

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

Ultra-violet bands of the hydrogen molecule. A. SCHAAFSMA and G. H. DIEKE (*Z. Physik*, 1929, **55**, 164—186).—The hydrogen spectrum has been investigated over the region 1250—1700 Å., and almost all lines have been arranged in the *B*—*A* band system. Oscillation levels up to $n=12$ have been found for the *A* state and up to $n=9$ for the *B* state. By applying combination conditions the terms have been isolated and the constants calculated. No lines belonging to other band systems lie in this region.

J. W. SMITH.

Some peculiar hydrogen bands. C. J. BRASEFIELD (*Physical Rev.*, 1929, [ii], **33**, 925—931).—Photographs of the secondary spectrum of hydrogen as excited by an electrodeless ring discharge were taken at pressures from 0.08 to 0.001 mm. A number of lines were found to be more intense at low than at high pressures, and were arranged into bands assumed to be $0 \rightarrow 0$, $1 \rightarrow 0$, $0 \rightarrow 1$, and $1 \rightarrow 1$ bands. The values of the moments of inertia are $I_0' = 3.8 \times 10^{-40}$, $I_1' = 5.5 \times 10^{-40}$, $I_0'' = 2 \times 10^{-40}$, and $I_1'' = 2.3 \times 10^{-40}$. The corresponding values of the nuclear separations are $r_0' = 2.14 \times 10^{-8}$, $r_1' = 2.57 \times 10^{-8}$, $r_0'' = 1.55 \times 10^{-8}$, and $r_1'' = 1.66 \times 10^{-8}$ cm. The emitter of these bands is thought to be either H_2^+ or doubly excited hydrogen.

N. M. BLYTH.

Intensity problem in the Stark effect in hydrogen. H. MARK and R. WIERL (*Z. Physik*, 1929, **55**, 156—163).—The intensity distribution in the Stark effect components of the H_α and H_β lines of hydrogen is different in collision excitation from that in resonance excitation with a field direction perpendicular to the direction of the positive rays. An analogy is drawn with the polarisation of light emitted by a moving hydrogen atom. The p -intensity (the electrical vector of the light parallel to the electric field and perpendicular to the velocity direction) is greater for collision excitation than for resonant excitation.

J. W. SMITH.

Asymmetry in the radiation from the hydrogen atom in the electric field. J. STARK (*Nature*, 1929, **124**, 125—126, and *Naturwiss.*, 1929, **17**, 568—569).—Observations on the hydrogen lines H_α , H_β , H_γ , and H_δ for the case of emission along the axis of a superposed electric field have revealed differences in the intensities for the two sides of the plane perpendicular to the axis. The asymmetry of radiation of the hydrogen atom in the electric field is incompatible with the Bohr—Epstein—Kramers theory, with the Heisenberg—Schrödinger theory, and with Sommer-

feld's theorem on the symmetry of the hydrogen atom.

A. A. ELDRIDGE.

Second order Stark effect in the Balmer series of hydrogen. II. H. R. VON TRAUBENBERG and R. GEBAUER (*Z. Physik*, 1929, **56**, 254—258; cf. this vol., 734).—The shifts of the higher components of H_γ towards the red end of the spectrum observed experimentally agree with the values now calculated from Schrödinger's theory, but not with Epstein's calculations from the old quantum theory.

J. W. SMITH.

Continuous spectrum of the hydrogen atom. D. CHALONGE and N. T. ZÉ (*Compt. rend.*, 1929, **189**, 243—245).—The capacity of the discharge in the experiments of Chalonge and Lambrey (this vol., 616) has been varied, and the form of the resulting intensity-wave-length curves indicates that the new spectra obtained are probably due to the superposition of the molecular and continuous atomic spectra of hydrogen. The latter accompanies (and its maximum intensity is produced before the limit of) the Balmer series, and a progressive enlargement of the lines of the latter, due to the Stark effect, is produced by a displacement of the maximum towards the higher wave-lengths.

J. GRANT.

Hydrogen atom-rays. I. Technical production of hydrogen atom-rays and the action of hydrogen atoms on the Schumann plate. II. Reflexion of hydrogen atoms at crystals and passage of the atoms through thin foils. H. KERSCHBAUM (*Ann. Physik*, 1929, [v], **2**, 201—212, 213—220).—I. The technique has been improved by the use of celluloid divisions in the tube for generating the hydrogen atom stream, and the use of Schumann plates for detection of the rays.

II. Reflexion experiments on thermally generated streams of hydrogen atoms impinging in two different angular regions (45 — 50° and 5 — 10°) on mica, gypsum, and celluloid show that the angle of incidence is equal to the angle of reflexion, with respect to the normal to the crystal. When the stream passed through very thin celluloid and mica foil no selective scattering could be observed. The passage of hydrogen atoms through neon has been studied in a preliminary way.

R. A. MORTON.

Detection of atomic scattering by measurement of the ionisation produced by a single *H*-particle. G. HOFFMANN and H. POSE (*Z. Physik*, 1929, **56**, 405—415).—A new method of detecting atomic scattering is described in which the ionisation



produced by each *H*-particle can be measured by means of a Duanten electrometer, which must be used in conjunction with a special type of ionisation chamber. The method is illustrated by measurements for *H*-particles produced by the bombardment of aluminium with α -particles from polonium.

J. W. SMITH.

Properties of the He₂ rotation terms. W. E. CURTIS and A. HARVEY (*Nature*, 1929, 124, 12).—Certain regularities exhibited by the rotation term differences of the various electronic states render possible the prediction (within a few cm.⁻¹) of most of the rotation terms at present missing; conversely, the interpretation of new bands is facilitated. Thus, two new branches of *P*- and *Q*-form (Dieke, Imanishi, and Takamine, this vol., 732) are recognised as *Q*- and *R*-branches of the 6*X* level of ortho-He₂.

A. A. ELDRIDGE.

Fine structure in the helium band lines. G. S. MONK and R. S. MULLIKEN (*Nature*, 1929, 124, 91).—Fine structure has been observed in the lines of a number of ortho-He₂ bands having 2³ π as their lower electronic state, but the 2³ Σ —3³ π band at 4650 Å. shows no evidence of fine structure. The bands at 6400, 5733, and 4546 Å. show qualitatively the same fine structure for all band lines which end on any given rotational level; other bands show a similar relation. An interpretation of the 2³ π fine structures is offered.

A. A. ELDRIDGE.

Analysis of the fine structure of D₃ line of helium. H. R. WEI (*Astrophys. J.*, 1928, 68, 246—256).—By using gratings of high resolving power and large dispersion in the high orders, the D₃ line of helium has been resolved into a triplet, a result which has been confirmed with an echelon spectrograph. The ratio of intensity is 4.5 : 3 : 1 and the separation ratio 10.3 : 1.

L. S. THEOBALD.

Regularities in the band spectrum of helium. Vibration quanta of He₂ and He₂⁺. W. WEIZEL and E. PESTEL (*Z. Physik*, 1929, 56, 197—214).—The fine structures of twelve bands in the spectrum of helium have been determined. Deductions are drawn concerning the vibration quanta and their dependence on the electron terms.

J. W. SMITH.

Isotope effect in the spectrum of neon. H. NAGAOKA and T. MISHIMA (*Proc. Imp. Acad. Tokyo*, 1929, 5, 200—202).—In order to study the effect of the two isotopes of neon and to compare results with Bohr's theory on the change of Rydberg constant, the interference fringes of neon, cooled in liquid air to obtain sharpness, were observed, and the lines measured and classified. The spectrum differed from the ordinary close doublets, and deviations from the calculated wave-length values were attributed to the isotope effect, and were in good agreement with calculated values of the shift to shorter wave-length based on the change of Rydberg constant.

N. M. BLYGH.

High-pressure carbon bands and the Swan system. R. C. JOHNSON and R. K. ASUNDI (*Proc. Roy. Soc.*, 1929, A, 124, 668—688).—Photographs of the high-pressure carbon bands have been obtained in the first order of a 21-foot grating, using large discharge tubes filled with carbon monoxide at a

pressure of 20—40 mm. and having at least one of the electrodes made of carbon. With tubes having a life of 4—6 hrs. the high-pressure bands were emitted strongly, and found to bear an exceptionally close resemblance in their fine structure to the Swan bands as developed under low-temperature conditions. Impurities such as hydrogen, carbon dioxide, and water vapour inhibit formation of the bands. The Swan system and the high-pressure carbon system are shown to have a common final state, hence the emitter responsible for both systems is a C₂ molecule. The inhibiting effect of hydrogen on the high-pressure system is definitely against a hydrocarbon emitter (cf. Johnson, A., 1927, 395). Four new high-pressure bands have been found in the near ultra-violet and two more in the near infra-red which, with the six known bands, form a single *n'* progression (*n'*=0). The bands consist of *P* and *R* branches only and the electronic transition involved is 3*P_n*^D→3*P_i*^P. A detailed examination of the structure of the *R* branches shows several anomalies and perturbations of an unusual type. The methods used by Hund and by Mulliken for the elucidation of the structure of diatomic molecules (cf. A., 1928, 105, 1166) are discussed, and Mulliken's application to the C₂ molecule is extended to cover the initial state of the high-pressure system. This is believed to be a normal 3*P* level and different in this respect from the two lower 3*P* levels, which are believed to be inverted.

L. L. BIRUMSHAW.

Spectrum of carbon. D. S. JOG (*Indian J. Physics*, 1929, 3, 451—461).—The wave-lengths of the carbon spectrum as given by a number of investigators being somewhat discordant, and a number of lines being unaccounted for, a re-examination was undertaken and the results are fully tabulated and discussed. The results of a search for inner transitions in the spectrum of C I of the type (2*L*₁*L*₂*M*₁←*L*₁2*L*₂*M*₁) are also given.

N. M. BLYGH.

Molecular binding and low ⁵S terms of N⁺ and carbon. L. A. TURNER (*Proc. Nat. Acad. Sci.*, 1929, 15, 526—528).—Herzberg's analysis (cf. A., 1928, 808, 1165) of the negative bands of nitrogen suggests that the dissociation of the excited molecular ion produces a normal atom and a normal atomic ion, whereas the dissociation of the normal molecular ion produces an atom and an ion, one of which is excited. The energy difference is 2.4 volts. Fowler's tables (cf. A., 1927, 489) show two lines for the excited state of nitrogen corresponding with 3*P*₂ and 3*P*₁ levels and 2.4 volts, indicating that the N⁺ ion rather than the nitrogen atom is excited. The correct fixation of the ⁵S terms of nitrogen and carbon is discussed.

N. M. BLYGH.

Ultra-violet band spectrum of nitrogen. R. T. BIRGE and J. J. HOPFIELD (*Astrophys. J.*, 1928, 68, 257—278; cf. A., 1928, 1294).—A more detailed examination of previous spectrograms together with recent spectrograms shows that the ultra-violet emission spectrum of nitrogen consists of a clearly-defined system of more than 60 bands, degraded towards the red. The weighted average wave-lengths of these bands are tabulated, together with the vibrational quantum analysis of the system. The

absorption spectrum of nitrogen also contains this system. Numerous additional emission and absorption bands are reported, and three new systems presumably are represented among the emission bands. Four new electronic levels in the neutral nitrogen molecule are thus evaluated, although one of these may be doubtful, since the corresponding system occurs only with commercial, partly-purified nitrogen and not with chemically pure nitrogen. The two most probable values of the heat of dissociation of nitrogen calculated from the vibrational constants of the several electronic levels are 11.9 and 9.5 volts, respectively.

L. S. THEOBALD.

Spectrum of ionised nitrogen (N II). L. J. FREEMAN (Proc. Roy. Soc., 1929, A, 124, 654—667).—The second group of terms based on the $2p'$ terms of N III (cf. Fowler and Freeman, A., 1927, 489) has now been investigated. Nine quintuplet multiplets have been observed, resulting in the identification of all the $3s'$, $3p'$, and $3d'$ terms. The deepest term, $2p'^5S$, has not been found. The term separations of O III are all about 2.3 times as great as those for N II. The differences in the energy levels when the series electron occupies various orbits is not much affected by the disposition of the inner electrons, since the two systems of N II quintuplets and triplets run nearly parallel, both in relative magnitudes and relative separations. Six new triplet combinations have been found, resulting in the identification of two new terms. For corresponding terms of the N II triplets and N III quadruplets, the separations are very similar in the two systems. About 75 N II lines are newly classified.

L. L. BIRCUMSHAW.

Simultaneous ionisation and dissociation of oxygen and intensities of the ultra-violet O_2^+ bands. E. C. G. STUECKELBERG (Physical Rev., 1929, [ii], 34, 65—67).—The formation of O^+ from the neutral molecule by a single impact of about 20 volts (cf. Hogness, A., 1926, 768; Smyth, this vol., 113) is explained from potential energy curves of the molecule and ion. The intensities of the ultra-violet O_2^+ bands were calculated from the same curves and found to be in good agreement with experiment.

N. M. BLYGH.

Spectra of phosphorus and arsenic in the extreme ultra-violet. Multiplets of As IV and As V. P. QUENEY (Compt. rend., 1929, 189, 158—159).—The principal lines of As V and As IV have been obtained by extrapolation, according to Millikan and Bowen's laws of regular and irregular doublets, from the homologous lines of Zn II, Ga III, and Ge IV, and of Zn I, Ga II, and Ge III, respectively. The results were confirmed experimentally.

J. GRANT.

Second spark spectrum of sulphur, S III. S. B. INGRAM (Physical Rev., 1929, [ii], 33, 907—913; cf. Gilles, this vol., 225).—With experimental data previously obtained (cf. A., 1928, 1068) the spectrum of S III is analysed. Most of the triplet terms predicted by the Hund theory are found and the strongest in the visible and extreme ultra-violet are classified. The ground term $3s^23p^2P_0$ gives the ionisation potential as 34.9 ± 0.4 volts. Complete term tables and a list of classified lines are given. The term $3s^23p.4s^3P$ is anomalous, having a total separation

of 450, whilst the p doublet of the ion is 950. The interval ratio of this term is 10 : 1, instead of 2 : 1 as given by Landé's rule. Combinations of this term with the ground term in the extreme ultra-violet are very weak.

N. M. BLYGH.

Excitation of visible "red" and "blue" argon spectra by electron collision. B. SCHULZE (Z. Physik, 1929, 56, 378—393).—The excitation of the arc and first spark spectra of argon in the visible region by electron collision has been investigated, the successive appearance of the different lines with increasing accelerating voltage being observed photographically. In contradiction to previous work the arc spectrum in the visible and near infra-red regions can be excited in seven stages between 13.3 and 15.7 volts. In all cases good agreement is obtained with the excitation potentials calculated from the series terms, thus affording a direct confirmation of the analysis of the "red" spectrum given by Meissner (A., 1926, 1186; 1927, 177). The excitation potentials of a series of lines of the first argon spark spectrum (the "blue" spectrum) were measured in a similar way, good agreement being obtained with the values calculated from the spectroscopic measurements of de Bruin (A., 1928, 450; this vol., 3).

J. W. SMITH.

Possibility of observing an emission spectrum of the calcium substratum in the galaxy. Y. ÖHMAN (Nature, 1929, 124, 179—180).

Intensities in the calcium spark spectrum. A. ZWAAN (Arch. Néerland, 1929, [iii], 12, 1—76).—Mathematical. The potential function is considered, the central field of the Ca^{++} ion being investigated, and the "Eigenfunktion" is calculated, the approximation method of Kramers being used. The probability of switch is also calculated, the doublet structure of the Ca^{++} spectrum being neglected. The following values were obtained for A and f : $4_2 \rightarrow 3_3$, $A = 1.3 \times 10^7$; $f = 0.09$; $4_2 \rightarrow 4_1$, $A = 1.55 \times 10^8$; $f = 1.08$. These values are high compared with those of Milne, and indicate that the calcium in the highest layers of the chromosphere is not in equilibrium.

A. J. MEE.

New series in the iron spectrum produced by a highly condensed spark. M. KAHANOWICZ (Atti R. Accad. Lincei, 1929, [vi], 9, 761—764).—Three doublets (5937.5, 5928; 5677.5, 5666.5; 5003, 5001 Å.), which may be regarded as due to a modification of the second Stark effect, are observed in the iron spectrum produced by a highly condensed spark. They belong to the series $\nu = R[1/2^2 - 1/(n/32)^2]$, where $n = [(4 \times 26) - 1]$, $[(4 \times 27) - 1]$, and $[(4 \times 31) - 1]$, respectively.

F. G. TRYHORN.

Spectral relations between certain iso-electronic systems and sequences. III. Ti I, V II, Cr III, Mn IV, and Fe V. H. E. WHITE (Physical Rev., 1929, [ii], 33, 914—924; cf. this vol., 734).—With the help of the irregular doublet law these spectra were analysed and wave-lengths, relative intensities, and designations are tabulated. About 40 lines for the electron transition $3d^34p - 3d^34s$ and about 12 lines for the transition $3d^34d - 3d^34p$ were traced through the first three elements, and in the former transition the multiplet $^5F' - ^5G'$ was traced as far as Fe V. The systematic increase in term separations

is given for the ${}^6F'$ and ${}^6G'$ terms arising from the electron configurations $3d^34s$ and $3d^34p$, respectively; the Landé interval rule and Hund's rule for relative term positions are found to be satisfied. A new type of Moseley energy level diagram for these and other elements is considered.

N. M. BLIGH.

Vector coupling in the nickel-, palladium-, and platinum-like spectra. J. E. MACK (Physical Rev., 1929, [ii], 34, 17—34).—The structure of the atomic states in which the outer electrons occur in configurations of nine d electrons and one s or p electron is chiefly considered. The $5d^96s$ and $5d^96p$ configurations are identified among the known levels of Pt I, and partly identified in Tl IV and Pb V. The lines observed in the condensed spark discharge of thallium $\lambda 868$ —1070 and lead $\lambda 477$ —1280 are tabulated. The relative energies, line intensities, and g -values of the levels of the d^9s and d^9p configurations of the sequences Ni I—Ge V, Pd I—Sn V, and Pt I—Pb V show a transition from LS or Russell-Saunders coupling to jj coupling with increasing atomic number and net charge. In the pure jj coupling the levels are arranged in groups, two in d^9s and four in d^9p . The positions of the d^9p groups observed for Hg III, Tl IV, and Pb V agree well with the positions calculated for jj coupling by Sommerfeld's regular doublet law. In the d^9p configuration of Tl IV and Pb V, only levels built upon $d^9D_{5/2}$ are observed.

N. M. BLIGH.

Spectra of Cu I, Cu II, and Mn II by means of a vacuum tungsten furnace. O. S. DUFFENDACK and J. G. BLACK (Physical Rev., 1929, [ii], 34, 35—43).—A high-temperature vacuum tungsten furnace for the study of the spectra of elements of high $b. p.$ is described. All previously observed absorption lines of Cu in the range of the quartz spectrograph were found and also six new lines from the $3d^94s$ level, 2618.381, 2824.375, 2882.81, 2961.177, 3010.84, 3194.103. CuH bands were also observed in absorption. The emission spectrum of Cu I was excited by resonance radiation from the furnace walls, the atoms being excited to the 2P state with emission of the lines 3247, 3274, 5106, 5700, and 5782. The excitation of Cu II and Mn II spectra by collisions of the second kind with ions of argon, neon, and helium was studied with reference in each case to the possible excess energy for excitation after ionisation; theoretical results were confirmed.

N. M. BLIGH.

Second spark spectrum of selenium (Se⁺⁺). D. K. BHATTACHARJYA (Nature, 1929, 124, 229).— PD , PP , and PS groups of $N_2O_1 \leftarrow N_2O_2$ have been located graphically at 24000, 28000, and 28400, respectively. Leading lines of these multiplets in the same transition are: ${}^3P_2 - {}^3D_3$ 23979 (4169.16 Å.), ${}^3P_2 - {}^3P_2$ 27482.6 (3639.6 Å.), ${}^3P_2 - {}^3S_1$ 28210.0 (3643.8 Å.).

A. A. ELDRIDGE.

Series spectrum of Se IV. P. PATTABHIRAMAYYA and A. S. RAO (Indian J. Physics, 1929, 3, 531—535).—An analysis of the spectrum of Se IV is tabulated showing: a classification of the identified lines with the terms and term values; the variation of the logarithms of doublet separations and the logarithms of the net nuclear charge; the comparative positions of some of the prominent members in the spectra of Ga I,

Ge II, As III, and Se IV; the progression of the terms in the spectra of these elements; and some unclassified pairs with their probable classification.

N. M. BLIGH.

Spectrum of trebly-ionised bromine. S. C. DEB (Nature, 1929, 123, 981).—The chief lines of the group $N_2(O_1 \leftarrow O_2)$ have been located, as follows: ${}^3P_2 - {}^3D_3$ at ν 36675.2, ${}^3P_2 - {}^3P_2$ at ν 40130.8, ${}^3P_2 - {}^3S_1$ at ν 42247; also ${}^1P_1 - {}^1P_1$ is at ν 42177.

A. A. ELDRIDGE.

Complexity of the terms of the resonance spectrum of tellurium vapour. W. KESSEL (Compt. rend., 1929, 189, 94—96; cf. Rosen, A., 1927, 608).—The author's method for the excitation of intense resonance radiation resulted in a well-developed series for tellurium vapour in which the fundamental element of each term was a doublet composed of lines of unequal intensities $\Delta\lambda = 0.5$ Å. apart, the frequencies being related by the formula $\nu = 0.53n^2 - 246.7n + 2294.3 + \Delta\nu$. The fundamental doublets were λ 4358.5, 4358.9 ($n=0$), and 4452.8, 4453.3 ($n=2$).

J. GRANT.

Temperature classification of the stronger lines of cerium and praseodymium. A. S. KING (Astrophys. J., 1928, 68, 194—245).—The furnace spectra of cerium and praseodymium obtained between 2000° and 2700° and at 1900°, respectively, have been examined, and lines arising from neutral and ionised spectra have been segregated by a comparison of furnace, arc, and spark spectra. This was facilitated by the addition of caesium, which suppresses the ionised lines normally appearing in the furnace spectrum. The furnace spectrum is especially effective in revealing lines of the neutral atom unrecognised in the arc and spark spectra. The prominent lines of cerium and praseodymium in the arc and spark spectra belong to the ionised atom, whilst at greater wave-lengths the neutral lines are stronger and form a large part of the arc spectrum. Tables of 1362 lines for cerium and of 1018 for praseodymium are given, the lines being selected for their prominence and suitability as a means of identification in either the neutral or ionised condition. Praseodymium is notable for the large number of complex lines which it shows both in the neutral and in the ionised spectra.

L. S. THEOBALD.

M-Series of rhenium. E. LINDBERG (Z. Physik, 1929, 56, 402—404; cf. A., 1928, 1078).—The discrepancies between the measurements of the author and those of Beuthe (*ibid.*, 1294) are discussed. New measurements have been made in which the previous observations have been confirmed and new lines measured.

J. W. SMITH.

Spectrum of trebly-ionised thallium (Tl IV). P. PATTABHIRAMAYYA (Indian J. Physics, 1929, 3, 523—529).—Tables are given of the scheme of multiplets formed by the combination of terms; the progression of the regular doublet law in the homologous spectra of Pt I, Au II, Hg III, and Tl IV; the progression of the difference in sub-levels in the spectra of the homologous series of elements; the progression of the ${}^3s^1P$, ${}^3s^1D$ multiplet in the sequence of the spectra, and a list of lines classified.

N. M. BLIGH.

Notation for atomic spectra. H. N. RUSSELL, A. G. SHENSTONE, and L. A. TURNER (*Physical Rev.*, 1929, [ii], 33, 900—906).—Suggestions and recommendations are made for adapting existing spectral notations to a standardised form suitable for designating multiplet, configuration, and series analyses.

N. M. Blich.

Possible origin of faint Fraunhofer lines. D. S. KOTHARI (*Nature*, 1929, 124, 90—91).—Many of the lines are ascribed to the combined effect of Raman scattering and ordinary absorption. It does not appear that the coronal spectrum is due to modification of strong Fraunhofer lines by Raman scattering.

A. A. ELDRIDGE.

Spectrum of the [solar] corona. E. M. LINDSAY (*Nature*, 1929, 124, 94).—The possibility that the unknown lines of the solar corona might be due to the occurrence of forbidden transitions between terms in the spectra of ionised iron (Fe II), calcium (Ca II), titanium (Ti II, Ti III), and argon (A II), and of the neutral titanium atom has been examined and dismissed. There is no evidence that they arise in second type collisions involving the metastable 18 terms of ionised calcium (Ca II).

Spectrum of the solar corona. I. M. FREEMAN (*Astrophys. J.*, 1928, 68, 177—193).—Thirty-three of the 38 lines of undisputed coronal origin have now been identified with emission lines in the spectrum of argon.

L. S. THEOBALD.

Measurement of the strength of sunlight. J. E. MOSS and A. W. KNAPP (*Analyst*, 1929, 54, 334—335; cf. Bagnall, this vol., 407).—It is suggested that Bagnall's reaction should be carried out in quartz vessels, since glass absorbs radiations shorter than 320 $\mu\mu$, and bottle glass probably absorbs still more of the ultra-violet spectrum. If it is known which wavelengths decompose the potassium iodide the value of any actinometer test is increased. Unless one unit of ultra-violet radiation liberates the same quantity of iodine from the nearly colourless potassium iodide solution as from the orange-coloured mixture of solutions of iodine and potassium iodide, the quantity of iodine liberated will not be directly proportional to the amount of ultra-violet radiation incident in the solution.

D. G. HEWER.

Black body [radiation] at the m. p. of palladium by the tube method. G. RIBAUD and S. NIKITINE (*Ann. Physique*, 1929, [x], 11, 451—482).—A more detailed account of work already published (this vol., 366).

Abnormal broadening of spectral lines. A. W. PORTER (*Trans. Faraday Soc.*, 1929, 25, 389—391).—The most probable origin of an abnormal broadening of spectral lines is considered to be the lack of uniformity in the distribution of the illumination falling on the working crystal. Consideration of a simple case illustrates the general nature of the effect of such illumination. A stationary mechanical oscillation in the crystal would also produce a broadening of the spectral lines.

L. L. BIRUMSHAW.

Hyperfine structure in doublets and its use for the determination of nuclear moments. H. SCHÜLER and H. BRÜCK (*Z. Physik*, 1929, 55, 575—

580).—Theoretical. Examination of the hyperfine structure of the doublet spectrum of thallium leads to a value, $i = \frac{1}{2}$, for a new momentum which is constant for all atomic states. From considerations of the intensities in the hyperfine structure it is concluded that the new momentum is a nuclear one.

W. E. DOWNEY.

Hyperfine structures in triplet spectra and their use for the determination of nuclear moments. H. SCHÜLER and H. BRÜCK (*Z. Physik*, 1929, 56, 291—296; cf. preceding abstract).—Triplet spectra are examined under the assumption that for a single isotope the nuclear moment is constant for all atomic states and forms a new quantum number i . In the case of cadmium the isotopes fall into two groups with $i = 0$ and $i = \frac{1}{2}$, respectively. Data so far available are tabulated and discussed.

J. W. SMITH.

Ultra-violet spark spectra in liquids. A. CAMPETTI (*Nuovo Cim.*, 1928, 5, 291—306; *Chem. Zentr.*, 1929, i, 480).—The spark spectra of cadmium, zinc, magnesium, calcium, copper, silver, gold, aluminium, lead, bismuth, and antimony under water and, in some cases, under petroleum or carbon tetrachloride have been studied. The continuous background arises chiefly from the central zone of the spark. The number of reversed lines generally increases as the far ultra-violet is approached. Usually lines corresponding with the first and second resonance potentials of an element are strongly reversed.

A. A. ELDRIDGE.

Spectral reflectances of common materials in the ultra-violet region. M. LUCKIESH (*J. Opt. Soc. Amer.*, 1929, 19, 1—6).—Using the photographic method spectral reflectance data are recorded graphically as a function of the wave-length for the following substances in separate groups: fabrics—linen, bleached wool, pongee silk, white blotting paper, and bleached cotton, the last-named having the highest reflectance; dry white pigments—white lead, stannic oxide, lithopone, titanium pigment, and zinc oxide; other dry powders—magnesium carbonate, slaked lime, wall plaster, kaolin, alumina, silica, opal glass, and graphite; some commercial paints, and the polished metals silver, aluminium, chromium, nickel, zinc, steel, tin; and porcelain enamel.

