containing a small amount of sulphuric acid gives mainly unchanged material together with a small amount of high-boiling material (not identical with the glycol acetate).

H. BURTON.

Transformation of camphene into isobornyl esters and decomposition of bornyl and isobornyl esters to camphene. G. BRUS and J. VÉBRA (Compt. rend., 1930, 191, 267–270).—The reaction between camphene and formic or acetic acid in presence of phosphoric or 50% sulphuric acid is shown to be reversible. Quantitative yields of isobornyl formate or acetate are, therefore, not obtained. The yields of crude products are, however, 94–98%. When isobornyl formate (10 parts) is distilled with phosphoric acid (1 part) at 20 mm., formic acid, camphene (86% of the theoretical amount), and a small amount (7%) of a diterpene, $C_{20}H_{32}$, b. p. 125–130°/1 mm., are obtained. Bornyl formate and acetate, and isobornyl acetate are decomposed similarly, and sulphuric acid, zinc chloride, or antimony trichloride can be used in place of phosphoric acid.

H. BURTON.

Solubilisation of some metallic salts of camphorcarboxylic acid in organic solvents. M. PICON (Compt. rend., 1930, 191, 137–139).—The neutral anhydrous camphorcarboxylates of neodymium, cerium, bismuth, gold, and uranium are soluble in the usual organic solvents and in olive oil. The camphorcarboxylates of calcium, copper, zinc, lead, and mercury become soluble after treatment with boiling benzene; such treatment does not increase the solubilities of the sodium, magnesium, and manganese salts.

C. C. N. VASS.

Treatment of cedrene with mercuric acetate. J. BELL (J.C.S., 1930, 1908–1910).—Prolonged treatment of cedrene with aqueous mercuric acetate affords an organo-mercury compound, $C_{16}H_{28}O_6Hg_2$, m. p. 193–195° (decomp.), which is possibly a mixture, mercurous acetate being precipitated. Oxidation of cedrene with mercuric oxide in glacial acetic acid gives a saturated alcohol, $C_{15}H_{26}O$, b. p. 140–150°/10 mm., d_4^{20} 0.9872, n_D^{20} 1.5071, which is probably the same product as is obtained by oxidation of cedrene with hydrogen peroxide (Henderson and Sword) and apparently identical with ψ -cedrol (Semmler and Mayer, A., 1912, i, 479).

J. W. BAKER.

Sagittol. A new sesquiterpene alcohol. E. YANOVSKY (J. Amer. Chem. Soc., 1930, 52, 3446–3448).—Distillation of the roots of *Balsamorhiza sagitta* (Pursh), Nutt., with steam gives about 0.5% (of dry cortex) of sagittol, $C_{15}H_{26}O$, m. p. 77–78°, $[\alpha]_D^{25} +26.15^\circ$ in alcohol (acetate).

H. BURTON.

Caryophyllene series. III. Clovene alcohol and α -caryophyllene alcohol. J. BELL and G. G. HENDERSON (J.C.S., 1930, 1971–1975).—The liquid

by-product obtained in the preparation of caryophyllene dihydrochloride (A., 1929, 931) is now shown to be a monohydrochloride, since it is converted by the action of silver acetate in glacial acetic acid and subsequent hydrolysis into a mixture of clovene and a tricyclic sesquiterpene alcohol, $C_{15}H_{26}O$, b. p. 146—154°/10 mm., d_4^{17} 0.9934, n_D^{17} 1.5039. The same alcohol is obtained by similar action of silver acetate on the product obtained by saturating clovene in dry ether with dry hydrogen chloride at 0°. Dehydration of α -caryophyllene alcohol either with phosphoric oxide or anhydrous oxalic acid yields a hydrocarbon the physical constants of which, b. p. 118—123°/12 mm., d_4^{17} 0.9252, n_D^{17} 1.5000, are closely similar to those of clovene. The action of phosphorus pentachloride on α -caryophyllene alcohol affords no crystalline chloro-derivative similar to that obtained from the β -alcohol (Wallach and Walker, A., 1893, i, 101), indicating that the α - and β -alcohols are structural isomerides. This view is confirmed by oxidation of the two alcohols with Beckmann's chromic acid mixture. β -Caryophyllene alcohol gives a viscous oily acid, $C_{10}H_{12}O_3$ (methyl ester, b. p. 170—180°/10 mm.; silver salt), whilst α -caryophyllene alcohol yields a crystalline dicarboxylic acid, $C_{13}H_{24}O_4$, m. p. 187° (yielding an anhydride, m. p. 49.5°, when heated above its m. p.), identical with an acid obtained by similar oxidation of the sesquiterpene by-product formed in the hydration of caryophyllene (Ruzicka). J. W. BAKER.

α -Tetrahydrofurfuryl chloride and ethers. W. R. KIRNER (J. Amer. Chem. Soc., 1930, 52, 3251—3256).— α -Tetrahydrofurfuryl chloride, b. p. 149—149.5°/721 mm., d_4^{20} 1.1102, n_D^{20} 1.4560, prepared from the corresponding alcohol by Darzens' method, is more stable and less reactive than furfuryl chloride. The following α -tetrahydrofurfuryl alkyl ethers are prepared from tetrahydrofurfuryl alcohol and the requisite alkyl halide (usually bromide) in presence of powdered potassium hydroxide: methyl, b. p. 140—141°/715.5 mm., d_4^{20} 0.9640, n_D^{20} 1.4292; ethyl, b. p. 152—154°/726 mm., d_4^{20} 0.9386, n_D^{20} 1.4298; n-propyl, b. p. 175—176.5°/728 mm., d_4^{20} 0.9248, n_D^{20} 1.4313; n-butyl, b. p. 194.5—196°/721 mm., d_4^{20} 0.9150, n_D^{20} 1.4357; isoamyl, b. p. 209—210° (corr.)/718 mm., 86.5—87.5°/10 mm., d_4^{20} 0.9040, n_D^{20} 1.4370; n-hexyl, b. p. 231—233°/708 mm., 107.5—108.5°/10 mm., d_4^{20} 0.9019, n_D^{20} 1.4407; allyl, b. p. 179.5—181°/707 mm., d_4^{20} 0.9571, n_D^{20} 1.4498, and benzyl, b. p. 141.5—143°/10 mm., d_4^{20} 1.0484, n_D^{20} 1.5174. Several of the ethers show anæsthetic action when injected peritoneally into mice and guinea-pigs. H. BURTON.

Methylfurfuraldehyde oxide as a by-product in the preparation of hydroxymethylfurfuraldehyde. J. P. C. CHANDRASENA (J.C.S., 1930, 2035).—In the preparation of hydroxymethylfurfuraldehyde by heating together sucrose and oxalic acid in aqueous solution under 3 atm. pressure (Troje, A., 1925, ii, 1210) a by-product, $C_{12}H_{10}O_5$, m. p. 120°, apparently identical with methylfurfuraldehyde oxide (Kiermayer, A., 1896, i, 144), is obtained. Oxidation with cold alkaline permanganate or 2N-nitric acid converts it into oxalic acid, but hot alkaline permanganate gives an unidentified substance, not melting at 250°. J. W. BAKER.

Preliminary formation of additive compounds in substitution reactions of aromatic types.
Bromination of ethyl 2-furylacrylate. H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 3349—3353).—When ethyl β -2-furylacrylate (1 mol.) is treated with bromine (1 mol.) in carbon disulphide at the ordinary temperature and the solution cooled to -10° , a dibromide, m. p. 70°, separates. Treatment of this with zinc dust and alcohol regenerates the original ester, whilst decomposition with alcoholic potassium hydroxide and subsequent hydrolysis affords 5-bromofurylacrylic acid (this vol., 479). The dibromide readily loses hydrogen bromide yielding ethyl 5-bromofurylacrylate. H. BURTON.

Tea tannin from green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 63—69).—From green tea a new tannin has been isolated (procedure described in detail) closely resembling that described by Deuss (A., 1923, i, 1046). Tea tannin, $C_{22}H_{18}O_{10}$ (+2H₂O), $[\alpha]_D^{25}$ -162.5° in alcohol, gives a blue colour with ferric chloride, but not the flavone reaction with magnesium and hydrochloric acid; it is gradually oxidised in air. By hydrolysis with 5% sulphuric acid it affords gallic acid, m. p. 237°, and a reddish-brown substance which yields phloroglucinol when heated with 50% potassium hydroxide at 180°. Treatment of the tannin with cold acetic anhydride and a trace of sulphuric acid or with acetic anhydride and anhydrous sodium acetate at 100° yields a hepta-acetyl derivative, $C_{22}H_{11}O_3(OAc)_7$, $[\alpha]_D^{25}$ -100° in benzene, which appears to contain 0.5—1 mol. H₂O. It is suggested that tea tannin is the gallic ester of tea catechin (cf. A., 1929, 934). C. W. SHOPPEE.

Synthesis and constitution of scutellarein. F. WESSELY and G. H. MOSER (Monatsh., 1930, 56, 97—105; cf. Robinson and Schwarzenbach, this vol., 785).—2:5-Dimethoxyresorcinol (Baker, Noduz, and Robinson, A., 1929, 326) is converted into 2:4-dihydroxy-3:6-dimethoxyacetophenone, m. p. 129°, by condensation with acetonitrile in presence of zinc chloride and ethereal hydrogen chloride. When this is heated with anisic anhydride and potassium anisate at 180—185° and the resulting product hydrolysed with aqueous-alcoholic sodium hydroxide, 5:7-dihydroxy-6:4'-dimethoxyflavone, m. p. 219° (slight decomp.) (diacetate, m. p. 149—150°), is obtained. This is demethylated by boiling hydriodic acid (d 1.7) to 5:6:7:4'-tetrahydroxyflavone, the tetra-acetate of which is identical with natural scutellarein acetate. Methylation of the dimethoxy-derivative with ethereal methyl-alcoholic diazomethane affords 5-hydroxy-6:7:4'-trimethoxyflavone, m. p. 188—189° (acetate, m. p. 169°), identical with the trimethyl ether from scutellarein, whilst methylation with an excess of methyl sulphate and potassium hydroxide in acetone at 60° furnishes 5:6:7:4'-tetramethoxyflavone, two modifications, m. p. 142° and 161°.

7-Hydroxy-5:8:4'-trimethoxyflavone, m. p. 258° (slight decomp.) (acetate, m. p. 194.5°), was isolated in one case from the condensation of the above acetophenone with anisic anhydride and potassium

anisate. When this was demethylated with hydriodic acid (d 1.7) and the product then acetylated, scutellarein tetra-acetate was obtained. 5:7:8:4'-*Tetra-methoxyflavone* has $m. p.$ 207—208°. H. BURTON.

5-Thiofluran. II. Action of phthaloyl chloride on *p*-bromoanisole and *p*-bromophenyl methyl sulphide. W. KNAPP (Monatsh., 1930, 56, 106—112).—*p*-Bromophenyl methyl sulphide reacts with phthaloyl chloride in presence of carbon disulphide and aluminium chloride at 40—50°, forming 2:8-dibromo-5-thiofluran, $m. p.$ 214—216° (cf. A., 1929, 186). Reduction of this with sodium amalgam and sodium in boiling alcohol affords 5-thiohydrofluoranic acid, $m. p.$ 215—216°, both bromine atoms being replaced by hydrogen. When an aqueous-alkaline solution of this acid is boiled for a long time in presence of air, 5-thiofluran, $m. p.$ 174—175° (corresponding sulphoxide, $m. p.$ 266—268°), is obtained.

p-Bromoanisole and phthaloyl chloride react as above furnishing 3':3'-dibromo-6':6''-dimethoxydiphenylphthalide, $m. p.$ 214—216°. H. BURTON.

Pyrrolidine derivatives from ethyl $\alpha\alpha'$ -dibromoadipate and secondary amines. R. C. FUSON and R. A. CONNOR (J. Amer. Chem. Soc., 1930, 52, 2985—2987).—The failure of dimethylamine to effect the cleavage of ethyl $\alpha\alpha'$ -dibromoadipate (cf. von Braun, Leistner, and Münch, A., 1926, 1128) is explained by the fact that the main product in this case is a salt-like substance, believed to be 2:5-dicarbethoxy-1:1-dimethylpyrrolidinium bromide, which, when distilled under reduced pressure, yields ethyl 1-methylpyrrolidine-2:5-dicarboxylate (cf. von Braun and Seeman, A., 1923, i, 1242; Le Sueur and Haas, J.C.S., 1910, 97, 173). H. E. F. NOTTON.

Action of Grignard reagents on *N*-methyl pyrrolidone. **Synthesis of substituted pyrrolines.** R. LUKES (Coll. Czech. Chem. Comm., 1930, 2, 531—544).—Grignard reagents react with *N*-methylpyrrolidone to give generally a mixture of monoalkyl- Δ^2 -pyrrolines (separated first as perchlorates) and dialkylpyrrolidines (subsequently isolated as picrates); a mechanism for the reaction is suggested. Thus magnesium methyl bromide and *N*-methylpyrrolidone, $b. p.$ 200°, d_4^{20} 1.0450, n_D^{20} 1.47118 (best prepared by electrolytic reduction of *N*-methylsuccinimide), at the ordinary temperature give 1:2-dimethyl- Δ^2 -pyrroline, $b. p.$ 125—127° [perchlorate, $m. p.$ 238°; chloroaurate, $m. p.$ 135—182° (decomp. : depends on the rate of heating); chloroplatinate], and 1:2:2-trimethylpyrrolidine, $b. p.$ 130—135° (picrate, decomp. about 250°); if the reaction mixture is warmed for several hours a small quantity of a base, $C_8H_{17}N$, $b. p.$ 146° (perchlorate, decomp. about 234°), is also formed. Magnesium ethyl bromide similarly yields 1-methyl-2-ethyl- Δ^2 -pyrroline, $b. p.$ 40—41°/10 mm., d_4^{20} 0.8779, n_D^{20} 1.48422 (perchlorate, $m. p.$ 209°; chloroaurate, $m. p.$ 115—117°), and 1-methyl-2:2-diethylpyrrolidine, $b. p.$ 168° (corr.) [hydrochloride; picrate, $m. p.$ about 235° (decomp.); chloroaurate, $m. p.$ 159—163°; chloroplatinate], whilst magnesium *n*-propyl bromide gives 1-methyl-2-*n*-propyl- Δ^2 -pyrroline, $b. p.$ 82°/30 mm.

(perchlorate), and 1-methyl-2:2-di-*n*-propylpyrrolidine, $b. p.$ 206.8°/738 mm. (corr.) (picrate).

Interaction between *N*-methylpyrrolidone (1 mol.) and magnesium phenyl bromide (3 mols.) yields only 2-phenyl-1-methylpyrroline, $b. p.$ 112°/15 mm., d_4^{20} 1.0083, n_D^{20} 1.57578 (hydrochloride + H_2O , $m. p.$ about 96°; perchlorate, $m. p.$ 117—118°; chloroaurate + H_2O , $m. p.$ 95—97°; chloroplatinate; picrate, $m. p.$ 140—141°). A. I. VOGEL.

Preparation of oxindoles and iodindoles. Q. MINGOIA (Gazzetta, 1930, 60, 509—515).—Indole and aqueous mercuric acetate give indole 2:3-dimercuriacetate, converted by hot saturated sodium chloride solution into indole 2:3-dimercurichloride, which with iodine in potassium iodide solution affords 2:3-di-iodindole, $m. p.$ 220° (decomp.). 3-Methylindole similarly gives 3-methylindole 2-mercuriacetate, converted successively into the chloride and 2-iodo-3-methylindole, $m. p.$ 197—198°, and 2-methylindole yields 2-methylindole mercuriacetate, giving successively the chloride and 3-iodo-2-methylindole, $m. p.$ 82°. These iodindoles are unaffected by moist silver oxide or by aqueous or alcoholic alkali; the above mercury compounds all decompose without melting.

C. W. SHOPPEE.

ortho- and para-Bz-Chloronitroquinolines. E. FOURNEAU, (M.) TRÉFOUËL, (MME.) TRÉFOUËL, and A. WANCOLLE (Bull. Soc. chim., 1930, [iv], 49, 738—755).—Seven of the eight possible chloronitroquinolines containing the chlorine and nitro-group in *o*- or *p*-positions to one another in the benzene ring have been synthesised by the Skraup-Knuessel reactions. 8-Chloro-5-nitroquinoline, $m. p.$ 145°, was obtained in 63% yield from 6-chloro-3-nitroaniline, or in 82.5% yield by nitration at 0° to -5° of 8-chloroquinoline, $b. p.$ 288°/760 mm., 163°/20 mm., similarly obtained in 55% yield from *o*-chloroaniline. 6-Chloro-3-nitroaniline, $m. p.$ 119°, was obtained in 77% yield by nitration of *o*-chloroaniline sulphate at 0°. 6-Chloro-5-nitroquinoline, $m. p.$ 129°, is similarly obtained from *p*-chloroaniline either together with an orange-yellow sulphate (?), $m. p.$ 155°, and a basic precipitate, $m. p.$ 126°, by nitration of 6-chloroquinoline, $m. p.$ 41—42°, $b. p.$ 159°/45 mm. (obtained in a yield of 85—88%), or together with 6-chloro-7-nitroquinoline, $m. p.$ 160°, by the Skraup reaction on 4-chloro-3-nitroaniline, $m. p.$ 103°, obtained in 70% yield by nitration of *p*-chloroaniline sulphate at 0°. 5-Chloro-8-nitroquinoline, $m. p.$ 136°, is obtained from *m*-chloroaniline, $b. p.$ 127°/33 mm., 230°/767 mm., either by nitration of the *m*-chloroacetanilide, $m. p.$ 78°, at -10° to 15°, hydrolysis of the 5-chloro-2-nitroacetanilide, $m. p.$ 118° (after separation of the 3-chloro-4-nitroacetanilide, $m. p.$ 144°, also formed), with 50% hydrochloric acid and condensation of the 5-chloro-2-nitroaniline, $m. p.$ 125° (yield 80.3%), or together with 7-chloro-8-nitroquinoline, $m. p.$ 186°, by nitration of the mixture of 5- and 7-chloroquinolines, $b. p.$ 144°/16 mm., obtained in 86.6% yield from *m*-chloroaniline. The constitution of 5-chloro-8-nitroquinoline is confirmed by its synthesis from 2:5-dichloroaniline. 5-Chloro-6-nitroquinoline, $m. p.$ 153°, is obtained, together with 7-chloro-6-nitroquinoline, $m. p.$ 155—156°, from 3-chloro-

4-nitroaniline, m. p. 157°, obtained by hydrolysis of 3-chloro-4-nitroacetanilide, m. p. 144°, also formed in the nitration of *m*-chloroacetanilide. On reduction and elimination of the amino-group it is converted into 5-chloroquinoline, a reaction which establishes its structure. The structure of 7-chloro-6-nitroquinoline is similarly established by its conversion into 7-chloroquinoline and 7-chloro-8-nitroquinoline.

R. BRIGHTMAN.

Stereoisomerism in polycyclic systems. VII. Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline. S. G. P. PLANT and R. J. ROSSER (J.C.S., 1930, 1840—1844).—Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline with sodium and boiling alcohol yields approximately equal amounts of the two stereoisomeric (*cis*- and *trans*-) forms, *A*, m. p. 61.5° (hydrochloride, m. p. 244—245°; *picrate*, m. p. 167—168°; *phenylcarbamyl*, m. p. 144°, and *benzoyl*, m. p. 139—140°, derivatives), and *B*, an oil (Perkin and Plant, A., 1928, 1258) (hydrochloride, m. p. 143—145°; *picrate*, m. p. 196°; *phenylcarbamyl*, m. p. 112.5°, and *benzoyl*, m. p. 146.5°, derivatives) of 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline, separated by fractional crystallisation of their hydrochlorides from ethereal-alcoholic solution. Electrolytic reduction affords the two forms *A* and *B* in the ratio 3 : 4, whilst with zinc and alcoholic hydrogen chloride the ratio is 3 : 5. Re-investigation of the product obtained by reduction with tin and alcoholic hydrogen chloride (Perkin and Plant, *loc. cit.*) by the improved method of separation indicates the presence of a small quantity of the *A* form (ratio 1 : 6). Similarly, re-examination of the product obtained by the reduction of 11-keto-5 : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline with sodium amalgam and boiling alcohol (*loc. cit.*) reveals the presence of a small amount of the *A*-isomeride, isolated as its hydrochloride, m. p. 244—245°.

J. W. BAKER.

Thiohydantoin from cystine and cysteine. Action of alkali. B. H. NICOLET (J. Biol. Chem., 1930, 88, 395—401, 403—407).—A solution of cystine in sodium hydroxide was treated with acetic anhydride (1 mol.), neutralised with hydrochloric acid, and evaporated; the residue containing *N*-acetylcystine was heated with ammonium thiocyanate and acetic anhydride to give a mixture of free sulphur, *cystine-bis*-NS-diacetyl-2-thiohydantoin, C₁₂H₁₄O₄N₄S₄, m. p. 208° (decomp.), and *cysteine*-NS-diacetyl-2-thiohydantoin, C₈H₁₀O₃N₂S₂, m. p. 142°; the latter compound was obtained also by the direct action of ammonium thiocyanate and acetic anhydride on cysteine, and its production (together with liberation of sulphur) from cystine was favoured by the presence of sodium acetate.

The above cysteine derivative when kept in solution in *N*-sodium hydroxide for 30 min. at the ordinary temperature yields a polymeride of 2-thio-5-methylenehydantoin, (C₄H₄ON₂S)_n; the same compound together with *cystine-bis*-N-acetyl-2-thiohydantoin, C₈H₁₀O₃N₂S₂, is formed by the action of 0.1*N*-sodium hydroxide on the cystine derivative described above for 5 min. at the ordinary temperature.

C. R. HARRINGTON.

Synthesis of iminazole derivatives from α-amino-acids. I. Synthesis of β-iminazolylpropionic acid. S. AKABORI (Proc. Imp. Acad. Tokyo, 1930, 6, 260—261).—Reduction of ethyl α-aminoglutarate with 2.5% sodium amalgam in cold, dilute hydrochloric acid and treatment of the semi-aldehyde formed with potassium thiocyanate affords β-2-thioliminazolylpropionic acid (+H₂O), m. p. 205—206.5°. This is converted by mild oxidising agents into β-iminazolylpropionic acid, m. p. 206—207° (lit. 208—209°).

H. BURTON.

Structure of the veronal molecule. C. M. ESCOLAR (Anal. Fis. Quím., 1930, 28, 495—500).—The changes of structure of the veronal molecule on addition of alkali to a 3.28% aqueous solution have been followed by measurements with the interferometer: the reading at first falls rapidly until about one equivalent of alkali has been added, and thereafter rises to approximately the initial value. The partition coefficient of veronal between water and ether diminishes from 5.8 to 0.7 as the *p*_H of the solution rises from 5 to 8. The physiological significance of these results is discussed with reference to the distribution of the hypnotic between the lipins and the blood. Analogous measurements with barbituric acid indicate that its structure differs from that of veronal.

H. F. GILLBE.

Skraup reaction with 4-aminoresorcinol dimethyl ether. K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 3196—3198).—The Skraup-Kneuppel reaction with 4-aminoresorcinol dimethyl ether gives, unexpectedly, *p*-phenanthroline [*picrate*, m. p. 255—256°; *chloroplatinate*, m. p. above 310°; *dihydrochloride*, not melted at 315°; *sulphate* (+H₂O), m. p. 233—234°; *chromate* (+2.5H₂O), m. p. 225—230°; *methiodide* (+H₂O), m. p. 268—269°; *dimethiodide* (+H₂O), m. p. 271°], oxidised to 3 : 3'-dipyridyl-2 : 2'-dicarboxylic acid, m. p. 215° (decomp.) [*sulphate* (+2H₂O), m. p. 218°].

H. BURTON.

Electrolytic reduction of 4-keto-3-phenyl-3 : 4-dihydroquinazoline. H. ITOMI (Mem. Coll. Sci. Kyōto, 1930, A, 13, 311—313).—Electrolytic reduction of 4-keto-3-phenyl-3 : 4-dihydroquinazoline with a lead cathode and aqueous-alcoholic sodium carbonate as the cathode solution at 25° gives 4-hydroxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m. p. 170—171°, in 40% of the theoretical yield. Both the above quinazolines are reduced to 3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m. p. 118—119°, when the cathode consists of copper coated with platinum-black and reduction is carried out at 50—60°.

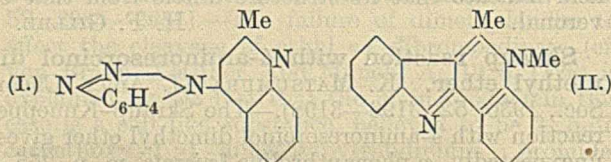
H. BURTON.

Formation of a phenazine compound from a diphenyl ether derivative. K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 3199—3204).—Nitration of diphenyl ether with potassium nitrate and sulphuric acid at 10—70° gives an 80% yield of 2 : 4 : 2' : 4'-tetranitrodiphenyl ether, which when reduced with stannous chloride and hydrochloric acid at 115—120° furnishes a mixture of 2 : 4 : 2' : 4'-tetra-aminodiphenyl ether, m. p. 129° (tetrahydrochloride, not melted at 310°; *tetrabenzoyl* derivative, m. p. 232—233°), and a small amount of a *diaminophenazine*, not melted at 320° (*sulphate*, anhydrous and +7.5H₂O;

triacetyl derivative, not melted at 320°). The tetraaminodiphenyl ether could not be converted into a phenoxazine derivative. H. BURTON.