N. M. Blich.

Reflecting power of some substances in the extreme ultra-violet. P. R. GLEASON (*Proc. Nat. Acad. Sci.*, 1929, 15, 551—557; cf. *Pfund*, A., 1926, 649).—The reflecting power was investigated quantitatively for the extreme ultra-violet region 585—1850 Å. A vacuum spectrograph was incorporated, the light analysed by and reflected from a concave speculum grating falling on a photographic plate directly or after reflexion from the surface. Curves showing the reflecting power as a function of the wave-length are given both for fresh and old surfaces sputtered or deposited and polished and of known opacity, in the case of aluminium, beryllium, brass, chromium, gold, nickel, platinum, silicon, silver, speculum, steel, stellite, fluorite, glass, and quartz. Platinum was easily the best reflector at the shortest wave-lengths, whilst nickel, crystalline quartz, and gold were the only others reflecting more than 10% at 585 Å.

N. M. Blich.

Sparking potential in hydrogen. E. MEYER (Helv. phys. Acta, 1928, 1, 14—17; Chem. Zentr., 1929, i, 970).—Progressive drying of hydrogen continuously diminishes the sparking potential. Small quantities of water in nitrogen depress the sparking potential. An explanation is offered.

A. A. ELDRIDGE.

Critical potentials and low tension-arcs in hydrogen. S. VENCOV (Compt. rend., 1929, 189, 27—30).—Different means of excitation and decomposition of the hydrogen molecule by electronic shock were obtained by various combinations of electric fields supplied by a potentiometric device. The principal critical potentials observed were due to molecular resonance (11.5 ± 0.5 volts), atomic ionisation resulting from thermal ionisation of H_2 molecules into atoms (13.6 ± 0.2 volts), molecular dissociation (16.5 ± 0.5 volts), and dissociation followed by double ionisation (29.7 ± 0.6 volts). The work of molecular dissociation of hydrogen is 3 volts. Examination of the corresponding spectra indicates a combination of the cumulative absorption of the radiations and the successive shocks necessary for ionisation (cf. Witmer, A., 1926, 552).

J. GRANT.

Photo-electric cells of alkali metals. S. ASAO (Mazda, 1928, 3, 155—165).—Cells in which the anode was a glass bulb bearing sodium, potassium, or their hydrides on the inner wall, and the cathode was a metallic ring, did not give reproducible results. Sodium was superior to potassium and the hydride increased the sensitivity. By filling the bulb with argon the anode current was considerably increased.

CHEMICAL ABSTRACTS.

Maximum excursion of the photo-electric long-wave limit of the alkali metals. H. E. IVES and A. R. OLPIN (Physical Rev., 1929, [ii], 34, 117—128).—The photo-electric long-wave limit, as the metals are deposited on platinum, moves from the short to the long wave-length of the spectrum, reaching a maximum and then receding. For sodium this maximum is in the visible region, but for potassium, rubidium, and caesium it lies in the infra-red, and for these a monochromatic illuminator was used by adapting a spectrometer with a "thalofide" cell. The photo-electric current was plotted against wave-length, and the maximum was found in each case to coincide with the first line of the principal series, or the resonance potential. This relation was found to hold for lithium, the maximum long-wave limit of which is thus shown to be greater than that of sodium. The special technique necessary for preparing and dealing with pure lithium metal is described. It is concluded that photo-electric emission is caused when sufficient energy is given to the atom to produce its first stage of excitation, and that atomic excitation is also the initial process in thermionic emission.

N. M. BLIGH.

Photo-electric effect of molten tin and two of its allotropic modifications. A. GOETZ (Physical Rev., 1929, [ii], 33, 373—385).—See this vol., 482.

Emission of electrons from cold metals. T. E. STERN, B. S. GOSSLING, and R. H. FOWLER (Proc. Roy. Soc., 1929, A, 124, 699—723).—The original formula of Fowler and Nordheim for the "auto-

electronic" current density (A., 1928, 681) is corrected, the numerical factor 6.8×10^7 being introduced in place of 2.1×10^8 . The nature of the comparison possible between the theory, which states a relation between the current density and the surface field, and the quantities actually observed—i.e., the total current passing between the electrodes and the applied voltage—is discussed. To derive the fullest information from the comparison, the emitting area A and the ratio of the surface field to the applied voltage are determined. This ratio depends not only on the large-scale geometry of the apparatus, but also on the micro-geometry of the irregularities of the cathode surface. The comparison yields fairly satisfactory results, except for the surprisingly small values of A derived. The theory is extended to include an examination of the space charge effect, which is found to be negligible, and an examination of the effect of surface films on the emission coefficient. If the cathode is of clean tungsten a much higher field must be applied to obtain a given auto-electronic emission than if it is covered with a layer of sodium, barium, caesium, or other electro-positive impurity. A formula is obtained for the emission through a surface layer under an applied field.

L. L. BIRCUMSHAW.

Connexion between spark potential and Volta-effect. R. BÄR (Helv. phys. Acta, 1928, 1, 186—192; Chem. Zentr., 1929, i, 725—726).

Experiments on the explanation of the selective outer photo-electric effect. III. Selective photo-electric effect with potassium films adsorbed on a platinum plate. R. SUHRMANN and H. THEISSING (Z. Physik, 1929, 55, 701—716; cf. A., 1928, 680, 1068; this vol., 114, 229).—The electron sharing per unit of energy was investigated for linearly polarised light in both the principal vector positions up to $300 \text{ m}\mu$, and with unpolarised light up to $240 \text{ m}\mu$, for variations of the thickness of potassium films adsorbed on a platinum surface. Only a very little of the potassium was distributed in the atomic state on the surface, but this possessed a normal sensitivity curve for the electric vector parallel to the plane of incidence, of which the long-wave limit was in the visible spectrum. With somewhat more potassium atoms than are necessary to make up a unimolecular layer a high spectral maximum is reached about $340 \text{ m}\mu$, and the vector ratio is strongly selective. With increasing thickness of the potassium layer the maximum is displaced towards the red and becomes small. The selectivity is retained as long as the layer is thin.

A. J. MEE.

Photo-electric and thermionic properties of molybdenum. M. J. MARTIN (Physical Rev., 1929, [ii], 33, 991—997).—The variation of the photo-electric sensitivity of a molybdenum surface during prolonged heat treatment was studied over 300 hrs. Thin molybdenum ribbons were heated at 1325° in a high vacuum and the photo-currents produced by the light from a quartz-mercury arc were measured with a quadrant electrometer. The sensitivity increased with time of heating, to a limiting value, and was accompanied by a shift in the long wave-length limit from 2600 to 3800 \AA . approx. The value 3.22 ± 0.16 volts was found for the photo-electric work function,

and the value 3.48 ± 0.07 volts for the thermionic work function as found from a graph of the emission as a function of the temperature. The photo-electric sensitivity decreased with rise of temperature by about 30% between 0° and 1000° . N. M. BLYTH.

Dependence of ionisation potential on atomic number. R. PEIERLS (Z. Physik, 1929, 55, 738—743).—The relationship between ionisation potential and atomic number recently discussed by Alexander (this vol., 487) is further investigated, and it is found that there are no deviations from theoretical expectations. A. J. MEE.

Influence of plastic deformation on the internal photo-electric effect in rock-salt crystals. M. PODASCHESKY (Z. Physik, 1929, 56, 362—369; cf. A., 1928, 1076).—Plastic deformation produces a marked influence on the primary photo-electric current in rock-salt crystals coloured by X-rays. On loading, the photo-electric current falls at first very rapidly, but finally comes asymptotically to a constant value, depending on the load applied. On removing the load, the preparation retains permanently the effect possessed at the time of unloading. The photo-electric sensitivity diminished in this way may be restored by prolonged illumination with X-rays. Ordinary elastic deformation produces no change in the photo-electric effect. J. W. SMITH.

Effects of a crystallographic transformation on the photo-electric and thermionic emission from cobalt. A. B. CARDWELL (Proc. Nat. Acad. Sci., 1929, 15, 544—551).—With the method previously used for iron (cf. A., 1928, 808) the photo-electric and thermionic emission from very carefully outgassed cobalt was investigated. Curves are given showing the change in photo-electric emission with rising temperature for a sample which, through supercooling from a critical temperature of about 850° , existed in the face-centred cubic form, and for a sample in the hexagonal close-packed form, obtained by very slow cooling from the same temperature. A more complex curve shows the effect with falling temperatures. Curves are given similarly to show the values of the thermionic current for rising and falling temperatures. During the transition process from one crystal lattice to another an intermediate structure is shown to exist, more sensitive photo-electrically and thermionically than the initial or final form. As contrasted with platinum and iron (cf. DuBridge, A., 1927, 391) the photo-electric sensitivity of cobalt is at no time independent of the temperature, and it is suggested that this is due to a change in the reflective power of the surface with temperature. N. M. BLYTH.

Ionisation by collision in monatomic gases. J. S. TOWNSEND and S. P. MACCALLUM (Proc. Roy. Soc., 1929, A, 124, 533—545; cf. A., 1928, 567, 1300).—A reply to Atkinson's criticisms and a discussion of his theories of ionisation (A., 1928, 809; this vol., 368). A number of contradictions are indicated. Examples, taken from the authors' work on helium and neon (*loc. cit.*), are given to show that the principles on which the theory of collisions of the second order is based are not supported by experiment. If the hypothesis which states that

very few electrons attain energy above that corresponding with the first critical potential were accepted, it would be impossible to obtain a consistent explanation of many simple phenomena observed in electric discharges in monatomic gases. Atkinson's second theory of conductivity includes many of the principal hypotheses forming the basis of Townsend's original theory of ionisation by collision.

L. L. BIRCUMSHAW.

Electrode function and ionic and electronic charges. F. KLINGELFUSS (Z. Physik, 1929, 55, 778—788).—Mathematical. The additional term to the sparking potential due to the free charge in air at atmospheric pressure causes a dielectric displacement. The calculations show that there is a difference in the size of the ionic and the electronic charges.

A. J. MEE.

Thermionic "A" and "b." E. H. HALL (Proc. Nat. Acad. Sci., 1929, 15, 504—514).—Experimental and thermodynamic evidence is reviewed, and shown to be consistent with views previously stated (cf. this vol., 482, 618) on the theory of conduction by electrons in two different states, free electrons or thermions, and associated or valency electrons. The possible identity of the thermionic and photo-electric work-functions is discussed.

N. M. BLYTH.

Theory of electron scattering in gases. A. C. G. MITCHELL (Proc. Nat. Acad. Sci., 1929, 15, 520—525).—The scattering of electrons in gases is treated using the Born collision theory in connexion with the Fermi statistical potential for atomic fields.

N. M. BLYTH.

Diffraction of electrons. P. TARTAKOVSKY (Z. Physik, 1926, 56, 416—420).—The diffraction by aluminium foil of electrons with velocities up to 1500 volts has been investigated. Diffraction rings were observed, corresponding with the Debye X-ray diagrams.

J. W. SMITH.

Mobility of ions in gases. R. J. VAN DE GRAAFF (Nature, 1929, 124, 10—11).—The author's method (A., 1928, 932) is improved.

A. A. ELDRIDGE.

Oscillations in ionised gases. L. TONKS and I. LANGMUIR (Physical Rev., 1929, [ii], 33, 990; cf. this vol., 367).—A correction.

N. M. BLYTH.

Simultaneous ionisation and excitation of diatomic molecules by impacts with positive ions and excited atoms. O. S. DUFFENDACK and H. L. SMITH (Physical Rev., 1929, [ii], 34, 68—80).—A study of mixtures of helium, neon, and argon with carbon monoxide and nitrogen, using a low-voltage arc and two separately controlled filaments, shows that impacts occur between a rare gas ion and a diatomic molecule leading to ionisation and excitation of the latter, and impacts of the second kind between excited helium and neon atoms and neutral carbon monoxide molecules leading to simultaneous ionisation and excitation of the latter. Several effects in similar mixtures in glow discharges are explained. Two new bands in the system due to ionised carbon monoxide and six new edges and a new band in the comet-tail system were found. Wave-lengths and a system analysis are given. From a study of the intensity distribution of the negative band systems of carbon

monoxide excited in mixtures with helium or neon a number of deductions on the degree of excitation of the CO ion in the two mixtures is made. The spectrum of carbon dioxide observed by Fox (cf. A., 1927, 916) is shown to be due to the carbon dioxide ion.

N. M. BLIGH.

New method of positive-ray analysis and its application to the measurement of ionisation potentials in mercury vapour. W. BLEAKNEY (Physical Rev., 1929, [ii], 34, 157—160).—The uniform magnetic field of a large solenoid is used to concentrate a narrow beam of electrons into a long straight path and at the same time to effect the separation of ions having different values of e/m . Preliminary values found for the ionisation potentials of Hg^{2+} , Hg^{3+} , and Hg^{4+} are 30, 71, and 143 volts, respectively.

N. M. BLIGH.

Velocity of formation of molecules from free atoms. V. KONDRATJEV and A. LEIPUNSKY (Z. Physik, 1929, 56, 353—361).—From the previously recorded intensity measurements in the continuous spectrum emitted by the reaction $Br' + Br = Br_2 + h\nu$ (A., 1928, 1075) the probability of molecule formation on collision between an active and a normal bromine atom is calculated. Another, independent, value of this magnitude is also deduced from the absorption coefficient in the region of continuous absorption. The probabilities calculated are of the order of magnitude of 10^{-8} — 10^{-10} , indicating that the formation of molecules in this manner is a very slow process.

J. W. SMITH.

Emission of anode rays of sodium and of chromium. A. POIROT (Compt. rend., 1929, 189, 150—151).—Moraud's work on lithium (A., 1927, 492) indicates that a stable emission is obtained from metals of low at. wt., and particularly from easily dissociable halogen salts. By an analogous method, however, a stable emission of long duration of anode rays of sodium and chromium was obtained from pure sodium dichromate. Emission commences at a temperature below the m. p. of the salt; strict control of the potential and of the temperature of the anode is essential.

J. GRANT.

Production of molecular rays of uniform velocity. B. LAMMERT (Z. Physik, 1929, 56, 244—253).—An apparatus by means of which molecular rays of mercury with velocities between certain limits can be separated is described. By measuring the intensities of the radiation over various velocity bands, a direct proof has been obtained of the applicability of the Maxwell distribution law to this case.

J. W. SMITH.

Ion rays. M. ZENTGRAF (Ann. Physik, 1929, [v], 2, 313—332; cf. Schmidt, A., 1926, 877; 1927, 397).—The relations between the current strength of ion rays and voltage have been studied at various temperatures and pressures. Apart from an irreversible decrease in emission with time, there is also an effect connected with impoverishment and subsequent recovery of the emitting surface. The effect is most marked with higher voltages and lower temperatures, whilst recovery is most rapid at the lowest voltages and the highest temperatures practicable. Emission of ion rays reaches saturation (a) with very

small voltages when the pressure is low, (b) more definitely at low temperatures than at high, (c) more markedly for the less volatile silver halides than for the more volatile thallium salts and cadmium iodide. The onset of emission depends on the pressure, the first ions appearing with lower voltages when the pressure is lower, but a small positive potential is always necessary. Visible discharge for the salts occurs at 300—400, 600—800, and 1600—2000 volts at pressures of 1, 10, and 100 mm., respectively. In a high vacuum no visible discharge occurs below 1900 volts. Experiments with cells filled with vaporized salts gave greatly increased currents, varying in the same sense as the voltage. Saturation is evident only at the lower pressures, and the discharge becomes luminous at lower voltages.

R. A. MORTON.

Passage of slow cathode rays through metals. II. A. BECKER (Ann. Physik, 1929, [v], 2, 249—263; cf. *ibid.*, 1927, [iv], 84, 779).—In the velocity range 4500—100 volts the following relations between the amount and velocity of the transmitted electrons have been found for thin metal foil. Apart from slow secondary electrons which reach a maximal fraction of the total electrons at a few hundred volts, the primary electrons are made up of (a) a very small fraction of unretarded electrons, (b) electrons more or less retarded, (c) electrons in a definite velocity region, corresponding with selective permeability to electrons. This last property decreases at first rapidly, then more slowly as the electron velocity decreases, and finally at voltages of the order of 100 volts the change becomes very small. Extension of the work to the smallest velocities consistent with adequate intensity shows that with thicknesses of nickel of 0.02 and 0.04 μ data can be obtained over the range 0.5—100 volts. From 2 to 10 volts the transmission-velocity curve increases rapidly, but beyond this point the rate of increase with increasing velocity is considerably reduced, the curve showing a flatter linear portion from 20 to 100 volts. Between 20 and 100 volts, there is evidence of selective distribution of electrons. True absorption of electrons contributes but little (compared with reflexion losses) to the total loss in intensity effected by the nickel foil; e.g., at 20 volts the transmission of a 0.02 μ thickness is 1.12×10^{-4} , whilst at 0.04 μ it is as high as 0.047×10^{-4} . The scattering of electrons occurs preferentially in certain directions.

R. A. MORTON.

Isotope of carbon, mass 13. A. S. KING and R. T. BIRGE (Nature, 1929, 124, 127).—A new, faint band, observed by the use of the vacuum electric furnace, corresponds with an assumed molecule $C^{13}C^{12}$. Six individual lines have been distinguished in the band.

A. A. ELDRIDGE.

Isotope of carbon, mass 13. R. T. BIRGE (Nature, 1929, 124, 182—183).—Evidence of the existence of the molecule $C^{13}O^{16}$ is presented by Hopfield's absorption spectrograms of carbon monoxide, and of the existence of the molecule $C^{13}N^{14}$ by King's furnace (emission) spectrogram of the CN band 3883 Å. It is also concluded that if isotopes of nitrogen exist, they are much less abundant in comparison with N^{14} than is C^{13} in comparison with C^{12} .

A. A. ELDRIDGE.

Atmospheric oxygen bands, and the relative abundance of the isotopes O^{16} and O^{18} . H. D. BABCOCK (Proc. Nat. Acad. Sci., 1929, 15, 471—477).—It has been pointed out by Giauque (this vol., 369) that the A' band described by Dieke (cf. A., 1927, 1005) indicates the existence of two oxygen isotopes of masses 16 and 18. Data for the A' band are revised and extended and by a special method of comparing intensities with the A band the relative proportion of O^{18} to O^{16} is deduced as 1:1250. A series of very weak doublets in the A and B bands has been detected; comparison with calculation indicates that they may be affected by some slight perturbation. N. M. BUGH.

Isotopes of oxygen. R. T. BIRGE (Nature, 1929, 124, 13—14).—Correction of an arithmetical error in the equation given by Dieke and Babcock (A., 1927, 1005) for the upper level of the atmospheric bands of oxygen [the corrected equation being $E_n = 13120.97 + 1418.69n - 13.925n^2 - 0.02n^3$ ($n = 0, 1, 2, 3$)] reduces the magnitude of discrepancies recorded by Giauque and Johnston (this vol., 369, 736).

A. A. ELDRIDGE.

At. wt. of antimony from different sources. R. K. McALPINE (J. Amer. Chem. Soc., 1929, 51, 1745—1750).—The density and at. wt. of antimony are independent of the geographical source of the metal (cf. Muzaifar, A., 1923, ii, 771). S. K. TWEEDY.

Mass numbers of the elements. Element formation. F. H. LORING (Chem. News, 1929, 139, 1—3).—Aston has pointed out (cf. this vol., 622) that there are no elements with mass numbers of 2, 3, 5, 8, etc. If a series of the type $2 \times 1/(2+1)$, $2 \times 2/(2+2)$ be worked out most terms give recurring decimals but a few do not. The latter correspond with the missing mass numbers, but there are numerous exceptions, e.g., sodium (23) gives a non-recurring decimal. It is suggested that these exceptions are due to the absorption of an atom of hydrogen.

A. R. POWELL.

Helicoidal classification of the elements. C. JANET (Chem. News, 1929, 138, 372—374, 388—393).—A new diagram of the classification of the elements, based on Moseley's law, has been derived by arranging the elements spirally around a cylinder.

H. F. GILLBE.

Evaluation of the α -radiation of the active deposit of actinium by measuring its β -radiation. M. NAHMLAS (J. Chim. phys., 1929, 26, 319—326).—A more detailed account of work already noted (this vol., 621).

Capture of electrons by swiftly-moving α -particles. B. DAVIS and A. H. BARNES (Physical Rev., 1929, [ii], 34, 152—156).—A stream of electrons from a thermionic source was superposed on a beam of α -particles from polonium, and the number of captures determined by subjecting the beam to a magnetic field and counting the scintillations due to the deflected α -particles for various electron velocities. As the latter increases the decrease in scintillations due to the smaller deflexion of α -particles which have captured an electron gives the percentage of captures. It was found that captures take place only at definite electron velocities which are related to those in the

Bohr orbits of ionised helium by the relations $v = u - w$ and $v = w' - u$, where u is the velocity of the α -particle, w and w' are two velocities of the electron at which capture takes place, and v is any circular Bohr orbit electron velocity. The number of captures plotted against voltage impressed on the electron stream gives a series of maxima on each side of the equivalent velocity of the α -particles corresponding with the energy levels of ionised helium. N. M. BUGH.

Spectrography by crystal diffraction of γ -rays of the radium group. M. FRILLEY (Ann. Physique, 1929, [x], 11, 483—568).—A summary is given of the nature and origin and the theory of the lattice spectroscopy of the γ -rays. A complete investigation was made of the spectrum of γ -rays from the radium group, and extended for the first time to the higher frequencies, to a wave-length of 16×10^{-11} cm., by a crystal-diffraction method using an adapted X-ray rotating-crystal spectrograph. Owing to the very short wave-length the reflexion angle of the highest frequency rays is less than $10'$. Results were in good agreement with those for corpuscular radiation except in the region of the K fluorescence rays of radium- B and $-C$, where strong γ -rays were detected which had not previously been observed. The wave-lengths of these support the theory attributing the emission of β - and γ -rays to the atom resulting from radioactive disintegration. The high intensity of the K radiation seemed to be due to the influence of nuclear γ -rays in the same region. Einstein's photo-electric law and Bragg's diffraction law were confirmed for these frequencies, and the evidence supported the electromagnetic wave-nature of the radiation.

N. M. BUGH.

Heat of β - and γ -radiation of radium. A. DORABIALSKA (Bull. Acad. Polonaise, 1928, A, 459—470).—See this vol., 116.

Temperature coefficient of radioactive disintegration. O. K. RICE (Proc. Nat. Acad. Sci., 1929, 15, 593—595).—It is shown that the low temperature coefficients found for radioactive changes are to be expected from the known sizes of atomic nuclei, on the basis of the new quantum-mechanical explanation of radioactivity (cf. Gamow, this vol., 7; Gurney and Condon, this vol., 374). A single quantum level is proved to be responsible for an ordinary radioactive decomposition up to or above 5000° .

N. M. BUGH.

Detection of atomic disintegration of aluminium by means of the Hoffmann electrometer. H. POSE (Naturwiss., 1929, 17, 624).—Disintegration experiments with aluminium foil 30μ thick, using polonium as a source of α -particles, show that the Hoffmann electrometer serves for the detection of liberated H -particles. A relatively large number of H -particles have ranges below 30 cm. of air, a second, smaller group range from 30 to 47 cm., whilst a third, much smaller group extend to 62 cm., when the number becomes very small. R. A. MORTON.

A Wilson apparatus for convenient low pressures. J. PETROVÁ (Z. Physik, 1929, 55, 621—627).—An apparatus is described which shows the tracks of both α - and β -rays at pressures down to 30 mm. W. E. DOWNEY.

Range of β -rays from radium-*D* by the Wilson method. J. PETROVA (*Z. Physik*, 1929, 55, 628—645).—Using the new apparatus (cf. preceding abstract), the distribution curve of the range of the β -rays from radium-*D* has been obtained. The curve shows two maxima corresponding with mean ranges, at normal pressure and 20°, of 0.80 and 1.58 cm. The maximum ranges are 1.3 and 2.4 cm., respectively. Some tracks between 2 and 4 cm. in length were observed.

W. E. DOWNEY.

Detection of atomic disintegration of aluminium by means of the tube electrometer. E. A. W. SCHMIDT (*Naturwiss.*, 1929, 17, 544—545).—Preliminary. Earlier work (*A.*, 1927, 494) is confirmed and extended.

R. A. MORTON.

Striations in high-frequency discharges. K. A. MACKINNON and J. K. ROBERTSON (*Nature*, 1929, 124, 55).

Luminous discharge in gases at low pressures. H. PETTERSSON (*Nature*, 1929, 123, 978—979).—A method for increasing the luminosity of the discharge in electrodeless tubes by electric oscillations of high frequency, and of causing the discharge to pass through narrow capillary tubes, has been applied to nitrogen, neon, carbon monoxide, and carbon dioxide. The last two undergo rapid dissociation. In spectrograms from the oxides of carbon all the Deslandres bands belonging to the first negative carbon spectrum between 2300 and 2900 Å. have been identified, and fainter bands of similar structure have been observed. The origin of the double bands near 2896 and 2883 Å. is probably different from that of the other bands of the series.

A. A. ELDRIDGE.

Stark effect of higher atoms and its interpretation in terms of the quantum theory. R. LADENBURG (*Physikal. Z.*, 1929, 30, 369—383).—A summary. Present-day quantum theories account satisfactorily for all the more important observations, and indeed partly for the very complicated phenomena arising from the action of electric fields on the series lines of the higher elements. Certain intensity anomalies (cf. Stark and Liebert, *Ann. Physik*, 1918, [iv], 56, 547, 589) concerning the changes in relative intensities with increasing field strength, observed with successive terms of the *P*—*P'* series of ortho-helium and lithium, remain to be explained. Neon, argon, oxygen, and some of the heavier elements exhibit effects which need investigation before a theoretical explanation can be arrived at. The interpretation of the Stark effect for the helium series provides support for the validity of the wave-mechanics quite as convincing as that given to the Bohr theory by the data for the Stark effect on hydrogen lines.

R. A. MORTON.

Paths of charged particles in electric and magnetic fields. W. BARTKY and A. J. DEMPSTER (*Physical Rev.*, 1929, [ii], 33, 1019—1022).—Mathematical. The velocity and directional focussing of a beam of charged particles, and a combination of electric and magnetic fields, are considered, suitable for positive-ray analysis experiments, or for determinations of the ratio of charge to mass.

N. M. BLYGH.

Dependence of ultra-violet reflexion of silver on plastic deformation. H. MARGENAU (*Physical Rev.*, 1929, [ii], 33, 1035—1045).—The behaviour of the minimum reflecting power of silver in the near ultra-violet was examined for surfaces under varying degrees of strain produced by polishing, etching, and electroplating. Reflexion curves were obtained by measuring incident and reflected intensities directly by means of two quartz photo-electric cells. Minima for different surfaces were found in the region 3160 Å., shifting to lower wave-lengths by about 20 Å. for unstrained surfaces. The results are explained as due to a change in the number of free electrons and hence in the index of refraction of the metal.

N. M. BLYGH.

Nature of the ultra-penetrating rays (cosmic rays). P. AUGER and D. SKOBELZYN (*Compt. rend.*, 1929, 189, 55—57).—Evidence is advanced in favour of the hypothesis that cosmic rays are not primary but secondary radiations, and are produced from an "ultra- γ " radiation which will not itself ionise directly (cf. Skobelzyn, this vol., 737).

J. GRANT.

Momentum distribution in hydrogen-like atoms. B. PODOLSKY and L. PAULING (*Physical Rev.*, 1929, [ii], 34, 109—116).—Mathematical.

N. M. BLYGH.

Problem of the ionised hydrogen molecule. C. Y. CHAO (*Proc. Nat. Acad. Sci.*, 1929, 15, 558—565; cf. Niessen, *A.*, 1927, 808; Wilson, *A.*, 1928, 574).—Mathematical. The energetics of the ionised hydrogen molecule are treated by the method of wave mechanics, with the introduction of approximations. The adiabatic transition of the energy levels when H_2^+ is dissociated into a nucleus and a H-atom is investigated.

N. M. BLYGH.

Molecular structure and properties of homopolymers. II. Structure of the carbon atom and isomerism in homologous series. A. DIBROVA (*Ukraine Chem. J.*, 1928, 3, 435—443; cf. *A.*, 1928, 827).—Assuming with Main Smith and others that all four valency electrons of the carbon atom are in orbit *L* but two are of quantum number 2₁ and the other two of quantum number 2₂, the differences in b. p. and density between primary, secondary, and tertiary saturated and unsaturated hydrocarbons are discussed both from the point of view of their probable molecular structure and polarisation.