Optical and photographic properties of sensitising and desensitising dyes of the cyanine and related types. O. BLOCH and F. M. HAMER.—See B., 1930, 928.

Synthesis in the indole series. IV. Derivatives of 2:3-benz- γ -carboline. W. O. KERMAK and J. F. SMITH (J.C.S., 1930, 1999—2010).—Condensation of 4-chloro-2-methylquinoline with *o*-phenylenediamine at 140°/20—30 mm. gives 4-*o*-aminophenylamino-2-methylquinoline, m. p. 220°, isolated as its dihydrochloride, m. p. 301°, and converted by nitrous acid into 4-(benztriazolyl-3')-2-methylquinoline (I), m. p. 149° (hydrochloride, m. p. 210°), which affords 5-methyl-2:3-benz- γ -carboline, m. p. 298° (for nomenclature, cf. Gulland, Robinson, Scott, and Thornley, this vol., 219), when heated in syrupy phosphoric acid. By similar methods are obtained 4-*o*-aminophenylamino-, m. p. 188° (hydrochloride, m. p. 294°), and 4-(benztriazolyl-3')-, m. p. 144° (hydrochloride, m. p. 221°), -6-methoxy-2-methylquinoline; and 15-methoxy-5-methyl-2:3-benz- γ -carboline + MeOH, m. p. 236°.



Condensation of *p*-anisidine with ethyl methylacetate at 37° for 3—4 days followed by heating to 250° gives 4-hydroxy-6-methoxy-2:3-dimethylquinoline + H₂O, m. p. 294°, converted by heating with phosphoryl chloride at 130—140° into the corresponding 4-chloro-derivative, m. p. 111°. This is converted as before into 4-*o*-aminophenylamino-, m. p. 193° [monohydrochloride, m. p. 125° (decomp.); dihydrochloride, m. p. 284° (decomp.)], and 4-(benztriazolyl-3')-, m. p. 201°, -6-methoxy-2:3-dimethylquinoline. The latter does not yield a crystalline base when heated with phosphoric acid, thus confirming the view that in the previous cases ring closure occurs not in the 5-, but in the 3-position as postulated. When 4-chloro-2-methylquinoline and phenylmethylhydrazine are heated together at 160—180°, 4-(β -phenyl- β -methylhydrazino)-2-methylquinoline, m. p. 237° (hydrochloride, m. p. 172°), is obtained, but cyclisation to 1:5-dimethyl-2:3-benz- γ -carboline, m. p. 173—174°, could not be effected. This derivative is, however, obtained when the phenylmethylhydrazone, m. p. 131—132°, of *o*-acetamidoacetophenone is treated with phosphorus oxychloride in boiling toluene. The constitution of this compound is proved as follows. Methyl sulphate in boiling benzene converts 5-methyl-2:3-benz- γ -carboline (above) into its methosulphate, m. p. 277° (decomp.), which is converted by ammonium hydroxide into the monohydrate, m. p. 262°, of the anhydronium base 4:5-dimethyl-2:3-benz- γ - ψ -carboline (II), the methosulphate, m. p. 292°, of which is identical with the methosulphate of 1:5-dimethyl-2:3-benz- γ -carboline. J. W. BAKER.

Ring synthesis of porphyrins with substituted and unsaturated side-chains. H. FISCHER and W. KUTSCHER (Annalen, 1930, 481, 193—214).—The yield of 4-carbethoxy-2:3-dimethylpyrrole-5-carboxylic acid (hydrolysed by 20% potassium hydroxide to the dicarboxylic acid, which is converted by heating in glycerol at 210° into 2:3-dimethylpyrrole) obtained by Piloty's method (A., 1912, i, 899) is much improved by careful control of the hydrogen-ion concentration. It is converted by chloroacetyl and acetyl chlorides and aluminium chloride in carbon disulphide into ethyl 4-chloroacetyl-, m. p. 103°, and 4-acetyl-, m. p. 137°, -2:3-dimethylpyrrole-5-carboxylate, respectively, the latter being reduced by the Wolff-Kishner method (sodium ethoxide and hydrazine hydrate in a sealed tube at 165°) to h emopyrrole, identified as its picrate. Ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate is converted by methyl-alcoholic sodium methoxide at 100° into methyl 3-methoxyacetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 139° [free acid, m. p. 188° (decomp.)], decarboxylated to 3-ethoxyacetyl-2:4-dimethylpyrrole, m. p. 89°, reduced by aluminium amalgam in ether to methyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 154—155°. Similar reduction of the ethyl ester of the 3-ethoxyacetyl derivative (free acid, m. p. 175—180°) affords ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate; ethyl 3-dimethylaminoacetyl-2:4-dimethylpyrrole-5-carboxylate is reduced to the 3- α -hydroxyethyl derivative (Fischer and Zeile, A., 1928, 902), but ethyl 3- β -dimethylamino-propionyl-2:4-dimethylpyrrole-5-carboxylate is reduced to ethyl 3-(γ -dimethylamino- α -hydroxypropyl)-, m. p. 122°, converted by anhydrous hydrogen chloride in ether or by benzoyl chloride into ethyl 3- γ -dimethylaminoallyl-, m. p. 95° (picrate, m. p. 182°; hydrochloride, m. p. 187°), -2:4-dimethylpyrrole-5-carboxylate. Bromination of ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate affords a monobromocompound, C₁₁H₁₃O₃NCIBr, m. p. 147°, the constitution of which is uncertain. By the action of formaldehyde and hydrogen chloride on the appropriate pyrrole derivative are obtained bis-(4-methoxyacetyl-3:5-dimethylpyrrol)methane, m. p. 245° (decomp.), and bis-(4-ethoxyacetyl-3:5-dimethylpyrrol)methane, m. p. 174°, which could not be converted into methenes. 3-Methoxyacetyl- and 3-ethoxyacetyl-2:4-dimethylpyrroles are converted by hydrogen cyanide in ether, in the presence of hydrogen chloride, into 3-methoxyacetyl-, m. p. 127°, and 3-ethoxyacetyl-, m. p. 121°, -2:4-dimethylpyrrole-5-aldehyde, respectively, whilst condensation of these products with the parent substances in the presence of 50% hydrobromic acid affords (4-methoxyacetyl-3:5-dimethylpyrrol)-(4-methoxyacetyl-3:5-dimethylpyrrolenyl)methene hydrobromide, m. p. 174° (free base, m. p. 143°), and (4-ethoxyacetyl-3:5-dimethylpyrrol)-(4-ethoxyacetyl-3:5-dimethylpyrrolenyl)methene hydrobromide, m. p. 169° (decomp.) (free base, m. p. 129°). Reduction of ethyl 3-cyanoacetyl-2:4-dimethylpyrrole-5-carboxylate with aluminium amalgam converts it into ethyl 3-(α -hydroxy- β -cyanoethyl)-2:4-dimethylpyrrole-5-carboxylate, m. p. 134—136°, dehydrated by hydrogen chloride in dry ether to ethyl 3- β -cyanovinyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 201°. Ethyl 3- β -cyanopropionyl-2:4-dimethylpyrrole-5-carboxylate,

m. p. 173° (obtained by heating the 3- β -chloropropionyl derivative with aqueous sodium cyanide), is similarly converted successively into ethyl 3-(α -hydroxy- γ -cyanopropyl)-, m. p. 113—115°, and ethyl 3- γ -cyanoallyl-, m. p. 160°, -2:4-dimethylpyrrole-5-carboxylate. Hydrolysis of the 3- β -cyanopropionylpyrrole ester with 20% sodium hydroxide converts it into 3- β -carboxypropionyl-2:4-dimethylpyrrole-5-carboxylic acid, m. p. 188° (dimethyl ester, m. p. 131°), which is decarboxylated to 2:4-dimethylpyrrole-3- γ -ketobutyric acid, m. p. 175°, which is also obtained by reduction of ethyl 3- β -cyanopropionyl-2:4-dimethylpyrrole-5-carboxylate by the Wolff-Kishner method. 2:4-Dimethylpyrrole-5-aldehyde is converted by sulphuryl chloride in ether into 4-chloro-3-methylpyrrole-2:5-dialdehyde, m. p. 145° (diphenylhydrazone, m. p. 178°). Condensation of ethyl 2:3-dimethylpyrrole-5-carboxylate with propionyl chloride in the presence of aluminium chloride in carbon disulphide gives ethyl 4-propionyl-2:3-dimethylpyrrole-5-carboxylate, m. p. 102°, hydrolysed to the free acid, m. p. 187°. The same acid is obtained by condensation of methyl α -aminoethyl ketone and propionylpyruvic acid. By the action of magnesium ethyl bromide on cryptopyrrole and treatment of the product with 5-chloroacetyl-2:4-dimethyl-3-ethylpyrrole is obtained 3:5-dimethyl-4-ethylpyrrolmethyle 3:5-dimethyl-4-ethylpyrrol ketone, m. p. 142—143° (coer.). In the conversion of ethyl 2:4-dimethylpyrrole-5-carboxylate into the 3-aldehyde-derivative a dimeride, $C_{18}H_{24}O_4N$, m. p. 236°, is obtained as a by-product, whilst in the preparation of ethyl 2:3-dimethylpyrrole-5-carboxylate by the Grignard reaction a polymeride, $C_{21}H_{26}O_2N_3$, m. p. 274—275°, probably a molecular compound of 2 mols. of the dimethylpyrrole with 1 mol. of the 5-carboxylate, is also obtained.

J. W. BAKER.

Chlorophyll series. III. Products of the phase test. J. B. CONANT and W. W. MOYER (J. Amer. Chem. Soc., 1930, 52, 3013—3023).—When methylphæophorbide is dissolved in a little pyridine and the solution diluted to about 0.1% with ether and shaken with one tenth of its volume of 25% methylalcoholic potassium hydroxide at 23° (phase-test reaction) for 5—10 min., products of two kinds are obtained: (a) a mixture of chlorins (acid numbers, 6—12) which cannot be isolated pure, since they change rapidly in ethereal solution into the purplish-brown compounds (acid numbers 7 and 18, respectively), phæopurpurin-7 (10—12% yield), $C_{35}H_{38}O_7N_4$, m. p. 200—205° on the block (dimethyl derivative, m. p. 233—235°), and phæopurpurin-18 (35—43% yield), $C_{34}H_{36}O_5N_4$, sinters at 250—280° (monomethyl ester, m. p. 275—278°); (b) chlorin-e and a monomethylchlorin (combined yield, 15%) of acid number 5. This is not identical with chlorin-e monomethyl ester, since further methylation gives an ester which differs in crystalline form from chlorin-e trimethyl ester. The formation of chlorin-e is completely repressed by replacing the methyl alcohol by ethyl or *n*-propyl alcohol, or by carrying out the reaction at -10°, whilst in boiling pyridine (Willstätter's conditions; cf. A., 1911, i, 659) chlorin-e is the main product and no unstable chlorins are formed. The unstable chlorins probably comprise two compounds

differing by a methoxyl group, one of which, the precursor of phæopurpurin-18, is identical with phytochlorin-g. On methylation, both yield dimethylphæopurpurin-7. Towards alkali the trimethyl ester of chlorin-e behaves very similarly to methylphæophorbide, yielding unstable chlorins at the ordinary temperature and chlorin-e at the b. p. Phæopurpurin-7 contains one methoxyl and one free propionic acid group. Phæopurpurin-18 has no methoxyl, but one free carboxyl and probably one lactone and one lactam group. It is hydrolysed in ether by methylalcoholic potassium hydroxide to a product, $C_{34}H_{38}O_6N_4$, apparently identical with Willstätter's chlorin-a (trimethyl ester, m. p. 239—240°). This reverts rapidly in solution at 140° and slowly at the ordinary temperature to phæopurpurin-18. Both phæopurpurins are almost completely converted by alkali at 150° under the conditions used by Treibs and Wiedemann (A., 1929, 941) into rhodoporphyrin. Details of the absorption spectra of the new compounds are given and their probable constitutions are discussed (cf. this vol., 225, 793). The formulæ given for phæopurpurin-18, chlorin-a, chlorin-e, $C_{34}H_{40}O_7N_4$, and their methyl esters differ by +4H from those obtained by assuming that these products are formed by simple hydrolysis and agree much better with the analytical results than do the latter.

H. E. F. NOTTON.

Glutathione. B. H. NICOLET (J. Biol. Chem., 1930, 88, 389—393).—Glutathione with ammonium thiocyanate and acetic anhydride yielded a compound, $C_{16}H_{19}O_6N_5S_3$, m. p. 155° after sintering at 140°; the product obtained by condensing this compound with benzaldehyde in presence of acetic acid and sodium acetate afforded, when hydrolysed with sodium hydroxide, a 50% yield of benzylidenethiohydantoin. The compound $C_{16}H_{19}O_6N_5S_3$ is therefore regarded as a bithiohydantoin in the formation of one of the thiohydantoin groups of which glycine must have taken part. It follows that glycine occupies a terminal position in the molecule of glutathione, and in conjunction with the evidence adduced by Hopkins (A., 1929, 1491) and by Kendall and others (this vol., 113, 945), that the latter compound is γ -glutamylcysteinylglycine.

C. R. HARRINGTON.

Glutathione. IV. Determination of structure. E. C. KENDALL, H. L. MASON, and B. F. MCKENZIE (J. Biol. Chem., 1930, 88, 409—423).—Evidence is adduced that glutathione is not hydrolysed during esterification with alcohol and hydrogen chloride and the previous work (this vol., 945) on the reaction between the ethyl ester hydrochloride and magnesium phenyl bromide is confirmed. By heating in aqueous solution at 62° for 120 hrs. glutathione was hydrolysed to glutamic acid and a dipeptide of glycine and cysteine, only a small amount of the latter having undergone conversion into the anhydride. After treatment of this dipeptide with sodium hypobromite or with nitrous acid the product still gave glycine (although in poor yield) on hydrolysis. The dipeptide was oxidised to the disulphide, the latter was condensed with 2:3:4-trinitrotoluene, and the product was hydrolysed with hydrochloric acid to a product, m. p. 190—195°, and glycine; the dipeptide was therefore cysteinyl-

glycine, which confirms the previously suggested (*loc. cit.*) constitution of γ -glutamylcysteinylglycine for glutathione. Whilst direct treatment of glutathione with hydrogen peroxide yields a product from which no glycine and only small amounts of succinic acid can be obtained by hydrolysis, large amounts of these compounds result from hydrolysis of the product of oxidation with hydrogen peroxide of the sulphonic acid corresponding with glutathione. C. R. HARRINGTON.

Condensation of 2:4-diketo-3-phenylthiazole with aromatic aldehydes. K. S. MARKLEY and E. E. REID (J. Amer. Chem. Soc., 1930, 52, 2981—2984).—All the aldehydes examined except resorcyaldehyde, γ -phenylpropaldehyde, and 2:4:6-trinitrobenzaldehyde give high yields of derivatives suitable for purposes of characterisation when refluxed with this reagent in glacial acetic acid in presence of sodium acetate (cf. Andreasch, A., 1918, i, 80; Ruhemann, J.C.S., 1909, 95, 117). The following 2:4-diketo-3-phenyl-5-arylidenthiazoles are described: -*p*-methylbenzylidene-, m. p. 192°; -*p*-hydroxybenzylidene-, m. p. 257.5°; -*o*-chlorobenzylidene-, m. p. 169—170°; -*vanillylidene*-, m. p. 234—235°; -*veratrylidene*-, m. p. 208—209°; -*furfurylidene*-, m. p. 218—219°; -*p*-anisylidene-, m. p. 199—200°; -*o*-anisylidene-, m. p. 138—139°; and -*m*-nitrobenzylidene-, m. p. 188°.

H. E. F. NOTTON.

Catalytic reduction of nicotine and metanicotine. W. R. HARLAN [with R. M. HIXON] (J. Amer. Chem. Soc., 1930, 52, 3385—3388).—Catalytic reduction (Adams) of nicotine hydrochloride in 95% alcohol gives a mixture of 25% of hexa- and 75% of octa-hydronicotine hydrochlorides. A mixture of nicotine and its hexa- and octa-hydro-derivatives can be separated by fractional crystallisation of the hydrochlorides and picrates. Similar reduction of metanicotine affords the dihydro-derivative; this can be reduced further to octahydrometanicotine.

H. BURTON.

Sparteine. III. K. WINTERFELD and W. IPSEN (Arch. Pharm., 1930, 268, 372—380).—Sparteine α -methoacetate, from the methiodide and silver acetate, is oxidised by mercuric acetate to a mercuri-derivative, which with hydrogen sulphide gives syrupy *dehydrosparteine methoacetate*. Attempts to convert this into crystalline salts were unsuccessful. It is oxidised by chromic and sulphuric acids to carbon dioxide and two products of amphoteric nature. These are obtained in better yield by oxidation and subsequent demercuration of the mercuri-derivative. The first is isolated as the *chloroplatinate*, m. p. 250° (also +H₂O), after removal of chromium and sulphate. The free base, C₇H₁₃O₂N, [α]_D²⁰ -51.6°, gives a positive pine-shaving reaction, contains a methylimino-group, and must therefore be derived from the nucleus which is concerned in methiodide formation. Since this nucleus has already been degraded to 2-methylpyrrolidine (A., 1929, 1186), the new product must be a 1:2-dimethylpyrrolidine-3-, -4-, or -5-carboxylic acid. The second product, a hygroscopic, optically inactive oil, gives a dark blue copper salt (N, 8.5%). H. E. F. NOTTON.

Strychnine and brucine. XI. Dihydrobrucine and some derivatives. O. ACHMATOWICZ, R. C. FAW-

CETT, (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1930, 1769—1772).—Catalytic reduction of brucine with palladised charcoal affords *dihydrobrucine*, m. p. 179—181°, +4H₂O, m. p. 70—72°, +1.5AcOEt, m. p. 48—50° [*methosulphate* +2H₂O, m. p. 242—244° after sintering at 215°; *methiodide* +H₂O, m. p. 283—285° after sintering at 245°, when prepared by the action of sodium iodide on the methosulphate, direct combination of dihydrobrucine with methyl iodide yielding a *compound*, m. p. 242—245° (decomp.)], and converted into *bisapomethylidihydrobrucine*, not melting at 320°, by a method similar to that used by Leuchs and Anderson (A., 1911, i, 746) for *bisapomethylbrucine*. The dihydrobrucine, m. p. 115°, described by Skita and Franck (A. 1911, i, 1017) cannot have been homogeneous (cf. Wieland and Münster, this vol., 936). Similar reduction of brucidine affords *dihydrobrucidine*, m. p. 172—172.5° (retains acetone of crystallisation tenaciously) [*dimethosulphate*, m. p. 270°], which is also obtained by electrolytic reduction of dihydrobrucine, whilst tetrahydrobrucine is reduced to *hexahydrobrucine*, m. p. 133°. J. W. BAKER.

Sinomenine and disinomenine. XVII. Methylsinomeninone. K. GOTO, T. NAMBO, and R. INABA (Bull. Chem. Soc. Japan, 1930, 5, 223—227).—Treatment of methylsinomenine with 2*N*-hydrochloric acid at 100° gives methylsinomeninone, m. p. 188°, [α]_D²⁰ +18.65° in chloroform (*oxime*, sinters at 100°, m. p. 170°, decomp. 213°; *methiodide*, decomp. 225—227°), in 70% yield; this with hydrogen and palladised charcoal yields dihydromethylsinomeninone, m. p. 128°, [α]_D²⁰ +71.05° in chloroform [*oxime*, m. p. 177°; *methiodide*, m. p. 248° (decomp.)], but with concentrated aqueous ammonia gives an amorphous substance.

The reactions of methylsinomenine are therefore not completely analogous with those of either sinomenine or its 1-bromo-derivative. An improved preparation of benzoylsinomenine [*oxime*, m. p. 249° (decomp.); *methiodide*, m. p. 237° (decomp.)] is given. R. J. W. LE FÈVRE.

Direct arsenation of benzene derivatives. C. S. HAMILTON and C. G. LUDEMAN (J. Amer. Chem. Soc., 1930, 52, 3284—3286).—The formation of *o*-carboxyphenylarsinic acid (Rosenmund, A., 1921, i, 370) and acetophenone-4-arsinic acid (G.P. 468,403) by the action of potassium arsenite on *o*-bromobenzoic acid and *p*-bromoacetophenone, respectively, is confirmed. *p*-Carboxyphenylarsinic and *o*-phenylenediarsinic acids are similarly prepared from *p*-bromobenzoic and *o*-bromophenylarsinic acids, respectively. Little or no arsenic acid was obtained using halogenonitrobenzenes and *p*-bromobenzenesulphonic acid. H. BURTON.

Arsinic acids of *p*-aminophenol. M. A. PHILLIPS (J.C.S., 1930, 1910—1916).—Nitration of *o*-acetamidophenylarsinic acid with mixed acids at 5° affords 5-nitro-2-acetamido-, reduced by sodium hyposulphite and 2*N*-sodium hydroxide at 10° to 5-amino-2-acetamido-, and converted by boiling 50% sodium hydroxide into 5-nitro-2-hydroxy-phenylarsinic acid. The last-named is reduced by various reagents to the corresponding 5-amino-acid, acetylated

to 5-acetamido-2-hydroxyphenylarsinic acid (cf. Benda, A., 1912, i, 61; Balaban, this vol., 354). 3-Oxalylaminophenylarsinic acid (G.P. 261,643; cf. Fournau and others, A., 1923, i, 983) is converted by potassium nitrate and sulphuric acid into the 2-nitro-5-oxalylamino-acid, hydrolysis of which with boiling 2*N*-hydrochloric acid to 2-nitro-5-aminophenylarsinic acid is accompanied by considerable fission of arsenic. Much less separation of arsenic occurs in the similar hydrolysis of 2-nitro-5-acetamidophenylarsinic acid, prepared as follows. 4-Nitro-*m*-phenylenediamine is converted by boiling acetic acid and acetic anhydride into a mixture of 4-nitro-3-aminoacetanilide, m. p. 200° (Kehrmann and Mermod, A., 1927, 260, give m. p. 178°) (deaminated to *p*-nitroacetanilide, and converted by the Sandmeyer reaction and subsequent hydrolysis into 3-chloro-4-nitroaniline), and the 1:3-diacetamido-compound. After diazotisation of the mixture, unchanged 4-nitro-1:3-diacetamidobenzene is removed and the diazonium salt converted into the required acid by the action of copper arsenite (cf. Bart, G.P. 250,264). Reduction of the 2-nitro-acid with sodium hyposulphite affords 2-amino-5-acetamidophenylarsinic acid. 2-Nitro-5-aminophenol (acetyl derivative, m. p. 200°; diacetyl derivative, m. p. 118°) is obtained either by diazotisation of 4-nitro-3-aminoacetanilide and subsequent treatment with 2*N*-solutions of sulphuric acid and copper sulphate, or by refluxing 4-nitro-1:3-diacetamidobenzene with 40% potassium hydroxide. It is converted by the Sandmeyer reaction into 5-chloro-2-nitrophenol. Application of the modified Bart method (above) to 4-nitro-3-aminophenol gives a 37% yield of 2-nitro-5-hydroxyphenylarsinic acid, monohydrate, m. p. 175°, resolidifying and melting again at 205°, which is also obtained by boiling 2-nitro-5-aminophenylarsinic acid with 25% sodium hydroxide. Reduction with ferrous sulphate and sodium hydroxide converts it into the corresponding 2-amino-acid (*N*-acetyl derivative, m. p. 230°; magnesium, barium, and calcium salts). 2:5-Diaminophenylarsinic acid, m. p. 220° (calcium and magnesium salts), is obtained by acid hydrolysis of either of its monoacetyl derivatives and on acetylation affords 2:5-diacetamidophenylarsinic acid + H₂O, m. p. 225° (decomp.) (calcium, barium, and magnesium salts). Nitration of 2-methoxyphenylarsinic acid (Johnson and Adams, A., 1923, i, 724) with mixed acids at 5° affords the 5-nitro-acid, reduced by ferrous sulphate and sodium hydroxide to 5-amino-2-methoxyphenylarsinic acid, decomp. 240—245° (acetyl derivative, decomp. 260—262°; monosodium + H₂O salt). Nitration of *m*-acetamidophenol with nitric acid (*d* 1.45) at 0° and hydrolysis of the two products (separated by fractional crystallisation from alcohol) so obtained affords 4-nitro-3-aminophenol and a 5-nitroaminophenol, m. p. 163°, which is not 2-nitro-5-aminophenol, the constitution of which is under investigation (Meldola and Stephens, J.C.S., 1906, 89, 925, state it to be 6-nitro-3-aminophenol).