A. FREIMAN.

Effect of a nuclear spin on the optical spectra. J. HARGREAVES (*Proc. Roy. Soc.*, 1929, A, 124, 568—591).—Mathematical. The motion of a single electron in a Coulombian field due to a nucleus possessing a $\frac{1}{2}$ quantum of spin is considered, and the results are compared with Jackson's recent work on the hyperfine structure of the optical spectrum of caesium (cf. this vol., 1). It is found that each of the electron spin fine structure levels splits up into two. The problem is dealt with on the lines of Pauli's treatment (cf. *A.*, 1927, 807), introducing, in addition to the electronic spin variables, similar ones for the nuclear spin. The method does not give the correct *S* levels, but empirical equations are constructed which give two levels. The calculated intensities of the Zeeman components of the transitions are found to be independent of the central field. A determination

of the numerical intensity ratios of the *D* and *P* series shows that the strongest lines are those in which there is no change in the spin configuration, whilst the next strongest are those in which there is one change, either that of the nucleus or that of the electron. So far as the energy levels are concerned, the results obtained are substantially the same as those of Jackson.

L. L. BIRCUMSHAW.

Electro-dynamics of the rotating electron. I. TAMM (Z. Physik, 1929, 55, 199—220).—Mathematical.

J. W. SMITH.

Heisenberg's indetermination principle and the quantum. G. E. M. JAUNCEY (Nature, 1929, 124, 57).

Distribution of charge in the carbon atom. G. W. BRINDLEY (Proc. Leeds Phil. Soc., 1929, 1, 402—411).—The distribution of charge in the carbon atom can be arrived at theoretically by a consideration of the *F* curve for carbon, *F* being the scattering power of the atom for X-rays, and a function of the glancing angle θ and the wave-length λ . The *F* curve for diamond is compared with the theoretical curve derived from the usual model of the carbon atom. The two curves do not agree well, the disagreement being greatest for large values of $\sin \theta$, where the calculated curve is known most accurately. In any investigation to determine the asymmetry of the carbon atom experimentally by X-ray methods, spectra which occur between $\sin \theta = 0.10$ and 0.30 will be specially important, as over this range the contributions of the *L* electrons to the *F* curve are varying most rapidly. Very little information can be derived about *L* electrons from a study of spectra at values of $\sin \theta$ greater than 0.40 .

A. J. MEE.

Forces between atoms and between molecules.
I. **Periodicity of interatomic forces.** D. AVDALIAN (Ukraine Chem. J., 1929, 4, 95—98).—The force *D* acting between atoms is calculated for the elements in the periodic table from Lindemann's formula $D = T_s / V^{2/3}$, *T*, being the absolute m. p. and a measure of the intensity of the atomic energy and $V^{2/3}$ the square of the amplitude of the vibration at the m. p. which is proportional to the energy of the vibration. The curve connecting *D* with the atomic numbers shows a series of minima and maxima, the minima separating the periods in the periodic tables.

A. FREIMAN.

Modern developments of wave mechanics and their bearing on the understanding of crystal structure. P. P. EWALD (Trans. Faraday Soc., 1929, 25, 402—409).—The general principles which have been advanced for the elucidation of the structure of atoms and atomic forces are reviewed and applied to problems of chemical action and of crystal chemistry. These include the Schrödinger picture of the atom, the Pauli exclusion principle and electron spin, the principle of energy shift by resonance, and the London-Heitler application to exchange energy. An account is given of Unsöld's and of Pauling's work on polar crystals and of recent work in connexion with exchange phenomena in metals. It is emphasised that the principle of exchange energy is important, not only for the homopolar, but also for the polar chemical linking.

L. L. BIRCUMSHAW.

Diatomic molecules according to the wave mechanics. I. Electronic levels of the hydrogen molecular ion. P. M. MORSE and E. C. G. STUECKELBERG (Physical Rev., 1929, [ii], 33, 932—947).—Mathematical.

N. M. BLIGH.

Scattering coefficient of hydrogen according to wave mechanics. J. A. STRATTON (Helv. phys. Acta, 1928, 1, 47—74; Chem. Zentr., 1929, i, 968).—A study of the intensity and spatial distribution of the unmodified component.

A. A. ELDRIDGE.

Structure of atomic nuclei. M. F. SOONAWALA (Indian J. Physics, 1929, 3, 489—492).—A table is constructed on the hypothesis that atomic nuclei are formed by the synthesis of protons, electrons, and rare gas nuclei, and its features are examined for evidence as to why the most favoured condensation of protons and electrons should give rise to the nuclei constituting matter. It is shown that the isotopes of the rare gases may, with the protons and electrons, give rise to the known groups of elements.

N. M. BLIGH.

Possible cause for the transformation of energy into matter. G. I. POKROVSKI (Z. Physik, 1929, 55, 771—777; cf. this vol., 623).—Mathematical. The gravitation effect of energy is discussed as a cause of the formation of new protons, and the determination of the upper limit of the elementary mass, *i.e.*, the mass of the proton, is mentioned. The value obtained is 1.67×10^{-24} g.

A. J. MEE.

Possibility of an experimental proof of the reciprocal annihilation of electrons and protons. C. LÖNNQVIST (Z. Physik, 1929, 55, 789—800).—The reciprocal annihilation of protons and electrons by collision is a hypothetical source of energy, the cosmic importance of which has been stressed by Eddington. Some indications of methods which could be used for the experimental proof of the occurrence of such annihilation are given. It is suggested that hydrogen nuclei, *i.e.*, free protons, are completely unprotected against electron bombardments, and hence they will be neutralised at their first encounter with an electron. Means for testing this are discussed.

A. J. MEE.

Relative masses of the proton, electron, and helium nucleus. E. E. WITMER (Nature, 1929, 124, 180—181).—Numerical relationships, possibly of a fundamental nature, are indicated, and the possibility that the helium nucleus is an ultimate particle is considered.

A. A. ELDRIDGE.

Effect of the addition of hydrogen and water on the radiation emitted from the carbon monoxide flame. W. E. GARNER and F. ROFFEY (J.C.S., 1929, 1123—1140; cf. A., 1928, 375).—The addition of hydrogen or water vapour diminishes the emission of radiation and increases the speed of flame of mixtures of carbon monoxide and oxygen under conditions of rapid cooling. This confirms Helmholtz's view that the radiation from flames is largely chemiluminescence. The emitters of the radiation are freshly formed activated molecules of carbon dioxide. The radiation is diminished in three stages: (1) from 0 to 0.04% H₂, where the decrease is proportional to $[H]^{1/2}$, (2) at 0.04%, where a marked step occurs, and (3) from 0.04 to 2%, where the decrease is

continuous but less rapid than in (1). Measurements of the speeds of the flame have been made, and the radiation-speed curves show a step at 0.04% H_2 . The speed increases with the addition of hydrogen or water. The general inference drawn from the results is that the decrease in radiation is due partly to chemical and partly to physical causes, the latter being mainly collisions of the second kind between activated carbon dioxide molecules and atomic hydrogen or protons. The occurrence of the step supports Bone's view that there are two distinct chemical mechanisms in the flame, one being dominant above 0.04% H_2 and the other below this concentration. The increase in speed of flame on the addition of hydrogen up to 0.04% can be interpreted as due to a rise of temperature consequent on the diminished radiation.

F. L. USHER.

Formation, pre-dissociation, and dissociation of molecules determined by vibration spectra. Sulphur monoxide. V. HENRI and F. WOLFF (J. Phys. Radium, 1929, [vi], 10, 81—106).—It follows from the principles of wave mechanics that a molecule is not necessarily formed when two atoms approach one another, but that combination depends on the mutual orientation of the magnetic moments of their valency electrons. Generally, the distribution of the valency electrons of two atoms the nuclei of which have been made to coincide should conform with Pauli's principle. In the case of nitrogen two kinds of diatomic molecule should be possible, one dissociating at 11.4 volts and the other at 3.8 volts, the latter kind being, in the author's view, identical with Rayleigh's active nitrogen. Analysis of the vibration spectrum makes it possible to calculate the energy of dissociation of a diatomic molecule into atoms of which neither, or one, or both may be activated. A new spectrum has been obtained by sparking dried sulphur dioxide at a pressure of 20—30 mm. It consists of a large number of bands at intervals of 40—60 Å. and extending to 2549 Å. The general character of the spectrum is that typical of a diatomic molecule, but differs greatly from the spectra of oxygen or sulphur. An analysis of the vibration spectrum shows that the molecules responsible for it are those of SO. The energy of dissociation of this compound into normal atoms has been calculated to be -148 kg.-cal., in striking agreement with the figure obtained from thermochemical data, viz., -146.2 kg.-cal. The moment of inertia of the molecule has been found to be 32×10^{-40} , giving 1.34 Å. as the distance between the oxygen and sulphur atoms.

F. L. USHER.

Effect of volume changes on the infra-red vibrations of simple crystals. E. O. SALANT (Proc. Nat. Acad. Sci., 1929, 15, 533—537).—Using the formula of Carpenter and Stoodley (cf. A., 1928, 694) it is shown how to calculate the effect of changing the distance apart of neighbouring ions in the crystal, and also the effect of volume changes on the wavelength of maximum reflecting power as given by the Havelock equation. The latter calculation is shown to require a knowledge of the change with volume of the dielectric constant and of the wave-length corresponding with the vibration frequency. The calcul-

ated results in the two cases are given for sodium chloride and for potassium chloride, bromide, and iodide.

N. M. BLIGH.

Near infra-red absorption spectra of calcite and strontianite. E. K. PLYLER (Physical Rev., 1929, [ii], 33, 948—951).—Thick specimens (2 cm.) cut at right angles to the optic axis were used, and for calcite bands were observed at 1.76, 1.9, 2.0, and 2.2 μ , similar to those found by Schaefer (cf. A., 1927, 5) in the near infra-red. Combination relationships were found to exist between these two sets of bands, with fair agreement of observed and calculated values. For strontianite the bands were at 1.89, 2.01, and 2.19 μ and of a similar type to those of calcite. The value 9.2 μ was calculated for the inactive fundamental, in good agreement with Nielsen's value 8.98 μ (cf. this vol., 119).

N. M. BLIGH.

Combination bands in the infra-red spectra of carbon tetrachloride and silicon tetrachloride. H. H. MARVIN (Physical Rev., 1929, [ii], 33, 952—953).—Assuming that the six Raman bands of carbon tetrachloride (cf. Pringsheim and Rosen, A., 1928, 1307) give the fundamental absorption frequencies, it is shown that their simple combinations account for almost all the absorption bands between 1 and 16 μ . The absorption bands of silicon tetrachloride are accounted for by similar combinations of six fundamental frequencies, the two systems and their combinations being very similar.

N. M. BLIGH.

Absorption spectrum of hydrogen chloride. C. F. MEYER and A. A. LEVIN (Physical Rev., 1929, [ii], 34, 44—52).—The vibration-rotation spectrum of hydrogen chloride consists of a fundamental band at 3.46 μ and a harmonic at 1.76 μ . Using a new spectrometer and very narrow slits, the lines of the fundamental were resolved, each into two lines due to the existence of the isotopes Cl³⁵ and Cl³⁷. The relative intensities of the lines in the two series agrees with the accepted proportion of the isotopes, 3:1 approximately. In the harmonic, good separation of the lines arising from the isotopes was obtained. Wave-number and intensity results for the two series of lines in each band are given.

N. M. BLIGH.

Analysis of the hydrogen chloride bands. W. F. COLBY (Physical Rev., 1929, [ii], 34, 53—56; cf. preceding abstract).—Wave-numbers for the two isotopes in the bands are fitted to a cubic formula of the rotational quantum number derived from Fues' energy expression (cf. A., 1926, 881), and tables are given of the wave numbers thus computed. From the formula the constants of the molecule were determined in accordance with the energy expression for the rotating dipole as derived by wave mechanics.

N. M. BLIGH.

Effect of temperature on the absorption bands of fused quartz in the infra-red. W. A. PARLIN (Physical Rev., 1929, [ii], 34, 81—91).—The absorption bands of thin quartz films, of thickness 2 mm. for the 3 μ region to 4×10^{-4} mm. for the 8 μ region, were investigated at the ordinary temperature and at 850°. The band in the region of anomalous dispersion at 9 μ shifted towards longer wave-lengths with rise of temperature. With higher resolution fine-structure

bands were found which did not shift with change of temperature, but underwent marked intensity changes. Several sharp bands between 2 and 4 μ did not change with temperature. A broad double band was found at 12.5 μ .
N. M. BLIGH.

Diatomic molecules according to the wave mechanics. II. Vibrational levels. P. M. MORSE (Physical Rev., 1929, [ii], 34, 57—64).—An exact solution is obtained for the Schrödinger equation representing the motions of the nuclei in a diatomic molecule, a simple form for the potential energy function being assumed, satisfying certain specified conditions. A formula is obtained for the allowed vibrational energy levels, and is found to satisfy experimental values. The normal molecular separation r_0 and the classical vibration frequency ω_0 are shown to be related by the empirical law $r_0^3\omega_0=K$, to a close approximation; K is the same constant for all diatomic molecules and all electronic levels. By the above results experimental data for various levels and molecules are analysed and a table of constants is obtained from which the potential energy curves can be plotted.
N. M. BLIGH.

Investigations in the spectral region 20—40 μ . L. KELLNER (Z. Physik, 1929, 56, 215—234).—Owing to its good transmission at wave-lengths of 20 μ and upwards, paraffin wax is a very suitable material for windows for a micro-radiometer for use in the long-wave infra-red region. It is gas-tight and owing to its selective absorption in the shorter-wave region up to about 16 μ it filters this out of the radiation.

The transmission of thin sheets of rock-salt over the range 20—37 μ has been measured and the extinction coefficient at different wave-lengths over this range calculated. The "residual rays" of fluor-spar have been measured over a similar range. In contradiction to previous observations (Rubens and Hettner, A., 1916, ii, 463), only one maximum was found, between 26 and 30 μ , the reflecting power rising to a maximum at about 32.8 μ .

J. W. SMITH.

Method of obtaining the optical constants of metallically reflecting substances in the infra-red. C. BOECKNER (J. Opt. Soc. Amer., 1929, 19, 7—15).—The method described, which is applicable to amorphous substances and to uniaxial crystals, consists in measuring the reflecting power of light, polarised in the plane of incidence, at two angles of incidence, and calculating the refractive index and the extinction coefficient by the Fresnel formula. The change of reflecting power with change of angle of incidence was also investigated. Curves are given for the reflecting power for angles of incidence of 5° and 68°, and for the refractive index and extinction coefficient of fused and crystalline quartz, plotted against wave-lengths. Experimental and calculated values of the reflecting power show good agreement.

N. M. BLIGH.

Infra-red emission bands under high dispersion. M. NEUNHOEFFER (Ann. Physik, 1929, [v], 2, 334—349).—The infra-red emission of burning hydrogen and carbon monoxide has been studied by means of a reflexion grating and thermopile, and quantitative absorption curves have been obtained

for the principal bands. The water bands exhibit rotation frequencies clearly, but the carbon dioxide bands show no sign of resolution at the same dispersion. The water band at 2.7 μ exhibits a single constant frequency difference of 24 ± 0.5 cm^{-1} , indicating one definite moment of inertia 2.3×10^{-40} at the temperature of the flame. When the temperature of the carbon monoxide flame is raised by inserting an electrically heated platinum spiral, the maxima near 4.3 μ are not changed in wave-length, but the percentage change in intensity is greater on the long-wave than on the short-wave sides of the bands. Addition of argon to the carbon monoxide does not shift the maxima, but the changes in intensity occur in a manner consistent with the fall in flame temperature. The bands near 2.7 μ for both water and carbon dioxide are similarly affected by variations in the environment, although the broadening of the short-wave band for water is more symmetrical when the gas is preheated.
R. A. MORTON.

Fluorescence and infra-red absorption. V. POSEJPAL (Compt. rend., 1929, 189, 159—161).—A generalisation of the author's theory (this vol., 120) in which it is shown that an effect analogous to the Raman and Cabannes-Daure effects exists for fluorescence spectra. The calculated and observed values of the wave-lengths of the fine bands of the fluorescence spectrum of benzene (liquid or vapour) are in close agreement. The theory also provides confirmation of the Haber-Lindemann formulae.
J. GRANT.

Infra-red registering spectrometer. P. LAMBERT and J. LECOMTE (Compt. rend., 1929, 189, 155—158).—The spectrometer consists of two 30° rock-salt prisms, one of which is fixed and receives the original source of light, whilst the other is supported on a movable platform which also carries a thermo-electric cell on to which the ray emerging from the second prism is directed. Wave-length-percentage transmission curves are obtained directly by passing a spot of light from a galvanometer (connected to the thermo-couple) across a light-sensitive paper held on a plate which travels in unison with the platform carrying the second prism. A wave-length range of 15 μ is obtainable.
J. GRANT.

Quantum theory of the Raman effect. E. AMALDI (Atti R. Accad. Lincei, 1929, [vi], 9, 876—881).

Incoherent scattering in gases. F. RASETTI (Nature, 1929, 124, 93).—A purely electronic transition has been observed in the scattering process with nitric oxide. By the use of apparatus permitting ultra-violet excitation of gases at 10 atm., good Raman spectra of hydrogen have been obtained.

A. A. ELDRIDGE.

Raman effect in diatomic gases. II. F. RASETTI (Proc. Nat. Acad. Sci., 1929, 15, 515—519; cf. this vol., 627).—With an improved experimental arrangement permitting the use of the 2536 mercury line as exciting light to obtain stronger scattering, experiments were conducted on nitrogen, oxygen, and hydrogen showing more clearly the relation between Raman transitions and band spectrum structure. Sharp, well-resolved Raman lines corresponding with

rotational transitions were obtained and photographed and their frequencies measured. The molecules are all in the *S* states, and the lines are discussed theoretically from the point of view of the new quantum mechanics. Oxygen gives a pattern of equally spaced lines, nitrogen presents a spectrum of alternating intensities, and the previously unknown moment of inertia of the nitrogen molecule in the normal state is found to be $(14.0 \pm 0.1) \times 10^{-40}$. The vibrational-rotational Raman spectra should give a *Q*-form branch and *PP*- and *RR*-form branches, but only the unresolved *Q*-form branch has been observed.

N. M. BLYTH.

Influence of temperature on Raman lines. Y. FUJIOKA (Nature, 1929, 124, 11).—Experiments with benzene, toluene, and carbon tetrachloride show that when the temperature of the scattering substance is raised, certain Raman lines become very diffuse. It is supposed that the diffuseness of Raman lines is due to molecular rotation, rise of temperature accelerating the rotation and causing broadening of the lines. The effect is most noticeable for close doublets.

A. A. ELDRIDGE.

Raman effect in carbon disulphide. A. S. GAVESAN and S. VENKATESWARAN (Nature, 1929, 124, 57).—The scattered spectrum of carbon disulphide gives two prominent frequency shifts, corresponding with 15.27 and 12.50μ , respectively. None of the infra-red absorption bands observed by Coblenz are represented in the scattered spectrum.

A. A. ELDRIDGE.

Relation between Raman spectra and ultra-violet absorption. A. LANGSETH (Nature, 1929, 124, 92).—On the assumption that the strongest band in the absorption spectrum of chlorobenzene is due to the electronic transition from the lowest level in the normal state to the lowest level in the excited state, a general analysis of the spectrum by means of the Raman frequencies has been made. The strongest frequencies of vibration in the excited state are: 318.8 , 519.0 , 523.9 , 929.8 , and 962.6 cm.^{-1}

A. A. ELDRIDGE.

Raman effect in carbon dioxide. P. N. GHOSH and P. C. MAHANTI (Nature, 1929, 124, 92–93).—The results of Rasetti (this vol., 241) support the linear model of the carbon dioxide molecule.

A. A. ELDRIDGE.

Raman effect in gases and liquids. P. N. GHOSH and P. C. MAHANTI (Nature, 1929, 124, 230).—Optically inactive vibrations are postulated.

A. A. ELDRIDGE.

Raman effect. A. DADIEU and K. W. F. KOHLRAUSCH (Physikal. Z., 1929, 30, 384–391).—The Raman frequencies for 25 aliphatic and aromatic compounds are given, and their classification with respect to groupings of the type C-C, C-O, etc. is discussed. The classification is by no means unequivocal; e.g., benzene exhibits not only the frequency $\nu = 3050$ which is characteristic of the aromatic C-H linking, but also shows the frequency $\nu = 2940$ which is ascribed to the aliphatic C-H linking. Anti-Stokes lines are recorded only with halogen derivatives. Investigation of mixtures of benzene and carbon tetrachloride and of solutions of naphthalene in carbon tetrachloride shows no reciprocal effects as regards

shifting of the Raman spectra. The acetic acid-water system disclosed no frequencies capable of indicating the occurrence of dissociation. The influence of temperature on the intensities of the Raman lines and the scattered (undisplaced) exciting lines has been studied for carbon tetrachloride. R. A. MORTON.

Raman effect of water. A. DADIEU and K. W. F. KOHLRAUSCH (Naturwiss., 1929, 17, 625–626).—The Raman frequency for water has been variously recorded as 3280 to 3450 cm.^{-1} , the mean of all the determinations being 3338 cm.^{-1} . Repetition has resulted in the observation that the Raman lines corresponding with three mercury lines are all double, the frequencies being 3324 and 3513 cm.^{-1} , respectively. The mean, 3419 cm.^{-1} , corresponds with 129 g.-cal./mol. for the energy necessary for the rupture of the O-H linking, whilst observed values are given as 120 and 147 g.-cal./mol. The observed Raman lines are shown to be not inconsistent with theory. R. A. MORTON.

Raman spectra of *p*-, *o*-, and *m*-xylenes. (MLLE.) W. CZAPSKA (Compt. rend., 1929, 189, 32–33).—The Raman spectra excited by the mercury lines $\lambda 4047$ to 4359 are different for the xylenes, but the frequencies $\Delta\nu 1371$ and 2918 are common to all three. The *o*- or *p*- and *m*-, but not the *o*- and *p*-isomerides have frequencies in common.

J. GRANT.

Raman spectra of sulphuric acid and the sulphates. S. K. MUKHERJEE and P. N. SENGUPTA (Indian J. Physics, 1929, 3, 503–505).—To investigate characteristic infra-red frequencies of salts in solution Wood's method (A., 1928, 1306) was used, involving only short exposure periods, and spectrograms were obtained of magnesium, sodium, and copper sulphates and of sulphuric acid. In the case of the sulphates modified lines were found at 4552.2 and 4213.7 \AA. The wave-number difference between the exciting and excited lines corresponds with infra-red absorption at 10.2μ . Sulphuric acid shows five modified lines corresponding with absorption at 11.01 , 10.96 , 17.9 , and 18.4 and 4.68μ . Each solution gave always the same frequency for the scattered components and this infra-red frequency is attributed to the SO_4 ion. N. M. BLYTH.

Scattering of light in quartz and solid amorphous substances which contain the SiO_2 group. E. GROSS and M. ROMANOVA (Z. Physik, 1929, 55, 744–752).—The spectra of radiations scattered by crystalline quartz, amorphous quartz, crown and flint glasses were investigated. It was found that in amorphous quartz and the glasses there were displacements in the spectra. For quartz, besides the already known but weak lines corresponding with wave-lengths 19.9 and 8.2μ , the very weak lines corresponding with wave-lengths 31.3 , 19.0 , 17.1 , 15.8 , 13.4 , 10.6 , and 9.8μ , were found. Amorphous substances containing the SiO_2 group have faded bands in their scattered spectra, instead of the lines found in the spectrum of crystalline quartz.

A. J. MEE.

Vibrational quantum analysis of red cyanogen bands. R. K. ASUNDI and J. W. RYDE (Nature, 1929, 124, 57).—The band at $\nu 14430$ is not the true

0—0 band of the system. Six new bands have been fitted in the existing n'/n'' table for the red cyanogen bands. Assuming ν 10937 to be the 0—0 band, the vibrational equation is: $\nu_{\text{head}} = 10937 + (1782n' - 13.5n''^2) - (2055n'' - 13.3n''^2)$. A. A. ELDRIDGE.

New bands in the spectrum of lanthanum oxide. G. PICCARDI (*Nature*, 1929, 124, 129).—The oxide has been completely vaporised by the use of the oxy-hydrogen flame; the spectrum then consists of bands only. Between 7000 and 2400 Å. 18 groups of bands have been recorded.

A. A. ELDRIDGE.

Absorption spectra of phthaleins of trihydric phenols. R. C. GIBBS and C. V. SHAPIRO (*J. Amer. Chem. Soc.*, 1929, 51, 1755—1766).—Data and curves are given for the absorption spectra of pyrogallolbenzein, gallein, sulphongallein (cf. Orndorff, A., 1925, i, 277; 1926, 949; 1927, 671), hydroxyquinolphthalein and -sulphonphthalein (cf. this vol., 822), and phloroglucinolsulphonphthalein, in (a) absolute alcohol, (b) concentrated sulphuric acid, and (c) aqueous potassium hydroxide. The results are interpreted along lines now familiar (cf. A., 1928, 570, 1019, 1374). In alcoholic solution pyrogallolbenzein is quinonoid, gallein mainly lactonoid, and sulphongallein and its dimethyl ether are internal complex salts. In sulphuric acid the first three compounds show closely related absorptions, as they do in aqueous potassium hydroxide. Phloroglucinol-sulphonphthalein is quinonoid in neutral solution; its orange-yellow alkaline solutions remain unchanged for some months. The quinonoid phthaleins, unlike those of lactonoid structure, show considerable differences in absorption with changes in the number and position of the hydroxyl groups.

H. E. F. NOTTON.

Absorption spectra of halogenated fluoresceins. R. C. GIBBS and C. V. SHAPIRO (*J. Amer. Chem. Soc.*, 1929, 51, 1769—1773).—The absorption curves of dibromo- (I), tetrabromo- (II, eosin), and tetrachloro- (III) -fluoresceins in alcohol and in sulphuric acid have been measured. Introduction of halogen produced no radical change in the absorption spectrum of fluorescein (cf. A., 1928, 526). The bands are displaced towards the region of longer wavelengths, the order of magnitude of the displacement being for the ultra-violet bands, II > I > III, and for the visible band, II > III > I. Accordingly, the halogen derivatives have, like fluorescein, a quinonoid and not an internal salt structure (cf. Orndorff, A., 1914, i, 542; 1927, 671). The results are compared with those previously obtained (cf. preceding abstract; Holmes, A., 1925, i, 255).

H. E. F. NOTTON.

Tautomerism of hydroxytriarylcarbinols. II. L. C. ANDERSON (*J. Amer. Chem. Soc.*, 1929, 51, 1889—1895; cf. A., 1928, 219, 285).—Data and curves are given for the absorption spectra of ethereal solutions of the following triphenylmethane derivatives: diphenyl-5-chloro-*o*-tolylmethane, diphenyl-5-bromo-*o*-tolylmethane, *p*-hydroxy-*m*-methoxytriphenylmethane, *p*-hydroxytriphenylmethane, and diphenyl-*o*-tolylmethane, and of the fuchsone and benzenoid and quinonoid carbinols derived from each, also of triphenylmethane and triphenylcarbinol. The

results are similar to those obtained in alcoholic solution (Orndorff and others, A., 1927, 764), and they afford further evidence for the existence of the quinonoid forms of the carbinols.

H. E. F. NOTTON.

Ferrous nitroso-compounds. H. I. SCHLESINGER and H. B. VAN VALKENBURGH (*J. Amer. Chem. Soc.*, 1929, 51, 1323—1331).—The absorption spectra of the complexes formed between ferrous phosphate and nitric oxide in phosphoric acid solutions and between ferrous chloride and nitric oxide in alcohol solutions are almost identical with the spectra of the ferrous sulphate-nitric oxide complex in sulphuric acid. The shift of the absorption bands towards the violet which occurs on dilution of the solution indicates a transition between two compounds. This transition appears to be determined by the activity of the water in the solution. The results support the views of Kohlschütter and Sazanoff (A., 1911, ii, 730). The spectra of numerous other salt solutions saturated with nitric oxide yielded no evidence of the existence of complex ions in these solutions. S. K. TWEEDY.

Absorption spectra of halogens and inter-halogen compounds in solution in carbon tetrachloride. A. E. GILLAM and R. A. MORTON (*Proc. Roy. Soc.*, 1929, A, 124, 604—616).—Measurements have been made of the absorption of solutions of chlorine, bromine, and iodine in carbon tetrachloride, using a Hilger quartz spectrograph in conjunction with a sector photometer. Summation curves are constructed on the assumption that solutions containing different halogens in stoichiometric proportions would obey the simple mixture law, and these are compared with experimental absorption curves obtained with solutions of definite inter-halogen compounds, and with experimental curves for mixtures in proportions corresponding with known compounds and with compounds the existence of which is doubtful. The results are in good agreement with those of previous investigators, whose work is summarised. It is shown that iodine chloride, iodine bromide, and bromine chloride (cf. Hanson and James, A., 1928, 1004; Barratt and Stein, this vol., 411) possess absorption bands of which the maxima are accurately measurable at 464, 487, and 380 μ , respectively. At the dilutions necessary for the investigation of absorption spectra all three compounds are to some extent dissociated; with iodine chloride the dissociation is scarcely detectable, with iodine bromide it remains slight, whilst with bromine chloride it is considerably greater. Solutions containing halogens in the proportions necessary for the formation of iodine trichloride, iodine tribromide, and bromine trichloride were found to contain the monohalide and free halogen only.

L. L. BIRCUMSHAW.

Effect of gases on the colour of iodine vapour, and the solvent action of various vapours on solid iodine. R. WRIGHT and T. MCGREGOR (*J.C.S.*, 1929, 1364—1367).—It has been observed that the colour of iodine vapour is not so deep in a vacuum as in air (cf. Dewar, *Proc. C.S.*, 1898, 241), nitrogen, oxygen, carbon dioxide, or argon. A qualitative spectroscopic examination showed increased absorption in presence of gases and a shifting of the head of

the absorption band towards the red. The spectra were identical whichever of the gases mentioned was present, and whether excess of iodine was used or less than would saturate the available space with vapour. The colour change is therefore not due to solubility of the iodine in the gas used or to chemical interaction between the gas and iodine. The vapour pressure of iodine has been found to be slightly less in air than in a vacuum. Experiments on the solubility of iodine in the vapours of several organic solvents have given indefinite results.

F. L. USHER.

Ultra-violet absorption curves of terpene alcohols. J. SAVARD (Bull. Soc. chim., 1929, [iv], 45, 398—402; cf. A., 1928, 1252).—The ultra-violet absorption of rhodinol, citronellol, linalool, and geraniol in hexane solution has been determined. The accepted constitutional formulæ for linalool and geraniol, and probably also for rhodinol and citronellol, are in agreement with the results of spectral analysis.

C. W. GIBBY.

Molecular absorption of iodine in the vacuum ultra-violet. H. SPONER and W. W. WATSON (Z. Physik, 1929, 56, 184—196).—Iodine vapour shows three distinct absorption series in the ultra-violet region. At very low pressures (the vapour pressure at -24°) there occurs only one series of bands at about 1750 Å. At higher pressures these bands broaden and become more intense, and new members appear. It has not yet been found possible to classify these bands. At about -4° a strong series of close, narrow bands begin to appear in the region 1950—1780 Å. Two possible systems for arranging this series are discussed. Strong absorption also occurs in the region 1600—1500 Å., but this could be observed only qualitatively.

J. W. SMITH.

Absorption of a crystal of dialogite. P. LEROUX (Compt. rend., 1929, 189, 162—163).—The pleochroic absorption phenomena observed for tourmaline (A., 1928, 934) have been shown to occur in the case of Colorado dialogite (MnCO_3) for the wave-lengths 3655—5790 Å., slight anomalies being due probably to small inclusions in the crystal which are absent from the purer tourmaline. The pleochroism of dialogite is most marked in the ultra-violet region.

J. GRANT.

Chlorides of sulphur. II. Molecular extinction coefficients. T. M. LOWRY and G. JESSOP (J.C.S., 1929, 1421—1435; cf. A., 1927, 505).—An account is given of observations of the extinction coefficients of chlorides of sulphur of compositions between that of the monochloride and that of the tetrachloride. Since the colour of sulphur chloride mixtures reaches a maximum at the approximate concentration of the dichloride and not of the tetrachloride, the deep red colour of these solutions is to be attributed to dichloride. Sulphur dichloride absorbs all wave-lengths less than 6200 Å. Sulphur monochloride has a maximum of selective absorption in the ultra-violet at 2660 Å. A colorimetric analysis of the system was made, using the wave-lengths 5220 and 5400 Å., to which chlorine and sulphur monochloride are completely transparent. Sulphur tetrachloride is not formed in appreciable quantities in the liquid chlorides of sulphur, which

behave as ternary equilibrium mixtures, to which the law of mass action can be applied in accordance with the equation $2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$. F. J. WILKINS.

Comparative spectrum analysis of *o*-, *m*-, and *p*-isomerides of certain benzene derivatives. J. SAVARD (Ann. Chim., 1929, [x], 9, 287—350).—The ultra-violet spectral absorption of the vapours of phenol, *o*-, *m*-, and *p*-cresols has been investigated at various temperatures. Except in the case of *p*-cresol two spectra, separated by definite intervals and corresponding, respectively, with the normal and activated state of the molecule, are found, their superposition giving rise to doublets and certain abnormalities in intensity. Vibration frequencies are greater in the normal than in the activated state. At the ordinary temperature *p*-cresol has a spectrum consisting of four regularly spaced groups between 2644 and 2848 Å., the intensity of lines in any particular series decreasing towards the extreme ultra-violet. The spectrum of *o*-cresol consists of a group of bands seemingly irregularly distributed between 2748 and 2784 Å. and a doublet at 2692 Å., whilst that of *m*-cresol consists of two groups, one consisting of seven bands and a doublet between 2642 and 2794 Å. and another group between 2750 and 2630 Å. Certain similarities exist between the spectra of the *o*- and *m*-compounds, which, however, are sharply differentiated from that of the *para*, these differences persisting with rise of temperature until absorption becomes total (at 31° for the *o*-, 43° for *m*-, and 41° for the *p*-compound). The spectra in the vapour state are similar to those in hexane solution (Klingstedt, A., 1923, ii, 201), but are shifted about 360 cm.^{-1} towards the violet. The spectra are represented by the following relationships: *ortho*, $1/\lambda = 36248$ (or 36412) + $704(p' - p_0) - 69p_0 + 245(q' - q_0) - 48q_0$; *meta*, $1/\lambda = 35983$ (or 36100) + $693(p' - p_0) - 76p_0 + 270(q_1 - q_0) - 48q_0$; *para*, $1/\lambda = 35339 + 808(p' - p_0) - 55p_0 + 209.5(q_1 - q_0) - 41q_0$, where p_0 and q_0 , p_1 and q_1 are whole numbers in the normal and activated molecules, respectively. The spectra of toluene (cf. Henri and Walter, A., 1923, ii, 275) and of phenol are represented, respectively, by $1/\lambda = 37421(37484) + 932(929)(p' - p_0) - 178p_0 + 263(q' - q_0) - 21(34) - q_0$, and $1/\lambda = 36350(37286) + 784(p_1 - p_0) - 62p_0 + 152(q_1 - q_0) - 38q_0$. On the basis of these results and those for dihalogenobenzenes (Errera and Henri, this vol., 377) the energy of activation, quantification of vibrations, degrees of vibrations, activation energy levels, and deformability of molecules are discussed. In each case similar differences between *o*-, *m*-, and *p*-positions are found.

J. W. BAKER.

Behaviour of various organic vapours in the high-frequency glow discharge. E. HIEDEMANN (Ann. Physik, 1929, [v], 2, 221—232).—Hydrogen passed through a heated palladium tube in a vacuum apparatus is perfectly pure even when various impurities are introduced into the surroundings of the palladium tube. The discharge phenomena in the vapours of ether, ethyl alcohol, acetone, acetic acid, chloroform, carbon tetrachloride, and benzene have been investigated qualitatively using a high-frequency discharge. In all cases decomposition was observed, a precipitate of carbon or a carbon com-

pound of high mol. wt. being formed. The product formed with benzene contains diphenyl, diphenylene, and higher isomerides. The kind of discharge used does not appear to determine the nature of the product, although composition varies with the current strength and potential gradient in the tube.

R. A. MORTON.

Quantum theory of fluorescence. E. SEGRÉ (Atti R. Accad. Lincei, 1929, [vi], 9, 887—892).

Thermophosphorescent radiations of hiddenite and kunzite. O. STUELMAN, jun. (J. Opt. Soc. Amer., 1929, 18, 365—369).—These minerals are lithium aluminium silicates differing in colour on account of various traces of impurities. The presence of traces of chromium and iron and the absence of potassium in hiddenite was confirmed by an examination of its visible and arc spectra. Spectrograms obtained showed that the thermophosphorescence of hiddenite consisted of an orange band from 0.7 to 0.589 μ and a faint green band with its maximum near 0.54 μ . The emission colours for kunzite were recorded over a temperature range of 210—420°. Attempts to obtain spectrograms were unsuccessful. Examination with colour filters indicated at 300° a yellowish-green band from 0.515 to 0.528 μ and an orange band from 0.570 to 0.650 μ , both widening with rise of temperature.

N. M. BLIGH.

Thermoluminescence excited by high-voltage cathode rays. (Miss) F. G. WICK and (Miss) E. CARTER (J. Opt. Soc. Amer., 1929, 18, 383—392).—The thermoluminescence produced by penetrating cathode rays was studied for Franklin fluorite, Ingleside calcite, and calcium sulphate plus manganese. After exposure of the specimens to the cathode rays observations were made of the maximum brightness and decay rate of the thermoluminescence (cf. A., 1927, 397), effects of varying the time of exposure, cathode tube voltage, and temperature. The effects produced are generally similar to those produced by X-rays, but in the latter case a higher subsequent excitation temperature is necessary, the saturation time is greater, and the effect is less permanent.

N. M. BLIGH.

Time-lags in fluorescence and in the Kerr and Faraday effects. E. GAVIOLA (Physical Rev., 1929, [ii], 33, 1023—1034).—Reports of time-lags (cf. Beams and others, A., 1926, 1069; 1927, 83, 610, 1007) are examined critically, and it is shown that the assumption of such time-lags cannot be sustained. Probable explanations of the causes of the erroneous views are given.

N. M. BLIGH.

Luminous effect in electrolysis at mercury electrodes. A. DUMANSKI, Z. ČESCHEVA, and A. BANOV (Z. physikal. Chem., 1929, B, 3, 440—442).—When aqueous solutions of sodium chloride, sulphate, carbonate, oxalate, or phosphate, potassium bromide or iodide, aluminium chloride, or hydrochloric or sulphuric acid are electrolysed at 12—70 volts with a mercury anode, the latter becomes luminous, the colour of the light emitted depending on the nature of the electrolyte. No luminosity is observed with sodium nitrate, sulphite, acetate, or borate, potassium hydroxide or chlorate, or nitric acid. The intensity of the

light increases with the applied *P.D.*, and with the electrolyte concentration up to 0.1*N*. The material of the cathode exercises no influence on the appearance. The phenomenon is dependent on the formation of an insoluble compound at the surface of the anode.

F. L. USHER.

Fluorescing power of solutions. Effect of concentration. Action of antioxygens. (MLLE.) F. VITTE (J. Chim. phys., 1929, 26, 276—287).—The variation of the fluorescing power of solutions with the concentration of the fluorescent substance has been investigated for fluorescein and erythrosin in alkaline solutions of constant p_H . For solutions of fluorescein the fluorescing power decreases exponentially with the concentration above a certain small concentration, below which the fluorescence is constant. The fluorescing power of erythrosin solutions increases with the concentration at first exponentially, then more rapidly, and finally remains practically constant. The fluorescing power of fluorescein in alkaline solution decreases rapidly with the concentration of added antioxygen (potassium iodide or resorcinol). A special form of fluorometer, in which the relative fluorescing powers of two solutions can be directly compared, is described.

O. J. WALKER.

Measurement of luminescence. J. PLOTNIKOV (Z. Elektrochem., 1929, 35, 432—434).—A method of measuring the intensities of various luminescent radiations has been devised by making use of Kruss' polarisation colorimeter.

H. T. S. BRITTON.

Influence of a magnetic field on the fluorescence of mercury vapour. H. NIEWODNICZANSKI (Z. Physik, 1929, 55, 676—689).—The increase in the intensity of the fluorescence of mercury vapour, excited by the line 2537 Å., reported by Franck and Grotrian (*ibid.*, 1921, 4, 89) is not confirmed. A magnetic field acting on the region where excitation takes place produces a periodic variation in the intensity of the fluorescence with increasing field strength. This behaviour is explained in terms of the Zeeman effect and the hyperfine structure of the line 2537 Å. to the effect that excitation of not too dense mercury vapour by the 2537 Å. line results first in the excitation of mercury atoms and not of mercury molecules.

W. E. DOWNEY.

Sodium chloride phosphor containing cuprous salt. (FRL.) M. FORRÓ (Z. Physik, 1929, 56, 235—243).—Sodium chloride phosphor containing 0.03—0.3% of cuprous salt shows an absorption band at 255 $m\mu$, the position of which is independent of the cuprous salt concentration. The breadth of this band varies in different specimens and is considered to depend on the degree of distortion of the crystal lattice ("internal temperature"). This conclusion is supported by the fact that the principal change in the absorption spectrum over the temperature range —193° to 500° is the gradual broadening of the band as the temperature rises. With 1% Cu, large changes are observed in the intensities in the absorption band after heating to 400° (cf. MacMahon, this vol., 239), but these revert to the previous values on keeping. Irreversible disturbance of the lattice occurs first on prolonged heating at about 600°.

J. W. SMITH.

Heterodyne null method of measuring dielectric constant. P. N. GHOSH and P. C. MAHANTI (*Nature*, 1929, 124, 13).—Sources of error are discussed. The dielectric constant of dry air, free from carbon dioxide, is $1.000579_{\pm 4}$ at *N.T.P.*

A. A. ELDRIDGE.

Dielectric polarisation of liquids. V. Atomic polarisation. C. P. SMYTH (*J. Amer. Chem. Soc.*, 1929, 51, 2051—2059).—The atomic polarisations, *P*, of numerous liquids are tabulated. In general, *P* is greater the greater is the number of atomic nuclei or groups in the molecule. The valency forces between these nuclei or groups, however, are insufficient to explain the differences in *P* in homologous and other series. The presence of electric doublets in the molecule, and dissymmetry of their arrangement, are conducive to higher values of *P*. In calculating the electric moment of a molecule *P* may be disregarded if the moment is high and the molecule is small and contains only one or two electric doublets.

S. K. TWEEDY.

Dipole moment as a characteristic property of a group. K. HÖJENDAHL (*Physikal. Z.*, 1929, 30, 391—397).—From Pohrt's measurements (*Ann. Physik*, 1913, 42, 569) of the dielectric constants of a series of organic vapours, dipole moments have been calculated. The results show that for mono-substituted homologues the dipole moment is roughly constant. Each polar group is thus apparently characterised by a constant "group moment" which can be regarded as a vector possessing a definite direction. Measurements have been made on the dielectric constants and refraction of 24 organic compounds dissolved in benzene. Experimental dipole moments can thus be obtained and compared with the data calculated from the vector-sum of the group moments. The results support the classical regular benzene structure in one plane and are not consistent with any of the alternatives. The experimental data for dinitro-, chloronitro-, and bromonitro-benzene, dinitronaphthalene, and nitrotoluene are in good agreement with the calculated values, but in the case of the nitroanilines, anisole, and nitroanisole considerable deviations occur. Substituent groups are divided into three classes: (a) those with positive poles pointing outwards, (b) those with negative poles pointing outwards, (c) those in which the group moment is oblique to the group. The groups NO₂, Cl, Br belong to one of (a) and (b) and Me, NH₂ to the other, but it is not possible to decide which set is positive and which negative.

R. A. MORTON.

Dielectric constant of desiccated oxygen. H. L. RILEY (*J.C.S.*, 1929, 1026—1028).—With a view to determine whether the change in its chemical and electrical properties observed on intensive drying of oxygen is accompanied by some fundamental change in the structure of the gaseous molecule such as would alter its dielectric constant, two precisely similar condensers were constructed, one containing oxygen dried over calcium chloride, the other oxygen intensively dried over phosphoric oxide, which was also placed in the condenser. Comparison over a period of 10 months showed no change in capacity

of the condenser attributable to the intensified drying.

C. A. SILBERRAD.

Additivity of molecular dipole moments. Constitution of C_α compounds. A. EUCKEN and L. MEYER (*Physikal. Z.*, 1929, 30, 397—402).—From the moments C—C, 0; H—O, 1.6; C=O, 2.3; Me—C, 0.4; H—C, 0.4; C—O, 0.7, and C—Cl, 1.5 the principle of additivity is found to apply satisfactorily to a variety of compounds with and without the capacity for free rotation. Stereochemical rotation of some groups accounts for the apparent moment of many C_α compounds.

R. A. MORTON.

Explanation of the orientation polarisation found in C_α derivatives. A. SCHLEDE, G. JUNG, and A. HETTICH (*Z. physikal. Chem.*, 1929, B, 3, 479—480).—The conclusions reached by Ebert, Eisenschitz, and Hartel (cf. A., 1928, 1308) regarding molecular polarisation in methane derivatives do not necessarily follow from their experimental results. A study of the dependence of molecular polarisation on temperature is being undertaken in order to decide between two possible interpretations.

F. L. USHER.

Electric moment of primary alcohols. P. C. MAHANTI and R. N. DASGUPTA (*Indian J. Physics*, 1929, 3, 467—475).—The electric moments of a number of primary alcohols have been calculated from measurements of the dielectric constants and densities of their solutions in benzene. To obtain a sharp null point the Nernst bridge method was used. The value obtained for each alcohol is nearly the same, indicating that the oxygen atom of the hydroxyl group in alcohols is similarly polarised.

N. M. BLIGH.

Electric moment and structure of derivatives of diphenyl. E. BRETSCHER (*Helv. phys. Acta*, 1928, 1, 355—361; *Chem. Zentr.*, 1929, i, 725).—*pp'*-Derivatives of diphenyl would have no electric moment only if the partial moments of the two rings were anti-parallel; the observation of an electric moment would admit a choice between various configurations. *pp'*-Difluoro-, -dichloro-, and -dibromo-diphenyl, and diphenyl itself have no electric moment, whilst the upper limits for the dipole moments of *pp'*-dimethoxy- and -diamino-diphenyl are reconcilable with a considerable value of the moment.

A. A. ELDRIDGE.

Dipole moment of antimony trichloride. O. WERNER (*Z. anorg. Chem.*, 1929, 181, 154—158).—The dipole moment calculated from measurements of the dielectric constant in benzene solution is $\mu = 3.64 \times 10^{-18}$, a value much greater than that for the corresponding iodide, 0.4×10^{-18} . Reasons for this are discussed.

J. S. CARTER.

Glass. III. Dielectric constants of glassy and liquid dextrose. F. R. CATOIR and G. S. PARKS (*J. Physical Chem.*, 1929, 33, 879—882; cf. A., 1928, 1189).—The dielectric constants for glassy and liquid dextrose have been measured over the range 200—423° Abs. by a resonance method. For glassy dextrose, the value of ϵ increases from 3.8 to 5.4 with a rise in temperature; between 293° and 310° Abs. the glass softens and ϵ rises; it reaches a

maximum of 23.9 at 378° Abs. and then slowly falls to 21.0 at 423° Abs. The values for glassy dextrose are similar to those of inorganic glasses and non-polar liquids, whilst those for liquid dextrose are similar to those of polar liquids. L. S. THEOBALD.

Kinetics of the change of optical properties [of crystals] with temperature. W. SCHMIDT and E. BAUER (Z. Krist., 1928, 68, 477—502; Chem. Zentr., 1929, i, 496).

[Optical properties of] potassium, rubidium, caesium, ammonium, and thallium tartrates. M. W. PORTER (Z. Krist., 1928, 68, 531—542; Chem. Zentr., 1929, i, 503).

Existence of liquid racemates. A. N. CAMPBELL (J.C.S., 1929, 1111—1123; cf. A., 1928, 1083).—The physical properties of liquid esters of racemic acid have been compared with those of corresponding esters of *d*-tartaric acid, to decide the question of the existence of liquid racemates. The following have been prepared: *n*-propyl racemate, m. p. 25°, b. p. 167°/11 mm., 286°/765 mm., d_{20}^{25} 1.1256, n_D^{25} 1.4413; isopropyl racemate, m. p. 34°, b. p. 154°/12 mm., 275°/765 mm., d_{20}^{34} 1.1214, n_D^{34} 1.4374; *n*-butyl racemate, b. p. 185°/12 mm., 320°/765 mm., d_{20}^{185} 1.0879, n_D^{185} 1.4451; isobutyl racemate, m. p. 58°, d_{20}^{58} 1.0160. The m. p. of *n*-propyl, isopropyl, and methyl dipropionyl-racemates are higher than those of the corresponding *d*-tartrates, and the inactive forms are therefore, in the solid state, true racemates. The f.-p. and solubility curves of the isobutyl tartrates have been determined, and lead to a similar conclusion. A little below 0° isobutyl racemate passes to the *dl*-conglomerate. Differences in b. p. and *d* of a number of racemates and *d*-tartrates have been established. The active forms have usually a higher refractive index, a lower dispersion, and a higher viscosity than the inactive. Determinations of the surface tensions show that the association of the active form is greater than that of the racemic. The conclusion is reached that there is a marked difference between the active and racemic forms of the liquid esters of tartaric acid. F. L. USHER.

Natural optical activity. W. KUHN (Z. physikal. Chem., 1929, B, 4, 14—36).—Mathematical. For very strongly rotating substances the refractive index for left circular light is very nearly the same as that for right circular light, the difference being only 1 in 10⁶. The parts of different spectral ranges concerned in optical activity are investigated. In many cases very weak absorption bands play an important part. Mathematically, the problem is investigated by obtaining qualitative and quantitative results for two coupled resonators oscillating perpendicular to each other. The results thus obtained can be applied to systems of more resonators. A quantitative relationship between circular dichroism and optical rotation inside and outside the absorption bands is obtained. A. J. MEE.

Elliptical polarisation produced by reflexion at the surface of solutions of fatty acids in water. C. BOUHET (Compt. rend., 1929, 189, 43—45).—The author's results (cf. this vol., 503) show that the curves relating the concentration/concentration of

saturated solution and ellipticity are all of the same form, although not completely superposable, and are displaced in general towards the smaller ellipticities when the number of carbon atoms increases. In all cases a constant ellipticity was obtained, and the surface area occupied by each acid molecule is then approximately 25×10^{-16} cm.² Conclusions reached from X-ray examination of the solid acids (Morrow, A., 1928, 224) were confirmed by these results and support Gibbs' hypothesis of the orientation of molecules perpendicular to the surface. J. GRANT.

Rotation-dispersion of optically active ammonium salts. E. WEDEKIND and G. L. MAISER (Z. Elektrochem., 1929, 35, 438—440).—The optical activity of *d*- and *l*-phenylbenzylallylmethylammonium *d*-camphorsulphonates, nitrates, and hydroxides was measured in various solvents using light of the wave-lengths 6650, 5770, 4920, and 4360 Å., respectively. In no case was the rotation, compared with the dispersion of the light used, anomalous, neither had the solvent any marked effect on the rotation-dispersion. Measurements were also made in acetone of the rotations of 1-methylallyltetrahydroquinolinium iodide and *l*-menthyl 2-isopropyl-tetrahydroisoquinolinium iodide acetate using the same sources of light. The results were anomalous. H. T. S. BRITTON.

Optical properties of amino-acids. II. Arginine and histidine. G. L. KEENAN (J. Biol. Chem., 1929, 83, 137—138).—*Arginine dihydrate* crystals are strongly doubly refracting and have n_a 1.528, n_β 1.549, n_γ 1.579; the anhydrous crystals have n_a 1.548, n_β 1.562, n_γ 1.610. Crystals of histidine have n_a 1.520, n_β indeterminate, n_γ 1.610.

C. R. HARRINGTON.

Microscopical study of electric double refraction in liquids. M. IWATAKE (Tech. Rep. Tôhoku, 1929, 8, 399—410).—A photomicrographic study has been made of the Kerr effect in nitrobenzene, *o*-nitrotoluene, pyridine, and carbon disulphide. Electrodes of various shapes were used, with a field intensity of 6000—7500 volts/mm. With the two Nicols crossed a bright layer, very close to the anode surface, appears with increasing potentials in nitrobenzene and pyridine. Under the same conditions with *o*-nitrotoluene a bright layer appears momentarily close to the cathode and subsequently disappears, to be followed by the appearance of a bright layer at the anode. With carbon disulphide the space between the electrodes is uniformly bright. The results suggest that the field in the gap is not uniform, due perhaps to the stratified settling of a non-homogeneous liquid substance in the gap. An explanation analogous to that of chromatic polarisation of uniaxial crystals, assuming the optical axis to be coincident with the electric field, is applicable. The effect is not shown by carbon disulphide. F. G. TRYHORN.

Measurement of optical activity in the extreme ultra-violet. W. KUHN (Ber., 1929, 62, [B], 1727—1731).—An apparatus is described and figured.

H. WREN.

Paramagnetic rotation of the plane of polarisation in the neighbourhood of absorption lines.

R. MINKOWSKI (Naturwiss., 1929, 17, 568—569).—Paramagnetic rotation in the neighbourhood of the caesium lines $1^2S_{\frac{1}{2}}-2^2P_{\frac{1}{2}}$ (8944 Å.) and $1^2S_{\frac{1}{2}}-2^2P_{\frac{3}{2}}$ (8521 Å.) has been detected. Quantitative experiments in the latter case show that within the limits of error ($\pm 15\%$) the paramagnetic effect in the neighbourhood of the line is in satisfactory agreement with calculations based on the Ladenburg-Kramers-Heisenberg dispersion formula. R. A. MORTON.

Quantum theory of valency. W. HEITLER (Naturwiss., 1929, 17, 546—547).—Theoretical.

R. A. MORTON.

Demonstration of the direct and reverse transformations of both forms of hydrogen. H. SENFTLEBEN (Z. physikal. Chem., 1929, B, 4, 169—173).—An apparatus which makes it possible to demonstrate the changes of one form of hydrogen into the other to large classes is described. A. J. MEE.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, B, 4, 113—141; cf. this vol., 479).—The preparation of pure para-hydrogen is described, together with systematic experiments on the conversion of one type into the other, the results of which have already been published. The pure para-form has m. p. 13.83° Abs., vapour pressure 787 ± 1 mm. at 20.39° Abs., the temperature at which the normal gas boils. The saturation pressure at the triple point is 53.0 ± 0.1 mm., whereas that for the normal gas is 53.9 ± 0.1 mm. The chemical and electrochemical properties of the two forms were also investigated. It is not to be expected that there will be any noticeable difference at ordinary temperatures. The strong lines in the para-hydrogen emission spectrum are the weak ones in the emission spectrum of ordinary hydrogen. The preparation of para-hydrogen provides proof of the accuracy of the new quantum theory. A. J. MEE.

Pseudo-components of hydrogen. A. SMITS (Physikal. Z., 1929, 30, 425—427).—The work of Bonhoeffer and Harteck (this vol. 479) and of Eucken (*ibid.*, 497) is an experimental realisation of certain aspects of the author's theory of allotropy. The implications of the discovery of ortho- and para-hydrogen are discussed. R. A. MORTON.

Structure of the molecules of N_2 , O_2 , and F_2 . A. T. WILLIAMS (J. Chim. phys., 1929, 26, 327—330).—A critical examination is made of certain consequences of the Lewis-Langmuir theory and particularly of the more recent theory of Niven (cf. A., 1927, 714) concerning the structure of the diatomic gaseous elements. It is concluded that these molecules are asymmetric. O. J. WALKER.