J. W. BAKER.

Properties and molecular state of organic arsenicals. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1930, 52, 2946—2951).—Contrary

to many published statements (cf., however, Palmer and Scott, A., 1928, 433; Steinkopf and Dudek, A., 1929, 1471), arsenobenzene and its *pp'*-dimethyl, m. p. 218—219°, and *pp'*-dimethoxy-, m. p. 230—232°, derivatives, obtained from the dichloroarylsines and hypophosphorous acid in hot acetone, are colourless and do not absorb oxygen. In presence of traces of catalysts, such as the strong mineral acids, iodine, halogenoarylsines, and triphenylmethyl bromide, they react rapidly, the amount of oxygen absorbed (1—2 mols. per mol. of arsenobenzene) depending on the catalyst chosen. Mol. wt. determinations show that aromatic arsenicals may be divided into three classes. (I) Compounds in which the arsenic atom is attached by single linkings to atoms other than arsenic, e.g., halogenoarylsines, triarylsines, and diarylsine oxides or sulphides, are colourless, unimolecular in solution, and stable towards oxygen. (II) Compounds in which arsenic is doubly linked to arsenic or some other atom, e.g., arylarsenious oxides, sulphides, and imides, and arsenobenzenes, are stable towards oxygen when pure and are associated (di- to quadrimolecular) in solution. (III) Compounds in which arsenic is singly linked to arsenic, e.g., tetraaryldiarsines and di-iododiarylsines, react instantly with oxygen and in solution may be partly dissociated into free radicals. Phenylarsenious sulphide has m. p. 174—176°.

H. E. F. NOTTON.

Diarsines. III. Di-iododiaryldiarsines. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1930, 52, 2937—2946).—*Di-iodo- α -naphthylarsine*, m. p. 106—108°, and *di-iodo-*p*-diphenylarsine*, m. p. 104—106°, are obtained from the arylarsenious oxide and hydriodic acid (*d* 1.7) at 100°. The following di-iododiaryldiarsines are prepared by the method of Michaelis and Schulte (A., 1881, 722): *-diphenyl-*, m. p. 176—177°, *-di-*p*-tolyl-*, m. p. 149—150°; *-di-*p*-anisyl-*, m. p. 135—137°; *-di- α -naphthyl-*, m. p. 176—178°, and *-di-*p*-diphenyl-*, m. p. 244—246° (decomp.). The mol. wt. of these derivatives does not deviate sufficiently from the normal to afford evidence of dissociation into free radicals. Di-iododiphenylarsine (I) is also formed (a) from phenylarsenious oxide, hydriodic acid, and phosphorous acid in absolute alcohol, (b) from arsenobenzene (1 mol.) and di-iodophenylarsine (2.5 mols.) in alcohol, (c) from arsenobenzene (1 mol.) and iodine (1 mol.) in benzene, and (d) from di-iodophenylarsine and mercury in bromobenzene, the apparatus and methods being similar to those used in the isolation of free radicals. The diarsine rapidly absorbs oxygen, probably forming first a peroxide which decomposes liberating iodine. This with I yields di-iodophenylarsine, the final result being given by the scheme $2(\cdot\text{AsPhI})_2 + \text{O}_2 \rightarrow 2\text{AsPhO} + 2\text{AsPhI}_2$. In presence of mercury twice this volume of oxygen is absorbed, owing to the occurrence of reaction (d). The oxygen absorptions of the products obtained in reactions (b) and (c) are in accordance with expectation, but in presence of a trace of iodine arsenobenzene (4 mols.) absorbs 5—6 mols. of oxygen, and in presence of a trace of di-iodophenylarsine 4—5 mols., instead of 4 mols. *Dibromodiphenylarsine* (2 mols.), m. p. 122—124° in nitrogen, from dibromophenylarsine and

arsenobenzene at 135°, absorbs between 1 and 2 mols. of oxygen in bromobenzene solution. Dichlorophenylarsine and arsenobenzene give a solution which absorbs oxygen, although no dichlorodiphenylarsine can be isolated from it. The diarsine I in benzene is slowly converted by mercury into arsenobenzene (95% of the theoretical) and triphenylarsine.

H. E. F. NOTTON.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. V. Nitration of benzyldiethylsulphonium picrate. A. POLLARD and R. ROBINSON (J.C.S., 1930, 1765—1769).—Treatment of benzyldiethylsulphonium picrate, m. p. 115—116°, prepared from the corresponding bromide, with nitric acid (*d* 1.51), first at 0° and then at the ordinary temperature, gives a mixture of *o*-, m. p. 118—120°, *m*-, m. p. 147—148° (about 28%), and *p*-nitrobenzyldiethylsulphonium picrates, m. p. 112—114° (about 61%). The nitro-salts are synthesised from nitrobenzyl halides, diethyl sulphide, and sodium picrate. It is now considered that the relatively greater deformation of the ionic centres in the sulphonium salt renders the sulphonium cation less effective than the ammonium in distributing a positive field over the nucleus (cf. A., 1928, 71).

o-Nitrobenzyldiethylsulphonium chloride develops an intense bluish-violet coloration when treated with sodium hydroxide in acetone solution. A solution of *p*-nitrobenzyldiethylsulphonium chloride in acetone gives an intense eosin-red coloration with aqueous-alcoholic potassium hydroxide. These colorations may be due to the formation of quinonoid betaines, $-\text{[NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{SR}_2\text{]}^+$.

H. BURTON.

Alternating effect in carbon chains. XXXIII. Nitration of aromatic sulphonium and selenium salts. J. W. BAKER and W. G. MOFFITT (J.C.S., 1930, 1722—1733).—Nitration of phenyldimethylsulphonium and *s*-selenium picrates with a mixture of nitric (*d*₄¹⁵ 1.53) and 95% sulphuric acids at 60° gives 94 and 99%, respectively, of the *m*-nitro-derivatives; no trace of the *o*- or *p*-nitro-compounds could be detected. The exclusive *m*-nitration shows that the possible influence of *op*-directive tautomeric electron displacements due to the presence of unshared electron pairs in the outer group of electrons is inoperative in orientation; the unshared pairs are effectively restricted by the charge on the atom. The damping effect of the extra electron group present in selenium is, however, clearly indicated by the formation of only 16% of the *m*-nitro-derivative by nitration of benzyldimethylselenium picrate with nitric acid (*d*₄¹⁵ 1.53) at -15°, whereas the corresponding sulphonium compound affords 52% of *m*-nitro-compound. The relationship between the directive action of various elements and their position in the periodic classification is discussed. The amounts of isomerides formed during nitration are determined by the bromination method (Goss, Ingold, and Wilson, A., 1926, 1132), or by oxidation to the nitrobenzoic acids and subsequent reduction and bromination (Flürscheim and Holmes, A., 1928, 403).

Prolonged treatment of phenyl methyl sulphide with methyl sulphate at 100° and addition of aqueous

sodium picrate to the resulting methosulphate give phenyldimethylsulphonium picrate, m. p. 101—102°. *m*- and *p*-Nitrophenyldimethylsulphonium picrates, m. p. 163° and 137°, respectively, are prepared similarly. Phenyldimethylselenium picrate, m. p. 87—89°, is obtained by the same process from phenyl methyl selenide. When a large excess of sodium picrate solution is used in the preparation of this salt, there is also obtained the double picrate,

$[\text{SePhMe}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{ONa}$, m. p. 136—144° (decomp.). Treatment of an alcoholic solution of *p*-chloronitrobenzene with the product from phosphorus pentaselenide, selenium, and aqueous-alcoholic sodium hydroxide affords *pp'*-dinitrodiphenyl selenide, m. p. 170—171°. Reduction of this with alkaline sodium sulphide and subsequent methylation with methyl sulphate gives *p*-nitrophenyl methyl selenide, m. p. 54—56°, converted as above into *p*-nitrophenyldimethylselenium picrate, m. p. 122—123°. Methylation of the product from *m*-nitrophenyl selenocyanate and aqueous-alcoholic sodium hydroxide furnishes *m*-nitrophenyl methyl selenide, m. p. 30—31°, convertible into *m*-nitrophenyldimethylselenium picrate, m. p. 156°. Benzyl bromide and dimethyl sulphide afford a hygroscopic bromide which with aqueous sodium picrate yields benzyldimethylsulphonium picrate, m. p. 134°. *o*-, *m*-, and *p*-Nitrobenzyldimethylsulphonium picrates, m. p. 150—153°, 167.5—168.5°, and 148.5—149°, respectively, are prepared similarly from the appropriate nitrobenzyl iodides. Prolonged digestion of dibenzyl diselenide with an excess of methyl iodide, conversion of the resulting tri-iodide into the hydroxide by the action of silver oxide in sulphurous acid, and treatment of this with aqueous picric acid gives benzyldimethylselenium picrate, m. p. 118°, also formed from benzyl bromide, dimethyl selenide, and aqueous sodium picrate. *o*-, *m*-, and *p*-Nitrobenzyldimethylselenium picrates have m. p. 145—148°, 132—134°, and 152°, respectively.

H. BURTON.

Triorgano-thallium compounds; thallium triethyl and thallium triphenylmethyl-diethyl. H. P. A. GROLL (J. Amer. Chem. Soc., 1930, 52, 2998—3002).—Thallium diethyl chloride and lithium ethyl in light petroleum in complete absence of air and moisture (cf. Schlenk and Holtz, A., 1917, i, 255) at the ordinary temperature give 79% of the theoretical of thallium triethyl, b. p. 54.6—54.8°/1.50—1.55 mm., decomp. 129°/760 mm. without boiling, f. p. between -80° and -183°, *d*₄²⁰ 1.971. It is also formed in small yield from alloys of thallium with 7%, 10%, or 15% of sodium and ethyl chloride at the ordinary temperature. It is stable towards oxygen, but is slowly decomposed by water to thallium diethyl hydroxide and ethane. The slowness of reaction arises from the immiscibility of the two liquids, since the trialkyl is violently decomposed by absolute alcohol. Syrupy thallium triphenylmethyl-diethyl, obtained in an impure state from thallium diethyl chloride and sodium triphenylmethyl, gives in moist air thallium diethyl carbonate and triphenylmethane.

H. E. F. NOTTON.

Preparation of magnesium phenyl chloride in absence of solvent. H. GILMAN and R. E. BROWN

(J. Amer. Chem. Soc., 1930, 52, 3330—3332).—When magnesium (0.15 atom) is heated with chlorobenzene (0.1 mol.) in an evacuated, sealed tube at 150—160° for 3 hrs., magnesium phenyl chloride is obtained in 85% yield. The solid Grignard reagent is dissolved in ether before use.

H. BURTON.

Combination of iron with proteins, amino-acids, and related compounds. C. V. SMYTHE and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 241—269).—The mode of combination of iron with the compounds named has been investigated (a) by determination of the concentration of ferric iron in solution in presence of the substance under test, for which the intensity of colour produced with thiocyanate was utilised, (b) by determining whether the iron compound is anodic or cathodic in character. The first method showed that marked reduction in the concentration of ferric iron in a solution (*i.e.*, formation of an undissociated iron compound) occurred on addition of α -hydroxy-aliphatic acids, unsubstituted and hydroxy-dicarboxylic acids, hydroxy- and dicarboxylic amino-acids, phosphoric and arsenic acids, glycerophosphoric and nucleic acids, caseinogen and gelatin; ordinary amino-acids had no effect. These results were confirmed by electrical transference experiments which showed the iron to be in the anodic condition in solutions of the above-mentioned compounds at suitable p_{aH} ; in some cases (*e.g.*, the dicarboxylic acids) the iron is held in the undissociated complex at reactions as acid as p_{aH} 2.0. The extra force necessary for the formation of this complex is thought to be derived from the residual negative charge of the substituent group; thus in the simplest case, lactic acid, the compound is formulated $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Fe}(x)_n$; the explanation is

elaborated to cover the more complex cases. The amount of iron bound in the complex with caseinogen can be accounted for by the dicarboxylic amino-acids and the phosphoric acid contained in the protein.

C. R. HARINGTON.

Combination between dyes and gelatin granules. L. M. C. RAWLINS and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 271—284).—The amount of Biebrich scarlet or of tropæolin-O which is taken up by gelatin granules at p_{aH} 2.2 or 3.5 at a fixed temperature depends on the time of contact; the ultimate amount of dye taken up corresponds, however, with that which combines with the same amount of gelatin in solution at the same reaction. Logarithmic plotting of the absorption data fails to give curves approximating to straight lines. The process is therefore regarded as one of chemical combination rather than of adsorption. In the case of the gelatin solutions a "protective colloidal" region was observed in which precipitation of the normally insoluble protein-dye complex failed to occur. On the assumption that the solubility of the protein is due to the orientation of its polar group to water, this phenomenon is ascribed to the progressive neutralisation of the polar groups by the dye; until a certain concentration of the latter is attained the number of free polar groups may suffice to maintain the complex in the soluble condition.

C. R. HARINGTON.

Mol. wt. of legumin. B. SJÖGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1930, 52, 3279—3283).—Solutions of legumin show an absorption maximum at 280 $\mu\mu$ and a minimum at 255 $\mu\mu$ both at p_{H} 6.5 and 12.4. Determinations of the mol. wt. by the method of sedimentation equilibrium give a mean value of 208,000 \pm 5000 at p_{H} 6.5—8.0 in phosphate buffers. The protein is stable at p_{H} 5—9, but at p_{H} < 5 and > 9 the molecules are disrupted. The molecules are spherical with a radius of 3.96 $\mu\mu$.

The mol. wt., sedimentation constant, molar frictional constant, and molecular radius of legumin are identical, within the limits of experimental error, with the corresponding constants for edestin (A., 1929, 1092), amandin and excelsin (this vol., 356), and *R*-phycoeyan, *C*-phycoeyan, and *R*-phycoerythrin (*ibid.*, 233).

H. BURTON.

Determination of organic halogen. P. W. ROBERTSON (J. Amer. Chem. Soc., 1930, 52, 3023—3024).—The method of Thompson and Oakdale (this vol., 799) is similar to that of the author (J.C.S., 1915, 107, 902; 1916, 109, 218), the latter being preferred.

H. E. F. NOTTON.

Determination of halogens in organic compounds. J. J. THOMPSON and U. O. OAKDALE (J. Amer. Chem. Soc., 1930, 52, 3466—3467).—The authors' method (this vol., 799) for the determination of halogen in organic compounds is preferred to that of Robertson (preceding abstract) since it is more rapid, more accurate, and applicable to iodo- as well as to chloro- and bromo-compounds.

H. BURTON.

Determination of sulphur in organic compounds. H. ZAHND and H. T. CLARKE (J. Amer. Chem. Soc., 1930, 52, 3275—3279).—The substance is oxidised with potassium nitrate and nitric acid, the nitric acid evaporated, the residue fused, and the amount of sulphate determined. The method can be used for the determination of sulphur in material containing as little as 0.02%, but fails with compounds yielding volatile sulphones.

H. BURTON.

Identification and determination of methyl alcohol in presence of ethyl alcohol. A. IONESCO-MATIU and C. POPESCO (J. Pharm. Chim., 1930, [viii], 12, 63—79).—A critical account and bibliography of existing methods are given, together with the results of experimental examination. The colour reactions of formaldehyde and formic acid with mercury compounds afford the foundation for the most suitable qualitative and quantitative methods. The redistillation in presence first of acid and then of alkali of the original distillate is necessary to obtain trustworthy results.

S. I. LEVY.

Micro-determination of cholesterol. R. OKEY (J. Biol. Chem., 1930, 88, 367—379).—Blood or other tissue is extracted with a mixture of alcohol and ether (*cf.* Bloor, A., 1928, 662); an aliquot portion of the filtered extract is evaporated in presence of excess of digitonin, the residue is washed with ether and then with warm water, and the remaining cholesterol digitonide is oxidised with standard potassium dichromate and sulphuric acid, the excess of dichromate being determined iodometrically. If cholesteryl esters are to be included the extract is hydrolysed with sodium hydroxide and the residue obtained on

evaporating the alkaline solution in an atmosphere of carbon dioxide is treated with slight excess of sulphuric acid and extracted with light petroleum. The latter is evaporated and the residue is taken up in alcohol and treated as above. C. R. HARRINGTON.

Rapid determination of furfuraldehyde. A. NOLL, F. BOLZ, and W. BELZ (Papier-Fabr., 1930, 28, 565—568).—Furfuraldehyde in aqueous or alcoholic solution is treated with a 7% solution of hydroxylamine hydrochloride, α -furfuraldoxime being formed, and an equivalent amount of hydrochloric acid liberated. The reaction is complete after shaking for 30 min. at the ordinary temperature or 1 hr. on the water-bath. The free acid is then titrated with 0.1*N*-sodium hydroxide, 1 c.c. being equivalent to 0.0096 g. of furfuraldehyde. The method has been applied to the determination of furfuraldehyde in the condensates and residual liquors in the sulphite pulp process. The furfuraldehyde is liberated from its hydrogen sulphite compound, the lignin residues are precipitated with alcohol, and the furfuraldehyde is determined as above. T. T. POTTS.

Colorimetric determination of tryptaflavin and rivanol. M. J. SCHULTE (Pharm. Weekblad, 1930, 67, 809—811).—The same colour is obtained with red fuming nitric acid as with nitrous acid. In strong sunlight the colour disappears within a minute. S. I. LEVY.

Micro-detection of alkaloids. G. D. LANDER (Analyst, 1930, 55, 474—476).—Fränkel's method of isolation and purification of alkaloids, primarily in saliva, is described in detail and the sensitiveness of the colour tests with various alkaloids is recorded. D. G. HEWER.

Apparatus for micro-catalytic hydrogenation. J. F. HYDE and H. W. SCHERP (J. Amer. Chem. Soc., 1930, 52, 3359—3363).—The apparatus described involves the use of the same principle as that of Warburg (A., 1925, i, 321). An accuracy of $\pm 2\%$ is obtained for the micro-scale hydrogenation of *d*-pinene, maleic, and dimethylacrylic acids. The apparatus can also be used for the determination of small amounts of gas absorbed or evolved during a reaction. H. BURTON.

Biochemistry.

Determination of blood [in blood-stained materials]. M. WAGENAAR (Z. anal. Chem., 1930, 81, 207—212).—Quantitative results are possible by the determination of nitrogen and iron content. Tabulated results of the ratio of nitrogen to iron of bloods of different mammalian origin are given. J. O. CUTTER.

Determination of hæmoglobin. Hæmoglobinometer. F. F. SCHWENTKER (J. Lab. Clin. Med., 1929, 15, 247—259).—A spectroscopic method is described. CHEMICAL ABSTRACTS.

Position of the violet band of oxy- and carbon monoxide-hæmoglobin. F. R. BERG and W. SCHWARZACHER (Z. physiol. Chem., 1930, 190, 184—188).—The violet band in the absorption spectrum of oxyhæmoglobin is at 4137 ± 2 and that of carbon monoxide-hæmoglobin is at 4180 \AA . No difference in this respect is discernible in the product from various animal species and that from man. J. H. BIRKINSHAW.

Decomposition of blood-pigments by dilute acids. G. BARKAN (Biochem. Z., 1930, 224, 53—62).—The view of Lintzel and Radeff (A., 1929, 338) that treatment of oxyhæmoglobin with dilute acid decomposes part of the pigment, liberating iron, is denied, since the amount of iron set free does not correspond with the amount of pigment disappearing. The iron liberated is the "labile" iron investigated previously by the author (A., 1928, 537; 1929, 87). P. W. CLUTTERBUCK.

Additive power of hæmatin. A. HAMSÍK (Z. physiol. Chem., 1930, 190, 199—221).—"Active" hæmatin like the α -metahæmins probably contains acetone or alcohol combined as a complex. This α -metahæmatin is converted into the anhydride

and inactivated by the loss of the additive substance. It is considered that acetone and alcohol (*a*) can drive out the oxygen from oxyhæmoglobin, whereby formation of methæmoglobin is induced, (*b*) can convert native globin into paraglobin, whereby cathæmoglobin is formed, (*c*) can drive out paraglobin from the complex and give acetone- and alcohol-hæmatin. The preparation and properties of the α -metahæmins and ψ -hæmins are described and the inactivation of active hæmatin is followed under various conditions. The coupling of globin with various hæmatin preparations in presence of pyridine and potassium cyanide is described. J. H. BIRKINSHAW.

Structure of hæmocyanin. A. SCHMITZ (Naturwiss., 1930, 18, 798).—When hæmocyanin is hydrolysed by *N*-sodium hydroxide and the precipitate extracted with alcohol, there is obtained a solution of the sodium salt of a complex copper compound. The free acid (C 44.9, H 7.1, N 12.5, Cu 6.3%) is obtained by acidification and purified by reprecipitation. It is greenish-blue, amorphous, yields no copper ion, and has an absorption spectrum similar to that of oxyhæmocyanin, with a maximum at $495 \text{ m}\mu$ and complete absorption below $425 \text{ m}\mu$. It is decomposed by hot concentrated hydrochloric acid with conversion of all the nitrogen into amino-nitrogen. Hæmocyanin is also similarly decomposed by trypsin. It is suggested that hæmocyanin consists of a protein combined with a complex copper compound which is of peptide nature and not a porphyrin. R. K. CALLOW.

Nature of the prosthetic group in *Limulus* hæmocyanin. J. B. CONANT and W. G. HUMPHREY (Proc. Nat. Acad. Sci., 1930, 16, 543—546).—The copper complex of the prosthetic group of the hæmo-

cyanin of the horseshoe crab (*L. polyphemus*) is isolated as a black powder (Cu 21.5, N 9.2, C 39.5, H 5.6, S 8.0%) by treatment of the whole blood with potassium hydroxide (10% of the blood) at 40–50°, washing the precipitate, dissolving in 50% acetic acid, removing copper sulphide by filtration, and reprecipitating with alkali. It is soluble in alkaline solutions only if ammonia or an amine is present to give green or brown solutions the spectra of which exhibit one broad band in the blue which extends into the extreme violet. Treatment of its solution in 50% acetic acid with concentrated hydrochloric acid removes the copper, hydrogen sulphide is evolved, and an amphoteric substance containing sulphur, insoluble at the neutral point, and a water-soluble, non-crystalline substance are formed. A similar amphoteric compound is obtained by precipitation with acetic acid after aërating a solution of the pigment in ammonia. The original material does not give either a pine splint or an Ehrlich test for pyrrole, but on fusion with potassium hydroxide a volatile substance giving a strong positive test is obtained. Reduction of the pigment with hydrogen iodide and phosphonium iodide, however, gave no trace of pyrroles. The pigment appears to be a complex salt of an unknown amino-acid containing sulphur, which forms highly-coloured complexes with amines, its function probably resembling that of protoporphyrin in hæmoglobin.

J. W. BAKER.

Plasma-protein in relation to suspension stability of erythrocytes and precipitation of serum-protein with aluminium sulphate. L. R. JONES (*J. Lab. Clin. Med.*, 1929, 15, 209–215).—An increase in the sedimentation rate of erythrocytes is often associated with an increase in the fibrinogen content of the blood or with a decrease in the albumin: globulin ratio. An increase in the precipitability of the serum-proteins with aluminium sulphate is associated with various pathological conditions; it does not appear to be related to the quantitative distribution of the plasma-proteins.

CHEMICAL ABSTRACTS.

Chemical constitution of serum- and tissue-proteins. II. A. BLANKENSTEIN and A. FISCHER (*Biochem. Z.*, 1930, 224, 211–222).—Further fractionation by salt solutions of serum-proteins (cf. this vol., 943) and of the proteins of pancreas, skeletal and heart muscle, spleen, liver, kidney, lung, thyroid, and brain is described together with determinations of the amounts of tryptophan, tyrosine, and cystine and of the nitrogen of the fractions in its various states of combination. Both the pseudoglobulin and the acid albumin of the serum-proteins are capable of separation into two fractions and the muscle-proteins into three fractions, the amino-acid contents of which are very different. It was not possible to identify any of the muscle-protein fractions with those of the serum-proteins. P. W. CLUTTERBUCK.

Specific refraction increments of serum-albumin and serum-globulin. G. S. ADAIR and M. E. ROBINSON (*Biochem. J.*, 1930, 24, 993–1011).—Crystalline horse serum-albumin (N, 15.6%) has been prepared by a method based on that of Hopkins. The specific refraction increment is a constant un-

affected by recrystallisation. In aqueous solution it is 0.00183 for the crystalline protein, but uncrystallised fractions of albumin show a higher increment. The refractive indices of solutions of alkali albuminates equilibrated with phosphate buffers have been measured and are represented by a simple empirical formula which can be used for calculations of the protein concentration from refractometric measurements. A calculation of the specific refraction increment of the protein from measurements of the refractive indices of the solution and the dialysate has been made by the application of Donnan's theory of membrane equilibrium. The preparation of clear solutions of horse serum-globulin (N 15.13%) is described. The refractive indices of solutions of isoelectric and of alkaline globulins equilibrated with phosphate buffers have been measured and the specific refraction increment of the protein has been calculated after making corrections for the effects due to the unequal distribution of ions. The mean value obtained for total globulin is 0.00186. Measurements have been made of the refractive indices of solutions of glycine, alanine, valine, and tryptophan.

S. S. ZILVA.

Determination of arginine in blood. C. J. WEBER (*J. Biol. Chem.*, 1930, 88, 353–359).—The method for the determination of arginine recently described (this vol., 755) has been applied to tungstic acid blood filtrates which, in the case of dog's blood, give a colour corresponding with 2–3 mg. of arginine per 100 c.c. of blood. That the chromogenic substance is in fact arginine is shown by its destruction by arginase and by the fact that arginine has been isolated (as the monoflavinate) from such blood filtrates.