Anomaly in the diamagnetism of gases. IV. Oxygen addition. A. GLASER (Ann. Physik, 1929, [v], 2, 233—248; cf. this vol., 628).—The pressure-diamagnetic susceptibility curves for argon-oxygen mixtures are linear, the susceptibility, however, decreasing with increasing concentration of paramagnetic oxygen and decreasing concentration of diamagnetic argon. Argon does not show the anomaly. The curves for carbon dioxide-oxygen mixtures show straight-line portions in certain higher-pressure regions, but in the pressure range

of the diamagnetic anomaly with pure carbon dioxide the oxygen content of mixtures plays a decisive part. With 0.1% O_2 the curve is a straight line, whilst with 0.15, 0.2, and 0.3% the anomalous behaviour increases progressively, but in the reverse sense to that encountered with pure carbon dioxide. Traces of oxygen as an impurity appear therefore to be extremely important in studying the diamagnetic anomaly. Hammar's results (A., 1926, 1197) are discussed from this point of view.

R. A. MORTON.

Paramagnetism through ions subjected to molecular forces. R. BRUNETTI (Atti R. Accad. Lincei, 1929, [vi], 9, 754—760).—Theoretical. The consequences of the severing of the bond existing between the vectors corresponding with the quantum numbers l and s in the case of atoms or ions in a strong force field are discussed. F. G. TRYHORN.

Paramagnetic properties of the rare earths. B. CABRERA and A. DUPERIER (Compt. rend., 1929, 188, 1640—1642; cf. A., 1925, ii, 618).—The Curie-Weiss law is satisfied by the sulphates and oxides of gadolinium, terbium, dysprosium, holmium, and erbium to a first approximation, but for those of praseodymium, thulium, yttrium, neodymium, europium, and probably of samarium the equation $(\chi+k)(T+\Delta)=C$ accords better with the experimental results. The constant k represents a susceptibility independent of temperature, paramagnetic and diamagnetic for the elements near samarium and yttrium, respectively, and due to deformation of the atom. J. GRANT.

Diamagnetism and space-charge distribution of atoms and ions. E. C. STONER (Proc. Leeds Phil. Soc., 1929, 1, 484—490).—The diamagnetic susceptibilities corresponding with the space-charge distributions obtained by the self-consistent field method of Hartree (A., 1928, 216) have been calculated for helium and for the ions Li^+ , Na^+ , K^+ , Rb^+ , and Cl^- . The experimental values for ionic susceptibilities are critically discussed and the calculated values are considered to be in good agreement with the experimental values for the positive ions. The calculated and experimental values for helium agree to within 1%, but the calculated value for the free chlorine ion is much greater than that observed for the ion in solution. The difference is discussed in relation to the space-charge distribution of an ion in a crystal. L. S. THEOBALD.

Mean square angular momentum and diamagnetism of the normal hydrogen molecule. J. H. VAN VLECK and (MISS) A. FRANK (Proc. Nat. Acad. Sci., 1929, 15, 539—544; cf. A., 1928, 572).—Using the wave function found by Wang (*ibid.*), the mean square electronic angular momentum is calculated for the normal hydrogen molecule and found to have the value $0.394h^2/4\pi^2$. Taking account of the summation over the various excited states, a simple method is found of calculating the correction to Pauli's formula or to Wang's calculation of the diamagnetism of the hydrogen molecule, and the value -4.2×10^{-6} is obtained. N. M. BLIGH.

Magnetic anisotropy of naphthalene crystals. S. BHAGAVANTAM (Proc. Roy. Soc., 1929, A, 124,

545—554).—Naphthalene crystals show a marked degree of magnetic and optical anisotropy. Two of the magnetic axes coincide with two of the crystallographic axes (*b* and *c*), whilst the third is a line perpendicular to both. The values -710 , -390 , and 1590×10^{-7} , respectively, were found for the principal susceptibilities along the *b* axis, along the *c* axis, and along a line perpendicular to both. Two of the axes of the optical ellipsoid also coincide with the *b* and *c* axes to within about 3° , and the values 1.775 , 1.932 , and 1.442 , respectively, have been found for n_D along the *b* axis, the *c* axis, and a line perpendicular to both. The fact that the direction of the maximum diamagnetic susceptibility coincides with that of the minimum refractive index explains the strong positive birefringence shown by aromatic liquids in a magnetic field. The experimental results indicate that the two molecules in the unit cell are oriented with their planes parallel to the *bc* plane, and not, as suggested by Bragg, to the *ac* plane. L. L. BIRUMSHAW.

Chemical combination as an electrostatic phenomenon. IX. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 386—389; cf. this vol., 867).—Methods of calculating the deformation constant α of an ion are described, and the results compared. The influence of the size of a cation on the extent of deformation produced is discussed, especially with regard to hydrogen and to organic compounds. H. F. GILLBE.

Valency of sulphur in dithionates. R. E. WINGER and D. M. YOST (Proc. Nat. Acad. Sci., 1929, 15, 462—464).—The shift in the *K*-absorption edges of various compounds of certain elements including sulphur is known to depend chiefly on the valency of the element in a given compound, shifting to smaller values with increasing valency. The *K*-absorption edge was examined for potassium dithionate and found to lie at 4992.8, between the values for quadri- and sexa-valent sulphur, indicating an equal valency of five for the two sulphur atoms in the dithionate in accordance with the usual view. N. M. BLIGH.

Effective strength of linking in polyatomic molecules. G. SCHWARZENBACH (Helv. Chim. Acta, 1929, 12, 820—821).—The conclusion of Ebel and Bretscher (this vol., 744, 745), that it cannot be assumed from thermochemical evidence that the strength of a C-C and a C-H linking is the same within narrow limits, is criticised. The view that the energy of fission of linkings of the same kind and nature has a constant value independently of the position and presence of other linkings and atoms in the molecule is discussed. L. S. THEOBALD.

Double sulphates and their components. V. Aluminium and chromium alums. F. KRAUSS, A. FRICKE, and H. QUERENGÄSSER (Z. anorg. Chem., 1929, 181, 38—54; cf. this vol., 665).—Measurements of the densities and isobaric dehydration curves and derived calculations of the heats of formation of the various hydrates of caesium, rubidium, and potassium aluminium alums and potassium chromium alum indicate that two types of alums must be distinguished. Potassium chromium alum exists with 0, 2, 6, and $12H_2O$. The aluminium salts exist with 0, 3, and $12H_2O$. J. S. CARTER.

Formation of associated or additive compounds in the crystalline state. W. KRINGS (Z. anorg. Chem., 1929, 181, 298—308).—From considerations based on the theory of polar compounds the heat of addition of 1 mol. of ammonia to 1 mol. of sodium chloride has been calculated and shown to be somewhat higher than, but of the same order of magnitude as, that determined experimentally. The mechanism of the formation of additive compounds with 5, 7, 9, and 10 and with fractional numbers of molecules of ammonia or water of crystallisation is discussed from the point of view of the co-ordination and polar theories. A. R. POWELL.

Quantum mechanics of chemical reaction. R. M. LANGER (Physical Rev., 1929, [ii], 34, 92—108).—The failure of classical mechanics applied to chemical phenomena and the difficulties of the "activation" hypothesis are discussed. Starting from the wave equation, it is shown that quantum mechanics can describe a typical chemical reaction, and that this can be generalised. It is found that a system may change from one configuration to another when a quantum level of the one has the same energy as a quantum level of the other. Examples of molecular rearrangements and decompositions are discussed and illustrated by *cis-trans*-isomerism, and the racemisation of pinene. The theory is also applied to catalysis and radioactive disintegration. The essential requirement is found to be that a molecular system should be capable of existing in physically distinguishable states of equal energy; the special problem is to find the perturbing potential causing the reactants to go over into the reaction products. N. M. BLIGH.

Parachor and chemical constitution. XI. Arsenic and selenium compounds. W. J. R. HENLEY and S. SUGDEN (J.C.S., 1929, 1058—1065).—The parachor of selenium (62.5) has been determined from those of five compounds in which it is bivalent (diphenyl selenide 445.6, diphenyl diselenide 506.5, phenylselenium bromide 321.4, *p*-bromophenyl selenocyanate 366.1, and *p*-chlorophenyl selenocyanate 349.3); that of arsenic (50.3) from those of the trichloride 212.0, the tribromide 253.5, phenyldichloroarsine 348.3, and diphenylchloroarsine 487.1. These values are in conformity with those of elements adjacent to them in the periodic table. The parachors of several higher valent compounds of selenium have also been determined (diphenyl selenoxide 461.6, phenylseleninic acid 299.5, and selenium oxychloride 181.1). All of these are in agreement with the values calculated on the assumption that the double linking is semipolar (460.9, 308.0, 189.5, respectively, as against 485.7, 332.8, and 214.3 for non-polar linkings). The two last are even lower than required for semipolar linkings. This is due to association. Thus the mol. wt. of a 20% solution of selenium oxychloride in benzene is 195.7 (theory 166.1); the parachor of the monohydrate of this compound is in favour of the structure $Se(OH)_2Cl_2$ with two singlet linkings. C. A. SILBERRAD.

Parachor and chemical constitution. XII. Fused metals and salts. S. SUGDEN and H. WILKINS (J.C.S., 1929, 1291—1298).—The parachors

of conducting liquids have been found to show both positive and negative anomalies. The parachor of a salt involves the constant for a polar linking, estimated at -1.6 units (cf. A., 1927, 714). Salts of organic bases which are dissociated in the fused state and in which all the atomic parachors are known with certainty afford a means of checking this value. Parachors of six out of ten such salts support the value -1.6 within the limits of experimental error, whilst those of the remaining four show considerable positive and negative anomalies. Thallous nitrate, stannous chloride, lead chloride, and the metals aluminium, tin, lead, and antimony showed positive parachor anomalies, too large in most cases to be accounted for by association of atoms or ions, and due apparently to some special condition of the metal atom not considered in the calculation. Approximate values for the atomic parachors of the alkali metals have been deduced from the observed parachors of various salts. The salts of the alkali metals, especially the fluorides, show large negative anomalies in their parachors.

F. L. USHER.

Parachor and chemical constitution. XIII. Some compounds of titanium and tin. F. B. GARNER and S. SUGDEN (J.C.S., 1929, 1298—1302).—The value 56.7 for the atomic parachor of tin has been deduced from the observed parachors of tin tetrachloride, tetrabromide, and tetraethyl. $[P]=45.3$ for titanium has been obtained from the parachor of titanium tetrachloride. These results harmonise with the values hitherto found for other elements of the fourth group. An additive compound, $\text{SnCl}_4 \cdot 2\text{POCl}_3$, m. p. 54.5° , b. p. $118-119^\circ$, has been isolated. This substance showed little conductivity in the fused state and is probably non-polar. A structure containing four singlet linkings is suggested, but the value of the parachor calculated on this assumption is lower than that experimentally observed ($[P]_{\text{obs.}}=691.6$, $[P]_{\text{calc.}}=665.5$). The explanation suggested is that the fused compound is partly dissociated into its components.

F. L. USHER.

Molecular volumes at absolute zero. III. Zero volumes, parachors, and molecular diameters. S. SUGDEN (J.C.S., 1929, 1055—1058; cf. A., 1927, 920).—A comparison of the author's work with that of Biltz (Nachr. Ges. Wiss. Göttingen, 1926, 45; A., 1927, 498) shows substantial agreement in the values of the atomic constants arrived at. The mean distances between molecules in 17 substances have been calculated, (a) at 0° Abs. (from zero volumes), (b) at unit surface tension (from parachors), and (c) at the critical temperature, and compared with molecular diameters as deduced from gas viscosity by Chapman's equation (cf. A., 1918, ii, 416). Results from (a) average 1.32 times the molecular diameter (except for $\text{H}_2=1.71$ and $\text{He}=1.92$); from (b) 1.78 with no marked variations; and from (c) about double (except for $\text{He}=2.64$, $\text{Cl}_2=1.60$, and $\text{Br}_2=1.69$).

C. A. SILBERRAD.

Theory of the equilibrium figures of small drops growing by diffusion in relation to the problem of form in physics. N. VON RASCHEVSKY (Z. Physik, 1929, 56, 297—307; cf. A., 1928, 474,

690; this vol., 509).—Since a slowly growing drop of the type previously considered is not spherical, the concentration varies along the surface, and hence also the surface tension. It is shown that the product of the surface tension and the curvature is constant for any point on the surface. This is discussed in connexion with the problem of shape determination in pure physical phenomena.
J. W. SMITH.

Wave-length of the *K* lines of copper using ruled gratings. J. A. BEARDEN (Proc. Nat. Acad. Sci., 1929, 15, 528—533).—A glass grating of 600 lines per mm., and a glass and speculum-metal grating each with 50 lines per mm. were used. The values obtained were $K\alpha=1.5422 \pm 0.0002$ and $K\beta=1.3926 \pm 0.0002 \text{ \AA.}$, differing appreciably from measurements using crystals, but probably more trustworthy. From the new results the following values of constants are calculated: the grating space of calcite 3.035 \AA. , $N=6.022 \times 10^{23} \text{ g.-mol.}$, $e=4.804 \times 10^{-10} \text{ e.s.u.}$, $h=6.604 \times 10^{-27} \text{ erg sec.}$, the fine structure constant $1/\alpha=136.6$ (cf. Eddington, this vol., 231).

N. M. BLYTH.

Optical line gratings for X-ray spectral analysis in the region $1-2 \text{ \AA.}$ H. SEEMAN and K. F. SCHOTZKY (Z. Physik, 1929, 55, 252—272).—The applicability of various types of line gratings with 100—1000 lines per mm. for different wave-lengths of X-radiation is discussed.
J. W. SMITH.

Iron, cobalt, nickel, and copper as deflexion lattices for the corresponding X-rays. S. PASTORELLO (Nuovo Cim., 1928, 5, 284—289; Chem. Zentr., 1929, i, 722).

New X-ray effect. C. V. RAMAN and P. KRISHNAMURTI (Nature, 1929, 124, 53).—X-Ray diffraction patterns of graphite show a notable amount of scattered radiation in the area surrounding the primary beam, terminating sharply at the first diffraction ring and reappearing with diminished intensity in the area between the first and second diffraction rings. The effect is ascribed to mobile electrons loosely associated with the crystal lattice.

A. A. ELDRIDGE.

Diffraction of X-rays by two-dimensional crystal lattice. W. L. BRAGG (Nature, 1929, 124, 125).—The effect observed by Linnick (this vol., 492), and attributed by that author to the effect of very thin layers of the mica crystal as independent two-dimensional gratings, is ascribed to ordinary diffraction by a three-dimensional grating, provided that the mica is assumed to consist of a number of flakes not quite parallel. The mechanism of diffraction is considered in relation to the simulation of a two-dimensional grating effect.
A. A. ELDRIDGE.

An X-ray effect of slow fracture. U. DEHLINGER (Naturwiss., 1929, 17, 545).—Strongly rolled sheet copper or silver was bent backwards and forwards until fracture occurred. Photographs of the last Debye lines taken at a place close to the fracture showed the *K* doublet of copper separated with great sharpness, no grains being recognised in the specimen. The lines shown at the unbent end of the sheet exhibited the usual diffuse effect.

R. A. MORTON.

Emission of soft X-rays by different elements, with reference to the effect of adsorbed gas. U. NAKAYA (Proc. Roy. Soc., 1929, A, 124, 616—641).—An extension of the work of Richardson and Robertson (A., 1927, 804). A more detailed investigation has been made of the effect of polishing the surface, the state of degassing of the photo-electric plate, and the conditions of oxidation of the target faces. The presence of adsorbed gas molecules on the photo-electric plate and target plays an important part in the absorption and excitation of soft X-radiation. The efficiency of liberation of photo-electrons is increased, the amount of increase being greater the more adsorbed gas molecules there are in the surface. The relative change in the value of i_p/i_i for different states of the adsorbed molecules on the plate is the same for the radiations produced by different targets. The excitation of soft X-rays for a given amount of thermionic current appears to be decreased by the presence of gas molecules on the target. A number of facts support this conclusion, such as the increase in i_p/i_i when the target is subjected to a heavy bombardment compared with the value for a long bombardment at low temperature, the increase when the oxide film on the target is reduced with hydrogen, and the variation of the value with time observed at high voltages. When all the targets and photo-electric plates are well degassed and the oxide films reduced with hydrogen, consistent values of i_p/i_i are obtained with an error of less than 3% up to 1000 volts. Curves plotted for 11 elements show that i_p/i_i does not vary proportionally with the voltage, as hitherto assumed. Measurements were also made at higher voltages, chromium, iron, and copper being examined from 1500 to 2000 volts, and manganese, nickel, and cobalt from 1500 to 4500 volts. The ratio i_p/i_i increases at first, but gradually approaches a constant value, and the curves showing the relation of i_p/i_i to voltage take the form of saturation curves.

L. L. BIRCUMSHAW.

Determination of particle size by the use of X-rays. H. MARK (Trans. Faraday Soc., 1929, 25, 387—389).—The factors influencing the experimental data in the determination of particle size are discussed, with special consideration of the cases of parallel and divergent radiation and of transparent and absorbing material. The fact that different crystals of a powder are not all of the same size and the possibility of lattice defects lead to serious difficulties. It is found that the intensity of reflexion from a distorted lattice differs from that from an undistorted lattice.

L. L. BIRCUMSHAW.

Intensity, sharpness, and reproducibility of Debye-Scherrer lines. H. MÖLLER and A. REIS (Trans. Faraday Soc., 1929, 25, 386).—A procedure has been developed whereby the intensity distribution of the lines in a Debye-Scherrer photograph can be deduced from the conditions of the experiment. A parallel beam is used and the intensity distribution in one line is determined for all angles of refraction, using the cross-section and absorption of the block. For high intensities and sharp lines, the cross-section must be accurately adjusted, varying with the absorption coefficient of the preparation. Conditions are

favourable when the cross-section of the line and the aperture width approximate respectively to the line given by an infinitely small focal spot and by an infinitely small preparation. I. L. BIRCUMSHAW.

Change of frequency of X-rays scattered by bound electrons. D. P. MITCHELL (Physical Rev., 1929, [ii], 33, 871—878).—With the high resolution obtainable by the use of the two-crystal X-ray spectrometer (cf. Davis and Purks, A., 1927, 804) the fine structure of scattered X-rays (cf. A., 1928, 1168) was investigated. Molybdenum $K\alpha_1$ X-rays were scattered by graphite, aluminium, and beryllium. Lines from graphite were shifted 0.0013, 0.0023, and 0.0113, and from aluminium 0.0023, 0.0055, and 0.069 Å. to the long-wave side of Mo- $K\alpha_1$. From beryllium the shifts were 0.0048 and 0.00065 Å. to the long- and short-wave side, respectively. The scattering electrons are shown to be ejected with zero kinetic energy, and the critical potentials obtained are 32, 57, and 279 volts for carbon, 57, 136, and 1550 volts for aluminium, and 16 and 119 volts for beryllium.

N. M. BLIGH.

Raman effect for X-rays. D. COSTER, I. NITTA, and W. J. THIJSSSEN (Nature, 1929, 124, 230).—It is impossible to account for the order of magnitude of the intensity of the anti-Stokes line for beryllium quoted by Mitchell (preceding abstract).

A. A. ELDRIDGE.

Effect of chemical combination on the absorption of X-rays at wave-lengths on each side of the K discontinuity. C. L. COTTRELL (Physical Rev., 1929, [ii], 33, 879—888).—The difference in the absorption of X-rays by free as compared with chemically combined iodine was investigated for wave-length bands on each side of the K absorption limit of this element, using the double ionisation chamber method. The reacting solutions were an alcoholic solution of iodine and an aqueous solution of sodium thiosulphate (cf. Morehouse, A., 1927, 707), the reaction being $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$. The results show that on the long wave-length side of the K limit the absorption coefficient of the free iodine is about 0.3% greater, and on the short wave-length side 0.5% smaller, than for the combined atom. Silver was also investigated.

N. M. BLIGH.

Diffraction of X-rays in liquids: benzene, cyclohexane, and certain of their derivatives. G. W. STEWART (Physical Rev., 1929, [ii], 33, 889—899).—With the apparatus and procedure previously reported (A., 1928, 465, 1079) an examination by the X-ray diffraction ionisation method was made of benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, ethyl- and isopropyl-benzene, cyclohexane, methyl- and 1:2-, 1:3-, and 1:4-dimethyl-cyclohexane, phenol, aniline, cyclohexanol and cyclohexanone, *m*-2- and -4-, *o*-4-, and *p*-2-xylene, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-tolyl methyl ether. The experiments give the effective thicknesses of the benzene and cyclohexane rings, the changes in these thicknesses with substitutions, and information on the orientation of molecules in the liquid state in support of the cybotactic theory. The benzene and cyclohexane rings show a flattened structure, having a

thickness of 4.7 and 5.1 Å., respectively, and the thickness is shown to depend on the relative positions of the substituents, *para*-substitutions giving the least thickness of ring, and the *meta*- usually giving less thickness than the *ortho*-position. All the hydroxy-compounds studied showed double molecules.

N. M. BLIGH.

X-Ray absorption limits and the distribution of electrons round the atom. B. B. RAY (Indian J. Physics, 1929, 3, 477—488).—Theoretical. Kossel's view of the absorption process and the fine-structure lines is developed to explain the secondary edges in compounds, and a general relation is found that for different elements in compounds of similar structure the separation of the *K* edge in the elementary atoms from that of corresponding edges of the same atoms in the compound is the same. The discontinuities in the curve for $\Delta(v/R) = K - K\beta_1$ and the atomic number from aluminium to zinc supports the Saha electronic distribution scheme rather than that of Stoner and Main Smith.

N. M. BLIGH.

Fine structure in the Compton effect. B. DAVIS and H. PURKS (Physical Rev., 1929, [ii], 34, 1—6; cf. A., 1928, 1168).—Using the double X-ray spectrometer (cf. A., 1927, 804) and a special X-ray tube with molybdenum target and large scattering angles of 155° and 163°, the displaced scattered radiation (Compton effect) from carbon and beryllium was investigated. The fine structure found for carbon was a relatively strong line, 0.0421 from Mo- $K\alpha_1$ position, and three weaker lines at 0.0012, 0.002, and 0.0109 Å. from the strong line. The displacement is 9% less than the theoretical. For beryllium a strong line was found at 0.0446 from Mo- $K\alpha_1$ position, a line at 0.0051 towards the long wave-lengths, and a weak line at 0.0009 towards the short wave-lengths.

N. M. BLIGH.

Experimental evidence for the filling of electron levels from the relative intensity of X-ray spectrum lines. S. K. ALLISON (Physical Rev., 1929, [ii], 34, 7—16).—The double line $L\beta_5$, representing the transitions $5_{32}, 5_{33} \rightarrow 2_{22}$, had been found much more intense in the uranium than in the tungsten *L* series (cf. A., 1928, 938). Intensity measurements involving this line are given for osmium, iridium, platinum, gold, thallium, lead, and bismuth, keeping high vacua in the X-ray tubes to avoid difficulties due to deposition of tungsten on the targets from the filaments. The curve showing the intensity ratio β_5/β_1 against atomic numbers rises with increasing atomic number and takes an upward jump between platinum and gold, indicating that gold is the first element in which 10 electrons occupy the 5_3 orbits approximately undisturbed in the solid state.

N. M. BLIGH.

Dependence of the number of crystal nuclei on the temperature. G. TAMMANN (Z. anorg. Chem., 1929, 181, 408—416).—A theoretical discussion on the dependence of formation of crystal nuclei in a liquid on the temperature and viscosity.

H. F. HARWOOD.

Diagram of the physical properties of crystals. J. KUNZ (Physikal. Z., 1929, 30, 463—464).—Theoretical.

R. A. MORTON.

Lattice determination in polycrystalline aggregates. K. WEISSENBERG (Trans. Faraday Soc., 1929, 25, 391—392).—Two methods have been developed which are of special value for investigating organic compounds of high mol. wt. In the first method a growth or deformation structure is obtained in which only a few distinct crystallite orientations occur in statistical preponderance. In the second, the preparation is made as long as possible in the direction of the beam and the interferences of the planes with the greatest spacing are strengthened.

L. L. BIRCUMSHAW.

Allotropy and the determination of densities by means of X-rays. N. H. KOLKMEIJER (Trans. Faraday Soc., 1929, 25, 392—397).—The difficulties of the X-ray and pycnometer methods of determining densities are discussed, and numerous examples are given of the discrepancies between the values obtained by the two methods, and also of those obtained by different observers using the same method. Since both methods are capable of giving values correct to within $\pm 0.1\%$, the discrepancies are probably mostly due to the presence of "physical impurities" in the material used. They may also be ascribed partly to the formation of mixed crystals. The possibility of testing the "physical purity" of a material by means of X-rays is illustrated by the determination of the densities of hexagonal (d_4^{18} 5.681) and cubic (d_4^{18} 5.683) silver iodide by the spectrographic method. A new precision camera is described.

L. L. BIRCUMSHAW.

X-Ray investigation of the structure of annealed carbon steel. G. KURDJUMOV (Z. Physik, 1929, 55, 187—198).—The changes which the crystal structure of hardened carbon steel undergoes on annealing have been investigated by the Debye-Scherrer method. The three steps in the process which have been observed by other methods are confirmed by the X-ray investigation. At the first change, which occurs at an appreciable velocity at 100—150°, the tetragonal structure breaks down; the second step, obtained by heating to 250°, is caused by the breakdown of the austenite; the third, which occurs only slowly at 300—400°, is associated with the formation of an α -iron-cementite mixture.

J. W. SMITH.

Lattice constants of quenched steels. S. SEKITO (Sci. Rep. Tôhoku, 1929, 18, 69—77).—The axial ratio of the tetragonal lattice which appears on the surface layers of quenched carbon steels (cf. Honda and Sekito, B., 1928, 753) diminishes with increasing depth until it reaches the value 1.00. The maximum value of this ratio is 1.07 with hypereutectoidal steels; the value decreases with decreasing carbon content and with decreasing quenching temperature.

A. R. POWELL.

X-Ray investigation of iron-nitrogen alloys. A. ÔSAWA and S. IWAIZUMI (Sci. Rep. Tôhoku, 1929, 18, 79—89).—Röntgenographic examination of the substances obtained by passing ammonia over finely divided iron at various temperatures has confirmed the existence of the compounds Fe_3N and Fe_2N . The former has a cubic lattice, $a = 3.86$ Å., in which the iron atoms have a face-centred distribution and one nitrogen atom is present in the elementary cube,

$d_{\text{calc.}}$ 6.57. Fe_2N has a close-packed hexagonal lattice, $a=2.743 \text{ \AA.}$, $c/a=1.59$, one nitrogen atom being present in every elementary parallelepiped, $d_{\text{calc.}}$ 5.02. Both compounds appear to form limited series of solid solutions with one another and with iron.

A. R. POWELL.

Röntgenographic investigations on aluminium at high temperatures. A. J. ALICHANOV (Z. Metallk., 1929, 21, 127).—X-Ray examination of aluminium of 99.5% purity at temperatures up to 593° showed that no change in the lattice structure takes place other than the normal expansion due to heating, and hence that aluminium does not undergo allotropic modification, at least up to 593° .

A. R. POWELL.

Intermetallic compound having a simple cubic lattice. A. ŌSAWA (Nature, 1929, 124, 14).—Antimony-tin alloys containing 43, 50, and 5.5% Sb, respectively, annealed for 200 hrs. at 240° , 270° , and 290° , slowly cooled to 240° , maintained at that temperature for 25 hrs., and then slowly cooled to the ordinary temperature, showed an X-ray spectrum indicating a simple cubic lattice.

A. A. ELDRIDGE.

X-Ray studies on alloys. A. F. WESTGREN and G. PHRAGMÉN (Trans. Faraday Soc., 1929, 25, 379—385).—A comparative study is made of the results of X-ray analyses of alloys, with the object of tracing the regularities governing the phenomena in this field of research. The structural analogies of intermetallic phases and their connexion with the concentration of valency electrons are considered (cf. A., 1926, 1084), and a graphical representation is given of the regularities found in some binary copper and silver alloys. Special reference is made to the unique crystal structure of manganese and to the fact that in some alloys where the ratio of valency electrons to atoms is 3 : 2 (e.g., Ag_3Al , Cu_5Si) the atoms are grouped as in β -manganese. The terms "solid chemical compound" and "solid solution" are discussed, and a short account is given of the change of the average volume of the atoms in alloys with varying composition. A marked contraction takes place in all cases where chemically unrelated metals are alloyed with each other, the contraction being too pronounced to make the linear dimensions additive. This is illustrated by reference to the system silver-cadmium.

L. L. BIRCUMSEAW.

Metallic state. J. D. BERNAL (Trans. Faraday Soc., 1929, 25, 367—379).—From the point of view of crystal chemistry, metallic substances occupy a position intermediate between ionic and homopolar substances, the transition from one state to the other being almost continuous. It is proposed to classify metals into metallic ionic, metallic homopolar, and truly metallic substances. One of the most important characteristics of the metallic state is the close-packed structure observed by X-ray analysis; the closeness is more marked in the truly metallic substances, decreasing in the direction of homopolar or ionic structures. The results of X-ray studies on intermetallic compounds are shown schematically, and the fact is stressed that, although the actual structures are mostly complicated, nearly all are

variants of the close-packed structure. The criteria for the existence of distortion in a metal crystal not only enable solid solutions to be distinguished from true metals, but also establish the existence of true intermetallic compounds. The electrical properties of intermetallic compounds indicate that they are to be considered as true metals, but the majority tend more to the homopolar or ionic types. The differences between metals in respect of their dissolving power is thought to have an important bearing on the theory of electrical conduction. A hypothesis as to the nature of superconductivity (cf. Kapitza, this vol., 632) is advanced, based on the assumption that a sudden freezing out of impurities occurs at the threshold temperature. A metal in the superconductive state is postulated as being extensively cracked but with an undistorted lattice. The importance of magnetic measurements is emphasised, and the structures of certain diamagnetic intermetallic compounds which follow the Hume-Rothery rules are explained in terms of homopolar linking. The empirical requirements of the metallic linking and their possible theoretical meaning are discussed.

L. L. BIRCUMSEAW.

X-Ray examination of the system Au-Hg. A. PABST (Z. physikal. Chem., 1929, B, 3, 443—455).—An investigation of the crystal structure of gold amalgams by the powder method. It was found necessary to anneal amalgams containing less than 20% Hg at temperatures up to 300° for 18—90 hrs. in order to develop the crystals. Amalgams containing up to 15% Hg gave diagrams showing a series of mixed crystals (cubic), the side of the unit cell increasing regularly with mercury content from 4.070 Å. (pure gold) to 4.107 Å. With more than 15% Hg a hexagonal phase appears along with the mixed crystals, the latter vanishing at 25% Hg. The constants for this phase are $a_0=2.908$, $c_0=4.791 \text{ \AA.}$, approximating closely to those of a hexagonal close-packed cell containing $\text{Au}_3\text{Hg}/2$. With increasing mercury content a number of new lines appear in the diagrams, those relating to the hexagonal phase finally disappearing at 60% Hg. The new lines are probably due to two crystalline phases of undetermined structure, containing 60% and 66—68% Hg, respectively.

F. L. USHER.

Crystal structure of solid nitrogen. L. VEGARD (Naturwiss., 1929, 17, 543).—The X-ray spectrum of solid nitrogen indicates a complicated cubic lattice. The edge of the elementary cube is 11.3 Å. long and the cell contains 64 atoms. The spectrum shows only lines satisfying the condition $\Sigma h=2n$, corresponding with a body-centred lattice. The space-group is probably O^8 .

R. A. MORTON.

Crystal structure of bismuth fluoride. O. HASSEL and S. NILSSEN (Z. anorg. Chem., 1929, 181, 172—176).—The structure is based on a face-centred lattice. The unit cube has $a=5.853 \pm 0.004 \text{ \AA.}$, and contains 4 mols.; $d_{\text{calc.}}$ 8.75.

J. S. CARTER.

Crystalline structure of thorium boride. G. ALLARD (Compt. rend., 1929, 189, 108—109).—The powder method indicated a simple cubic structure with $a=4.32 \text{ \AA.}$ and one mol. of ThB_6 per unit cell. The six boron atoms are assumed to be situated at the

points of an octahedron with the thorium atoms at the centre which coincides with that of the lattice.

J. GRANT.

Crystal form of calcium sulphate. L. S. RAMSDALE and E. P. PARTRIDGE (Amer. Min., 1929, 14, 59—74).—"Soluble anhydrite" is identical in crystal structure with the hemihydrate, which is zeolitic in character. The transition temperature of gypsum to anhydrite in contact with water is 38° (?), and from gypsum to hemihydrate 98° .

CHEMICAL ABSTRACTS.

Crystal structure of dimethyldiethylammonium chlorostannate. R. W. G. WYCKOFF and R. B. COREY (Amer. J. Sci., 1929, [v], 18, 138—144).—Laue and oscillation spectral photographs have been taken of crystals of dimethyldiethylammonium chlorostannate; they have tetragonal holohedral symmetry. The unit cell has $a_0=9.065$, $c_0=14.12$ Å., and contains two molecules. It belongs to the space-group $4Di-6$, the tin and chlorine atoms having the positions: tin (a) 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; chlorine (e) $00u$; $00\bar{u}$; etc., (h) $\bar{w}v0$; $v\bar{w}0$; etc., where $u=0.177\pm 0.01$, w =about 0.23 , and v =about 0.13 . The structure is probably a distorted calcium fluoride arrangement. The nitrogen atoms are probably at (d) of $4Di-6$ (D_{2h}^6); the distribution of the carbon atoms is not determined.

C. W. GIBBY.

Structure of sillimanite and mullite. W. H. TAYLOR (Z. Krist., 1928, 68, 503—521; Chem. Zentr., 1929, i, 497—498).—A dark brown specimen of sillimanite had $a:b:c=0.980:1:0.757$; a 7.43 ± 0.03 , b 7.58 ± 0.04 , c 5.74 ± 0.02 Å. The space-group V_6^6 is preferred to C_{2v}^6 . The unit cell contains 4 mols. of Al_2SiO_5 . Crystallographically and optically, mullite is almost identical with sillimanite; the unit cell contains 1.5 mols. of $3Al_2O_3, 2SiO_2$. Kaolinite, $Al_2O_3, 2SiO_2, 2H_2O$, monoclinic prismatic, reveals in its X-ray diagram no similarity with mullite or sillimanite. The appearance of mullite lines in the diagram of ignited kaolin may be due to the formation of $Al_2O_3, 2SiO_2$, which would have a structure similar to that of sillimanite and mullite.

A. A. ELDRIDGE.

Enargite group. Structure of sylvanite, Cu_3VS_4 . W. F. DE JONG (Z. Krist., 1928, 68, 522—530; Chem. Zentr., 1929, i, 497).—Enargite, Cu_3AsS_4 , and famatinite, Cu_3SbS_4 , give almost identical Debye diagrams. Sylvanite, Cu_3VS_4 , containing Cu 51.20, V 14.20, S 34.60%, is cubic, a 10.750 ± 0.005 Å., with 8 mols. in the unit cell, space-group O_h^2 .

A. A. ELDRIDGE.

X-Ray study of microcrystalline ferric hydroxide minerals. J. BÖHM (Z. Krist., 1928, 68, 567—585; Chem. Zentr., 1929, i, 498—499).— α - Fe_2O_3, H_2O , rhombic holohedral, has a 4.60 , b 10.01 , c 3.04 Å., $a:b:c=0.459:1:0.303$, d 4.195 ; the γ -form has a 3.85 , b 12.5 , c 3.07 Å., $a:b:c=0.308:1:0.246$, d 3.97 . Most of the ferric oxide minerals examined afforded the Debye diagram of the α -form, together, in some cases, with lines arising from impurities, particularly silica. The varying water content is ascribed to adsorption. γ - Fe_2O_3, H_2O was not observed in minerals. Hämatites are of two types according to the direction of fibrillation.

A. A. ELDRIDGE.

Is the lattice of tetragonal mercuric cyanide a molecular or a radical lattice? O. HASSEL (Z. anorg. Chem., 1929, 180, 370—373).—The author maintains the interpretation put forward in a previous paper (cf. Z. Krist., 1926, 64, 217).

F. L. USHER.

Is the lattice of tetragonal mercuric cyanide a molecular or a radical lattice? R. FRICKE (Z. anorg. Chem., 1929, 180, 374—376; cf. A., 1928, 821).—A reply to Hassel (preceding abstract).

F. L. USHER.

Lattice dimensions and phase range of the magnetic substance Fe_xSb_y . I. OFTEDAL (Z. physikal. Chem., 1929, B, 4, 67—70; cf. A., 1927, 924).—The previous determination of the lattice constants of a member of the ϵ -phase in the system iron-antimony has been repeated with a new preparation, as Hägg's results (cf. this vol., 749) were not in agreement. The new result fully confirms the previous one. Some explanation of the difference is given.

A. J. MEE.

X-Ray analysis of solid carbon disulphide. J. DE SMEDT (Physica, 1929, 9, 5—8).—For a tetragonal structure, $a=b=8.12$ Å., $c=3.77$ Å.; the unit cell contains 3 mols.; $d_{calc.}$ 1.51, $d_{obs.}$ 1.55.

CHEMICAL ABSTRACTS.

Crystal structure of cis-ethylene oxide-dicarboxylic acid. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 68, 586—594; Chem. Zentr., 1929, i, 474—475).—The substance is monoclinic, $a:b:c=3.118:1:0.998$, $\beta=91^\circ 10'$; the unit cell contains 8 mols. of $C_4H_4O_5$; space-group C_{2h}^2 .

A. A. ELDRIDGE.

Crystal structure of indigotin and fumaric acid. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 68, 543—566; Chem. Zentr., 1929, i, 473—474).—Indigotin is monoclinic, $a:b:c=1.897:1:1.741$, $\beta=107^\circ 30'$; the unit cell, a 11.00 , b 5.8 , c 10.1 Å., contains 2 mols. of $C_{16}H_{10}O_2N_2$; space-group C_{2h}^2 . Fumaric acid is monoclinic, $a:b:c=0.503:1:0.438$, $\beta=111^\circ 5' \pm 5'$; the unit cell, a 7.6 , b 15.1 , c 6.65 Å., contains 6 mols. of $C_4H_4O_4$; space-group C_{2h}^2 . Yardley's results (A., 1925, ii, 1126) are criticised.

A. A. ELDRIDGE.

Crystal structure of pentaerythrityl tetraacetate. H. MÖLLER and A. REIS (Z. Krist., 1928, 68, 385—386; Chem. Zentr., 1929, i, 192).—The results of Knaggs (A., 1928, 464) are supported.

A. A. ELDRIDGE.

X-Ray examination of insulin, edestin, and hæmoglobins. W. H. GEORGE (Proc. Leeds Phil. Soc., 1929, 1, 412—415).—The powder method was used with soft X-rays from a copper or iron anticathode. No traces of crystalline diffraction effects could be obtained with insulin, edestin, or pure, freshly-prepared hæmoglobins of sheep or horse blood. It was found, however, that an old sample of methæmoglobin gave Laue diagrams, but these were probably due to decomposition products or impurities. The extreme importance of blind experiments when powder methods are used is stressed.

A. J. MEE.

Translation lattice of cellulose hydrate. K. WEISSENBURG (Naturwiss., 1929, 17, 624).—Preliminary.

R. A. MORTON.

X-Ray diffraction in liquids and solutions and the molecular structure factor. P. KRISHNAMURTI (Indian J. Physics, 1929, 3, 507—522; cf. this vol., 751).—An examination was made of substances consisting of symmetrical molecules, in the liquid state and in solutions of different concentrations. Tetranitromethane gave two rings for the liquid, of spacings 5.49 and 3.02 Å., and gave in dilute benzene or cyclohexane solution a strong scattering at small angles and a faint maximum at 3.02 Å. The strong inner ring in the liquid is due to diffraction by neighbouring molecules and is intermolecular; the faint outer ring is due to the structure factor of the molecule and is intramolecular. Hexamethylenetetramine gave in concentrated aqueous solution a broad inner maximum and an outer one at 2.86 Å.; in more dilute solutions the water ring was superposed on the latter, shifting its position to smaller angles. Dilute solutions of carbon tetrachloride in cyclohexane gave faint outer maxima in approximately the same position as in the pure liquid. The calculation of the distance between planes containing the maximum number of molecules per unit area, rather than the distance between neighbouring molecules, is discussed.

N. M. BLIGH.

What circumstance conditions the solidification in the plastic deformation of solid isotropic bodies? H. HENCKY (Z. Physik, 1929, 55, 145—155).—Theoretical.

J. W. SMITH.

Electromotive behaviour of single zinc crystals. M. STRAUMANIS (Nature, 1929, 124, 56).—No variations in the potentials of different, artificially prepared, planes of single crystals of zinc against a neutral zinc sulphate solution could be observed (cf. Anderson, this vol., 127), although the potential varied with the composition of the electrolyte and with the previous treatment of the metal. A similar equality was observed with zinc-cadmium alloys containing up to 0.2% Cd.

A. A. ELDRIDGE.

Determination of crystal potentials by diffraction of high-voltage electrons. A. G. EMSLIE (Nature, 1929, 123, 977—978).—Preliminary experiments with calcite, galena, and antimony, in which $\sqrt{V} \sin \theta$ varied rapidly with ϕ , where V is the energy of the electrons in volts and ϕ is the inner potential of the crystal, indicated that the method may be of importance for precise measurement of ϕ .

A. A. ELDRIDGE.

Effect of gases on the electric charges developed by heated metals. D. H. BANGHAM and D. R. LEWIS (J.C.S., 1929, 1140—1149; cf. A., 1914, ii, 330).—The rate of development of the charge on a cylinder of gold gauze suspended in a Jena glass tube after successive earthings, when heated at 468° and 497°, has been studied in the presence of oxygen, nitrogen, and hydrogen. With oxygen, increase of pressure caused a marked shift of the equilibrium potential towards the positive side, and the rate of attainment of the final potential, even at low pressures, was considerably slower than in a vacuum. The ions responsible for the current are not charged atoms or molecules of oxygen, but are similar to those shown by Richardson to be emitted by "new" wires, probably

sodium and potassium ions. Nitrogen gave results similar to those with oxygen. Hydrogen, on the other hand, caused a displacement of the equilibrium potential toward the negative side, and facilitated the emission of ions, the saturation current at a pressure of 0.0238 mm. being nearly four times its normal value in a vacuum.

F. L. USHER.

Magnetostriction of diamagnetic substances in strong magnetic fields. P. KAPITZA (Nature, 1929, 124, 53).—Change of shape due to distortion produced by a magnetic field on the binding forces between atoms (atomic magnetostriction) has been observed with bismuth and other diamagnetic substances. It appears probable that the linkings between the atoms which lie further apart are weakened, whilst those between the closer atoms are strengthened.

A. A. ELDRIDGE.

Magnetic permeability of nickel in feeble oscillatory fields. R. G. LOYARTE (Univ. Nac. La Plata, Estud. Cien., 1928, 209—216).—Israel's observation of complicated permeability of nickel for oscillations of wave-lengths 28—60 cm. is attributed to the dependence of damping on the period.

CHEMICAL ABSTRACTS.

Determination of magnetic permeability of iron wires at high frequency by means of Wheatstone's bridge. K. KREIELSHEIMER (Z. Physik, 1929, 55, 753—770).—A method is described for the determination of the high-frequency resistance of iron wires by direct bridge measurements. From this the magnetic permeability may be obtained. With copper wire the resistance obtained agreed with the theoretical value to within $\pm 4\%$; this relatively large error is due to the comparatively small value of the resistance to be measured. For the permeability of iron the error is $\pm 1.7\%$.

A. J. MEE.

Theory of the plasticity of metals. H. SHŌJI (Sci. Rep. Tōhoku, 1928, 18, 1—9).—Mathematical; modifications of the expression previously deduced to define plasticity (Z. Physik, 1928, 51, 728) are introduced.

A. R. POWELL.

Strength and plasticity of rock-salt crystals. E. SCHMID and O. VAUPEL (Z. Physik, 1929, 56, 308—329).—In agreement with the views of Sohncke (Ann. Phys. Chem., 1869, 137, 177) the breaking strength of rock-salt crystals is characterised by a limiting stress which can be withstood perpendicular to the cubic faces. The various possible slip mechanisms are discussed. Tempering produces a lowering of the elastic limit and of the tensile strength of rock-salt crystals. Experiments carried out with crystals stressed under water have led to results conflicting with the theory of the Joffé effect (A., 1924, ii, 384).

J. W. SMITH.

Heat effect in the stretching of brass crystals. M. MASIMA and G. SACHS (Z. Physik, 1929, 56, 394—396).—The amount of work dissipated in heat during the stretching of brass crystals has been followed by measuring the rise of temperature during the process. It was found that considerably more heat was liberated on each change in the slip mechanism than during simple slip on one slip plane.

J. W. SMITH.

Specific resistance of cupric sulphide and its temperature coefficient. K. FISCHBECK and O.

DORNER (Z. anorg. Chem., 1929, 181, 372—378).—The specific resistance of cupric sulphide has been determined, using a spiral of the material prepared by immersing a copper spiral 70 cm. long and 0.1 mm. in diameter in sulphur vapour. Three series of experiments under varying conditions gave values for the specific resistance ranging from 36.76 to 42.33 microhm per cm., and a temperature coefficient of 0.0037; this latter is markedly higher than the value found by Bädeker (cf. A., 1907, ii, 327). The resistance is proportional to the temperature over the whole range investigated, between -80° and $+400^{\circ}$.

H. F. HARWOOD.

Influence of extension and contraction of the surface in the phenomenon of triboelectricity of mercury. V. POLARA (Nuovo Cim., 1928, 5, 127—136; Chem. Zentr., 1929, i, 203).

Photo-*E.M.F.* in selenium. R. L. HANSON (J. Opt. Soc. Amer., 1929, 18, 370—382).—Three types of selenium cells and the arrangements for a detailed study of photo-*E.M.F.* are described, and this was found over a wide range of applied *E.M.F.* to be independent of the current through the cell and to be related linearly to the intensity of illumination. The photo-*E.M.F.* sensitivity has a maximum for the visible spectrum in the region 490 m μ . It is shown that the photo-*E.M.F.* cannot be a thermal *E.M.F.*; the former was found to have no direct relation with the photo-electrical conductivity effect.

N. M. BLIGH.

Electrical conductivity of vapours of salts. H. QUERENGÄSSER (Z. Elektrochem., 1929, 35, 459; cf. this vol., 634).—The work of Schmidt (A., 1927, 397), Kahra (this vol., 229), and Birkenberg (*ibid.*) is acknowledged.

H. T. S. BRITTON.

Contact potential measurements with adsorbed films. I. LANGMUIR and K. H. KINGDON (Physical Rev., 1929, [ii], 34, 129—135).—Contact *P.D.* were measured between a clean unheated tungsten filament, and the same filament coated with an adsorbed film of thorium, caesium, oxygen, or a mixture of caesium and oxygen. The method used was intended to minimise surface contamination errors. The values found for the contact potentials between cold surfaces are, Cs,O,W—W, 3.1; Cs,W—W, 2.8; Th,W—W, 1.46; W—O,W, 0.8 volts. These values do not agree with those calculated from the thermionic emission constants.

N. M. BLIGH.

Specific heats of para-hydrogen in the solid, liquid, and gaseous states. K. CLUSIUS and K. HILLER (Z. physikal. Chem., 1929, B, 4, 158—168).—A method for obtaining para-hydrogen in large quantities is described. The specific heats of the liquid and solid para-form and its m. p. were determined; within the experimental error, the values obtained agree with those for ordinary hydrogen. The specific heat of para-hydrogen exceeds the classical value for a diatomic molecule at 115° Abs., and at 160° Abs. has the value 2.79 g.-cal. The possibility of obtaining the pure ortho-form is discussed.

A. J. MEE.

Detection of a transformation of ortho- into para-hydrogen by determinations of specific heat. A. EUCKEN and K. HILLER (Z. physikal. Chem., 1929, B, 4, 142—157).—See this vol., 497.

A. J. MEE.

Determinations of the specific heat of [air,] nitrogen, and carbon dioxide at high temperature. M. CHOPIN (Compt. rend., 1929, 188, 1660—1662).—The author's methods (this vol., 44) show that for $200-1000^{\circ}$ $C_p=6.82+0.00058t$ for nitrogen and $8.9+0.61(t/100)^{0.673}$ for carbon dioxide. Air has C_p equal to that of nitrogen at 500° but 1% higher than that at 1000° . The results are compared with those of other workers.

J. GRANT.

Specific heats, heats of formation, and decomposition pressures of strontium halide hydrates. G. F. HÜTTIG and C. SLONIM [in part with L. TRIP and O. MAIER] (Z. anorg. Chem., 1929, 181, 65—77).—The above quantities have been experimentally determined and the molecular heats and total energy contents at temperatures between 50° and 350° Abs. calculated therefrom. Measurements on the dehydration of barium halide hydrates are included.

J. S. CARTER.

Lithium. VII. Specific heats, heats of formation, decomposition, pressures, and densities of lithium halide hydrates. C. SLONIM and G. F. HÜTTIG [with O. MAIER] (Z. anorg. Chem., 1929, 181, 55—64).—Determinations of the above quantities have enabled calculations to be made of the molecular heats and total energy contents at temperatures between 50° and 350° Abs.

J. S. CARTER.

Thermal data on organic compounds. V. Revision of the entropies and free energies of nineteen organic compounds. G. S. PARKS, K. K. KELLEY, and H. M. HUFFMAN (J. Amer. Chem. Soc., 1929, 51, 1969—1973).—From experimental measurements made at sufficiently low temperatures, it is found that the molal heat capacity (*C*)—temperature curves fall into two not dissimilar classes, one for aliphatic and one for cyclic compounds. In each class the various curves are essentially similar and a standard curve has been constructed which holds up to 90° Abs. In either class the equation $C_p=(A+BT)C_p$ holds quite accurately, where *A* and *B* are constants characteristic of each substance (determined by substituting known values of *C* and *T* in the equation) and C_p is the heat capacity on the standard curve at *T*. The entropy values at 25° of several organic compounds are revised, and revised values for the free energies of the compounds are calculated therefrom with an accuracy which is limited almost entirely by the accuracy of the heats of combustion involved in the calculation. The general principle that the entropy of an organic compound changes in a definite, additive manner with changes in its constitution is confirmed.

S. K. TWEEDY.

Specific heats of important metallurgical substances. W. A. ROTH and W. BERTRAM (Z. Elektrochem., 1929, 35, 297—308).—Two new types of calorimeter, designed to eliminate errors caused by evaporation of the calorimeter water on introducing the heated substance undergoing test, were used, viz., the "buffer-calorimeter" (cf. Roth, A., 1925, ii, 949) and an all-metal calorimeter in which the heated body is inserted in a silver vessel, fitted into a block of aluminium which is surrounded by a water-jacket (cf. Jaeger and Rosenbohm, A., 1928, 469).

The following data were obtained: α -Quartz,

transition point 575° , mean specific heats, at 96° , 0.1911; at 455° , 0.2325; at 503° , 0.2330. β -Quartz, $c = 0.1794 + 0.0001645(t - 20) - 0.000000085(t - 20)^2$ for $t = 575^\circ$ to 898° . Amorphous silica obtained by hydrolysing silicon tetrachloride, $c = 0.1782 + 0.000104(t - 20) - 0.0000000403(t - 20)^2$ for $t = 50^\circ$ to 933° . Quartz-glass (d^{18} 2.2058), $c = 0.1782 + 0.0001231(t - 20) - 0.00000004937(t - 20)^2$ for $t = 96.5^\circ$ to 855° . Calcium oxide, $c = 0.1823 + 0.0000879(t - 20) - 0.0000000366(t - 20)^2$ for $t = 417^\circ$ to 852° . Calcium metasilicate (d^{18} 2.9163), $c = 0.1749 + 0.0001107(t - 20) - 0.0000000485(t - 20)^2$ for $t = 50^\circ$ to 884° . Alumina, $c = 0.1930 + 0.0001382(t - 20) - 0.0000000705(t - 20)^2$ for $t = 96^\circ$ to 914° . Cryolite (artificial, d^{18} 2.9482) α -modification: transition point 565° , $c = 0.2251 + 0.0001977(t - 20) - 0.0000001086(t - 20)^2$, β -modification: from 565° to m. p., 1000° . $c = 0.2359 + 0.0001977(565 - 20) - 0.0000001086(565 - 20)^2 + 0.000100(t - 565)$. Calculation gave 1.24 kg.-cal. as the heat of transition and 16.64 kg.-cal. as the heat of fusion per mol. Sodium chloride, $c = 0.2006 + 0.00007024(t - 20) - 0.0000000375(t - 20)^2$ for $t = 99^\circ$ to 785° , m. p. 800° ; calculated heat of fusion 7.41 kg.-cal./mol. Iron (chief impurities, 0.18% P and 0.39% Mn), for temperatures up to 750° (transition point) $c = 0.1060 + 0.00006003(t - 20)$; calculated heat of transition 0.324 kg.-cal./g.-atom.

The specific heats of several iron ores were measured; the heats of formation of calcium metasilicate at temperatures varying from 20° to 900° were calculated.

H. T. S. BRITTON.

Thermal conductivity of copper, nickel, and some alloys of nickel. W. C. ELLIS, F. L. MORGAN, and G. F. SAGER (Rensselaer Polyt. Inst. Bull., 1929, 21, 1—23).—One end of a wire (0.25 cm. diam.) of the metal was heated by a coil through which a periodic current was passed so that a sinusoidal variation of temperature was produced in that end. At two points on the wire, separated by 2.3—4.69 cm., the temperatures were continuously recorded by thermocouples. The velocities (V_1, V_2) of two heat waves of different periods (T_1, T_2) were deduced from the time lag determined as the time elapsing between similar indications (passing through the zero) of the two galvanometers connected with the thermocouples. The thermal conductivity q (=g.-cal./cm./sec./ $^\circ\text{C}$.) is given by an equation, for which mathematical proof is furnished. The chief results are ($\kappa \times 10^5$ = electrical conductivity = mhos/cm., c = specific heat): copper (electrolytic) q 0.919, κ 5.58; nickel (Driver Harris R—12), q 0.168, κ 0.966; "Climax" (Fe 70, Ni 30), d 8.01, q 0.116, q 0.0329, κ 0.1052; "Climax 193" (Fe 68, Ni 29, Cr 2, Mn 1), d 8.01, c 0.114, q 0.0324, κ 0.1071; "nichrome IV" (Ni 80, Cr 20), d 8.39, c 0.104, q 0.0358, κ 0.0939; nichrome (Ni 62, Cr 12, Fe 26), d 8.40, c 0.107, q 0.0325, κ 0.0911; "Advance" (Cu 55, Ni 45), d 8.78, c 0.094, q 0.0546, κ 0.2032; Monel (Ni 70, Cu 28, Fe 2), d 8.94, c 0.132, q 0.0832, κ 0.2346. The results for copper and nickel show the accuracy of the method. The figures for the ratio thermal conductivity/electrical conductivity show that the Wiedemann-Franz law does not apply to these alloys.

C. A. SILBERRAD.

Specific heat of pure iron at high temperatures. S. UMINO (Sci. Rep. Tôhoku, 1929, 18, 91—107).—The mean specific heat of iron increases abruptly at the A3, A4, and m. p., but between these points it increases linearly with rise of temperature. The true specific heat remains constant between the A2 and A3 points, where it decreases suddenly, then rises linearly to the A4 point, where there is a sudden increase to a value which remains constant to the m. p., after which it increases rapidly with further rise of temperature. The portions of the true specific heat-temperature curve just below and just above the γ -iron range fall on the same straight line. The heats of transformation at the A3 and A4 points and the latent heat of fusion are 5.60, 1.86, and 65.65 g.-cal./g., respectively. The ratio of the heats of transformation at the A3 and A4 points, namely 3 : 1, is the same as the ratio of the changes of length at the same points.

A. R. POWELL.

Calculation of latent heats of vaporisation of hydrocarbons and alcohols. J. W. SCHULTZ (Ind. Eng. Chem., 1929, 21, 557—559).—By the use of a Dühring line giving vapour pressures with a molal entropy line constructed from known latent heats, values have been determined for the latent heats from 0° to their respective critical temperatures for benzene, *n*-heptane, *n*-hexane, *n*-octane, ethyl and propyl alcohols. Comparison with determined results shows good agreement except in the region of the critical temperature, but this can be corrected graphically by making the latent heat-temperature curve intersect the abscissa at zero for the critical temperature. With ethyl and propyl alcohols it was found that by constructing the Dühring and entropy lines using methyl alcohol for reference instead of water as with the hydrocarbons, the points fell on a straight line over a much wider range of temperature.