C. R. HARRINGTON.

Determination of carbamide in blood. O. FOLIN and A. SVEDBERG (*J. Biol. Chem.*, 1930, 88, 77–83).—Improvements in the technique of the urease method for determination of carbamide in blood (cf. Folin and Wu, A., 1919, ii, 308) are described.

C. R. HARRINGTON.

Determination of blood-carbamide-nitrogen by direct Nesslerisation. J. M. LOONEY (*J. Biol. Chem.*, 1930, 88, 189–195).—Protein-free blood filtrate is treated with urease and, when conversion of carbamide into ammonium carbonate is complete, with gum ghatti solution and with Nessler's reagent; the colour is compared with that produced on Nesslerisation of a standard solution of ammonium sulphate containing similar amounts of gum ghatti and of urease.

C. R. HARRINGTON.

Micro-determination of non-protein-nitrogen, carbamide, uric acid, and sugar in unclaked blood. O. FOLIN and A. SVEDBERG (*J. Biol. Chem.*, 1930, 88, 85–96).—The application of standard micro-methods for the determination of the above-named substances in blood filtrates free from material of corpuscular origin (this vol., 630) is described; 0.1–0.2 c.c. of blood is required for each of the determinations.

C. R. HARRINGTON.

Determination of blood-sugar. E. R. NORRIS and W. E. GIBB (*J. Lab. Clin. Med.*, 1929, 15, 281–284).—Folin's micro-method gives results which agree closely with Folin and Wu's macro-method and with

Myers and Bailey's modification of Lewis and Benedict's method. Gibson's micro-method gives inconsistent results. CHEMICAL ABSTRACTS.

Determination of blood-sugar. I. Reduction of alkaline copper reagents by dextrose and other substances. II. Effect of different deproteinising agents on the determination of blood-sugar. S. L. TOMPSETT (Biochem. J., 1930, 24, 1148—1163, 1164—1171).—I. The amount of reduction of the Shaffer-Hartmann alkaline copper reagent by pure dextrose is greater when carried out in an atmosphere of nitrogen than when carried out in air. When the potassium salts are not incorporated in the reagent but added as a separate solution after reduction, the reduction is the same whether carried out in an atmosphere of nitrogen or air and the results are identical with those obtained when the reduction of the reagent containing the potassium salts is carried out in an atmosphere of nitrogen. The amount of reduction by dextrose of alkaline copper solutions containing copper sulphate, tartaric acid, and sodium carbonate depends on the relative concentrations of the two latter substances. Hydrogen carbonates can replace tartrates in alkaline copper solutions. Glycine, aspartic acid, glutamic acid, tryptophan, and cystine affect the reduction of alkaline copper reagents by dextrose only under certain conditions. Uric acid and creatinine in concentrations found in pathological bloods do not appreciably affect the determination of blood-sugar. Urea when present in a concentration of 200 mg. per 100 c.c. of blood has no influence on blood-sugar determinations. Potassium oxalate used as an anti-coagulant in a concentration of 1% in blood has no influence on the reduction values. The composition of a modified alkaline copper reagent and a modified technique for the determination of dextrose in blood filtrates are described. The method is based on the reduction of an alkaline copper solution, dissolution of the cuprous oxide in an acid iodide-iodate-oxalate solution, and titration with thiosulphate.

II. The non-sugar substances present in the tungstic acid filtrates in the method described above do not appreciably affect the results. The sugar content of tungstic acid filtrates as determined by the Folin-Wu, Folin, and Shaffer-Hartmann methods is low. Part of the sugar in a tungstic acid filtrate is in combination with other substances in the filtrate.

S. S. ZILVA.

Reducing power of a mixture of two kinds of sugar in equal concentrations. P. SCHWARTZ (Biochem. Z., 1930, 224, 193—201).—The amounts of copper (mg.), as determined by Benedict's method, equivalent to various amounts of pure dextrose, levulose, galactose, arabinose, and maltose, and the similar values for the reducing power of mixtures of equal concentrations of dextrose and levulose, dextrose and galactose, dextrose and arabinose, dextrose and maltose, are tabulated. The total reducing power of the mixtures is not equal to the sum of the separate reducing powers of the two sugars, but is much more nearly equal to half the sum of the reducing power of each sugar in double the concentration. P. W. CLUTTERBUCK.

Nature of blood-sugar. L. B. WINTER (Biochem. J. 1930, 24, 851—855).—Blood-sugar consists mainly of α -glucopyranose, which can be obtained in crystalline form from the deproteinised blood by precipitation with lead acetate and then with barium hydroxide in methyl alcohol and subsequent decomposition of the barium compound. S. S. ZILVA.

Determination and regulation of blood-clotting function in childhood. I. N. KUGELMASS, F. W. BANCROFT, and M. STANLEY-BROWN (Amer. J. Dis. Children, 1930, 39, 471—486).—The index of the clotting function of the blood ($I = [\text{prothrombin}][\text{fibrinogen}]/[\text{antithrombin}]$) is normally 0.5 ± 2 . Tendencies to clot ($I > 1.0$) or bleed ($I < 0.2$) may be influenced by diet. CHEMICAL ABSTRACTS.

Action of simple hæmolysins. E. PONDER and J. F. YEAGER (Proc. Roy. Soc., 1930, B, 106, 506—531).—Time-dilution and percentage hæmolysis curves were determined for simple hæmolytic systems (saponin, sodium taurocholate, sodium oleate, and washed erythrocytes) over greater ranges of dilution than in previous work. It is shown that the reaction should be expressed by an equation of the n th order rather than by one of the first order, as has been previously supposed. It is tentatively suggested that a reaction between the cell component and aggregates of different numbers of lysin molecules would explain this. The value for n was $1.0-3.0$ under normal conditions, but varied with the nature of the lysin, the type of the erythrocyte, the temperature, and with the presence of different electrolytes in the system. The application of these findings to the calculation of the "resistance constant" R for the comparison of different systems containing the same lysin is discussed. It is pointed out that the values for R previously obtained must be less than the true values when the reactions are considered as of the n th order, and that the effects of different inhibitors must be greater than has been previously supposed. G. F. MARRIAN.

Effect of variations in cell content of hæmolytic systems. E. PONDER (Proc. Roy. Soc., 1930, B, 106, 532—542).—The author's hypothesis (A., 1926, 969) of a limited zone of action round the erythrocyte to explain the relation between the quantity of lysin used and the number of cells present is revised in view of the fact that hæmolysis must be considered as an n th order reaction (see preceding abstract), and to include experiments covering a greater range of cell concentration. Equations showing this relationship are developed. The observed values for the quantity of lysin used were found to agree closely with those predicted. The value (ρ) for the radius of the "zone of action" was found to be larger than previously given. Calculations of ρ for different types of red cells and various simple lysins confirmed the author's previous conclusion that the magnitude of ρ depends on the resistance to hæmolysis of the cells in the system, although this relationship is not so exact as was supposed. G. F. MARRIAN.

Chlorohæmoglobin reaction in cadaverous tissues. A. D. VOLTA (Boll. Soc. Ital. sperim., 1928, 3, 37—39; Chem. Zentr., 1929, i, 1591).—The colour

reaction previously described (A., 1929, 459) is intense and rapid with putrescent parts which already show traces of cadaverous decomposition. The reaction detects incipient sepsis when other signs of decomposition are lacking. L. S. THEOBALD.

Fibrillar structures in the albuminous layer of the egg of the fowl. G. C. HERINGA and S. H. VAN KEMPE VALK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 530—532).—The albuminous layer surrounding the egg yolk consists of a series of strata, the outer layers being clear and transparent, whilst the rest is opaque. The membranes are of fibrillar structure. The fibrils are dissolved on digestion with pepsin and hydrochloric acid at 37°, when the albumin of a hard-boiled egg is dissolved completely. In a raw egg the membranes are dissolved less readily than the remainder of the albumin, and when sections are prepared from a frozen egg the membranous structures remain in connexion even after digestion. The membranes are completely soluble in alkaline trypsin. Evidence is obtained that the fibrils are composed of a keratinic substance. J. W. SMITH.

Glutathione content of organs, especially of muscle. E. GABBE (Klin. Woch., 1930, 9, 169—170; Chem. Zentr., 1930, i, 1952).—Of the glutathione in the lungs and arterial blood, 50—70% is present in the thiol form, whilst of that in the liver and spleen 98—100% is present in the thiol form. In resting animals the glutathione content of the muscle was 32—41 (average 37) mg. per 100 g., being depressed by vigorous exercise to 12—30 (average 23) mg. per 100 g. A. A. ELDRIDGE.

Glutathione. IV. Determination of structure. E. C. KENDALL, H. L. MASON, and B. F. MCKENZIE.—See this vol., 1299.

Glutathione. B. H. NICOLET.—See this vol., 1299.

Internal secretion in insects. III. Digestive enzymes of the silkworm. O. SHINODA (J. Biochem. Japan, 1930, 11, 345—367).—Optimal p_H values for the proteases, amylase, maltase, and invertase are recorded. Cellulase and cytase are absent. The disaccharide and dipeptide enzymes are localised in the intestinal epithelium.

CHEMICAL ABSTRACTS.

Co-enzyme content of various animal tissues. E. SYM, R. NILSSON, and H. VON EULER (Z. physiol. Chem., 1930, 190, 228—246).—The co-enzyme content of various animal organs was determined and an attempt made to correlate this with the sugar metabolism. Striped muscle shows the highest co-enzyme content, unaffected by stimulation. Nerve substance has a high co-enzyme content compared with connective tissue. The cortex of the kidney and adrenal has about double the co-enzyme content of the medulla. The muscular layer of the intestine contains co-enzyme. J. H. BIRKINSHAW.

Structure of simple nucleic acids. E. ANNAU (Z. physiol. Chem., 1930, 190, 222—227).—Guanylic acid from pancreas is identical in crystalline form of the tertiary sodium salt, specific rotation of the secondary sodium salt, and velocity of hydrolysis with the product obtained from yeast. J. H. BIRKINSHAW.

Microchemical tests for phenolic substances in the exoskeleton. H. SCHMALFUSS and H. BARTHMEYER (Mikrochem., 1930, 8, 245—251).—A minute quantity of the substance is powdered and then moistened with 0.008—0.25 c.c. of water and the suspension transferred to a test-tube. After heating for 2 min. in a water-bath the liquid is filtered. Into the filtrate is dipped a strip of filter-paper impregnated with at least a day-old preparation of the enzyme obtained from the larvæ of *Tenebrio molitor*, L. The preparation is kept for 3 days at 38° in a sealed tube; in the presence of melanogenic substances a grey or brown colour develops in the test paper. For the detection of *o*-dihydroxybenzene derivatives a drop of the filtrate is rubbed on a white tile with a fine rod which has been dipped in a 5% solution of ferric chloride; a green colour which becomes red on addition of a trace of sodium carbonate indicates the presence of the above-named compounds. Phenolic substances may be detected in a similar way by the blue to green colour produced with sodium hydrogen carbonate and a suspension of 2:6-dichloro-1-quinone-4-chloroimide in water or by means of Millon's reaction. A. R. POWELL.

Determination of lactic acid in muscle. E. ERNST and I. TAKÁCS (Biochem. Z., 1930, 224, 145—150).—The muscle is frozen in carbon dioxide snow-ether mixture, pulverised, extracted with ether, and the ether removed. The lactic acid in the filtered aqueous extract of the residue is then determined by permanganate titration (see following abstract). The recovery of added lactic acid is 90—94%.

P. W. CLUTTERBUCK.

Permanganate titration in a heated medium. E. ERNST and G. HORVÁTH (Biochem. Z., 1930, 224, 135—144).—In carrying out determinations by permanganate oxidation in hot acid solution, an error is caused by the fact that the permanganate is itself oxidised as well as the substance to be determined. The amount of self-reduction is shown to be proportional to the total amount of permanganate used and a standardisation curve is constructed which permits the reading off from the total permanganate used of the amounts concerned with self-reduction and oxidation of the substance. With this modification small amounts (10 γ) of lactic acid can be determined. P. W. CLUTTERBUCK.

Detection of ergosterol in human skin. H. HENTSCHEL and L. SCHINDEL (Klin. Woch., 1930, 9, 262; Chem. Zentr., 1930, i, 1952).—The sterol obtained from the cutis and epidermis of cadavers contained 0.42% (adult) or 0.15% (new-born) of ergosterol. A. A. ELDRIDGE.

Absorption spectrum of cholesterol from human brains. I. H. PAGE and W. MENSCHICK (Naturwiss., 1930, 18, 735).—Cholesterol from adult brains exhibits in the ultra-violet an "end" absorption similar to the purified product, whilst cholesterol from the brain of young and newly-born infants and of foeti shows a certain amount of absorption due to the presence of other substances. Two absorption maxima at 2820 and 2930 Å. are assigned to ergosterol, but the third maximum due to ergosterol (at 2700 Å.) is completely masked by unknown substances or

mixtures. The brain may absorb ergosterol along with nourishment or vitamin-*D* may accumulate during the period of bone formation, increasing the amount of ergosterol in cholesterol-rich organs. The regularity of the occurrence of considerable absorption at 2500—2600 Å. in the cholesterol from infant and foetal brains but not from adult brains seems to substantiate the latter hypothesis.

W. R. ANGUS.

Cholesterol in the earth-worm. A. DE WAELE (Bull. Acad. roy. Belg., 1930, [v], 16, 592—597).—After keeping for several days in sand, worms were extracted with ether, the extract being then evaporated and the residue twice saponified with 15% alcoholic potassium hydroxide. The material obtained by ethereal extraction of the resultant soap gave, after recrystallisation, the reactions of pure cholesterol. The results obtained by Dorée (cf., B., 1909, 373) are vitiated by the presence of impurities, probably phytosterol. The cholesterol content of earth-worms is 0.922 g. per kg. H. J. DOWDEN.

Fat from *Cypridina*. M. KOTAKE and Y. KIMOTO (Proc. Imp. Acad. Tokyo, 1930, 6, 237—238).—The fats extracted from *Cypridina* by light petroleum were hydrolysed with alcoholic potassium hydroxide. The portion insoluble in alcohol consists essentially of cholesterol (40% of total fats). The portion soluble in alkali yielded by extraction with ether a small crystalline fraction (6%), $C_{17}H_{34}O_2$, m. p. 53—56°, possibly mixed crystals of palmitic and stearic acids, and a residue which on hydrogenation afforded a crystalline acid (20%), $C_{20}H_{40}O_2$, m. p. 68.5—70°, which showed no depression of m. p. when mixed with dihydrologanic acid. The principal acid of *Cypridina* fat is probably laganic acid. No significant amount of highly unsaturated acids is present. T. H. MORTON.

Composition of the fatty acids present as glycerides in the liver oil of the thresher shark (*Alopias vulpes*). J. A. LOVERN (Biochem. J., 1930, 24, 866—869).—The amount of squalene (if any) must be very low in this oil. In this respect and in the composition of the fatty acids, namely, the absence of unsaturated acids of the C_{24} group and the high content of unsaturated acids of the groups C_{20} and C_{22} , it resembles skate-liver oil.

S. S. ZILVA.

Radium in aquatic organisms. W. VERNADSKY (Compt. rend., 1930, 191, 421—423).—The extent and significance of the presence of radium in aquatic organisms (*Lemna*) are discussed. F. O. HOWITT.

Colorimetric determination of proteins of the cerebrospinal fluid. P. B. MATZ (J. Lab. Clin. Med., 1930, 15, 370—385).—Colorimetric modifications of Hewitt's and Wu's methods for the determination of albumin, globulin, and total protein are described. Non-meningitic and non-syphilitic cerebrospinal fluid contains albumin (average) 3.4, globulin 0.13, total protein 48 mg. per 100 c.c. Markedly higher values and a lower albumin : globulin ratio are associated with paresis and multiple sclerosis.

CHEMICAL ABSTRACTS.

Vitamin content of milk used in infant feeding. I. G. MACY and J. OUTHOUSE (Amer. J. Dis. Children,

1929, 37, 379—400).—Human milk contains about the same amount of vitamin-*A*, but only half as much -*B*, as cow's milk; it is deficient in the anti-rachitic factor, whereas cow's milk contains a small quantity.

CHEMICAL ABSTRACTS.

Variations in component fatty acids of butter due to changes in seasonal and feeding conditions. T. P. HILDITCH and J. J. SLEIGHTHOLME (Biochem. J., 1930, 24, 1098—1113).—The influence of added fat in the diet of cows, although definite, is small. Much more profound changes in fatty acid composition appear to be caused by conditions such as change from outdoor to indoor life, character of diet, and seasonal changes in temperature. These differences lie mainly in the variation of the amount of unsaturated acids present and the amount of the lower saturated acids—butyric to lauric; palmitic acid appears to be the most constant, whilst the stearic acid content varies somewhat erratically from one butter to another. Butter-fat is characterised by amounts of butyric to myristic acids more or less specific to cow's milk-fat, and of palmitic, oleic, and linoleic acids not widely dissimilar from the proportions of the same acids found in the body or storage fats of the same class of animal. S. S. ZILVA.

Solubility of cholesterol in the bile. O. MERKEL-BACH (Schweiz. med. Woch., 1929, 59, 12 pp.; Chem. Zentr., 1930, i, 1963).—By precipitation with digitonin after esterification the variable cholesterol content of the bile was confirmed. The solubility of cholesterol in the bile is favoured by a high content of bile acids. The mechanism of formation of cholesterol and cholic acid in the organism is discussed. A. A. ELDRIDGE.

Determination of bile acids. Bile salts in urine. C. L. DUCCO and P. T. PANZA (Semana méd., 1930, 37, 1193—1198).—With body fluids Pettenkofer's reaction is not sensitive to 1 in 1000. In sodium glycocholate solution traces of impurities cause considerable variations in surface tension, rendering the stalagmometric method inexact. The determination is most exact when performed at p_H 2.0. In solutions less concentrated than 0.1% practically all of the bile salt is adsorbed on charcoal. Hence the surface tension is determined at p_H 2 and after treatment with charcoal, the bile salt content being determined by reference to a table. Urine contains 0.10—0.25 g. per 1000 calculated as sodium glycocholate. CHEMICAL ABSTRACTS.

Mechanism of sugar excretion. I. Dextrose. T. G. NI and P. B. REHBERG (Biochem. J., 1930, 24, 1039—1046).—There is no difference between sugar excretion after one sugar injection and a second following shortly after. The content of dextrose in the reabsorbed fluid is very variable. The reabsorption of dextrose goes on even when the blood-sugar is far above normal and is not decreased with increasing blood-sugar. The increase in reabsorption becomes less as the blood-sugar rises. Glycosuria must be due to the failure of the reabsorption of the sugar to increase as fast as its filtration increases with rising blood-sugar. The concentration difference between urine and blood at the site of reabsorp-

tion is probably the limiting factor of reabsorption of dextrose.

S. S. ZILVA.

Fastness of dyes to perspiration. I. Composition of human perspiration. C. C. N. VASS and B. A. MCSWINEY (J. Soc. Dyers and Col., 1930, 46, 190—195).—The maximum and minimum values for freshly-shed sweat from normal males and females were: p_H , 7.35 and 5.10 (females, 6.80 and 6.35); ammonia-nitrogen, 7.00 and 2.55 mg. per 100 c.c. (11.1 and 2.6); urea-nitrogen, 32.92 and 11.10 mg. per 100 c.c. (27.72 and 13.63); amino-acid-nitrogen, 9.2 and 2.4 mg. per 100 c.c. (8.7 and 4.7); dextrose, 26.4 and 9.4 mg. per 100 c.c. (35.0 and 12.0); and chlorides calc. as NaCl, 5.01 and 2.65 g. per 1000 c.c. (3.87 and 2.23). The dextrose content of sweat from stout healthy women is about twice that of sweat from normal women; the amount of dextrose in the sweat of stout men is only about 50% greater than in that of normal men. With few exceptions freshly-shed sweat is faintly acid, but on keeping its reaction becomes alkaline owing to decomposition, which results in a marked increase of the ammonia-nitrogen content and a disappearance of the urea-nitrogen, these changes being due to bacteria normally associated with freshly-shed perspiration. A. J. HALL.

Plasma-proteins [in disease]. H. J. WIENER and R. E. WIENER (Arch. Int. Med., 1930, 46, 236—265).—The fibrinogen, serum-globulin and albumin contents of human plasma have been determined in health and in a number of diseases, including cirrhosis of the liver, diabetes mellitus, benign glycosuria, and liver, gall-bladder, and renal affections. Cholesterol, chlorides, non-protein-nitrogen, uric acid, and calcium have also been determined. In mild infections, the albumin is slightly decreased and the fibrinogen content is increased, whilst in more severe infections the albumin is more markedly decreased and the globulin increased. In cirrhosis of the liver there is a decrease in the albumin and an increase in the globulin. No significant change in the serum-proteins occurs in diabetes mellitus and benign glycosuria.

W. O. KERMACK.

Excretion of chloride in achlorhydria. R. S. HUBBARD (J. Biol. Chem., 1930, 88, 361—366).—Patients with achlorhydria show a high rate of urinary excretion of chloride on awakening and a low rate of excretion for 1 hr. after breakfast.

C. R. HARINGTON.

Blood-serum-proteins in anæmic conditions. C. ACHARD and M. HAMBURGER (Compt. rend., 1930, 191, 309—311).—An abnormally low content of all fractions of proteins (albumin, globulin, and myxoprotein) is observed in the serum in cases of pernicious anæmia and also, although not invariably, in anæmias accompanying other pathological conditions. When cure takes place both the amount of serum-protein and the erythrocyte count rise to normal.

R. K. CALLOW.

Crystalline derivatives of an acid present in liver, active in pernicious anæmia. R. WEST and M. HOWE (J. Biol. Chem., 1930, 88, 427—431).—Concentrated liver extract was saturated with picric acid and extracted with a mixture of butyl alcohol and ether; the aqueous solution, after removal of

picric acid and organic solvents, was cleared with excess of lead hydroxide and with lead acetate and barium hydroxide. The filtrate was freed from lead and barium and precipitated with phosphotungstic acid; the solution obtained by decomposition of the precipitate with barium hydroxide was concentrated in a vacuum, treated with excess of barium hydroxide, and precipitated with alcohol. The barium salt was decomposed to give an alcohol-insoluble water-soluble product with C 46.6%, H 6.9%, N 10.6%; none of the nitrogen is in the amino-condition, but after acid hydrolysis one half is found in this form and in fact to be present as β -hydroxyglutamic acid. The other (unidentified) hydrolysis product is a neutral compound which is precipitated with phosphotungstic acid. The acid is highly active therapeutically in pernicious anæmia and gives a crystalline *quinine* salt, $C_{20}H_{24}O_2N_2 \cdot C_{10}H_{18}O_6N_2$, $[\alpha]_D -97^\circ$, which retains the therapeutic activity.

C. R. HARINGTON.

Anæmic lipæmia. M. HEKI (J. Biochem., Japan, 1930, 11, 369—390).—The distribution of total fatty acids, total cholesterol, and lipid phosphorus in the blood, liver, lung, kidney, spleen, heart, and skeletal muscles of anæmic rabbits has been determined.

CHEMICAL ABSTRACTS.

Preputial calculus. COULLAUD (J. Pharm. Chim., 1930, [viii], 11, 31—34).—A calculus weighing 645 g., found in a case of phymosis, was separated into four concentric layers. The outermost contained calcium carbonate, phosphate, and oxalate and magnesium ammonium phosphate (I), the second (120 g.), a larger proportion of I, but no calcium oxalate, the third (20 g.), almost entirely I, with uric acid, sodium urate, and traces of calcium salts, and the centre (4 g.), uric acid with traces of I and of calcium carbonate. The urine contained crystals of calcium oxalate and phosphate and of uric acid.

H. E. F. NOTTON.

Effect of vitamin injury on the origin of cancer. R. ERDMANN and E. HAAGEN (Arb. Reichsgesundh.-Amt, 1929, 61, 141—152; Chem. Zentr., 1930, i, 1323).—Alternating nutrition with food rich in vitamin and with the vitamin content enriched by vitamin-B favours the formation of tumours.

L. S. THEOBALD.

Cancer chemotherapy. IX. Reaction of the blood in cancer. F. BISCHOFF, M. L. LONG, and E. HILL (J. Pharm. Exp. Ther., 1930, 39, 425—433).—The mean p_H value of the plasma of 15 untreated cancerous subjects was 7.50, whilst that of 15 normal individuals was 7.46. Statistical analysis shows that the difference is probably significant. The carbon dioxide tension for the cancer group was lower than that of the normal group, the hydrogen carbonate content of the two groups being very nearly the same.

W. O. KERMACK.

Comparison of effects of arginine and thyroxine on tumour growth-rate in the mouse. E. GILROY (Biochem. J., 1930, 24, 1181—1187).—Injections of thyroxine into mice retard the rate of tumour growth without an accompanying loss of body-weight during a 12-day period of treatment. Substitution of arginine for thyroxine causes a renewal of rapid growth, but if arginine be given previously

the substitution of thyroxine does not cause a permanent deflexion of the curve. If both are given to the same animal the rate of growth is similar to that of untreated controls if arginine is given daily, but if less often, the effect of thyroxine predominates.

S. S. ZILVA.

Fluid exchange. VIII. Fluid and gas exchange in diabetes insipidus. K. KIMURA, S. ABE, and T. YAMAGUCHI (Tohoku J. Exp. Med., 1930, 15, 70—90).—Circulation of fluid between tissues and blood is abnormally active in diabetes insipidus. Chlorides tend to accumulate in the tissues, and tissue respiration is decreased.