H. S. GARLICK.

Supercooled water. L. HAWKES (Nature, 1929, 124, 225—226).—Water cooled at -17° to -22° may remain isotropic, and possibly hard. A deposit on cooling pipes at -22° consisted of a mixture of water drops and ice.

A. A. ELDRIDGE.

Properties of some very dry organic substances. J. TIMMERMANS (Bull. Soc. chim. Belg., 1929, 38, 160—162).—Benzene, *p*-xylene, and cyclohexane, dried in sealed tubes with phosphoric oxide for 35 months, failed to show the marked alterations in f. p. and surface tension observed by Baker. The views of Smits (A., 1928, 1189) are cited as an explanation of this apparent contradiction (cf. Lenher, this vol., 872).

B. W. ANDERSON.

Theoretical basis of the kinetic theory of gases. V. GLUMAC (Z. Physik, 1929, 56, 432—434).—The fundamental equation of the kinetic theory of gases is shown to follow directly from the Bernoulli formula $p/\rho + P + c^2/2 = \text{constant}$.

J. W. SMITH.

Extension of Avogadro's law. Application to the liquid state. I. N. LONGINESCU (J. Chim. phys., 1929, 26, 312—313).—The equation $P_i/n = \text{constant}$ is derived as a general statement of Avogadro's law for fluids. The total pressure (P_i) is equal to the sum of the external (P_e) and internal (P_i) pressures, and n is the number of molecules in unit volume. For gases

$P_i = P_e$, for liquids $P_i = P_v$. In the case of different liquids having the same internal pressure it follows that $M/D = \text{constant}$, *i.e.*, that the density is a measure of the mol. wt. O. J. WALKER.

Relation between the internal pressure of fluids and some physico-chemical properties. I. N. LONGINESCU (J. Chim. phys., 1929, 26, 314—316).—An expression is obtained for the internal pressure of fluids assuming that the forces between the molecules can be represented by m^2/d^x , where d is the distance between two g.-mols., x is a constant ($=5$), and m is the "attractive mass" of a g.-mol. The latter quantity is additive and independent of temperature, pressure, and volume, but depends on the nature of the linking. The additivity of the attractive mass has been verified in 40 cases, and from it several formulæ involving the critical data of fluids can be derived. O. J. WALKER.

Effect of a gas on the pressure of a vapour. L. A. SAYCE and H. V. A. BRISCOE (J.C.S., 1929, 1302—1307).—The unsaturated vapour pressure exerted by a given concentration of ether is considerably lower in the presence of an indifferent gas (carbon dioxide at 500 mm.) than in a vacuum. The effect is even more marked with pentane vapour. The results disagree with Campbell's view (cf. A., 1915, ii, 516) that the diminution of the saturated vapour pressure of a liquid in the presence of a gas is to be attributed solely to the adsorption of gas in the liquid surface. F. L. USHER.

Saturated vapour pressures and the latent heat of evaporation. N. A. KOLOSovski (J. Russ. Phys. Chem. Soc., 1929, 61, 681—684).—Levalt-Ezerski's attempt (A., 1928, 1083) at generalising and extending the applicability of Magnus' equation for vapour pressures to all types of liquid is discussed and criticised. It is shown that his equation $\lambda = 2.3026aRT_0 = \text{constant}$, where λ is the latent heat of evaporation, is impossible and the agreement obtained between calculated and observed data is attributed to a confusion between λ , the total latent heat of evaporation, and λ_i , the internal latent heat of evaporation. A. FREIMAN.

Vapour-pressure constant of neon. K. CLUSIUS (Z. physikal. Chem., 1929, B, 4, 1—13).—The specific heats of solid and liquid neon from 11° Abs. were determined. The heat of vaporisation of neon at 0° Abs. is found to be 447.6 g.-cal. From this the vapour-pressure constant of neon is calculated to be 0.39 ± 0.04 , which is in good agreement with the theoretical value of 0.37. It is shown that the assumption of different quantum weights for neon is not justified, as it is not also for argon and hydrogen. A. J. MEE.

Generalisation of the third law of thermodynamics for the case of gases. B. A. MESTSCHERSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 775—779).—Polemical against Kolosovski (this vol., 387). A. FREIMAN.

Change of coefficient of expansion of normal liquids with temperature. K. M. STACHORSKI (Ukraine Chem. J., 1928, 3, 457—462).—The expression $\alpha = 0.17T_c/T(T_c - T)$ permits the calculation of the coefficient of expansion (α) of normal liquids for

temperatures between the b. p. and f. p. Using the data in Landolt-Börnstein tables, α is calculated for *n*-pentane, *n*-hexane, benzene, ether, ethyl acetate, ethyl propionate, fluoro benzene, chlorobenzene, carbon tetrachloride, and stannic chloride. For temperatures near the b. p. α can be assumed to be 0.18. The equations of Thorpe and Rücker (J.C.S., 1884, 45, 135), Oswald (A., 1912, ii, 230), and Davies (*ibid.*, 426) are shown to be incorrect, whilst the equations of Herz (cf. 1917, ii, 441) and of Kolosovski (A., 1927, 302) are simply limiting cases of the author's equation. For the case of associated liquids the "metacritical" temperatures (A., 1911, ii, 189) are calculated by means of the equation $T_m = T/(1 - 0.17/\alpha T)$ for ethyl alcohol, ether, and acetic acid. The results suggest that the degree of association of acetic acid does not change between its b. p. and its critical temperature. A. FREIMAN.

Vapour pressure of isopropyl acetate. C. J. HAGGERTY and J. F. WEILER (J. Amer. Chem. Soc., 1929, 51, 1623—1626).—The vapour pressures, measured between 0 and 90° by the method of Smith and Menzies (A., 1910, ii, 1037), are given by the equation $\log p(\text{mm.}) = 14.2517 - 2.0972 \log T - 2170.1/T$. The calculated b. p. is 88.2° and the calculated molal heat of vaporisation 7900 g.-cal. Determinations of the entropy of vaporisation indicate that isopropyl acetate is a normal liquid. S. K. TWEEDY.

Vapour pressure of ethylene chloride between -30° and 100°. J. N. PEARCE and P. E. PETERS (J. Physical Chem., 1929, 33, 873—878).—The vapour pressure of ethylene chloride between -30° and 100° has been determined; between -30° and 90° it can be represented, with an accuracy of less than 1 mm., by $\log p = -4481.12/T - 52.3092 \log T + 0.07153T - 0.000041847T^2 + 128.756$. Interpolation from the vapour pressure-temperature curve gives b. p. 84.1°/760 mm.; the molal heat of vaporisation at the b. p. is 7745 g.-cal.; the molal entropy of vaporisation is 21.68 g.-cal. and t_c (calc.) is 321.9°. L. S. THEOBALD.

Hydrocyanic acid. II. H. SINOSAKI and R. HARA (Tech. Rep. Tôhoku, 1929, 8, 297—342).—Measurements of the vapour density of hydrogen cyanide have been made at temperatures between 0° and 190°, and at pressures between 100 and 830 mm. The relation between PV/T and P , for 1 g. of hydrogen cyanide, is given for the 0°, 30°, and 60° isotherms by $PV/T = R - bP - cP^2$, and for the 100° and 189° isotherms by $PV/T = R - bP$. The relationships between b and c and T are given respectively by $(\log b)^2 = -2.6393 + 0.010449T$, and $\log c = 4.4533 - 0.029123T$. At constant volume the relation between P and T is not linear, but is represented by a curve, of which the curvature increases as the volume diminishes. Taking into account the association of its molecules, the behaviour of hydrogen cyanide may be expressed with an accuracy of 0.1% by an equation of the Keyes type $P = [2308.61T(1 - y/2)]/[V - 12.82e^{-78.12/y}] - 10^6 \times 28.235/[v^2 + 10^6 \times 0.290]$, $\log(V - 8)y = 15.33363 - 226.026/T - 5.7511 \log T$. The association factor of hydrogen cyanide was calculated from Keyes' equation at a series of temperatures and volumes. The value in general is small, the maximum recorded being 0.06549 at 30° and a volume of 1000 c.c./g. From

measurements of the density of liquid hydrogen cyanide between 0° and 30°, the following equation, having a probable accuracy of 2 in 150,000, was derived: $V_t = V_0(1 + 0.00200201t + 10^6 \times 6.175t^2)$.

F. G. TRYHORN.

Densities of single crystals of iron, nickel, and aluminium. S. KAYA (J. Study Met., 1928, 5, 385—386).—The densities of single crystals exceed those of polycrystals by 0.037, 0.110, and 0.034%, respectively.

CHEMICAL ABSTRACTS.

Density measurements at high temperatures. IX. Densities of molten gold, gold-silver, and silver-copper alloys. W. KRAUSE and F. SAUERWALD (Z. anorg. Chem., 1929, 181, 347—352).—Determinations of the densities by the buoyancy method at temperatures ranging from 18° to 1300° show that in all these cases the specific volumes have a linear relationship to the temperature and the composition of the alloy.

H. F. HARWOOD.

Density of molten metals and alloys. Y. MATUYAMA (Sci. Rep. Tôhoku, 1929, 18, 19—46).—The density of tin, copper, cadmium, lead, and zinc and of seven binary alloys and six ternary alloys of these metals has been measured at temperatures between the m. p. and about 500°. The values of d for the molten metals at the m. p. found by extrapolation are: tin 6.986, bismuth 10.067, cadmium 8.017, lead 10.667, and zinc 6.562; these figures agree closely with those calculated from the expansion of the solid metal and the change of volume during melting. The coefficient of expansion of all the metals tested in the liquid state is almost independent of the temperature, having only a small tendency to decrease with rising temperature. The atomic volume of the molten alloys tested is somewhat greater than that of the mean atomic volume of the constituents; the maximum deviation of about 1% occurs with alloys containing a little more than 50 at.-% of the constituent of lower d . The equation of van Laar and Lorenz connecting the heat of mixture and volume change in alloys holds good for tin-cadmium, lead-cadmium, tin-zinc, and cadmium-zinc alloys.

A. R. POWELL.

Densities of co-existing liquid and gaseous nitrous oxide. E. L. QUINN and G. WERNIMONT (J. Amer. Chem. Soc., 1929, 51, 2002—2008).—The densities of liquid nitrous oxide (D) and of the saturated vapour (d) were determined by a modification of the method of Young (J.C.S., 1891, 59, 929) over the range of -50° to 40°. The results above 0° agree with those of Villard (A., 1894, ii, 379). The law of rectilinear diameter is accurately obeyed. The critical density is 0.459 and the molecular volume at 0° Abs., calculated by Sugden's equation, is 28.1 c.c. The equations for D and d deduced for carbon dioxide by Lowry and Erickson (A., 1928, 11) do not hold satisfactorily when applied to nitrous oxide.

S. K. TWEEDY.

Densities of liquid potassium and sodium. E. RINCK (Compt. rend., 1929, 189, 39—41).—Determinations of density from the pressure exerted on a nickelled copper plunger suspended in the doubly fractionated liquid metal gave results between the m. p. and 65° represented to within 1/500 by the straight lines $d_{Na} = 0.9835 - 0.000260(t - 96.5)$ and

$d_K = 0.826 - 0.000222(t - 62.4)$. Extrapolation to 900° enabled the constant of the Lorenz law (A., 1924, ii, 761) to be calculated for the system $Na + KCl \rightleftharpoons K + NaCl$.

J. GRANT.

Limiting volume of molecules. W. HERZ (Z. Elektrochem., 1929, 35, 457—458).—The ratios molecular refraction: $b_c (= RT_c/8p_c)$, the value of the characteristic constant in van der Waals' equation at the critical point) calculated for numerous liquids, vary from 1.75×10^3 to 6.98×10^3 . Several of the liquids which gave values lower than 3×10^3 had a low b. p. or were strongly associated, whilst those corresponding with values higher than 5×10^3 either had high b. p. or contained sulphur, bromine, or iodine.

H. T. S. BRITTON.

Volume changes in the softening range of glassy substances. G. TAMMANN and W. JELLINGHAUS (Ann. Physik, 1929, [v], 2, 264—284).—Selenium, salicin, and colophony have been investigated in the glassy condition. The determination of volumes in relation to temperature and pressure in the softening range disclosed that the isotherms for lower temperatures and for higher temperatures intersect at pressures below 1000 kg./cm.² Hence the volume of the material at high constant pressure at first decreases with rising temperature and then increases. Thus the volume isobars at high pressures exhibit weakly marked minima in the softening range. The results are interpreted theoretically.

R. A. MORTON.

Compressibility of carbon monoxide at 0° and various other temperatures, from 50 to 130 atm. S. GOIG BOTELLA (Anal. Fis. Quím., 1929, 27, 315—350).—A new series of determinations has been made of the isotherms of carbon monoxide at 0°, 12.44°, and 20.22°, in an apparatus resembling that of Amagat but with refinements whereby an error of not more than 0.02% is obtained. The isotherms, which have in each case been carried beyond the minimum on the pv - p curve, show that as regards its compressibility carbon monoxide comports itself normally, its behaviour resembling that of nitrogen. Amagat's results are confirmed substantially. Minimum values of pv were found at about 90, 80, and 70 atm. for 0°, 12.44°, and 20.22°, respectively. Full details are given for correcting the observations, for determining the normal volume of the gas taken, and for the use of the compressibility of hydrogen as a reference standard.

H. F. GILLBE.

Compressibility of carbon monoxide at 0° above 50 atm. S. GOIG (Compt. rend., 1929, 189, 246—248).—A summary of the methods and results of observations at 0° between 53.58 and 127.67 atm. (cf. preceding abstract).

J. GRANT.

Viscosity of vapours of organic compounds. I. T. TITANI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 433—460).—A new capillary viscosimeter has been devised which can be used with small quantities of gases at various temperatures; it is based on the resistance offered to a mercury column in passing through a narrow glass tube. The viscosities of 16 organic vapours, sulphur dioxide, and air have been determined at several temperatures between 20° and 120°, the results agreeing with Sutherland's formula.

The molecular diameters calculated from the kinetic theory of gases are in general agreement with those deduced from van der Waals' constant b calculated from the critical data. Except in a few cases, notably acetylene and allylene, the cube roots of the molecular volumes at the b. p. are proportional to the molecular diameters. The viscosities at 0°, Sutherland's constant, and the molecular diameters for the gases investigated are tabulated. J. W. SMITH.

Viscosity of ether at low temperatures. E. VAN AUBEL (J.C.S., 1929, 1111).—The author shows that his relation between fluidity (ϕ) and temperature, $\phi = m + n \log(t_c - t)$, where m and n are constants (A., 1921, ii, 575), is, down to -92.2° , in agreement with the results of Archibald and Ure for ether (A., 1927, 404), the values used in the calculation being: $t_c = 193.8^\circ$, $m = 4003.46$, and $n = -1599.7$.

C. A. SILBERRAD.

Dielectric constant of binary mixtures. I. Methylene and ethylidene halides in benzene. P. C. MAHANTI and R. N. DAS-GUPTA (J. Indian Chem. Soc., 1929, 6, 411—417; cf. this vol., 242).—The dielectric constants of solutions of methylene and ethylidene chlorides, bromides, and iodides in benzene have been measured by the modified Nernst bridge method and the dipole moments calculated. The following values for the latter are given in electrostatic units: methylene chloride 1.61×10^{-18} , bromide 1.89×10^{-18} , iodide 2.12×10^{-18} ; ethylidene chloride 1.95×10^{-18} , bromide 2.12×10^{-18} , iodide 2.30×10^{-18} . The results afford further support for the mechanism of the molecular model previously suggested.

F. L. USHER.

Dielectric polarisation of liquids. IV. Dependence of molar refraction on concentration in mixtures. C. F. SMYTH, E. W. ENGEL, and E. B. WILSON, jun. (J. Amer. Chem. Soc., 1929, 51, 1736—1744).—The values of n_D^{20} were measured for several liquid pairs. The molecular refractivities of the components of a mixture are independent of the concentration to within 0.07%, indicating that the contribution to the polarisation of the electronic shifts induced in a molecule is practically independent of the surrounding molecules. This result does not support Sidgwick's views on the nature of molecular association in hydroxyl compounds. The fact that, e.g., alcohols, which according to Sidgwick are associated, fail to show a change of refraction on evaporation greater than that shown by supposedly unassociated substances also affords evidence that actual sharing of electrons between molecules during association of hydroxyl compounds does not occur.

S. K. TWEEDY.

Viscosity of binary systems with guaiacol as a component. N. A. PUSCHIN and T. PINTER (Z. physikal. Chem., 1929, 142, 211—226).—The authors discuss the trustworthiness of viscosity-concentration diagrams in their application as criteria for the existence of association or dissociation in binary systems. The viscosity and density of the binary mixtures of guaiacol with phenylhydrazine, quinoline, pyridine, aniline, *o*-toluidine, acetone, benzene, toluene, and mono- and di-methylaniline have been determined at 30°. The viscosity-composition and density-com-

position curves have been compared with the m. p.-composition curves. It is shown that the compounds of guaiacol with the first five amines as indicated by the thermal analysis are characterised by a maximum in the viscosity-composition curve. The position of the maximum shows that, except in the case of phenylhydrazine, the compounds are largely dissociated at 30°. The viscosity-composition curves of guaiacol with the other five substances are convex to the concentration axis. It is suggested that in these systems the association of guaiacol is less. F. J. WILKINS.

Viscosity formula for binary mixtures, association of the constituents being taken into consideration. III. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, 4, 149—152; cf. this vol., 500).—The equation of Dunstan and Wilson (J.C.S., 1907, 91, 90) connecting η and mol. wt. can be written in the form $\log \eta = a + bM$. Data for the paraffins and their simpler derivatives show a to have the mean value of -3.22 , almost independent of temperature, whilst b varies with temperature and from one homologous series to another. For various liquids at 25° the values of b and of the field-constant k (*loc. cit.*) are practically the same when both are compared with those for benzene. L. S. THEOBALD.

Lowering of the vapour pressure in concentrated solutions of two volatile components. E. KORDES (Z. anorg. Chem., 1929, 181, 203—224).—From Raoult's law it is deduced that the relative lowering of the vapour pressure of two volatile liquids in concentrated solutions may be expressed: $(P_b - p_b)/P_b : (P_a - p_a)/P_a = a : b$, where P_a and P_b are the vapour pressures of the two components in the pure state, p_a and p_b the corresponding partial pressures in the solution, and a and b the concentration in mol.-% of the respective liquids. If P_x is the total vapour pressure of the solution, it follows that $p_b/p_a = (b + a[(P_x - P_a)/P_a]) / (a + b[(P_x + P_b)/P_b])$. Thus if the composition of the liquid phase and the values of P_a and P_b are known, the composition of the vapour phase can be calculated if the total vapour pressure of the solution is determined. The calculated values for the systems nitrogen-oxygen at 74.7° Abs., water-formic acid at 80°, water-acetic acid at 80.09°, and acetone-chloroform at 55.1° agree reasonably well with those found experimentally. In the case of acetone-chloroform mixtures at 28° the calculated values are lower than the experimental values owing to the formation of the 1:1 compound. Molecular association in the vapour phase has no appreciable effect on the validity of the equations. The second equation may be modified to give the composition of the vapour phase at the b. p. of the mixture by substituting the relative molecular proportions of the compounds, b'/a' , for the relative partial pressures on the left-hand side. If c is the equilibrium constant of the system, then $a'/b' = p_a/p_b = (a/b)(P_a/P_b)^c$; for an ideal system c should equal 1, and the extent of its deviation from this value indicates the extent by which the system deviates from the ideal. For oxygen-nitrogen the deviations are very small, but for chloroform-acetone mixtures the value of c rises from -2 to $+4$ with increasing acetone concentration and for water-acetic acid mixtures from 0.2 to 2.3

with increasing acidity, although for mixtures containing 20–80 mol.-% of acid the value of c is approximately 1. The form of the various equations deduced for the lowering of the vapour pressures of the components of mixtures is similar to that of the equations previously deduced for the position of the eutectic point (cf. A., 1927, 1132). A. R. POWELL.

Determination of the b.-p. diagrams of high-boiling liquid mixtures. E. KORDES and F. RAAZ (*Z. anorg. Chem.*, 1929, **181**, 225–236).—The apparatus of Ruff and Korschak (A., 1927, 102) has been used to determine the b. p. and vapour pressure of the systems mercury–cadmium and sodium chloride–potassium chloride and the composition of the vapour phase has been calculated by the method described in the preceding abstract. In the metal system the b. p. of the mixture rises in a smooth curve convex to the axis of composition, whereas the curve giving the composition of the saturated vapour phase is concave to this axis. In the salt system the curve is slightly concave to the axis of composition, joining the b. p. of the two constituents, 1411° for potassium chloride and 1430° for sodium chloride, and passing through a maximum at 1437° with 50–70 mol.-% of sodium chloride. The saturated vapour curve is almost identical with the b.-p. curve.

A. R. POWELL.

Binary azeotropes. XIV. M. LECAT (*Ann. Soc. Sci. Bruxelles*, 1929, **49**, B, ii, 109–118; cf. this vol., 756).—A further list is given of 81 positive azeotropes and 47 negative azeotropes, of 10 which are almost positive and 8 which are almost negative. The list includes 58 non-azeotropic pairs in which the isobar is convex towards the concentration axis, 34 in which it is concave, and 23 in which it is practically rectilinear; also 20 other non-azeotropic systems, and 10 in which rapid reaction takes place.

C. W. GIBBY.

Azeotropism in binary systems containing a phenol. M. LECAT (*Ann. Soc. Sci. Bruxelles*, 1929, **49**, B, ii, 119–143).—467 binary systems in which one constituent is phenolic have been investigated. Negative azeotropism is shown with alcohols (except glycol), ketones, and esters, positive azeotropism with glycol, acids, nitro-derivatives, halogen derivatives, and hydrocarbons, whilst amides, amines, and ethers generally exhibit no azeotropism. C. W. GIBBY.

Concentrated solutions. V. P. SCHSCHOKIN (*Z. anorg. Chem.*, 1929, **181**, 137–153; cf. Mortimer, A., 1923, ii, 299).—Investigation of the f.-p. curves of a large number of binary systems has shown that the individual branches are represented by the equation $S = ke^{-a/T}$, where S is the concentration of the crystallising constituent, T the absolute temperature of the commencement of crystallisation, and k and a are constants, provided that the heat of fusion of the constituent derived from thermodynamic considerations is not greatly different from the actual value. Deviations from the exponential relation are indicative of reaction between the constituents. If binary mixtures of a substance A with substances B and C conform to the requirements of the exponential relation, this relation will also hold for mixtures of B and C . If the system $A-B$ obeys the relation and

the system $A-C$ does not, the relation will not apply to the system $B-C$.

J. S. CARTER.

Liquid mixtures of tellurium and sodium telluride. I. Specific resistance as a function of composition and temperature. II. Phase diagram of the system tellurium–sodium telluride. C. A. KRAUS and S. W. GLASS (*J. Physical Chem.*, 1929, **33**, 984–994, 995–999).—I. The specific resistances of liquid mixtures of tellurium and sodium telluride have been measured at concentrations up to 54 at.-% Na and at temperatures between 300° and 500°, using a fused quartz cell of the type previously described (Kraus and Johnson, A., 1928, 1181). Mixtures rich in tellurium conduct well and behave as metallic conductors, whilst those rich in sodium telluride approximate to fused salts and conduct electrolytically. In all cases, the specific resistance decreases almost exponentially with a rise in temperature. Contrary to Pellini and Quercigh (A., 1910, ii, 1062), sodium telluride and tellurium appear to be completely miscible in the liquid state and the curves indicate the formation of the compound Na_2Te_6 with a congruent m. p. at 436°. A method for the preparation of these alloys by the addition of tellurium to sodium dissolved in liquid ammonia is described.

II. The equilibrium diagram for the system tellurium–sodium telluride has been determined by thermal analysis and shows complete miscibility of the components (see above). In addition to the normal telluride Na_2Te , the compounds Na_2Te_2 and Na_2Te_6 exist, the former showing a transition point at 355° and the latter a congruent m. p. at 436°, in agreement with the temperature found by the electrical method. Eutectics corresponding with the solid phases Na_2Te_2 and Na_2Te_6 , and Na_2Te_6 and tellurium, occur at 319° and 43 at.-% Na and 402.5° and 12.5 at.-% Na, respectively.

L. S. THEOBALD.

Copper–aluminium [alloys] containing tin or cobalt. E. MORLET (*Compt. rend.*, 1929, **189**, 102–104).—Manganese (1–6%) increases the hardness and electrical resistance of copper–aluminium alloys containing 80–90% Cu and dissolves in the α - and γ -constituents without formation of a special constituent. Less than 6% of tin is dissolved when the aluminium content is below 80%, but otherwise a special δ -constituent is produced. Tin induces fragility. Cobalt dissolves in the α - and (α + eutectic)-constituents to the extent of 1.27% and 1.66%, respectively, but higher proportions produce special constituents in each case.

J. GRANT.

Constitution of copper–beryllium alloys. G. MASING and O. DAHL (*Wiss. Veröff. Siemens-Konz.*, 1929, **8**, [1], 94–100).—The system beryllium–copper has been investigated by microscopical and conductivity methods up to 12% Be. The saturated α -solid solution contains 2.8% Be at the peritectic temperature 865°, 1.72% at the eutectoid temperature 578°, and 0.75% at 400°. The eutectoid composition is 6% Be and the (α + γ)-field extends from 1.72 to 11% at 578°. The β -field is bounded by slightly convex lines joining the eutectoid point with the peritectic at 4.2% and the solidus at 10.5%,

respectively. Numerous photomicrographs showing the characteristics of the various phases in copper-beryllium alloys are included. A. R. POWELL.

Magnetic measurements on iron-beryllium alloys. O. VON AUWERS (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 236—247).—The saturation value, coercivity, remanence, and permeability of beryllium-iron alloys containing up to 4% Be have been determined before and after heat treatment. With more than 3% Be the coercivity and wattage losses increase very rapidly, especially when carbon is also present; these alloys are therefore of no value for electrical apparatus. Alloys with less than 3% Be and some silicon have similar properties to silicon-iron alloys. The maximal permeability, μ_{max} , remanence, B_r , and coercivity, H_c , are related by the expression $\mu_{max} = 0.488B_r/H_c$. A. R. POWELL.

Changes in the etching structure of beryllium-copper alloys during ageing. G. MASING and O. DAHL (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 149—153).—During the ageing of beryllium-copper alloys at 350° the α - and β -crystals on etching with ammoniacal copper sulphate solution show a series of crystallographically regularly oriented lines which gradually increase in number and intensity. This phenomenon is ascribed to the gradual precipitation of γ from supersaturated α and from the breakdown of the β -phase. The lines are most intense when the hardness is at a maximum; further heating results in their slow disappearance. A. R. POWELL.

Changes during the ageing of beryllium-copper alloys observed by röntgenographic methods. O. DAHL, E. HOLM, and G. MASING (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 154—186).—The α -solid solution phase in beryllium-copper alloys has a face-centred cubic lattice which in the case of the alloy with 2.5% Be has a parameter of 3.564 Å. compared with 3.619 Å. for pure copper. The γ -phase has a body-centred cubic lattice, $a = 2.70$ Å., in which the copper and beryllium atoms are regularly distributed, corresponding with the compound CuBe. On ageing the alloy with 2—2.5% Be at 350° the presence of γ is shown in the röntgenograms after 10 min.; at 150° the (331) line of the α -phase begins to become fogged after 4 hrs., indicating the beginning of the separation of γ , which causes a certain amount of internal stress. Wire which has been drawn after quenching hardens on ageing more rapidly and at lower temperatures than unworked wire. The crystals of the γ -phase after ageing have the same fibrous structure as the original α -crystals but are differently oriented, the (110) planes instead of the (111) planes being parallel to the direction of rolling. A. R. POWELL.

Aluminium and its solid solutions with silicon. W. KÖSTER (Z. anorg. Chem., 1929, 181, 295—297).—A criticism of the work of Anastasiadis (this vol., 501), the results of which are considered to be erroneous owing to insufficient annealing. The most probable boundary of the α -solid solution phase in the aluminium-silicon system is that found by Dix and Heath (B., 1928, 126). A. R. POWELL.