CHEMICAL ABSTRACTS.

Hypophysectomy and pancreas diabetes in the toad. B. A. HOUSSAY and A. BIASOTTI (Semana Méd., 1930, 37, 1207).—Pancreatectomy produces hyperglycæmia and glycosuria, but with simultaneous hypophysectomy the former does not develop unless part of the pituitary gland is reimplanted under the skin.

CHEMICAL ABSTRACTS.

Chemistry and metabolism in experimental yellow fever in *Macacus rhesus*. A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1930, 46, 290—305).—Blood from *M. rhesus* in the final stages of yellow fever infection has a high concentration of non-protein-nitrogen, and usually an increase in urea concentration which is small in proportion to the non-protein-nitrogen. It also shows an increase of amino-acid-nitrogen large in proportion to that of non-protein-nitrogen, and of residual nitrogen, and a normal uric acid content. The creatinine content of the blood is usually increased.

W. O. KERMAK.

Cholesterol content of blood in filaria. T. C. BOYD and A. C. ROY (Indian J. Med. Res., 1930, 17, 949—953).—Values were 0.12—0.22 (average 0.146)%, instead of (normally) 0.116%.

CHEMICAL ABSTRACTS.

Disturbance of metabolism produced by bony and non-bony injury, with notes on certain abnormal conditions of bone. D. P. CUTHBERTSON (Biochem. J., 1930, 24, 1244—1263).—In normally healing fractures there is little change in the metabolism of calcium. There is, however, a marked loss of nitrogen, phosphorus, and sulphur, the rate of loss following the injury reaching a maximum about the second to sixth day and then gradually declining, but persisting even after 1 or 2 months. This loss can be traced mainly to the catabolism of muscle. The administration of irradiated ergosterol to these cases does not alter their metabolism apart from a slight increase in the urinary excretion of calcium, nor does it improve the clinical condition of the patient. Irradiated ergosterol can have a beneficial effect in certain types of pathological fracture and abnormal bone conditions. There is a catabolic loss of sulphur, nitrogen, and phosphorus resulting from the injury of tissue other than bone. There is no coincident increase in the non-protein-nitrogen and inorganic phosphorus of the blood corresponding with the increased catabolism in the cases of fracture and non-bony injury. Changes occur later which appear to involve a raising of the level of these elements. A

few cases of abnormal bone metabolism are discussed in so far as they illustrate some phases of calcium and phosphorus metabolism.

S. S. ZILVA.

Lactic acid content of blood in hepatic disease. E. MASSOBRO and M. MICHALOV (Minerva Med., 1930, 1, 650—656).—In mild cases not involving the parenchyma the blood-lactic acid is unchanged; it is considerably increased in severe cases, in heart disease, and in liver stasis.

CHEMICAL ABSTRACTS.

Action of the cinchona and certain other alkaloids in bird malaria. J. A. GOODSON, T. A. HENRY, and J. W. S. MACFIE (Biochem. J., 1930, 24, 874—890).—Only alkaloids belonging to or derived from the cinchona series showed marked remedial action in canaries infected with *Plasmodium inconspans*. Of the natural alkaloids the most active was hydroquinine, followed by quinidine, quinine, cinchonidine, and cinchonine in descending order, differing, however, little in activity. Hydrogenation of quinidine, cinchonidine, and cinchonine, unlike that of quinine, does not increase the activity. Among alkaloidal drugs having some reputation as remedies for malaria slight activity was observed only in *Alstonia scholaris* and *A. constricta*. The former species probably owes its activity to echitamine, which showed slight action. Activity is restored to quitenine and the analogous carboxylic acids derived from quinidine, cinchonidine, and cinchonine by esterification; the activity rises as the mol. wt. of the alcohol used for esterification is increased, and reached a maximum at butyl- or amyl- quitenine. The following esters were prepared by passing dry hydrogen chloride into a mixture of the acid and the alcohol and heating: *methylquitenine* (not obtained crystalline), m. p. 170°, $[\alpha]_D^{20}$ —130° in chloroform (*monohydrochloride*, m. p. 153°, $[\alpha]_D^{20}$ —189° in water); *n-propylquitenine*, m. p. 170°, $[\alpha]_D^{20}$ —143° in chloroform (*monohydrochloride*, m. p. 187°, $[\alpha]_D^{20}$ —225° in water); *isopropylquitenine*, m. p. 189°, $[\alpha]_D^{20}$ —142° in chloroform (*monohydrochloride*, $[\alpha]_D^{20}$ —231° in water); *n-butylquitenine*, m. p. 142°, $[\alpha]_D^{20}$ —143° in chloroform (*monohydrochloride*, $[\alpha]_D^{20}$ —227° in water); *dihydrochloride*, $[\alpha]_D^{18}$ —250° in water); *isobutylquitenine*, m. p. 154°, $[\alpha]_D^{20}$ —144° in chloroform (*monohydrochloride*, m. p. 248°, $[\alpha]_D^{20}$ —223° in water); *n-amylquitenine*, m. p. 135°, $[\alpha]_D^{20}$ —135° in chloroform (*monohydrochloride*, m. p. 195°, $[\alpha]_D^{20}$ —217° in water); *isoamylquitenine*, m. p. 160°, $[\alpha]_D^{20}$ —136° in chloroform (*monohydrochloride*, $[\alpha]_D^{17}$ —222° *optylquitenine monohydrochloride*, m. p. 181°, $[\alpha]_D^{20}$ —191° in water, and *dihydrochloride* not crystalline, m. p. 164°; *benzylquitenine*, m. p. 161°, $[\alpha]_D^{24}$ —128° in chloroform (*monohydrochloride*, m. p. 233°, $[\alpha]_D^{20}$ —175° in water); *ethylquitenidine*, m. p. 139°, $[\alpha]_D^{20}$ +163° in chloroform (*monohydrochloride*, m. p. 242°, $[\alpha]_D^{17}$ +151° in water); *isoamylquitenidine monohydrochloride*, m. p. 245°, $[\alpha]_D^{17}$ +132° in water; *ethylcinchotenidine*, m. p. 180°, $[\alpha]_D^{20}$ —115° in chloroform (*monohydrochloride*, $[\alpha]_D^{20}$ —165° in water); *isoamylcinchotenidine monohydrochloride*, m. p. 152°, $[\alpha]_D^{17}$ —151° in water; *ethylcinchotenine monohydrochloride*, $[\alpha]_D^{17}$ +130° in water; *isoamylcinchotenine*, m. p. 147—149° (*monohydrochloride*, m. p. 145°, $[\alpha]_D^{20}$ +117° in water).

S. S. ZILVA.

Constituents of blood-serum in myxœdema.

C. ACHARD and I. ORNSTEIN (Compt. rend., 1930, 191, 311—312).—In twelve cases of myxœdema the blood-serum had the normal content of proteins, cholesterol, and sodium, but the total lipin content was slightly high, and calcium content slightly low.

R. K. CALLOW.

Fat metabolism. I. Fat tolerance in obesity.

H. R. RONY and A. J. LEVY (J. Lab. Clin. Med., 1929, 15, 221—228).—The blood-fatty acid normally increases after ingestion of cream; obese subjects behave irregularly. The plasma-cholesterol is normal in both cases. A high or low fat tolerance in obese subjects is usually associated, respectively, with a high or low sugar tolerance. CHEMICAL ABSTRACTS.

Liberation of a histamine-like substance from the lung in œdema. E. PESERICO (Minerva Med., 1930, 1, 692—700).—The presence in the blood of a substance behaving like histamine is discussed.

CHEMICAL ABSTRACTS.

Experimental production of pellagra in rats.

I. V. R. LEADER (Biochem. J., 1930, 24, 1172—1180).—Pellagra can be induced in rats in 17—25 days on a synthetic diet containing starch and sucrose and just sufficient marmite to prevent polyneuritis, administered when the animals begin to manifest the deficiency of the vitamin-B complex. In the absence of sucrose from the diet pellagra does not appear, but all the rats develop polyneuritis. Increased amounts of sucrose do not increase the severity of the symptoms. Rats suffering from polyneuritis develop pellagra after the marmite dose is raised sufficiently to protect them from the disease, and in the case of those on a sugar-free diet when sugar is added. Rats, like human beings, have a seasonal immunity from pellagra.

S. S. ZILVA.

Nature of the sugar in pentosuria. I.

GREENWALD (J. Biol. Chem., 1930, 88, 1—7).—The urine was cleared with lead acetate, and the filtrate was further precipitated with basic lead acetate and sodium hydroxide; the precipitate was decomposed with carbon dioxide, and the filtrate, after removal of traces of lead with hydrogen sulphide, was concentrated. The resulting solution was treated with mercuric sulphate (in molecular proportion to the nitrogen content) and neutralised with barium hydroxide, and the filtrate, freed from mercury, was concentrated to small bulk and treated with excess of alcohol; after filtration, the concentration and precipitation with alcohol were repeated. The final filtrate was concentrated and treated with an amount of *p*-bromophenylhydrazine equal in weight to the apparent dextrose content. Application of this procedure to the urines of four patients exhibiting pentosuria resulted in the isolation of xyloketose-*p*-bromophenylhydrazone. The conclusions of Levene and La Forge (A., 1914, i, 1027) are therefore confirmed.

C. R. HARRINGTON.

Post-mortem blood chemistry in renal disease.

S. H. POLAYES, E. HERSHEY, and M. LEDERER (Arch. Int. Med., 1930, 46, 283—289).—Blood from patients who died from various diseases has been analysed in respect of urea and creatinine, and the results have been compared with those obtained from the same

patient before death. No definite relation was found between the urea contents of the blood before and after death. The *post-mortem* creatinine figures in various diseases were on an average 0.5—1.7 mg. per 100 c.c. higher than those obtained during life.

W. O. KERMAK.

Absorption spectrum of blood and its relation to rickets. R. C. GIBBS, J. R. JOHNSON, and C. V. SHAPIRO (Naturwiss., 1930, 18, 764).—Suhrmann's statement (this vol., 132) that solutions of blood from rachitic rats give a different absorption spectrum from that obtained with a solution of blood from normal animals was not confirmed. It is therefore concluded that his results were accidental and that no effective change in the blood-pigments results from a change in pathological state.

W. R. ANGUS.

Effect of administration of phosphorus, anti-rachitic treatment, and spontaneous healing on calcium of the blood-serum of rachitic rabbits. B. HAMILTON, L. KAJDI, and D. MEEKER (J. Biol. Chem., 1930, 88, 331—336).—The increase in the phosphorus of the blood-serum of rachitic rabbits which occurred in cases of spontaneous healing, or was brought about by administration of phosphate, cod-liver oil, or irradiated ergosterol, or by the action of ultra-violet light, was frequently accompanied by diminution in the blood-calcium.

C. R. HARRINGTON.

Anomaly of copper metabolism. F. HAURWITZ (Z. physiol. Chem., 1930, 190, 72—74).—In two cases of Wilson's disease (pseudosclerosis) the liver contained 5.9 and 4.8 mg. of copper per 100 g. (normal value about 0.3) and the abdominal ganglia 2.8 and 3.1 mg. (normal value about 0.55). The iron content of the liver was normal.

J. H. BIRKINSHAW.

Metabolism of the lung-fish, *Protopterus aethiopicus*. H. W. SMITH (J. Biol. Chem., 1930, 88, 97—130).—Lung-fish were induced to aestivate under artificial conditions, and, after varying periods, were transferred to a metabolism chamber. The fasting but active lung-fish utilises oxygen at the rate of about 20 c.c. per kg. per hr., of which about 50% is employed in the oxidation of protein, the nitrogen appearing almost equally as carbamide and as ammonia. Of the total metabolism of the active fish about 15% is estimated to be due to muscular tone and movement. During aestivation the fish is completely immobilised and is enveloped, except for the oral aperture, by an impervious cocoon; secretion of urine is entirely suspended. The oxygen consumption of the aestivating fish falls, at 20°, to about 8 c.c. per kg. per hr.; the metabolic rate may be raised by rise of temperature or by injection of thyroxine without awaking the fish. The reduction of the metabolism must involve non-mechanical as well as muscular processes. Energy during aestivation is derived largely from the catabolism of protein, of which the nitrogen accumulates in the tissues almost exclusively as carbamide; this, together with sulphate which also accumulates, is excreted at a very high rate during the first days of the post-aestivation period. No significant accumulation of ammonia, creatine, or phosphate is observed; acetone sub-

stances and uric acid were absent from the tissues during aestivation. C. R. HARINGTON.

Carbohydrate metabolism of normal and tumour tissue. I. Measurement of the respiratory quotient. F. DICKENS and F. ŠIMER (Biochem. J., 1930, 24, 905—913).—Thin slices of tissue are suspended in carbon dioxide-free Ringer solution buffered by means of phosphate and in equilibrium with pure oxygen. The carbon dioxide formed in respiration is absorbed by barium hydroxide solution and the diminution in pressure which occurs is used for the calculation of respired oxygen. After a definite time all the carbon dioxide is expelled from the barium hydroxide, phosphate, and tissue by addition of excess of strong acid, and the resulting positive pressure is used for the calculation of the total carbon dioxide at the end of the experiment. This figure corrected for the carbon dioxide present at the beginning of the experiment gives the amount formed in respiration during the experimental period. The greatest error to be expected in the value of R.Q. is 0.02.. S. S. ZILVA.

Oxidations in central and peripheral nervous tissue. E. G. HOLMES (Biochem. J., 1930, 24, 914—925).—Various types of tissue composing the central nervous system have different rates of oxygen consumption; the activity of grey matter whether in the central system or in the peripheral nerve is much higher than that of the white matter. The distributions of indophenol oxidase and of cytochrome run approximately parallel both to each other and to the rate of oxygen consumption of the different types of tissue. The greatly increased oxygen uptake which grey matter displays in the presence of dextrose depends on the conversion of the sugar into lactic acid and disappears if this conversion is prevented by fluoride. Other substances besides lactic acid, probably not of a carbohydrate nature, which are not easily removed by washing are also responsible for some of the oxygen uptake by brain-tissue. S. S. ZILVA.

Lactic acid oxidation in brain with reference to the "Meyerhof cycle." E. G. HOLMES and C. A. ASHFORD (Biochem. J., 1930, 24, 1119—1127).—Although a "Meyerhof quotient" (total lactic acid disappearing/lactic acid oxidised) was obtained, no synthesis of carbohydrate from that portion of the lactic acid which disappeared, but was not accounted for by the oxygen uptake, could be demonstrated in brain. S. S. ZILVA.

Transformation of pyruvic acid into lactic acid in the liver. Y. KHOUVINE, E. AUBEL, and L. CHEVILLARD (Compt. rend., 1930, 191, 446—448).—The addition of pyrophosphate to macerated liver with sodium pyruvate incubated at p_H 7.4 favours the formation of lactic acid, but has no influence on the amount of lactic acid derived from pyruvic acid. The carbon dioxide evolution and oxygen consumption lead to the conclusion that an enzyme allows pyruvic acid to function as a hydrogen acceptor and thus form lactic acid. F. O. HOWITT.

Energetics of muscular contraction with increased formation of lactic acid. O. MEYER-

HOF, E. LUNDSGAARD, and H. BLASCHKO (Naturwiss., 1930, 18, 787—788).—When creatinephosphoric acid is hydrolysed, a considerable amount of energy is liberated which during muscular activity is employed partly for anaërobic contraction. When the muscle is poisoned with iodoacetic acid, formation of lactic acid is inhibited without affecting anaërobic contraction and the whole of the phosphagen is simultaneously decomposed, even more quickly than in normal muscle. By a comparison of the total anaërobic development of tension with the decomposition of phosphagen, it is shown that the whole of the energy for anaërobic contraction with the poisoned muscle is derived from phosphagen. P. W. CLUTTERBUCK.

Methylglyoxal as an intermediate product of carbohydrate degradation. E. WIDMANN and E. SCHNEIDER (Biochem. Z., 1930, 224, 157—169).—Macerates of normal and diabetic human blood-corpuses, of red and white corpuses separately, and of acetone preparations of human red cells, are able to convert magnesium hexosediphosphate into methylglyoxal in the same way as macerates of the blood cells of sheep, horses, and rabbits (this vol., 360). Human red and white cells have per c.c. the same glycolytic power but per cell the glycolytic power of the white cell is about twenty times that of the red cell. Macerates of red and white cells give with magnesium hexosediphosphate yields of methylglyoxal corresponding with 71.5 and 70.3% of the sugar used. Macerates of pus, on the other hand, gave negative results. P. W. CLUTTERBUCK.

Use of sodium sulphite as fixing agent for acetaldehyde in surviving tissues and hearts. M. KORTSCHAGIN and M. LEVITOV (Biochem. Z., 1930, 224, 63—68).—A buffered mixture containing sodium sulphite can be used for fixing acetaldehyde in surviving tissues and hearts. P. W. CLUTTERBUCK.

Carbohydrate metabolism of the normal newborn infant. II. Effect on the concentration of blood-sugar of feeding various sugars. H. M. GREENWALD and S. PENNEL (Amer. J. Dis. Children, 1930, 39, 493—503).—The blood-sugar in infants does not increase after breast-feeding during the first 48 hrs., but may do so after the second day. Dextrose is most readily absorbed. CHEMICAL ABSTRACTS.

Passage of carbohydrate through the animal organism. F. HOLTZ and E. SCHREIBER (Biochem. Z., 1930, 224, 1—52).—After administration of dextrose solutions to dogs, the absorption in the stomach, the emptying of the stomach, the filling of and the absorption in the intestine, and the amount and character of the fluids secreted and absorbed are studied and the movements of these organs followed by the usual barium-X-ray technique. Stomach absorption was investigated both in normal and in anaesthetised animals in which the stomach was ligatured above and below. Dextrose solutions of known concentration and containing a known amount of colloidal silicic acid are introduced into the stomach. Changes in silicic acid concentration indicate the changes due to dilution by secretions and permit the calculation of the sugar concentration after allowing

for these dilutions. Comparisons of this with the actual sugar concentration indicates whether or not absorption has occurred. In twelve experiments with normal animals three showed no absorption and nine an absorption of about 2 g. of dextrose per hr. per m.² body-surface, whilst in all of seven experiments of the second type, smaller but positive absorption was obtained. The volumes of gastric juice, its p_{H} , and content of chloride, nitrogen, etc. are tabulated.

P. W. CLUTTERBUCK.

Intermediate metabolism of foreign sugars. E. H. FISHBERG and B. T. DOLIN (Arch. Int. Med., 1930, 46, 321—332).—A method is given for the determination of galactose or xylose in the presence of dextrose in 0.2 c.c. of blood, the principle being to remove the dextrose by treatment with a suitably-prepared yeast suspension. In normal human subjects the reducing non-fermentable fraction is approximately 28 mg. per 100 c.c., but is increased in uræmia, diabetes, and lactation. Galactose and xylose introduced into the blood-stream of a rabbit disappear at a rate proportional to their concentration in the blood. Xylose disappears much more slowly from the blood-stream of rabbits suffering from uranium nephritis and more quickly from rabbits made diabetic by phloridzin. Galactose disappears abnormally slowly from the blood-stream of rabbits suffering from uranium nephritis and from the blood of those gradually poisoned by phosphorus. In human beings, galactose disappears slowly from the blood of patients with nephritis and diabetes.

W. O. KERMAK.

Embryos. IV. Accumulation of glycogen in the bodies of developing chick embryos. V. Accumulation of glycogen in the liver of developing chick embryos. G. E. VLADIMIROV (Biochem. Z., 1930, 224, 69—78, 79—82).—IV. [With M. J. DANILINA.] The increase in the absolute amount of glycogen in the embryo follows the same law as the increase in weight and is calculable from the expression $\log G = 6.31 \log t - 6.01$. This holds even before the internal secretory glands have become active. Part of the glycogen is utilised at hatching. Fat may serve as a source of glycogen in the second half of the incubation period. The liver is very rich in glycogen and heart-muscle is richer than skeletal.

V. The ratio of the weight of the liver to the total weight of the embryo is constant from the 13th day to the time of hatching, the growth of the liver following the same law as that of the whole body. Liver-glycogen forms 40% of the total glycogen of the embryo (cf. A., 1926, 1268).

P. W. CLUTTERBUCK.

Metabolism of tributyrin. R. E. DAVIS (J. Biol. Chem., 1930, 88, 67—75).—When tributyrin was administered orally to hens it was digested to the extent of about 90% in the first experiment and less in subsequent experiments with the same bird owing to the toxicity of the material. Tributyrin was stored to some extent by rats after injection but not after oral administration of the fat, although in the latter case it was digested and absorbed; the butyric acid was probably largely synthesised into higher acids during absorption. Administration of tri-

butyrin to normal and phloridzinised rats on a carbohydrate-free diet increased the ketonuria.

C. R. HARRINGTON.

Lipins of blood-plasma in normal dogs in the post-absorptive state and in fasting dogs. D. GLUSKER (J. Biol. Chem., 1930, 88, 381—387).—Figures are given for the total fatty acids and the total cholesterol of the blood-plasma of 10 dogs in the above-named conditions. C. R. HARRINGTON.

Effects of cystine diet on keratin composition in rabbit wool. J. BARRITT, A. T. KING, and J. N. PICKARD (Biochem. J., 1930, 24, 1061—1065).—There was a large increase in the sulphur content of the fur of individual Angora buck rabbits between two successive 3-month periods, January to April and April to July, whether fed on a normal diet or on a diet containing added cystine. The weight of the fleece was also not influenced by the inclusion of cystine in the diet. S. S. ZILVA.

Comparative biochemistry. V. Behaviour of 2-methylquinoline in the organism of the rabbit and the hen. VI. Behaviour of nitrocinnamic acid in the animal organism. M. TAKAHASHI (J. Biochem. Japan, 1930, 11, 437—441, 441—444).—2-Methylquinoline is partly oxidised and partly paired with glycine to form pyridine-2 : 3-dicarboxylic acid. In rabbits *o*-nitrocinnamic acid is only sparingly oxidised or paired; in the hen it is oxidised to nitrobenzoic and then to succinic acid.

CHEMICAL ABSTRACTS.

Carbamide of rat's blood in pregnancy and lactation on diets containing varying amounts of protein. H. T. PARSONS (J. Biol. Chem., 1930, 88, 311—330).—Large increases were observed in the concentration of carbamide in the blood of pregnant and lactating rats as the result of diets rich in protein, particularly if this dietary treatment were preceded by partial nephrectomy. The greatest increase was observed during lactation and appeared to be associated with an effect (possibly emotional) of the act of suckling. C. R. HARRINGTON.

Nitrogen and calcium metabolism in calves during the period of milk feeding. E. A. SOKOLOV (Nauch. Agron. Zhur., 1929, 6, 429—437).

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism in older children on mixed diet containing a large or small quantity of milk. A. M. COURTNEY and A. BROWN (Arch. Dis. Childhood, 1930, 5, 17—22).—A diet which contains eggs and vegetables but only a small quantity of milk does not provide sufficient calcium and phosphorus. Marked individual differences in the amounts secreted were observed.

CHEMICAL ABSTRACTS.

Calcium and phosphorus concentration in the large and small intestines of children. A. M. COURTNEY (Arch. Dis. Childhood, 1930, 5, 23—27).—The contents of the large intestine, *post mortem*, contained more calcium and less phosphorus than those of the small intestine.

CHEMICAL ABSTRACTS.

Effect of the contents of the radicle of germinated grain on calcium and phosphorus metabolism. M. RUBNER (Deut. med. Woch., 1930, 56,

295—297; Chem. Zentr., 1930, i, 2271).—The normal organism is enriched in calcium and phosphorus. A. A. ELDRIDGE.

Influence of bile acids on calcium metabolism. T. SEKITO (J. Biochem. Japan, 1930, 11, 390—406).—Laparotomy alone has no effect on the blood-calcium of the rabbit. Hypocalcæmia resulting from the discharge of bile from a gall-bladder fistula can be remedied by administration of bile acids. In experimental obstructive icterus hypercalcæmia alternates with hypocalcæmia.

CHEMICAL ABSTRACTS.

Retention of calcium on diets rich and poor in fat. M. C. MALLON, R. JORDAN, and M. JOHNSON (J. Biol. Chem., 1930, 88, 163—167).—No constant effect of dietary fat on the retention of calcium in normal young women could be observed.

C. R. HARRINGTON.

Behaviour of potassium in the organism. I. Potassium and sodium contents of different organs. II. Fluctuations in excretion of potassium, sodium, and chlorine by the kidney. III. Fluctuation in potassium concentration of the plasma after administration of potassium salts and in diuresis, and its relation to the elimination of potassium in urine. M. NORN (Skand. Arch. Physiol., 1929, 55, 162—183, 184—210, 211—229; Chem. Zentr., 1930, i, 1580).—I. The potassium content of the heart is less than that of the skeletal muscles, but the sodium content is greater. The sodium content of the kidney compared with that of muscle is very high.

II. The excretion of potassium, sodium, and chlorine by the kidneys is lower during the night than the day; with persons awake at night and asleep during the day, the reverse is the case. Muscular activity has no effect on the secretion. The reduction in secretion is not attributable to a general depression of renal activity, since the secretion of calcium is unchanged, whilst that of magnesium is greater at night than during the day. Narcosis appears to exert an influence similar to that of sleep.

III. The administration of potassium chloride to rabbits is accompanied by a marked increase in the potassium content of the plasma; this brings about an increase in the excretion of potassium by the kidneys.

L. S. THEOBALD.

Value of potassium iodide as a supplement to the ration of growing chicks. T. S. HAMILTON and C. H. KICK (J. Agric. Res., 1930, 41, 135—137).—Addition of potassium iodide to chicken food, at the rates of 0.5 and 1.0 mg. per 100 g. body-weight, in no way affected the rate of growth of chicks.

A. G. POLLARD.

Ionic theory of nerve excitation. N. VON RASCHEVSKY (Z. Physik, 1930, 63, 660—665).—The observations of Hill on the motion of ions in an electric field between two parallel impermeable membranes are brought into line with the theory of nerve excitation.

A. J. MEE.

Hysteresis in biophysics. N. VON RASCHEVSKY (Z. Physik, 1930, 63, 666—671).—A heterogeneous system with several equilibria, possessing the property

of reacting to certain "configurations" brought about by external conditions, is considered. A. J. MEE.

Biological significance of intermediate compounds. E. ABDERHALDEN (Naturwiss., 1930, 18, 429—431).—The importance in biological processes of intermediate compounds such as the polypeptides, hexosephosphates, and the enzyme-substrate complexes is discussed; such compounds may have considerable bearing on the action of hormones, vitamins, and immunising agents.

H. F. GILLBE.

Physiological reaction of salts. M. GÓRSKI (Rocz. Nauk. Roln. Lés., 1929, 22, 27—32).—The dependence of the adsorption of salts on p_H is expressed diagrammatically.

CHEMICAL ABSTRACTS.

Iodine investigations at Bad Hall in Upper Austria. T. VON FELLEBERG (Biochem. Z., 1930, 224, 176—192).—Water from the various bore-holes at Bad Hall gave in one case only 1.23 mg. but in all others values between 11.1 and 47.5 mg. of iodine per litre. The soil of Bad Hall is rather poor in iodine and the iodine-containing water must come from low-lying strata. The drinking water and stream-water are very rich in iodine and must also be enriched by water from deep strata. The Hall water gives off small amounts of iodine into the air. The milk supply is rich in iodine. By bathing for $\frac{1}{3}$ hr. in the water (63 g. of salts with 13.3 mg. of iodine per litre) an absorption of iodine through the skin is detected by subsequent urine analysis of about 0.48 mg. corresponding with 36 c.c. of bath water. Iodine can be detected in sweat.

P. W. CLUTTERBUCK.

Determination of traces of iodine in organic materials. T. VON FELLEBERG (Biochem. Z., 1930, 224, 170—175).—Various modifications of the author's method of determining traces of iodine in which ashing in an open vessel is replaced by ashing in a tube (McClelland, A., 1928, 607; Reith, A., 1929, 337, 414, 1410; Schwaibold, A., 1929, 337, 1256) are examined and gave low results, it being often difficult either to avoid formation of tarry material or to absorb quantitatively the whole of the fumes developed. Details are given of an improved method which combines a preliminary fusion with potassium hydroxide in a nickel dish with subsequent burning of carbon in a heated tube after removal of water-soluble material. The fumes from the tube are collected in potassium hydroxide and together with the residual ash are combined with the water-soluble material and the iodine is finally determined by titration. Using the method, calf's blood is shown to contain 1.2 and 1.14 γ per 10 c.c. and the mean of six determinations of 142 γ of iodine added to the blood was 144.5 γ .

P. W. CLUTTERBUCK.

Effect of organic fluorine compounds on the animal organism. I. Action of fluorobenzene, *p*-fluorotoluene, and *p*-fluoroacetanilide and the state of fluorine in the blood. K. LANG (Arch. exp. Path. Pharm., 1930, 152, 361—376).—Feeding organic fluorine compounds to rabbits does not increase the fluorine content of the blood, which is almost entirely inorganic, nor does it increase the time required for clotting. Feeding of fluorobenzene,

p-fluorotoluene, or *p*-fluoroacetanilide causes no accumulation of fluorine in the various organs except the heart and, in smaller degree, the lungs. Dogs fed regularly with fluorobenzene grow thin and show intense salivation, but no definite product of metabolism can be isolated. The fate of *p*-fluoroacetanilide is also obscure, but *p*-fluorotoluene gives rise to *p*-fluorobenzoic acid, of which 5 g. are obtained from the urine on feeding 26 c.c. of *p*-fluorotoluene in small daily doses.

P. G. MARSHALL.

Pharmacology of gold compounds. I. B. VON ISSEKUTZ and M. LEINZINGER. II. B. VON ISSEKUTZ and Z. DIRNER. III. B. VON ISSEKUTZ and I. MÉHES (Arch. exp. Path. Pharm., 1930, 152, 288—305, 306—317, 318—340).—I. Sodium chloroaurate has a characteristic affinity for proteins and will cause agglutination of blood-corpuscles and check the swelling of gelatin. The hæmolytic action is strongly inhibited by blood-serum, falling from 1:150,000 to 1:15,000 in the presence of 2% of serum. Potassium auricyanide, which is lipoid-soluble, produces no inhibition of the swelling of gelatin and has no appreciable hæmolytic activity. "Sanocrysin" resembles it in this respect and is bound only to the extent of 20% by serum. Most other gold compounds resemble gold chloride and sodium chloroaurate in their properties.

II. A study of the toxicity of gold compounds on various organisms such as bacteria, yeast, and paramoecium. Gold chloride is a general protoplasmic poison and is more effective in killing bacteria than is "sanocrysin." Potassium auricyanide shows the strongest antiseptic action, probably by virtue of the inhibiting action of the cyanogen group on oxidative processes. Its toxic effect on frogs and rats is only slightly diminished by sodium thiosulphate. "Krysolgan" and "triphyl" have a toxicity similar to that of "sanocrysin," whilst "solganal" has only one tenth the toxicity.

III. Neutralised gold chloride solutions in a concentration greater than 1:2500 produce a digitalis-like action on the isolated frog's heart, a considerable proportion of the gold being bound in the surface layers of the heart-muscle. Frog's gastrocnemius is similarly contracted. In cats gold chloride produces a lowering of blood-pressure and increase in the respiration rate. "Krysolgan" and "solganol" produce similar effects in smaller degree. The tonus of isolated rabbit's gut is raised by gold chloride (and by "sanocrysin" in larger doses) and lowered by gold cyanide.

P. G. MARSHALL.

Influence of crystalline glutathione on the physiological action of arsenic compounds. S. M. ROSENTHAL and C. VOEGLIN (J. Pharm. Exp. Ther., 1930, 39, 347—367).—Intravenous injection into rats of the minimum lethal dose of 3-amino-4-hydroxyphenylarsenious oxide or of sodium arsenite does not cause death if the animals have previously received an injection of a solution of glutathione in the ratio of 10 mols. of the tripeptide to 1 g.-atom of arsenic. Trypanosomes exposed *in vitro* to the action of arsenious oxide retain their power to infect rats if glutathione is present, and the inflammation produced in the ear of the rabbit by injection there of solutions

of arsenious oxide is prevented if glutathione is added to the solutions. The rate of oxidation of glutathione by oxygen with hæmin as catalyst is reduced if arsenious oxide or its 3-amino-4-hydroxyphenyl derivative is present in concentrations of the same order as that of the glutathione. Lower concentrations of arsenic compound have no effect, although there may be more than sufficient arsenic compound present to combine with all the hæmin used. Concentrations of sodium cyanide, very low in relation to the concentration of glutathione, produce marked inhibition of the oxidation. It is probable that the action of compounds of trivalent arsenic on living cells involves chemical reaction between the compounds and glutathione and possibly also between the compounds and other constituents of the protoplasm which contain thiol groups.

W. MCCARTNEY.

Local anæsthetics derived from dialkylamino-propanediols. I. Phenylurethanes. T. H. RIDER (J. Pharm. Exp. Ther., 1930, 39, 457—467).—The local anæsthetic activity of the hydrochlorides of the phenylurethanes and diphenylurethanes of dialkylaminopropanediol (cf. this vol., 897) has been investigated on the sciatic nerve of the frog and on the rabbits' cornea. With increase in the size of the alkyl group the local anæsthetic action increases. In the lower homologues it is greater in the diphenyl than in the monophenyl series, whereas in the higher homologues the reverse is the case. The compounds have a marked precipitating action on proteins, and this probably masks the local anæsthetic action to some extent, especially in the diphenyl series, where precipitating power is very pronounced. Diisobutylaminopropanediol monophenylurethane hydrochloride is six times as strong as cocaine on the rabbit's cornea and more than three times as strong as either novocaine or cocaine in an interdermal wheal, whilst it appears to be less toxic than either of these two drugs.

W. O. KERMACK.

Comparison of the effect on the circulation and the narcotic action of barbituric acid derivatives. M. VOGT (Arch. exp. Path. Pharm., 1930, 152, 341—360).—The action of the following compounds is reported: diethyl- (veronal), dipropyl- (propional), phenylethyl- (luminal), cyclohexenylethyl- (phanodorm), diallyl- (dial, curral), isopropylallyl- (numal), isobutylallyl- (sandoptal), isoamylethyl- (amytal), isopropylbromoallyl- (noctal), and *sec*-butylbromoallyl- (pernocton)-barbituric acids. The whole group produces lowering of blood-pressure and reduction of the respiratory volume. Veronal has the least and pernocton the greatest circulatory effect in the dosage necessary to produce narcosis, other derivatives being intermediate. The lethal dose for a 20-g. rat is 9.0 mg. of veronal and 1.8 mg. of pernocton. The therapeutic ratio is greatest (3.0) for phanodorm and least (1.2) for noctal.

P. G. MARSHALL.

Pharmacological actions of harmalol. J. A. GUNN and A. J. L. SIMONART (Quart. J. Pharm., 1930, 3, 218—237).—Investigation of the pharmacological actions of harmalol and comparison with harmaline show that the replacement of the methoxyl group in the latter by hydroxyl is accompanied by a reduction of the toxicity by subcutaneous injection

to 40% for laboratory mammals, but the toxicity for frogs is unchanged. Harmalol does not produce the clonic convulsions characteristic of harmaline. Harmaline is 30—60 times as toxic for protozoa (*Colpidia*) as harmalol. Otherwise the action of the two alkaloids on voluntary and involuntary muscle runs parallel with their toxicity. R. K. CALLOW.

Pyrethrum flowers. IV. Relative toxicity of pyrethrins I and II. C. B. GNADINGER and C. S. CORL (J. Amer. Chem. Soc., 1930, 52, 3300—3307).—The toxicity of pyrethrins I and II, isolated from Japanese *Pyrethrum* flowers and partly purified through their semicarbazones (cf. Staudinger and Ruzicka, A., 1924, i, 700), has been determined towards house flies (*Musca domestica*) using the oil-spray method of Peet and Grady (J. Econ. Entomol., 1928, 21, 612). Pyrethrin II is about 80% as toxic as pyrethrin I. The determination of the total pyrethrin content of *Pyrethrum* flowers by the authors' copper reduction method (B., 1929, 996) is an accurate index of their toxicity. H. BURTON.

Study of toxicity [of rotenone] using goldfish. W. A. GERSDORFF (J. Amer. Chem. Soc., 1930, 52, 3440—3445).—The toxicity of rotenone to goldfish in concentrations of 0.015—4 mg. per litre of water (containing 1 part of acetone in 1000) is studied at $27 \pm 0.2^\circ$. H. BURTON.

Histamine and alkalosis. R. RAFFLIN and P. SARADJICHVILI (Compt. rend. Soc. Biol., 1929, 102, 559; Chem. Zentr., 1930, i, 1325).—The subcutaneous injection of histamine into mentally-deficients is accompanied by alkalosis of the blood and urine, the result of elimination of chlorine in the gastric and urinary secretions. L. S. THEOBALD.

Chemotherapy of quinoline compounds. I. Action of certain quinoline compounds on *Paramecia*. U. BRAHMACHARI, T. BHATTACHARYYA, R. BANERJEA, and B. B. MAITY (J. Pharm. Exp. Ther., 1930, 39, 413—415).—8-Aminoquinoline and quinolyl-8-glycineamide are without toxic action on *paramecia* in concentration of 1—2000, whereas 6-aminoquinoline and quinolyl-6-glycineamide kill at a concentration of 1—2000, but not at a concentration of 1—4000. 8-Amino-6-hydroxyquinoline and 6-hydroxyquinolyl-8-glycineamide are highly lethal, but 8-amino-6-methoxyquinoline (1—2000) is without action. W. O. KERMACK.

Idiosyncrasy to quinine, cinchonidine, and ethylhydrocupreine and other laevorotatory alkaloids of the cinchona series. Further chemical delimitation of the idiosyncrasy; alteration in sensitiveness. W. T. DAWSON and F. A. GARBADE (J. Pharm. Exp. Ther., 1930, 39, 417—424).—A male subject exhibiting sensitiveness to quinine and related alkaloids is not sensitive to quitenine and cinchotenidine, but is sensitive to the ethyl, amyl, and isoamyl esters of quitenine. Sensitiveness is shown to laevorotatory propyl-, isopropyl-, isobutyl-, and isoamyl-hydrocupreine and to quinoline. The sensitiveness to isoamylhydrocupreine did not exist at the beginning of the experiments, but set in later, indicating apparently an increase of sensitiveness of the subject. W. O. KERMACK.

Fate of apomorphine after subcutaneous injection. F. BAMFORD (Analyst, 1930, 55, 502—503).—Four rabbits were injected subcutaneously with (1) 160 mg. of morphine hydrochloride, (2) 160 mg. of apomorphine hydrochloride, (3) as (2), and (4) 6 mg. of apomorphine hydrochloride. After 1 hr. the rabbits were killed and the stomachs and contents of (1) and (2) and the contents only of (3) and (4) extracted by the Stas-Otto process. Only the extracts from (1) and (2) gave precipitates with the usual alkaloid precipitants and the colour reactions of the morphine group, and in (2) the extracted apomorphine was free from morphine.

D. G. HEWER.
Enzyme purification; pancreatic amylase. H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Biol. Chem., 1930, 88, 295—304).—Commercial pancreatin is extracted with 10 parts of 87% glycerol at the ordinary temperature, the mixture is centrifuged, and the supernatant fluid is diluted at 0° with 5 parts of a phosphate buffer solution so that the final p_H is 5.8; the solution is again centrifuged and the mother-liquor is treated with an alcoholic suspension of aluminium hydroxide at 0° . The enzyme is eluted from the precipitate with dilute sodium hydroxide (final p_H 7.0—7.3) and is again precipitated by addition of a mixture of equal parts of alcohol and ether. The resulting preparation (0.7 g. from 10 g. of pancreatin) has an amyolytic activity about eight times as great as that of the original material. Control of the p_H is important throughout and is checked by electrometric determinations, which can be made in presence of alcohol or glycerol. The purified preparation has the properties of a protein and is free from carbohydrate; it exhibits proteolytic activity. C. R. HARRINGTON.

Action of powdered organs on pancreatic amylase. A. BADREAU (J. Pharm. Chim., 1930, [viii], 11, 20—31).—Desiccation of salivary glands of the ox, stomach mucosa of the pig, pancreas of the pig, ox, and horse, bile, and pig's intestine gives powders of p_H 6—6.2, all of which, except the bile and stomach powders, show amyolytic power. The amount of starch hydrolysed by a mixture of pancreas powder (0.05 g.) with 0.2 g. of one of the others is greater than that hydrolysed under similar conditions by the two glands separately. Addition of larger quantities of the second gland, or of a mixture of glands, does not produce a further exaltation. Similarly, the amyolytic action of mixtures of any two of the other glands, whether both or only one is active, is greater than that of the two separately. The activity of pancreatic amylase is also increased by thymus and liver powders and by glycine and tyrosine, whilst peptone causes the greatest increase of any of the substances tried. It is suggested that the effect of all these products is due to the amino-acids which they contain, and that the latter may be co-enzymes necessary for the activity of this enzyme. H. E. F. NORTON.

Enzymic hydrolysis of phloridzin. E. A. MOELWYN-HUGHES (J. Gen. Physiol., 1930, 13, 807—817).—Data on the velocity of hydrolysis of phloridzin by acids (A., 1928, 374), compared with those of

other glucosides, showed that the lability of phloridzin towards acids resembles the fructosides rather than the normal glucosides. Emulsin had no action on phloridzin, whereas maltase and maltase-free invertase hydrolysed it. The action of maltase is considered to be due to small amounts of invertase known to be present. The phloridzin sugar prepared by hydrolysis had $[\alpha]_D +44.61^\circ$. *B. pestis* fermented phloridzin sugar less readily than dextrose. It is concluded that phloridzin is not a normal glucoside, and the tentative suggestion that it is a derivative of a γ -hexose is put forward.

G. F. MARRIAN.

Inactivation of pancreatic lipase by heat. I. H. MCGILLIVRAY (Biochem. J., 1930, 24, 891—904).—Purified pancreatic lipase is inactivated by heat in accordance with the unimolecular law, the optimum stability being at p_H 6.0. The critical increment for the heat-inactivation process in 50% glycerol is sensibly the same, namely of the order of 46,000 g.-cal., at p_H 6.0, 8.01, and 5.0. In 25% glycerol and at p_H 6.0 the critical increment is 47,800 g.-cal. With unpurified lipase the course of inactivation by heat in 80% glycerol is unimolecular, whereas in the water extract of the dried gland powder the unimolecular coefficient decreases with time. The unpurified lipase is also most stable at about p_H 6.0. At p_H 6.0 and in 80% glycerol the critical increment for the process in unpurified extracts is of the order of 100,000 g.-cal., whereas in 50% glycerol the value is 57,500 and in water 35,000. At p_H 9.3 the critical increment of unpurified extract containing 80% glycerol is of the order 92,000 g.-cal.

S. S. ZILVA.

Action of arsenate on hexosephosphatase. M. G. MACFARLANE (Biochem. J., 1930, 24, 1051—1057).—Hexose-mono- and di-phosphate can be hydrolysed by washed dried yeast in the absence of co-enzyme. Arsenate accelerates the rate of production of phosphate from hexosediphosphate only in the presence of yeast extract and the acceleration has not been obtained without an accompanying fermentation. Fluoride inhibits this acceleration. Fractionation of the boiled yeast extracts used indicates that some other factor besides the co-enzyme is necessary for the reaction.

S. S. ZILVA.

Crystalline pepsin. I, II. Isolation and properties. J. H. NORTHROP (J. Gen. Physiol., 1930, 13, 739—766, 767—780).—I. Commercial pepsin was dissolved in dilute sulphuric acid and precipitated by half saturation with magnesium sulphate. The precipitate was suspended in water, dissolved by the addition of sodium hydroxide, so that the p_H did not rise above 5.0, reprecipitated by the addition of sulphuric acid to p_H 3.0, and dissolved in sodium hydroxide at 45°. After inoculation and slow cooling a crystalline paste separated. The proteolytic activity of the crystals was about 5 and 2.5 times that of the original pepsin when measured by the hydrolysis of caseinogen and the liquefaction of gelatin. It had the characteristic properties of a protein; the nitrogen content, optical rotation, and proteolytic activity were constant for six different preparations and remained unchanged throughout seven crystallisations. Data from solubility determinations in differ-

ent salt solutions, the rate of activation by heat and alkali, and the determination of its diffusion coefficient suggest that it is a pure substance. The possibility that it is a solid solution is not, however, excluded. The rate of inactivation at 65° (p_H 3.0) was found to follow the course of a unimolecular reaction.

Sera of rabbits injected with active and denatured preparations gave precipitin reactions with either active or denatured pepsin solutions. Both sera inhibited the action of the enzyme.

II. The effects of temperature, p_H , and varying concentrations of sodium sulphate on the solubility of crystalline pepsin were studied. The substance has a minimum solubility at p_H 2.75 corresponding with its isoelectric point. Migration experiments and a titration curve confirm this figure. Different methods of determining the mol. wt. (osmotic pressure, diffusion coefficient, phosphorus content, chlorine content, and sulphur content) gave values ranging from 33,000 to 40,000. A summary of the chemical and physical properties of the substance is given.

G. F. MARRIAN.

Action of pepsin on gelatin. R. K. CANNAN and E. MUNTWYLER (Biochem. J., 1930, 24, 1012—1020).—The changes in acid- and in base-binding capacities which accompany the digestion of gelatin by pepsin have been determined with the aid of hydrogen electrode titration curves, and it was found that the main chemical effect of pepsin is the hydrolysis of peptide linkings between the α -amino- and α -carboxyl groups of amino-acids. Pepsin produced marked changes in the physical condition of gelatin before any increase in titratable groups could be demonstrated. Each peptide linking hydrolysed rendered 14—15 atoms of nitrogen soluble in 80% alcohol.

S. S. ZILVA.

Action of the latex of *Ficus carica* on proteins. S. VISCO (Atti R. Accad. Lincei, 1930, [vi], 11, 688—691).—The action of the latex on the proteins of egg-white does not proceed further than the formation of secondary proteoses.

T. H. POPE.

Rate of liberation of arginine in tryptic digestion. J. A. DAUPHINEE and A. HUNTER (Biochem. J., 1930, 24, 1128—1147).—In the case of caseinogen and gelatin the initial rate of liberation by arginase of arginine or of an arginine complex is so great that half of their total potential arginine is easily set free within 3 hrs. With Witte peptone this liberation is only slightly slower, whilst with edestin and fibrin free arginine appears much more gradually. Egg-albumin exhibits a peculiar behaviour in that the liberation of arginine, like that of free amino-groups in general, commences only after a latent period of one or two days. With fibrin the total amount of arginine liberated by trypsin was only two thirds of the amount obtainable on complete hydrolysis, and with caseinogen, gelatin, edestin, egg-albumin, or Witte peptone four fifths. These fractions appear to be characteristic. In the acid hydrolysis of gelatin arginine is liberated less rapidly and at a more regular rate than in its tryptic digestion.

S. S. ZILVA.

Protein constituents and their enzymic conversions. M. BERGMANN (Naturwiss., 1930, 18,

465—468).—The structure and reactions of certain amino-acids and related compounds are described with special reference to the action of enzymes.

H. F. GILLBE.

“Activation” of proteolytic enzymes. H. A. KREBS (Naturwiss., 1930, 18, 736).—Priority of publication is claimed over Waldschmidt-Leitz, Purr, and Balls (this vol., 1217). W. R. ANGUS.

[Biochemical factors in] heredity. IV. H. VON EULER, H. DAVIDSON, and D. RUNEHJELM (Z. physiol. Chem., 1930, 190, 247—261; cf. A., 1929, 1497).—The catalase content of chlorophyll-normal and chlorophyll-defective mutants of barley was determined at different stages of germination. One strain had a ratio green : white of 2.5, another 2.2, another green : light green 1.5 (etiolated, yellow : light yellow, 1.4). A further strain green : yellowish-green had a similar ratio. J. H. BIRKINSHAW.

Cytochrome and the catalase action of yeast. H. VON EULER and H. HELLSTRÖM (Z. physiol. Chem., 1930, 190, 189—198).—Hæmochromogen of yeast shows absorption bands at 557 and 525 $m\mu$ coinciding with those of pyridine hæmochromogen and a third at 586 $m\mu$ unaffected by oxidation and reduction. 60% pyridine extracts hæmochromogen, the extract giving a strong band at 586 $m\mu$ and a very weak one at 557 $m\mu$ which is strengthened by reduction. The 586 $m\mu$ band disappears on the addition of hydrazine hydrate. Cytochrome on addition of pyridine is apparently resolved into two different porphyrin or porphyratin complexes of which one is hæmin. Heating yeast to 65° or treatment with chloroform or acetone causes three of the five cytochrome bands to disappear, 550 and 521 $m\mu$ remaining. The catalase action is strengthened.

J. H. BIRKINSHAW.

Selective fermentation. I. Alcoholic fermentation of dextrose, lævulose, and mannose mixtures. H. SOBOTKA and M. REINER (Biochem. J., 1930, 24, 926—931).—All the types of yeast examined fermented dextrose and lævulose at a rate of 2 to 1 or higher. This rate is influenced by the nature of the culture medium. There is no correlation between selective fermentation and invertase or maltase content. Dextrose and mannose were fermented at a rate of about 2—3 : 1, whilst in the case of lævulose and mannose the ratio was about 1.4 : 1.

S. S. ZILVA.

Fourth and fifth fermentation processes of sugar. C. NEUBERG and M. KOBEL (Naturwiss., 1930, 18, 427—429).—The existence has been established of a fourth mode of fermentation of hexoses, which follows the second and third processes and results in the production of pyruvic acid and glycerol, whilst in a fifth mode of decomposition, according to the equation $C_6H_{12}O_6 = 2H_2O + 2CO_2 + CHO$, an 85% yield has been obtained by employment of 2 : 4-dinitrophenylhydrazine to isolate the methylglyoxal formed. The significance of these reactions in plant and animal organisms is indicated.

H. F. GILLBE.

Co-zymase. XVII. H. VON EULER and K. MYRBÄCK (Z. physiol. Chem., 1930, 190, 93—100; cf. A., 1929, 1340).—The best preparations of co-

zymase show an activity coefficient of about 70,000—80,000 units. The composition corresponds with an adenine-carbohydrate (pentose)-phosphoric acid complex. On this basis about 80% of the co-zymase is accounted for. Further fractionation of a highly active preparation yields some inactive fractions, the total activity of all fractions being considerably less than that of the original. Co-zymase may also be inactivated by enzymes, e.g., liver nucleotidase, but the phosphoric acid liberated is much less than corresponds with the amount of co-zymase rendered inactive. The activating action of boiled yeast juice is probably the resultant of several factors. In the determination of the activity of co-zymase different preparations of apozymase give different results, although with fresh apozymase from a given strain of yeast the results are comparable.

J. H. BIRKINSHAW.

Effect of different amounts of toluene on the fermentation of sugar by fresh and dried yeast. G. SELIBER (Biochem. Z., 1930, 224, 202—210).—The intensity of fermentation by living yeast is depressed by 10—50% in presence of toluene, but increasing the amount of toluene from 2 to 40% does not affect the extent of inhibition. A greater effect is obtained by triturating yeast with toluene. Dried yeast is more sensitive to toluene except when drying has been prolonged, when the total fermenting power is very low and toluene has little effect.

P. W. CLUTTERBUCK.

Growth acceleration in protozoa and yeast. H. H. DARBY (J. Exp. Biol., 1930, 7, 308—316).—The allelocatalytic phenomena in the growth of *Paramecium* do not occur if a small volume of suitable medium is used. The optimum growth of yeast is at p_H 4.4.

E. BOYLAND.

Oxalic acid as a reagent for isolating tubercle bacilli. Growth of acid-fast, non-pathogenic organisms on different media, and their reaction towards chemical reagents. H. J. CORPER and N. UYEI (J. Lab. Clin. Med., 1930, 15, 348—369).

CHEMICAL ABSTRACTS.

Oxidation of hydrogen and hydrocarbons by bacteria. J. TAUSZ and P. DONATH (Z. physiol. Chem., 1930, 190, 141—168).—Both *B. aliphaticum liquefaciens* and the methane bacterium are able to oxidise hydrogen in presence of air. The former organism oxidises all the longer-chain paraffins beginning with pentane. The olefines are not attacked nor are the cyclic hydrocarbons except those with a long side-chain (e.g., cetylbenzene). The methane bacterium oxidises all the paraffins and propylene and butylene, but not benzene or cyclohexane. The bacterial oxidation of hydrogen proceeds with methylene-blue as acceptor, indicating hydrogen activation. In the oxidation of hexane, the intermediate formation of unsaturated hydrocarbons was established. J. H. BIRKINSHAW.

Culture media containing urea. III. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1930, 12, 141—145; cf. this vol., 503).—Two series of experiments have been carried out on the influence of urea on the fermentation of milk. The acidity developed, determined by titration, is somewhat less in presence

of urea; it is concluded that lactic acid bacteria can decompose urea to give ammonia, and that *B. fluorescens liquefaciens* can ferment lactose to lactic acid.

S. I. LEVY.

Oxidation-reduction studies in relation to bacterial growth. I. Oxidation-reduction potential of sterile meat broth. II. Method of poisoning the oxidation-reduction potential of bacteriological culture media. B. C. J. G. KNIGHT (Biochem. J., 1930, 24, 1066—1074, 1075—1079).—I. The oxidation-reduction potential of completely deaerated sterile, buffered meat broths has been measured over a range p_{H} 4—10.5. The potentials indicated by Clark's dyes are more negative than those shown by an electrode in broth alone. When oxygen is removed the potential of the broth drifts to a definite level depending on p_{H} .

II. The negative potential drift is balanced by passing into the medium a controlled stream of very dilute oxygen in nitrogen, the concentration and rate of flow of the gas mixture being adjusted until there is equilibrium between the rate of reduction of the broth system and its rate of oxidation by the oxygen. Much greater precision can be given to the electrode readings and the poisoning of the potential is made more refined by the addition of small quantities of oxidation-reduction dyes with a span of potential covering the desired level.

S. S. ZILVA.

Mechanism of opsonin and bacteriotropin action. IV. Isoelectric points of certain sensitised antigens. M. McCUTCHEON, S. MUDD, M. STRUMIA, and B. LUCKÉ (J. Gen. Physiol., 1930, 13, 669—681).—The isoelectric points of *Mycobacterium avium* and *M. chelonae*, determined by cataphoresis, showed a progressive shift from about p_{H} 2.5 to 5.7 after sensitisation with increasing amounts of homologous rabbit immune serum, the mean isoelectric point of the globulins of the sera used being p_{H} 5.1—5.2. This phenomenon was not due to the deposition of residual fibrinogen on the bacteria since when plasma was used instead of serum slightly, lower results were obtained. The shift in isoelectric point was accompanied by agglutination, and changes in surface properties of the bacteria.

G. F. MARRIAN.

Possible mechanism of diphtheria toxoid formation. L. F. HEWITT (Biochem. J., 1930, 24, 983—992).—Eighty-five % of the amino-nitrogen present in fresh diphtheria toxins remains free in completely detoxified toxoids prepared by incubation with formaldehyde. Reducing and oxidising agents and methyl alcohol failed to produce a detoxified toxoid. Slight reducing conditions are maintained when toxin is incubated with formaldehyde.

S. S. ZILVA.

Effect of intravenous injection of urethane on the secretion of adrenaline in cats. S. KODORNA (Tohoku J. Exp. Med., 1930, 15, 11—16).—Hypersecretion of adrenaline is observed; it is prevented by cutting the splanchnic nerves.

CHEMICAL ABSTRACTS.

Calcium of cerebrospinal fluid and of blood-serum with reference to parathyroid hormone. S. MORGULIS and A. M. PERLEY (J. Biol. Chem., 1930,

88, 169—188).—Oral administration of calcium salts and production of experimental jaundice were without effect on the calcium of the blood-serum or cerebrospinal fluid of dogs. Increase in the serum-calcium of dogs by direct injection of calcium salts or by their oral administration in combination with parathyroid hormone and decrease in the serum-calcium brought about by parathyroidectomy had little or no effect on the calcium of the cerebrospinal fluid. No evidence was obtained of the transfer of calcium to the red blood-corpuses as the result of parathyroidectomy, or of the existence in blood of a slowly dissociable organic calcium compound. The diffusible calcium determined by dialysing blood-serum against cerebrospinal fluid was practically constant in amount irrespective of whether the dogs were normal, or had received injections of calcium salts with or without parathyroid hormone, or had been parathyroidectomised. The parathyroid hormone has therefore no apparent effect on the distribution of calcium between the blood-serum and the cerebrospinal fluid.

C. R. HARRINGTON.

Influence of the thyroid on the protein metabolism of individual organs. O. STEPPUHN and A. SMIRNOVA (Biochem. Z., 1930, 224, 83—90).—The authors' previous work on the autoprotoleolysis of entire animal bodies (A., 1926, 1174) is extended to individual tissues, the autolysis of rabbits' liver, muscle, heart, and brain being investigated at p_{H} 3.4, 7.4, and in water after 24 and 48 hrs.' incubation at 37°, the tissues being obtained from normal animals and animals to which had been administered thyroid gland either as dry preparation by stomach tube or thyroxine by injection. Changes in the rate of autolysis are exceptionally marked in the case of liver and heart-muscle pulp, much less with skeletal muscle, and scarcely appreciable with brain.

P. W. CLUTTERBUCK.

Effect of secretin on blood-sugar. M. YASUDA (J. Biochem. Japan, 1930, 11, 479—503).—Insulin hypoglycaemia is accompanied by a corresponding fall in inorganic phosphorus; hyperglycaemia causes a fall in plasma-phosphorus. Under the influence of thyroxine and amino-acids the effect of sympathetic stimulation is manifested in so far as both hyperglycaemia and hypophosphataemia are produced. Only with injection of pancreatic secretin is the former accompanied by the latter. The internal secretion of the pancreas is not promoted by its external secretory activity.

CHEMICAL ABSTRACTS.

Hormones of the anterior pituitary lobe. I. B. ZONDEK (Klin. Woch., 1930, 9, 245—248; Chem. Zentr., 1930, i, 1955).—A description of biological tests for the hormones, and a definition of units.

A. A. ELDRIDGE.

Effect of posterior pituitary extract on respiratory metabolism. E. SCHILL and J. VON FERNBACH (Z. ges. exp. Med., 1929, 67, 551—557; Chem. Zentr., 1930, i, 1955).

Stability of aqueous solutions of the oxytocic principle of the pituitary gland. J. H. GADDUM (Biochem. J., 1930, 24, 939—944).—The rate of destruction of the principle in the aqueous extract has

been measured at different hydrogen-ion concentrations and at different temperatures.

S. S. ZILVA.

Pituitary gland. VII. Separate identity of the pressor and melanophore principles. L. HOGGEN and C. GORDON (*J. Exp. Biol.*, 1930, 7, 286—292).—By the action of sodium hydroxide the pressor activity of pituitary extracts can be removed whilst the melanophoric activity remains. E. BOYLAND.

Isolation and preparation of vagotonin, a new pancreatic hormone. H. PÉNAU and D. SANTE-NOISE (*Compt. rend.*, 1930, 191, 342—344).—Extraction of minced pancreas with 0.05*N*-alcoholic sulphuric acid, followed by processes of fractional precipitation and ultra-filtration to remove compounds of low mol. wt., yields vagotonin as a white, water-soluble powder, with properties quite distinct from those of insulin. It acts on the oculo-cardiac reflex in doses of less than 0.1 mg. per kg., and has a slow hypoglycaemic effect.

R. K. CALLOW.

Crystalline insulin. XI. Does insulin cause an initial hyperglycaemia? E. M. K. GELLING and A. M. DE LAWDER (*J. Pharm. Exp. Ther.*, 1930, 39, 369—385).—The initial temporary hyperglycaemia which immediately follows injection of commercial insulin is caused by non-dialysable impurities which are present. The impurities are not completely destroyed by alkali solutions of sufficient concentration to render insulin inactive. Crystalline insulin does not cause initial hyperglycaemia.

W. MCCARTNEY.

Insulin. XII. Crystalline insulin. H. JENSEN and A. DE LAWDER (*Z. physiol. Chem.*, 1930, 190, 262—272).—A non-crystalline preparation of pig's insulin showing activity equal to that of crystalline ox insulin had a lower sulphur content (2.7 instead of 3.1%). Crystalline insulin precipitated by heating with 0.1*N*-hydrochloric acid cannot be reconverted into the crystalline form. An attempt was made to account for the low activity of acetylinsulin. Part of the acetyl is probably attached to an amino-group. Acetylation at higher temperatures yields a product of lower activity than acetylation at 0°. Compounds of insulin formed with benzaldehyde and benzoyl chloride are inactive and the activity cannot be regenerated. The action of dilute alkali hydroxide eliminates not only sulphide-sulphur but also ammonia or an amine. The ammonia removed seems to be related to the loss of activity which also occurs.

J. H. BIRKINSHAW.

Determination of insulin secretion. B. A. HOUSSAY, J. T. LEWIS, and V. G. FOGLIA (*Rev. soc. Argentina biol.*, 1929, 5, 15—31).—Determinations of blood-sugar were made on fasting dogs anaesthetised with chloralose; the pancreas was removed and insulin injected into the jugular vein. In a fasting anaesthetised animal with normal blood-sugar the pancreas secretes about 0.01 unit per kg. per hr. to maintain the blood-sugar at the normal level. When the blood-sugar is high, 0.1 unit is at first secreted, the quantity falling when the normal level is reached.

CHEMICAL ABSTRACTS.

Action of insulin on the glycogen distribution in normal animals. M. W. GOLDBLATT (*Biochem.*

J., 1930, 24, 1199—1209).—The observation made on young rabbits (A., 1929, 609) that insulin produces a very large rise in hepatic glycogen without any simultaneous considerable fall in muscle-glycogen is confirmed on kittens. This rise is not a necessary sequel of a high degree of hypoglycaemia. The increase in liver-glycogen consequent on the injection of insulin into starving young rabbits cannot be explained by changes occurring in glycogen and free sugar in other parts of the body nor is it associated with changes in blood constituents other than diminution in sugar and inorganic phosphorus. Under the conditions described glycogen formation from endogenous sources is definitely increased.

S. S. ZILVA.

Oestrin. IV. Chemical nature of crystalline preparations. G. F. MARRIAN (*Biochem. J.*, 1930, 24, 1021—1030; cf. this vol., 821).—Of the total oestrus-producing material in the ethereal extract of acidified urine, 32% has been obtained as a pure crystalline substance, $C_{18}H_{24}O_3$, m. p. 264—266°, $[\alpha]_{5461}^{20} + 38^\circ$. The substance is feebly acidic, being soluble in aqueous alkali. It is precipitated from alkaline solution by carbon dioxide. A triacetate, m. p. 120—122°, insoluble in aqueous alkali, has been prepared. Determinations of the base-binding power and approximate pK of the substance show that one hydroxyl group is acidic; it gives colour reactions characteristic of phenolic substances. The activities and m. p. of the material precipitated from alkaline solution by carbon dioxide and of the material obtained by regenerating the acetate are the same as those of the original substance. It is not appreciably volatile at 165°/0.001 mm.

S. S. ZILVA.

Crystalline menoformone. E. DINGEMANSE, S. E. DE JONGH, S. KOBER, and E. LAQUEUR (*Dent. med. Woch.*, 1930, 56, 301—304; *Chem. Zentr.*, 1930, i, 1954).—Menoformone, dissolved in a little benzene, was adsorbed on fuller's earth, which was then boiled with benzene, the residue from which was extracted with much light petroleum. The precipitate obtained on cooling was treated with potassium hydroxide and extracted with 70% alcohol and the solution shaken with benzene. The menoformone was then recovered by shaking the acidified solution with benzene, and was recrystallised as needles or plates from 70% alcohol. The substance contains not more than 25 carbon atoms in the molecule; it gives only a faint coloration with antimony pentachloride in chloroform solution.

A. A. ELDRIDGE.

Relaxative hormone of the corpus luteum. Purification and concentration. H. L. FEVOLD, F. L. HISAW, and R. K. MEYER (*J. Amer. Chem. Soc.*, 1930, 52, 3340—3348).—Details are given for the extraction of the relaxative hormone (named relaxin) from the corpus luteum tissue of sows' ovaries. The method involves extraction with acidified alcohol, removal of proteins and fats from the extract, and subsequent treatment of the resulting water-soluble extract as follows: (a) the evaporated extract is dissolved in acetic acid and the relaxin (contaminated with sodium chloride) crystallises, or (b) the extract is treated with picric acid whereby the active material is precipitated. This is freed from picric acid by dissolving in acetic acid, re-precipitating with ether,

dissolution of the solid in water, adjusting the solution to p_{H} 5.4, and centrifuging the precipitated active material. The purified product contains about 11% N and 0.035 mg. constitutes a guinea-pig unit. Relaxin is soluble in acetic acid, slightly soluble in water, and insoluble in organic solvents. Acid and neutral solutions are stable, whilst alkaline solutions are unstable. The activity of aqueous solutions is destroyed by boiling for 10—15 min., and the solid gradually loses its activity when heated above 50° in the air. Relaxin is oxidised by potassium permanganate (with loss of activity) and it is destroyed by pepsin and trypsin. Relaxin can be isolated from the serum of pregnant rabbits; it is associated with the pseudoglobulin fraction.

H. BURTON.

Effect of cryptorchidism and of castration on the chemical composition of rats. V. KOREN-CHEVSKY and M. DENNISON (Biochem. J., 1930, 24, 954—960).—The amount of intra-abdominal fat is increased in cryptorchid and to a greater extent in castrated rats. The nitrogen content is slightly decreased in both-sided cryptorchid and in castrated rats. This decrease, however, is chiefly due to the increased proportion of fat in these animals. There is a slight increase in the content of solid matter in both-sided cryptorchid and in castrated rats.

S. S. ZILVA.

Properties of the comb-growth-promoting substance obtained from testes and urine. E. C. DODDS, A. G. H. ALLAN, and E. J. GALLIMORE (Biochem. J., 1930, 24, 1031—1038; cf. Dodds, Greenwood, and Gallimore, Lancet, 1930, i, 683).—The activity of this factor is destroyed by pepsin, trypsin, and oxidation, but survives with acids and alkalis. The benzene solution of the active substance can be washed with concentrated acids and alkalis and the active substance can be extracted from a 50% aqueous alcohol solution with light petroleum. The hormone can be distilled in a high vacuum, but only after previous purification and drying. When injected into male castrated rats or mice the atrophied seminal vesicles regain their normal size. The extracts from testes do not produce œstrus.

S. S. ZILVA.

Carotene and vitamin-A. Transformation of carotene into vitamin-A as shown by a study of the absorption spectra of rat-liver oils. N. S. CAPPER (Biochem. J., 1930, 24, 980—982; cf. Moore, this vol., 962).—The band at 325 $m\mu$ attributed to vitamin-A is absent from the absorption spectra of liver oils of rats suffering from vitamin-A deficiency, but is shown by liver oils of similar rats which have been subsequently cured by massive doses of carotene, which does not show this band.

S. S. ZILVA.

Vitamin-A of butter. R. A. MORTON and I. M. HELBRON (Biochem. J., 1930, 24, 870—873).—The unsaponifiable matter from butter shows ultra-violet absorption similar to that of carotene, an increasing absorption on the ultra-violet side of 380 $m\mu$, identical with that of the vitamin-A of liver oils, and an ultra-violet absorption of an unidentified substance characterised by a maximum near 272 $m\mu$. Carotene and vitamin-A can be determined spectroscopically with

some degree of accuracy. The blue colour given by the unsaponifiable matter from New Zealand butter with antimony trichloride was characterised by a band at 592 $m\mu$ (carotene) and at 624 $m\mu$ (vitamin-A). In the case of a Danish butter the latter band was very sharp whilst the former was absent.

S. S. ZILVA.

A diatom (*Nitzschia closterium*, W. Sm.) as a source of vitamin-A. B. AHMAD (Biochem. J., 1930, 24, 860—865).—The oil obtained from the diatom possesses a very high vitamin-A activity and gives a strong colour reaction with antimony trichloride. The greater part of the biological activity of the oil is probably due to carotene synthesised by the organism and extracted with the oil.

S. S. ZILVA.

Vitamin content of marine plankton. J. C. DRUMMOND and E. R. GUNTHER (Nature, 1930, 126, 398).—An examination of phytoplankton and zooplankton for vitamin-A and vitamin-D showed positive tests for vitamin-A in the former and for vitamin-D in the latter. The small amount of vitamin-D present in zooplankton appears to result from irradiation in surface waters and not from a prolonged diet of phytoplankton.

L. S. THEOBALD.

Isolation of the antineuritic vitamin. N. STECHOW and L. WAMOSCHER (Arch. Pharm. Inst. Univ. Berlin, 1927, 13, 145—147; Chem. Zentr., 1930, i, 1961—1962).—In experiments with rice bran, precipitation with potassium bismuth iodide, but not that with lead acetate, afforded active preparations.

A. A. ELDRIDGE.

Heat-stability of the (antidermatitis, "anti-pellagra") water-soluble vitamin-B₂. II. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 932—938).—An extract made from washed brewer's yeast by boiling in dilute acetic acid after being heated in acid solution (p_{H} 2.5) for 4 hrs. at 119° retained its power to cure the skin affection in rats, due to deprivation of vitamin-B₂, completely in doses equivalent to 0.5 g. of yeast (dry wt.) and less completely in doses equivalent to 0.16—0.33 g. of yeast. The same extract treated in alkaline solution (p_{H} 10.3—9.6) failed to cure the skin affection in doses equivalent to 0.5 g. or 1.0 g. in three out of four cases. The acid extract promoted the growth of rats on diets deficient in vitamin-B₂, whilst the alkaline extract did not.

S. S. ZILVA.

Experimental scurvy. VII. Effect of vitamin-C given parenterally to guinea-pigs fed on a vitamin-free diet. T. NAGAYAMA and T. TAGAYA. **VIII. Carbohydrate metabolism of guinea-pigs fed on a diet free from vitamin-C.** Y. KOZA (J. Biochem. Japan, 1930, 11, 445—460, 461—477).—**VII. Hypodermic administration of vitamin-C prevents experimental scurvy.**

VIII. Lack of vitamin-C has no direct effect on the liver- or muscle-glycogen of the guinea-pig.

CHEMICAL ABSTRACTS.

Vitamin-C and the rat's diet. G. A. HARTWELL (Biochem. J., 1930, 24, 967—972).—The addition of vitamin-C to a synthetic diet produces no improvement in the rate of growth or reproduction of the rat.

S. S. ZILVA.

Fat-soluble vitamins. XXX. Effect of feeding with irradiated yeast on antirachitic value of cow's milk. H. STEENBOCK, E. B. HART, F. HANNING, and G. C. HUMPHREY (J. Biol. Chem., 1930, 88, 197—214).—Daily administration to cows of 10 g. of irradiated yeast had no effect on the milk but increased the vitamin-A content of the butter; 50 g. of irradiated yeast daily caused definite increase in the vitamin-A of the milk, and as much as 200 g. could be given daily without adverse effect on the amount or the fat-content of the milk.

C. R. HARINGTON.

Is vitamin-D a single substance? G. VON WENDT (Klin. Woch., 1930, 9, 166—167; Chem. Zentr., 1930, i, 1961).—Experiments on the massive feeding of rats with "vitophos" suggest the possibility that several different substances may exhibit the effects of vitamin-D.

A. A. ELDRIDGE.

Sinkage [of pulp-wood]. II. Seasonal distribution of water and gas in trees. R. D. GIBBS (Canad. J. Res., 1930, 2, 425—439; cf. B., 1930, 907).—The distribution of water and gas, together with the seasonal changes, in balsam, jack pine, birch, and poplar have been investigated. The water content of freshly-cut soft woods, with the exception of balsam, is relatively uniform, very high in sapwood, and low in heartwood. The gas content of heartwood is higher than that of sapwood; thus the higher is the proportion of heartwood the lower is the tendency of logs to sink. An apparatus for the measurement of volume of wood samples is described, and the seasonal distribution of water and gas is illustrated by means of curves and tables.

T. T. POTTS.

Effect of turbulence [of the atmosphere] on the carbon dioxide exchange in plants. P. LEHMANN (Forts. Landw., 1929, 4, 745; Bied. Zentr., 1930, 59, 312—318).—Variations in the carbon dioxide content of the air at short intervals and under varying conditions are recorded. The effect of wind velocity, temperature, and environmental conditions on local changes in the moisture and carbon dioxide in air, and the resulting influence on the carbon dioxide assimilation of plants, are discussed.

A. G. POLLARD.

Assimilation of carbon dioxide under the influence of radioactivity in the development of cells containing chlorophyll. J. STOKLASA, J. ČAKIR, and J. PĚNKAVA (Biochem. Z., 1930, 224, 102—134).—The amounts of carbon dioxide assimilated and expired by a cell containing chlorophyll changes with its age. The action simultaneously of β - and γ -rays and the action of γ -rays alone increase the assimilation of carbon dioxide, the increase being different for cells at different stages of development. Simultaneous action of β - and γ -rays using 200 and 250 g. of "nasturan" (=0.0354 and 0.04425 mg. of radium) causes a decrease in the respiration of young cells. Radium emanation causes a decrease of assimilation at all stages of the cell development, the greatest effect being obtained with a young cell and decreasing with age. Emanation also causes an increased respiration, the increase being greatest with the young cell.

P. W. CLUTTERBUCK.

Photosynthesis. I. The formaldehyde hypothesis. II. First sugar of carbon assimilation and nature of the carbohydrates in the narcissus leaf. E. C. BARTON-WRIGHT and M. C. PRATT (Biochem. J., 1930, 24, 1210—1216, 1217—1234).—I. The production of formaldehyde in Klein and Werner's experiments (A., 1926, 439) is not due to photosynthetic activity of the plant, but to the action of light on carbonic acid and hydrogen carbonates in their solutions.

II. Only hexoses and sucrose are formed in the leaf of the daffodil *Narcissus pseudonarcissus*, L. Investigation of the carbohydrates indicates that the hexose and not sucrose is the first sugar of photosynthesis.

S. S. ZILVA.

Storage and other carbohydrates in a Natal succulent and a Natal geophyte and their behaviour before, during, and after the winter resting season. J. W. BEWS and J. E. VANDERPLANK (Ann. Bot., 1930, 44, 689—719).—The succulent type studied was *Portulacaria afra* (Jacq) and the geophytic type *Hypoxis rooperi* (Moore). The pentosan content of the leaves of the former is 49.9% and the hexosan content 45.5% higher on the north (sunny) side than on the south side. The carbohydrate content of *H. rooperi* is highest in the spring and least in dying leaves, except for the hexosan fraction, for which the reverse is true. The hexosans, the chief products of photosynthesis, increase largely during the day and decrease by night. In neither plant does the water content directly affect the carbohydrates. The large carbohydrate reserves are drawn on only to a small extent for the production of spring leaves.

P. G. MARSHALL.

Influence of temperature on composition and quality of peas (*Pisum sativum*, L.). V. R. BOSWELL (Proc. Amer. Soc. Hort. Sci., 1928, 25, 21—26).—The sugar: starch ratio, the temperature during development, and the time of maturity were studied.

CHEMICAL ABSTRACTS.

Enzymic change in ripening barley. H. LÜERS, H. FINK, and W. RIEDEL (Woch. Brau., 1930, 47, 393—397, 405—409).—With progressive ripening the catalase content of barley shows an increase which is followed by a decrease at the resting stage, and finally reaches a value which remains constant during storage. The content of catalase appears to be dependent on external influences such as climate. During ripening the diastatic power of the barley increases steadily, but decreases at the conclusion of that condition. At p_H 4.6 there is an optimum for the diastatic action. Apart from slight changes with the barely ripe barley, the oxidation-reduction system shows no appreciable quantitative changes during the ripening process. Post-mortal respiration decreases markedly during ripening.

C. RANKEN.

Significance of glutamine in germination. R. NUCCORINI (Annali Chim. Appl., 1930, 20, 239—244).—Comparison of the proportions of glutamic and aspartic acids in the proteins of *Ricinus* seeds and wheat with those of the glutamine and asparagine extractable from the germinating seeds indicates that, unlike asparagine, glutamine may be regarded

as a direct product of the hydrolysis of the proteins during germination. T. H. POPE.

Transport of nitrogenous substances in the cotton plant. V. Movement to the boll. E. J. MASKELL and T. G. MASON (Ann. Bot., 1930, 44, 657—688; of this vol., 965).—Of six samples, three had the bolls removed and after 5 days the increase of the various nitrogen fractions was determined. In the upper regions of the leaves, wood, and bark the nitrogen response is always significant, and that of the crystalloid nitrogen is greater than that of the protein. The carbohydrate concentration is also increased, in the leaves chiefly on account of sucrose and in the bark entirely so. The p_H of the sap is increased in all tissues except the bark of the upper regions. Fertilisation of the bolls causes a marked increase in carbohydrate and water uptake and a much smaller increase in nitrogen uptake, such increase being greater in the ovules than in the carpels. After the fourth day the concentrations of all nitrogen fractions except amino-acid are higher in unfertilised than in fertilised ovules. The p_H of the sap of normal ovules continues to rise after the fourth day but falls in unfertilised ovules, whilst in the carpels no difference is detectable until after the sixth day. The nitrogen gradients into the boll during growth indicate that organic nitrogen enters from the sieve-tubes as residual rather than asparagine-nitrogen. P. G. MARSHALL.

Physiological reaction of ammonium salts and nitrates. A. MAKSIMOV (Rocz. Nauk Rol. Lés., 1929, 22, 33—88).—Plants altered the reaction of a solution of single salts only to a certain value which varied for different plants. With physiologically acid salts the final values were for grain crops p_H 3.3, and for leguminous crops p_H 4.1. The course of the change was irregular. Between 0.001 and 0.02N the concentration of the salt solution does not affect the final value. The physiological reaction of ammonium nitrate is not definite, but is determined by the reaction of the medium. CHEMICAL ABSTRACTS.

Improvement of the metabolism of plants by physiological culture without change in the soil. N. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], 11, 712—717).—Improved results are obtained with *Cattleya*, maize, beans, potatoes, sugar beet, tobacco, and tomato plants supplied with a mixture of the soluble and insoluble salts actually existing in the plants and in doses corresponding with the requirements of the whole crop. T. H. POPE.

Development of seedlings from seeds treated with solutions of nitrates. B. N. AXENTSEV (Biochem. Z., 1930, 223, 387—393; cf. A., 1929, 1345).—Although the early development of seeds of *Amaranthus retroflexus*, L., is stimulated by treatment with solutions of sodium nitrate, later stages of the growth of seeds so treated may be either more or less vigorous than those of untreated seeds, and the effect of treatment with the nitrate may be modified according as growth takes place in the dark or in light. W. MCCARTNEY.

Ripening and composition of the Texas magnolia fig. H. P. TRAUB and G. S. FRAPS (Proc. Amer. Soc. Hort. Sci., 1928, 306—310).

CHEMICAL ABSTRACTS.

Leaves of *Solanum pseudocapsicum*. M. G. BREYER-BRANDWIJK (Bull. Sci. pharmacol., 1929, 36, 541—550; Chem. Zentr., 1930, i, 1163).—Alcohol extracts an alkaloid (0.25—0.53% of the dry substance) which is not volatile with steam. Solanine is not present. A. A. ELDRIDGE.

Alcohol-soluble proteins of varieties of *Holcus sorghum*. D. B. JONES and F. A. CSONKA (J. Biol. Chem., 1930, 88, 305—309).—The seeds of dwarf yellow milo and of feterita contain alcohol-soluble proteins which are closely similar in composition to each other and to that derived from kafir (Johns and Brewster, A., 1917, i, 108) except that tryptophan is absent from the protein of milo. C. R. HARRINGTON.

Crystalline globulin of banana seeds. G. L. KEENAN and J. D. WILDMAN (J. Biol. Chem., 1930, 88, 425—426).—Banana seeds contain a crystalline globulin similar in properties to those previously observed in squash and cantaloupe seeds (cf. Jones and Gersdorff, A., 1923, i, 883). C. R. HARRINGTON.

Carotenoid from the seed-hulls of the spindle-tree (*Euonymus europæus*). L. ZECHMEISTER and K. SZILÁRD (Z. physiol. Chem., 1930, 193, 67—71).—The arillus of the seeds on extraction with ether and treatment with alkali yields a carotenoid, red crystals, m. p. 201° (corr.), $[\alpha]_D^{25}$ -63° ($\pm 20\%$). The absorption spectrum is identical with that of zeaxanthin. The natural pigment appears to be an ester of which the substance described is the alcoholic component. J. H. BIRKINSHAW.

African *Chaulmoogra* species. E. PERROT and M. T. FRANÇOIS (Bull. Sci. pharmacol., 1929, 36, 551—554; Chem. Zentr., 1930, i, 1163).—*Caloncoba Welwitschii* seeds afford an oil (44%) having m. p. 38°, d_4^{25} 0.942, n_D^{25} 1.4750, $[\alpha]_D^{25}$ $+54.8^\circ$, acidity (oleic%) 7, saponification value 184; iodine value (Hanus) 84; the fatty acids had m. p. 56°, acid value 203, average mol. wt. 275, iodine value (Hanus) 90, $[\alpha]_D^{25}$ $+55.5^\circ$. Oil from *Oncoba echinata* and *Caloncoba glauca* (yield 19%) is similar. A. A. ELDRIDGE.

Composition of wallflower-seed oil. J. VAN LOON (Rec. trav. chim., 1930, 49, 745—753; cf. Matthes and Boltze, A., 1912, i, 601).—The oil, obtained in 20% yield by extraction of the ground seeds of the wallflower (*Cheiranthus cheiri*, L.) with light petroleum, has d_4^{25} 0.9155, n_D^{25} 1.4718, acid value 2.5, saponification value 176.4, ester value 173.9, iodine value (Wijs) 137.0, Reichert-Meissl value 0.5. The total fatty acids (94.5% of the oil) consist of saturated (mainly palmitic) (4.9%), erucic (40.6%), oleic (4.9%), linoleic (24.7%), and linolenic (19.4%). The oil contains glycerol (3.9%) and solid unsaponifiable matter (1.1%). H. BURTON.

Composition of soya beans under the conditions prevailing in the middle Volga district. V. KHARICHKOV and E. VAGANOVA (Masloboino Zhir. Delo, 1930, No. 2, 64—66).—Variations of the oil and protein contents with the soil and climatic conditions are recorded. Early or dense sowing increases the protein and decreases the oil content; humidity increases the oil content. CHEMICAL ABSTRACTS.

Cephalins of soya bean. B. SUZUKI and U. NISHIMOTO (Proc. Imp. Acad. Tokyo, 1930, 6, 262—265).—Details are given for the extraction of the cephalins from the oil-free alcoholic extract of soya bean. Hydrolysis of these with 3% sulphuric acid gives cholamine, stearic, linoleic, linolenic, and β -glycerophosphoric acids. Treatment of the cephalins with bromine in light petroleum affords (a) soluble and (b) insoluble fractions, hydrolysed to (a) stearic and tetrabromostearic acids, and (b) stearic and hexabromostearic acids. The original mixture contains, therefore, α -stearo- γ -linoleo- and α -stearo- γ -linoleo- β -cephalins. H. BURTON.

Occurrence of lysolecithin in polished rice. M. IWATA (Proc. Imp. Acad. Tokyo, 1930, 6, 212—215).—Washed, polished rice contains 0.2% of lysolecithin which may be extracted by repeated digestion with 94% alcohol, evaporating to a syrup, and pouring into ether. The crude material is purified by precipitating the alcoholic solution with warm alcoholic cadmium chloride, removing the cadmium, and recrystallising from absolute alcohol and chloroform. Lysolecithin, $[\alpha]_D^{20} -4.52^\circ$, softens at 100° , decomposes at $262-264^\circ$, and on hydrolysis yields palmitic acid, choline, and glycerophosphoric acid, the first two being obtained in almost theoretical yield. P. W. CLUTTERBUCK.

Phototoxic substance from *Hypericum crispum*. Z. MÉLASJOANNIDÈS (Arch. Inst. Pasteur Hellén., 1928, 2, 161—165; Chem. Zentr., 1929, i, 1576).—In an attempt to isolate the phototoxic substance from *Hypericum crispum*, 0.16 g. of a red, amorphous substance, slightly soluble in water and giving a characteristic spectrum, was obtained from 100 g. of the dried plant. L. S. THEOBALD.

Rice starch. V. Comparative studies on rice, boiled rice, and mochi. W. S. TAO (Bull. Chem. Soc. Japan, 1930, 5, 209—214).—The chemical change undergone by rice during cooking (either simple boiling with water, or steaming and pounding into mochi-cake) is mainly hydrolysis to water-soluble reducing sugars and polysaccharides. Both boiled rice and mochi give large quantities of soluble sugars when treated with diastase or saliva; with the former enzyme both maltose and dextrose are obtained but with the latter only maltose. In both reactions dextrin is produced.

The chemical changes caused in rice starch by cooking resemble those in the germination of rice seeds except that the velocity of conversion of starch into soluble sugars is greater in the former, and the change of starch into carbon dioxide and water takes place only in the latter. R. J. W. LE FÈVRE.

Biochemical relations between formaldehyde, sugars, and plant acids. H. SCHMALFUSS (Z. angew. Chem., 1930, 43, 500—503).—A lecture. A. R. POWELL.

Variations in content of sugars and related substances in olives. P. F. NICHOLS (J. Agric. Res., 1930, 41, 89—96).—The picric acid determination of reducing sugars and sucrose in the water extract of olives is unsatisfactory if basic lead acetate is used for clarification. After clarification with mercuric nitrate, the remaining reducing substances can be

removed by yeast. All of the 17 varieties of olive studied showed a maximum total sugar content about midway in their production season, and the ratio of simple to total sugars usually declined as the season progressed. E. HOLMES.

Constitution of the principal sugar of *Rhodymenia palmata*. H. COLIN and E. GUÉGUEN (Compt. rend., 1930, 191, 163—164).—The principal sugar of *Rhodymenia palmata* is an α -monogalactoside of glycerol (secondary alcohol group) and is the typical sugar of many *Floridæ*. C. C. N. VASS.

Biochemical studies on the bamboo. I. S. KOMATSU (Reprint Chikashige Anniversary Vol., Kyoto, 1930, 119—138).—An investigation of the carbohydrates and nitrogenous substances of the mature mandrake (*Phyllostachys quilioi*) and its shoots is recorded. The polysaccharide content of the nodes increases with age, whilst the water, ash, and total nitrogen decrease. The pentose content is constant throughout the life of the shoot, but the pentosan-hemicellulose decreases. Crystalline *l*-xylose (m. p. $145-150^\circ$, $[\alpha]_D^{20} +19.21^\circ$) and glyceronic acid isolated from the shoot-juice indicate the course of the hexose catabolism. The juice also contains oxalic, tartaric, citric, and lactic acids. The variation in moisture, carbon dioxide, oxygen, and gaseous nitrogen in the culm runs parallel with the total reducing sugar content of the aqueous extracts. F. O. HOWITT.

Hydrolytic products of oroboside: dextrose and orobol. M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1930, 12, 765—772).—See this vol., 456.

Hexacosanol, a new C_{26} alcohol of the fatty series extracted from the bark of *Amelanchier vulgaris*, Mœnch. J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 758—764).—The bark is dried, extracted with boiling 60% alcohol, and the residue digested with boiling 95% alcohol. The lipid and fatty matter thus obtained is saponified, the benzene-soluble substances are separated, and hexacosanol, m. p. 77.5° (corr.), is obtained in the pure state by crystallisation from ethyl acetate. The acetate, iodo-derivative, and the acid formed on oxidation are described. F. O. HOWITT.

Piceoside in the bark of the black willow. M. BRIDEL and J. RABATÉ (J. Pharm. Chim., 1930, [viii], 11, 561—572).—See this vol., 825.

Constituents of corncockle seed. III. Githagoic acid and githagonolic acid. Degradation of githagenin. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1930, 190, 1—14; cf. A., 1929, 857).—Githagenin on oxidation with permanganate in acetone yielded the dibasic githagoic acid, $C_{25}H_{44}O_5$, m. p. 359° , $[\alpha]_D^{20} +91.6^\circ$ (methyl ester, $C_{30}H_{48}O_5$, m. p. 247° , $[\alpha]_D^{20} +77^\circ$). The presence of an alcoholic or a ketonic group could not be detected. Alkali fusion of githagenin gave githagonolic acid, $C_{25}H_{38}O_4 \cdot H_2O$, m. p. 364° [methyl ester, m. p. $234-235^\circ$; acetyl derivative, m. p. 328° (decomp.); methyl ester of acetyl derivative, m. p. 171°]. Acetylgithagonolic acid was produced as a by-product in the acetylation of githagenin. Oxidation of acetylgithagenin with chromic acid in aqueous acetic acid at $60-70^\circ$ gave

acids I and II (*methyl ester of I*, $C_{29}H_{42}O_6$, m. p. 279°; *methyl ester of II*, m. p. 189°). Treatment of the methyl ester I with hydroxylamine hydrochloride yielded the *oxime*, $C_{29}H_{43}O_6N$, m. p. 222°. Oxidation of githagic acid with chromic acid in boiling acetic acid gave an *acid (dimethyl ester)*, $C_{46}H_{38}O_6$, m. p. 265°).
J. H. BIRKINSHAW.

Determination of the saponin content of indigenous *Gypsophila paniculata*. L. G. MATOLCSY (Ber. Ungar. pharm. Ges., 1929, 5, 33—42; Chem. Zentr., 1929, i, 1592).—A method for the determination of the foam number (1667 in this case) is described. The viscosity and surface tension increase with concentration, whilst the former decreases with temperature. Different parts of the root contained from 0.15 to 8.36% of saponin (mean 7.06%). Haemolytic indices are recorded.

L. S. THEOBALD.

Microscopical and chemical examination of the tissue of the bamboo stalk. S. OGURI and M. NARA (J. Soc. Chem. Ind. Japan, 1930, 33, 236—238b).—Photomicrographs of longitudinal and transverse sections of bamboo stalk are shown and the proportions of the main constituents (cellulose, lignin, and pentosans) are determined.
F. R. ENNOS.

Jute fibre. II. Hemicelluloses. J. K. CHOWDHURY and T. M. SAHA (J. Indian Chem. Soc., 1930, 7, 347—356).—Jute fibre is extracted with chloroform to remove resin and fat and delignified by treatment with a slow current of chlorine dioxide gas. The residue is extracted successively with benzene, 95% alcohol, boiling water, and 17.5% sodium hydroxide. The extracted material is isolated by evaporation of the solvent or by concentration and addition of alcohol. The hemicelluloses are precipitated repeatedly from their solutions by alcohol and subsequently hydrolysed by 2.5% sulphuric acid. Galactose, laevulose, arabinose, xylose, uronic acids, and pectins are identified among the products of hydrolysis. It appears improbable that the insoluble calcium salt method gives a quantitative measure of the pectin.

Pectins and hemicelluloses of jute may be removed almost completely by treatment in an autoclave with water at 2—3 atm. for 4 hrs. The residue is similar in properties to α -cellulose.
H. WREN.

Hemicelluloses. II. Hemicelluloses of maize cobs. I. A. PREECE (Biochem. J., 1930, 24, 973—979).—Hemicellulose of maize cobs has been separated into four fractions, hemicellulose *A* which yields on hydrolysis xylose and uronic acid, *B1* and *C1* yielding varying proportions of xylose, uronic acid, and methylpentose, and *C2* which gives arabinose, uronic acid, and methylpentose. In all cases the proportion of pentose residues present far exceeded the combined proportions of residues of methylpentose and uronic acid. The separation was carried out by Norris and Preece's method (cf. this vol., 383). Hemicellulose *C* was fractionated by precipitation of *C1* directly with Fehling's solution and *C2* with acetone from the filtrate.
S. S. ZILVA.

Preparation of skeletal substances from incrustated cell walls of plants by means of chlorine

dioxide. E. SCHMIDT, Y. C. TANG, and W. JANDEBEUR (Naturwiss., 1930, 18, 734).—Preparations of these skeleton substances have previously been made by a two-stage reaction with chlorine dioxide. It has been found that direct preparation may be effected at the ordinary temperature in presence of suitable inorganic or organic compounds which are stable towards chlorine dioxide. The new method gives a better insight into the constitution of the cell wall and results on red beech are recorded. The method is applicable to the determination of cellulose in lignin.
W. R. ANGUS.

[Impurities in] wood and animal charcoals. D. I. MACHT (J. Pharm. Exp. Ther., 1930, 39, 343—346).—Saline extracts of animal charcoal and of blood charcoal, but not those of wood charcoal, had a detrimental effect on the growth of seedlings of *Lupinus albus*. This effect may be due to the presence in the animal charcoal of substances which could modify the effects produced by solutions of compounds having powerful physiological actions.
W. McCARTNEY.

Kinetics of penetration. II. Penetration of carbon dioxide into *Valonia*. A. G. JACQUES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1930, 13, 695—713; cf. this vol., 110).—The rate of penetration of carbon dioxide is believed to be of the first order, although the velocity coefficient decreases. The latter phenomenon was found not to be due to differences in the shape and size of the cells. It is suggested that individual differences in the permeability of the cells used is the cause. The velocity coefficients at p_H 4.8 (carbon dioxide undissociated) and at p_H 6.8 (carbon dioxide 75% dissociated) were nearly the same. The rate of penetration of carbon dioxide depends on the concentration of the undissociated carbon dioxide in the sea-water, rather than the concentration of ions. It is concluded that there is little penetration of ions.

G. F. MARRIAN.

Bioelectric potentials. I. Effects of potassium and sodium chlorides on *Nitella*. W. J. V. OSTERHOUT (J. Gen. Physiol., 1930, 13, 715—732).—Experiments on the concentration effects of potassium and sodium chloride solutions in *Nitella* were carried out by the technique previously described (cf. A., 1929, 1112). When it was assumed that diffusion potentials predominated, the calculated *P.D.* agreed closely with the observed values. On the basis of phase boundary potentials the calculated figures were not satisfactory. It is concluded that diffusion potentials predominate.
G. F. MARRIAN.

Cell sap of *Halicystis*. L. R. BLINKS and A. G. JACQUES (J. Gen. Physiol., 1930, 13, 733—739).—Analyses of the sap obtained from growing cells of *Halicystis* gave the following results expressed in mols. per litre: Cl 0.6028, Na 0.5570, K 0.0064, Ca 0.0080, Mg 0.0167, and a trace of sulphate. The p_H of the fresh sap was 6.2.
G. F. MARRIAN.

Mineral content of mushrooms. H. RAMAGE (Nature, 1930, 126, 279).—All parts of a button mushroom have a high potassium and low calcium content; the skin contains lithium and most of the

iron present. Phosphorus varies from 1 to 3% in the dried material, the gills containing most. Silver and copper are present in all parts, the stem containing least. The skin, the white, and the gills (dried material) contain more than 0.02% of copper and more than 0.01% of silver (gills <0.05%). L. S. THEOBALD.

Separation from *Laminaria* of a complex compound containing labile iodine. P. DANGEARD (Compt. rend., 1930, 191, 337—339).—If a stalk of *Laminaria flexicaulis* is immersed in sea-water, small amounts of iodine are liberated in the first few hours. At the end of two or three days iodides appear from which iodine is liberated by acids. In fresh water iodides are also set free in the initial period. The labile iodine is supposed to be in the form of a complex compound, decomposed by acids, of an iodide and a thermo-stable oxidising agent. R. K. CALLOW.

Boron content of oranges. C. S. SCOFIELD and L. V. WILCOX (Science, 1930, 71, 542).—A relationship between the boron content of irrigation water and that of the leaves and fruit is established.

L. S. THEOBALD.

Potassium and sodium contents of plants growing in salt lagoons or on the sea shore. G. BERTRAND and M. ROSENBLATT (Bull. Soc. chim., 1930, [iv], 47, 639—642).—See this vol., 823.

Biology of metals. III. Localisation of lead within the cell of the growing root. IV. Influence of lead on mitosis and cell size in the growing root. F. S. HAMMETT. V. Selective fixation of lead by root nuclei in mitosis. F. S. HAMMETT and E. S. JUSTICE. VI. Nature of the lead compound deposited in the growing root. F. S. HAMMETT (Protoplasma, 1928, 5, 135—141; 1929, 535—542, 543—546, 547—562).—In plants grown for 24 hrs. in lead nitrate solution (1 in 10⁴) the lead was combined in especially high concentration with the nuclei and walls of the cells. The deposit is a compound of lead with an organic thiol compound, possibly glutathione.

CHEMICAL ABSTRACTS.

I. Precipitation of silicic acid in plants. II. Comparison of the precipitation of silicic acid and of calcium salts in plants. A. FREY-WYSSLING (Ber. deut. bot. Ges., 1930, 48, 179—183, 184—191).—I. The phenomenon of silica precipitation in plants is represented as the elimination of non-assimilable matter and is characteristic of tropical and sub-tropical flora. The higher temperature at which rock disintegration occurs leads to a higher silica content in the soil solution than occurs in temperate and polar zones. Silica is precipitated mainly in the peripheral tissues of transpiratory organs and is localised along the conducting vessels.

II. The deposition of silica in plant-tissue occurs in a similar manner and in corresponding tissues to that of calcium salts. In warmer regions plants take up amounts of calcium and silica in excess of their physiological requirements. Calcium hydrogen carbonate enters the plant from the soil solution and its subsequent deposition as calcium carbonate represents merely the elimination of unutilisable surplus. Oxalic

acid, however, is a product of plant metabolism and its precipitation as calcium oxalate is an excretory function. A. G. POLLARD.

Toxicity of some aliphatic alcohols [to plants]. W. S. EISENMENGER (Plant Physiol., 1930, 5, 131—156).—Ethyl alcohol (up to 0.0012M) stimulated, but other aliphatic alcohols retarded, the growth of soybean seedlings. Low concentrations of calcium nitrate also had a stimulating effect, but increased the toxicity of some of the alcohols. The toxicity does not increase regularly with increase in the number of carbon atoms in the molecule, and *n*-alcohols are not more toxic than *iso*-alcohols.

CHEMICAL ABSTRACTS.

Simple instrument for micro-manipulations. A. N. RICHARDS (J. Biol. Chem., 1930, 87, 463—466).—Technical. C. R. HARRINGTON.

Micro-determination of mercury in organic material. K. O. MÖLLER (Biochem. Z., 1930, 223, 379—386).—Unless precautions are taken, mercury is lost by volatilisation during the destruction of organic matter when determinations of the metal are carried out by the usual methods. A satisfactory method is described. W. MCCARTNEY.

Determination of manganese in animal material. J. T. SKINNER and W. H. PETERSON (J. Biol. Chem., 1930, 88, 347—351).—The material is incinerated, the ash is extracted with dilute phosphoric acid, the filtered extract is treated with potassium periodate, and the permanganate formed is determined colorimetrically; 0.01 mg. of manganese may be determined with an error of about $\pm 10\%$, the use of phosphoric acid avoiding the difficulties otherwise encountered owing to precipitation of calcium sulphate. C. R. HARRINGTON.

Determination of sulphur and phosphorus in plants. G. BERTRAND and L. SILBERSTEIN (Bull. Soc. chim., 1930, [iv], 47, 95—99).—See this vol., 120.

Improved design of Van Slyke apparatus for the determination of amino-nitrogen. S. J. FOLLEY (Biochem. J., 1930, 24, 961—964).—Rubber connexions are obviated in the deaminising chamber and in the Hempel pipette of this design.

S. S. ZILVA.

Should lipins be calculated as fat? H. FINCKE (Chem.-Ztg., 1930, 54, 598).—Polemical against Rewald (cf. *ibid.*, 134); the author supports his opinion that lipins should not be included in determinations of "fat content" of materials.

E. LEWKOWITSCHE.

Analysis. X. Determination of fats. L. PIX-CUSSEN and S. KOLODNY (Biochem. Z., 1930, 223, 347—351).—The acids obtained from fats by hydrolysis under pressure with water, zinc, and zinc oxide are converted into lead salts. The salts of unsaturated acids are dissolved in ether and of the ether-insoluble salts some are dissolved by chloroform. After the organic matter in the three fractions has been destroyed by treatment with nitric acid and hydrogen peroxide, the lead is determined colorimetrically as sulphide. W. MCCARTNEY.