Germanium. XXXI. Alloys of germanium: silver-germanium. T. R. BRIGGS, R. O. McDUFFIE, and L. H. WILLISFORD (J. Physical Chem., 1929, 33, 1080—1096).—The equilibrium diagram for the system silver-germanium has been determined from thermal and metallographic data for temperatures between 600° and 1000°. The solid phases in equilibrium with the fused mass are pure germanium and a solid solution of germanium in silver. When saturated, this solid solution contains 6—7 at.-% Ge at 650°. No stable compounds are formed in the range investigated and the alloys form a simple eutectic series; the eutectic temperature is 650° and the eutectic composition 74 at.-% Ag. The specific conductances of the alloys from pure silver to the eutectic are low when compared with the values calculated from the mixture rule and lead to the conclusion that in the fine-structure of these particular alloys germanium predominates as the continuous phase. Comparison of this system with the silver-silicon and silver-tin systems shows it to be intermediate between silver and tin as regards the properties of the silver alloys. Photomicrographs are reproduced. L. S. THEOBALD.

Crystalline form in the formation of solid solutions. V. Thermal and X-ray analyses of the systems $\text{CoCl}_2\text{-FeCl}_2$ and $\text{MnCl}_2\text{-FeCl}_2$. A. FERRARI, A. CELERI, and F. GIORGI (Atti R. Accad. Lincei, 1929, [vi], 9, 782—789).—No decomposition of the mixed crystals in these systems could be detected by the thermal method. An X-ray examination of the system $\text{CoCl}_2\text{-FeCl}_2$ shows that with increasing percentage of ferrous chloride the cobalt chloride lattice is increased in size (7.05—7.155 Å.), whilst the rhombohedral angle remains constant at 60°. In the second system, a doubling of lines was observed due to the occurrence in the mixed crystals of a rhombohedral lattice with an angle different from 60° which is peculiar to pure ferrous chloride. In this case with increasing manganese chloride content a increases from 7.16 to 7.20 Å., α from 60° 17' to 61° 25', and c/a decreases from 2.434 to 2.370. F. G. TRYHORN.

X-Ray study of the formation of zinc silicates. A. PABST (Z. physikal. Chem., 1929, 142, 227—232).—Mixtures of zinc oxide and silica in the proportions required for the formation of zinc ortho- and metasilicates were heated at varying temperatures and powder photographs of the products were prepared. Zinc metasilicate is not formed, the orthosilicate being always obtained even when the composition corresponds with the metasilicate. Further, the results support the statement of Tammann (A., 1926, 921) that the reaction between zinc oxide and silica begins at 775°. F. J. WILKINS.

Miscibility of phenol with aqueous salt solutions. G. CLAXTON and H. M. DAWSON (Proc. Leeds Phil. Soc., 1929, 1, 416—420).—The solubility of phenol in aqueous solutions containing varying amounts of salts is determined. In all cases the exponential formula $S = S_0 \cdot e^{-km}$ is obeyed, where S_0 and S are the concentrations in pure water and in the aqueous solution, respectively, m is the molar concentration of the salt, and k is a constant. The

salts used were sodium chloride, sodium sulphate, and calcium chloride. It would be expected, however, that S_0 would be independent of the nature of the dissolved salt. This is not the case. The deviation is probably connected with the interionic forces which are responsible for the deviations shown by electrolytes in dilute solutions. The constant k also varies with the nature of the salt. A. J. MEE.

Solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°. G. L. FREAR and J. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 2082—2093).—The solubility of calcite at 25° is recorded for various partial pressures (p) of carbon dioxide. The solubility product (in terms of activity) is 4.82×10^{-9} . The concentration of calcium hydrogen carbonate in solution varies approximately as the cube root of p . The solubility of calcite in solutions of gypsum and of sodium chloride at values of p up to 1 atm. was also measured. No solid solution or double salt formation occurs when these salts are present in solid phase. The ratio of the solubility of calcite in a dilute salt solution of constant concentration to that in water is independent of p . The activity coefficients of calcium hydrogen carbonate are calculated; they are higher than usual for salts of the uni-bivalent type. S. K. TWEEDY.

Solubility of magnesium carbonate (nesquehonite) in water at 25° and pressures of carbon dioxide up to 1 atm. W. D. KLINE (J. Amer. Chem. Soc., 1929, 51, 2093—2097).—The solubility at 25° of magnesium carbonate trihydrate is recorded for pressures of carbon dioxide up to 1 atm. At high pressures the trihydrate is the stable solid phase, but below $p=0.0004$ atm. magnesium hydroxide becomes the stable salt. There is no evidence of definite basic carbonates. The solubility product (in terms of activity) is 1×10^{-5} for magnesium carbonate and about 5×10^{-12} for magnesium hydroxide. S. K. TWEEDY.

Solubility of the phosphates of calcium in aqueous solutions of sulphur dioxide. W. M. MEBANE, J. T. DOBBINS, and F. K. CAMERON (J. Physical Chem., 1929, 33, 961—969).—The system lime-phosphorus pentoxide-sulphur dioxide-water has been investigated analytically at 0° and 25° in relation to the possibility of a technical process for the manufacture of monocalcium phosphate or superphosphates. The addition of sulphur dioxide to aqueous suspensions of the phosphates of calcium increases the solubility of both the lime and the phosphoric acid, the former to a greater extent than the latter. Three solubility curves have been obtained. For small concentrations of phosphoric acid the solubility of sulphur dioxide in the liquid phase rises to a maximum and then falls, the solid phases being calcium sulphite and a series of solid solutions of which dicalcium phosphate is a limiting member. For medium concentrations of phosphoric acid the solubility of sulphur dioxide again reaches a maximum and the solid phases consist of the mono- and di-phosphates. For high concentrations of phosphoric acid the solubility of sulphur dioxide is approximately constant and negligible, and the solid phase is monocalcium phosphate. Treatment of a

phosphatic rock with sulphur dioxide yields a solution in which the ratio P_2O_5/CaO is only slightly greater than in the dicalcium salt, and the large percentage of water to be removed makes the process impracticable on a large scale. L. S. THEOBALD.

Germanium. IV. Solubility of germanium dioxide in acids and alkalis. W. PUGH (J.C.S., 1929, 1537—1541).—The solubility at 25° of germanium dioxide has been determined in hydrochloric acid solutions (up to 7.62*N*), in sulphuric acid solutions (up to 95%), and in sodium hydroxide solutions (up to 0.1*N*). As an acid oxide its solubility is repressed by hydrochloric acid, reaching a minimum of 0.074 g./100 c.c. at an acid concentration of 5.3*N*. In sulphuric acid the solubility falls steadily with increase of acidity, no evidence occurring of the formation of germanium sulphate. Solutions in sodium hydroxide solution are colloidal and may contain salts of condensed germanic acid. F. G. TRYHORN.

Oxidisability of silicon and its solubility in hydrofluoric acid. C. BEDEL (Compt. rend., 1929, 189, 180—182).—The author has failed to repeat Sanfourche's experiments (this vol., 1030), which suggested that the solubility of silicon in hydrofluoric acid is the result of previous oxidation in air. The catalytic effect of impurities is regarded as a more likely explanation (cf. this vol., 756). J. GRANT.

Solubility of arsenic tri- and penta-sulphides. R. HÖLTJE (Z. anorg. Chem., 1929, 181, 395—407).—The solubility of the two sulphides in pure water and hydrogen sulphide solution at 0° has been determined by an analytical method, the sulphide being digested with the solvent for several days, the solution filtered through a Zsigmondy ultra-filter, and the dissolved arsenic determined iodometrically in the filtrate. One litre of water at 0° dissolves 0.89 mg. of arsenic trisulphide and 1.36 mg. of the pentasulphide, but in the presence of 0.002% of hydrogen sulphide these amounts are reduced to 0.23 mg. and 0.27 mg., respectively. Higher concentrations of hydrogen sulphide increase the solubility of the sulphides, but this effect is offset by the presence of hydrochloric acid, being probably due to the formation of small amounts of arsenic thio-acids. For analytical purposes the precipitation of arsenic trisulphide by hydrogen sulphide from a solution containing hydrochloric acid is complete as soon as the solution has become saturated with the gas, but in the case of the precipitation of the pentasulphide by the addition of acid to a thioarsenate solution it is preferable to keep the liquid over-night before filtration; removal of the excess of hydrogen sulphide is unnecessary. H. F. HARWOOD.

Solubilities of the soluble electrolytes. I. Relationships between the temperature coefficients. A. F. SCOTT (J. Physical Chem., 1929, 33, 1000—1014).—A theoretical paper in which certain relationships between the temperature coefficients of solubility are deduced and an explanatory theory is outlined. The ratio of the temperature coefficients for a pair of salts which fulfil certain conditions is independent of the temperature. The

ratio at different temperatures is identical for all salts with the same dominant ion, *i.e.*, an ion which, in a saturated solution of a very soluble salt, controls the water molecules to the exclusion of the weaker ion. The solubilities of potassium chloride, bromide, and iodide and of rubidium and caesium chlorides are represented by the equation $N_{\text{salt}} = aN_{\text{KCl}} + b$, where N is number of mols. of water per mol. of salt and a and b are specific constants. Between 0° and 100° the ratio of the temperature coefficients for any of these salts is determined by the characteristic constant a . The significance of the discontinuities now revealed in the solubility curves of various salts is also discussed. L. S. THEOBALD.

Factors affecting solubility. L. J. WEBER (Z. anorg. Chem., 1929, 181, 385—394).—Correlation of Rothmund's solubility determinations for lithium carbonate, silver sulphate, and potassium bromate in the presence of various non-electrolytes with Traube's surface tension values for the latter shows that the diminution of solubility increases in inverse ratio to the surface tension of the added non-electrolyte. Experiments with potassium sulphate also indicate a relationship between solubility and surface tension, but the results are less easily interpreted than those preceding. Similar data for potassium hydrogen tartrate, sodium oxalate, potassium chlorate, and lead chloride in the presence of 21 non-electrolytes agree with the first series in the case of the alkali salts, but the results for lead chloride are untrustworthy owing to the formation of compounds. Conversely, salts which lower the surface tension of water increase the solubility of certain non-electrolytes, *isoamyl alcohol*, for example, being 275 times as soluble in a 30% solution of sodium cinnamate as in pure water. H. F. HARWOOD.

Solubility and dissolution velocity of solids. N. E. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 369—374).—Regarding the process of dissolution of a solid in a liquid as a gradual change and applying the ideas developed by Richardson for the emission of electrons from hot bodies, it is deduced that the critical increment of solution is given by $E = Q' + RT/2$, where Q' is the heat of dissolution of the dissolving substance, and that $K/C\sqrt{T} = \text{const.}$, where K is the dissolution coefficient and C the solubility. On the other hand, the diffusion theory of dissolution leads to $E = W + RT$, where W for most of the solids investigated is identical with the latent heat of fusion, and $d \log_e K/dT = d \log_e \phi/dT + 1/T$, where ϕ is the fluidity.

Experiments on the solubility of benzoic acid at 20° , 40° , and 60° according to Wilderman's method (Z. physikal. Chem., 1908, 66, 445) support the conclusions of the author's theory rather than those of the diffusion theory. A. FREIMAN.

Solubilities of inorganic salts. S. S. URAZOVSKI (Ukraine Chem. J., 1929, 4, 7—12).—Fajans' theory (Naturwiss., 1923, 11, 1165) which attempts to explain the different solubilities of inorganic salts by the different degrees of deformation of their outer electronic shells is shown to be incorrect. It is suggested that the solubilities are determined by the difference in the atomic numbers between the cation

and anion and that the solubility is lowest when the difference is a minimum, and *vice versa*.

A. FREIMAN.

Distribution of trichloroacetic acid between water and organic solvents. L. M. ANDREASOV (Ukraine Chem. J., 1928, 3, 463—465).—The distribution of trichloroacetic acid between water and benzene, water and nitrobenzene, water and chloroform, water and carbon disulphide, and water and carbon tetrachloride has been determined. In benzene, nitrobenzene, chloroform, and carbon disulphide double molecules are formed, whilst in carbon tetrachloride the acid exists in single molecules. These results disagree with those found by ebullioscopic and cryoscopic methods by other workers.

A. FREIMAN.

Attempted measurement of the partition coefficient of a colloid, gelatin, between two liquids. R. M. WOODMAN and P. H. GALLAGHER (J. Physical Chem., 1929, 33, 1097—1106; cf. A., 1926, 676).—Measurements of the distribution of gelatin between water and cresol have been attempted, and a partition hypothesis relating to the mechanism of the formation of the emulsions and of the dual types (*loc. cit.*) which complicate the system is advanced. The gelatin is said to be in the colloidal state in both solvents, but the large experimental errors preclude the possibility of determining whether any difference in partition accounts for the formation of two types of emulsion. The partition coefficient, calculated on the simple law, largely favours the cresol. The hypothesis that cresol extracts the gelatin completely from the aqueous solution is untenable, and on the assumption that the partition is mainly determined by the mutual solubility of the two solvents the value 66.6 in favour of the cresol is obtained. This agrees with the experimental values of 73 and 69 found for two different concentrations of gelatin at 13.5° . The stability of the water-in-cresol and the instability of the cresol-in-water emulsions are explained by the fact that the partition coefficient favours the cresol layer. L. S. THEOBALD.

Adsorption with active charcoal. E. ENGEL (Svensk Kem. Tidskr., 1929, 41, 157—168).—The nature of the adsorption of gases by charcoal is discussed. The "resistance time" of a charcoal, *i.e.*, the length of time required for a definite amount of charcoal to remove a substance from a current of air charged with the vapour of the materials, is given by Mecklenburg's equation, $R = k/vC(V - Qh)$. The values of R , k , and h have now been determined for four different varieties of charcoal, using chlorine, carbonyl chloride, and chloropicrin as the substances to be removed. The results show that for one and the same charcoal adsorption takes place most readily with the substance of greatest mol. wt., but no regularity between the different samples is traceable. Only one of the samples gave results conforming to Freundlich's formula for adsorption isotherms, the other three showing marked divergences. In the removal of a constituent from a gas current by passage through charcoal, the speed of the gas current, the size of the charcoal particles, and the presence of moisture all have a marked influence

on the efficiency of the adsorption, and these factors must therefore be taken into account in technical applications.

H. F. HARWOOD.

Sorption of water vapour by activated charcoals. II. Isothermals in presence of air. A. J. ALLMAND, R. CHAPLIN, and D. O. SHIELDS (J. Physical Chem., 1929, 33, 1151—1160; cf. A., 1928, 471).—Data relating to the rates of sorption and desorption of the charcoals previously described (*loc. cit.*) show that the rates, in general, are less than 0.5 mg. of water vapour per g. of charcoal per mm. pressure difference per hr., that sorption is less rapid than desorption at low and medium pressures but more rapid at higher pressures, that the three charcoals investigated show little difference between each other or when evacuated at 270° or 800°, and, finally, that for any given isotherm the maximum rate of sorption or desorption occurs in the intermediate pressure range over which a small pressure difference corresponds with a large change in the amount of water vapour sorbed. All the isotherms studied show considerable hysteresis and those given by the different charcoals previously evacuated under practically identical conditions differ considerably from each other. Lastly, the effect of the temperature of outgassing is quite definite, for charcoals outgassed at 800° compared with those outgassed at 270° show a larger increase in weight on saturation with air, a higher saturation value, more marked hysteresis, and a greater tendency to retain water after passing dry air at 25°. A discussion of results is reserved.

L. S. THEOBALD.

Sorption of water vapour by activated charcoals. III. Isothermals in presence of nitrogen. A. J. ALLMAND and P. G. T. HAND (J. Physical Chem., 1929, 33, 1161—1166).—A repetition of previous work (cf. preceding abstract) with a current of nitrogen replacing that of air shows that oxygen has no retarding effect on the processes concerned with the adsorption of water vapour by charcoal. The rates of sorption and desorption and the isotherms are similar to those obtained in the presence of air; the hysteresis is of the same magnitude, and the effect of a higher outgassing temperature is even more marked.

L. S. THEOBALD.

Heat of adsorption of oxygen on [coconut] charcoal. M. J. MARSHALL and H. E. BRAMSTON-COOK (J. Amer. Chem. Soc., 1929, 51, 2019—2029).—The differential heat of adsorption, Q , was measured down to very low oxygen concentrations. The Q - c curves, c being the concentration of the oxygen in the charcoal, tend to flatten near $Q=70,000$ g.-cal. (Keyes and Marshall, A., 1927, 207) and then rise abruptly, so that at $c=0$ Q is about 89,600 g.-cal. A curve constructed from the results shows the apparent distribution of activities of the elementary spaces on the carbon surface; the curve does not, as a whole, resemble the probability curve, and three possible explanations of the shape of the curve are discussed. At least 85% of the total elementary spaces have heats of adsorption below 8000 g.-cal. The results are best explained by the multimolecular layer theory of Keyes and Marshall. The specific

surface of the carbon is estimated to be $3-6 \times 10^4$ cm.² per g.

S. K. TWEEDY.

Interferometric investigation of adsorption by pure carbon from non-aqueous binary systems. F. E. BARTELL and C. K. SLOAN (J. Amer. Chem. Soc., 1929, 51, 1637—1643).—The adsorption of 1-bromonaphthalene, benzene, and ethyl carbonate from dilute solution in ethyl alcohol conforms to Freundlich's adsorption isotherm at the low solute concentrations investigated. The order of adsorption from dilute solutions is the same as that of the adhesion tension of the pure solutes against carbon, a result which would probably be universal if external factors did not interfere.

S. K. TWEEDY.

Adsorption by pure carbon from non-aqueous binary systems over the entire concentration range. F. E. BARTELL and C. K. SLOAN (J. Amer. Chem. Soc., 1929, 51, 1643—1656).—The work described in the preceding abstract is extended to the entire concentration range, additional binary systems also being investigated. The component with the higher adhesion tension against carbon is adsorbed to the greater extent, although the other component when it is present at very low concentration is preferentially adsorbed, which causes the adsorption curves to be S-shaped. The adsorption is represented by an equation similar to that used by Ostwald (A., 1923, ii, 128); this equation is derived on the assumption that the adsorption of each component follows Freundlich's adsorption isotherm. Gibbs' adsorption principle is restated in terms of adhesion tension, which restatement indicates the importance of many factors usually ignored in the formulation of the principle, *e.g.*, electrical properties of the boundary layer etc. Adsorption from binary systems by silica, as in the case of carbon, depends on the adhesion tension of the adsorbed component against silica.

S. K. TWEEDY.

Charcoal as an adsorbent. II. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1929, 61, 587—594).—The adsorption of organic and inorganic acids on sugar charcoal prepared by carbonisation at 500° increases with the capillary activity of the acid. In the case of charcoal similarly prepared at 800°, the adsorption follows the reverse order. This difference is due to the presence of amorphous carbon in the first and of microcrystalline carbon in the second product. Neither of these charcoals adsorbs alkalis if they are previously freed from adsorbed carbon dioxide. Similar effects are obtained with wood charcoal, provided that this has previously been freed from inorganic salts. The inactivation of charcoal by prolonged heating at high temperatures appears to be due to the coating of its surface with graphite.

R. TRUSZKOWSKI.

Adsorption and volume of solution. A. RABINERSON (Kolloid-Z., 1929, 48, 231—237).—Measurements of the adsorption of succinic and acetic acids by vegetable charcoal show that when the amounts of adsorbent and adsorbed material are kept constant the degree of adsorption decreases with increasing volume of solution. Over a fairly wide region, the following equation was found to be valid: $x = kv^{-1/n}$,

where x is the amount adsorbed, v is the volume, and k and n are constants. The exponent $1/n$ is not identical with that of the ordinary adsorption equation: it has a lower value. Comparison of the curves relating the amount adsorbed to the amount of adsorbent and the curves relating the amount adsorbed to the amount of substance before adsorption shows that in each case the former curve passes through higher values, and leads to an explanation of the variation of the amount of adsorption with the volume. In regions of high concentration or low volume the x - v curve changes its sign, and the complete curve consists of two branches, the first rising and the second falling.

E. S. HEDGES.

Influence of hydrogen-ion concentration on the adsorption of weak electrolytes by pure charcoals. H. J. PHELPS and R. A. PETERS (Proc. Roy. Soc., 1929, A, 124, 554—568).—The importance of this subject with respect to enzyme chemistry is emphasised, and previous work is briefly reviewed. Commercial norit charcoal, purified by Miller's method (A., 1926, 898) and activated by heating to redness in a vacuum, was used, and various p_H values were obtained, in the case of simple acids and bases, by partial neutralisation with strong acids and bases, and in the case of other substances by the addition of small amounts of buffer solutions. The equilibrium p_H values were determined by the bubbling hydrogen electrode except in the case of very dilute histidine and histamine solutions, where the colorimetric method was made. The analytical methods adopted for the determination of propionic and hexoic acids, succinic acid, n -propylamine and n -butylamine, and glycine, alanine, glutamic acid, aspartic acid, histidine, and histamine are described. Propionic, hexoic, and succinic acids are decreasingly adsorbed with increasing alkalinity between the limits p_H 3.0 and 7.0, and the change follows approximately the ionisation curves of the acids. In the case of n -propylamine and n -butylamine adsorption increases with increasing alkalinity, but the effect is not directly correlated with the ionisation of the base. In accordance with the observations of Michaelis, no pronounced adsorption is found for glycine, alanine, or aspartic acid at any p_H . The adsorptions of histidine and histamine are compared. They give similar adsorptions from p_H 4.0 to 7.3, after which that of histidine slightly decreases with increasing alkalinity, whilst that of histamine rises to completion at p_H 10.0. The results with histidine can be explained by the classical theory of the dissociation of the amino-acids, but those with glycine, alanine, and aspartic acid require further explanation. It is inferred that adsorption proceeds through the medium of the non-ionised molecule, in contradiction to the theory of Bartell and Miller that adsorption takes place through the medium of the ion (cf. A., 1924, ii, 734). The results are considered to be consistent with Langmuir's theory of adsorption from solution.

L. L. BIRCUMSHAW.

Adsorption of iodine, bromine, and some halides by carbon in different organic liquids. J. TRIVIDIC (Rev. gén. Colloid., 1929, 7, 14—24, 67—73).—Measurements have been made of the

adsorption of iodine and bromine by two kinds of activated vegetable charcoals in a number of different organic liquids including alcohols, saturated chlorinated hydrocarbons, and aromatic hydrocarbons. Contrary to the result obtained by Davis (J.C.S., 1907, 91, 1666), the adsorption of iodine and bromine by activated charcoal proceeds in accordance with the formula of Freundlich. For a series of liquids of similar chemical constitution there appears to be a relation between the quantities of iodine fixed by the carbon and the mol. wt. and densities of the liquids. There also exists a relation between the quantities of iodine or bromine adsorbed by carbon in mixtures of two solvents and the quantities adsorbed in each of the pure liquids, and in these mixtures the adsorption is again in accordance with the Freundlich formula. Measurements of the adsorption of alkali halides in aqueous-alcoholic solution by charcoal gave inconclusive results because of the small degree of adsorption.

E. S. HEDGES.

Adsorption of sulphur dioxide by platinised asbestos. D. O. SHIELDS (J. Physical Chem., 1929, 33, 1167—1174).—The sorption of sulphur dioxide by platinised and ordinary asbestos has been determined at 25° and at pressures up to 40 mm. Sorption is reversible, without the occurrence of hysteresis, and the isotherm is represented in both cases by Langmuir's equation $q = abp/(1 + ap)$, where q is the quantity of gas adsorbed per gram of adsorbent, p is the equilibrium pressure (mm.), and a and b are constants. The adsorption by platinised asbestos is much the greater.

L. S. THEOBALD.

Adsorption of sulphur dioxide by platinum-black. D. O. SHIELDS (J. Physical Chem., 1929, 33, 1175—1183).—The adsorption of sulphur dioxide by platinum-black has been measured at 25° and at pressures from 0 to 175 mm. The process is irreversible, 84 volumes of gas at N.T.P. per unit volume of platinum being adsorbed, and 54 volumes being retained even after 8½ hrs. at 250°. There appears to be a strong, irreversible adsorption accompanied by a weaker and more nearly reversible effect which shows some hysteresis. This last may be due to oxidation of sulphur dioxide to the trioxide at active centres of the platinum-black. The curve obtained on subsequent adsorption follows a course parallel to the desorption curve and not to the first adsorption curve, indicating that adsorbed impurities are not responsible for the hysteresis.

L. S. THEOBALD.

Low-pressure adsorption on a washed glass surface. H. S. FRANK (J. Physical Chem., 1929, 33, 970—976).—The adsorption of water vapour by a surface of pyrex glass washed by hot chromic acid solution has been measured at 25° over the range 5.2×10^{-3} to 8.7×10^{-2} mm. by means of a new form of all-glass manometer. A high-frequency ultramicro-meter method was used to follow the movement of the diaphragm. The results indicate that the adsorption is a slow but reversible process and that an acid-washed glass surface is not plane, but is covered by a layer of silica gel (cf. Frazer, Patrick, and Smith, A., 1927, 722; Latham, this vol., 134).

L. S. THEOBALD.

Adsorption on glass and determination of the adsorbing surface. N. S. SCHENKER (J. Russ. Phys. Chem. Soc., 1929, 61, 413—421).—The adsorption of methyl-violet BB, diamond-fuchsin, and brilliant-safranin on glass-wool has been studied. The total adsorbing surface was found by measuring the length and thickness of each separate thread. The thickness of a thread was determined by means of a precision micrometer screw which had a total internal reflexion prism attached to its head so as to facilitate the taking of readings and make them more accurate. The concentration of dye in the 0.2 c.c. of solution used was determined by means of a specially adopted König-Martens spectrophotometer. The adsorption of methyl-violet BB was found to be 1.78×10^{-7} g./c.c. and of diamond-fuchsin 1.79×10^{-7} g./c.c., agreeing closely with the values found by Schmidt and Durau (A., 1924, ii, 238). The author also determined by the method of Paneth and Thimann (A., 1924, ii, 612) the thickness of the adsorbed layer and found it to be unimolecular in the case of methyl-violet BB and of diamond-fuchsin and to cover about 83% of the glass surface, whilst the layer of the brilliant-safranin is assumed to be unimolecular.

A. FREIMAN.

Adsorption of certain acids by wool. W. W. PADDON (J. Physical Chem., 1929, 33, 1107—1108).—Wool adsorbs tartaric acid less readily than hydrochloric or sulphuric acid from boiling aqueous solutions. In concentrations up to 2 mg.-mol. of acid/250 c.c. sulphuric acid is more readily adsorbed than hydrochloric acid, but at higher concentrations the reverse is the case. No evidence of compound formation between the wool and the acid has been obtained.

L. S. THEOBALD.

Adsorption of electrolytes by crystalline surfaces. II. (MLLE.) L. DE BROUCKÈRE (Bull. Soc. chim. Belg., 1929, 38, 212—222).—See this vol., 757.

Influence of ammonia on the adsorption of copper or nickel salts. M. GELOSO and (MLLE.) L. S. LÉVY (Compt. rend., 1929, 189, 175—177).—Known volumes of a standard solution of iron alum were added to ammoniacal solutions of ammonium sulphate and copper or nickel sulphate and the precipitated ferric oxide was analysed after 3 hrs. at 22°. The adsorption of the copper or nickel salt is influenced considerably by the concentration of ammonia which is not itself detectable in the precipitate, but may have been adsorbed and subsequently removed by washing. Alternatively it may exert its effect simply by an increase of the p_H value.

J. GRANT.

Adsorption of gases and vapours and the Langmuir theory. H. ZEISE (Z. Elektrochem., 1929, 35, 426—431).—The Langmuir adsorption isotherm is discussed, and new interpretations are given to the coefficients involved therein (cf. A., 1928, 1182). The contentions of Póányi (this vol., 256) are criticised.

H. T. S. BRITTON.

Potential theory of adsorption. M. PÓÁNYI (Z. Elektrochem., 1929, 35, 431—432).—A reply to Zeise (preceding abstract) and a statement of the principles underlying the author's purely physical theory.

H. T. S. BRITTON.

Shapes of drops, and the determination of surface tension. B. B. FREUD and W. D. HARKINS (J. Physical Chem., 1929, 33, 1217—1234).—A theoretical paper in which the drop-weight method is discussed under the three heads: the hanging, detached, and detaching drop. The theory of the first is treated mathematically. Profiles of hanging and detaching drops taken by a motion-picture camera are reproduced.

L. S. THEOBALD.

Capillary phenomena in non-circular cylindrical tubes. W. O. SMITH and P. D. FOOTE (Ind. Eng. Chem., 1929, 21, 567—568).—Expressions are deduced relating the surface tension of a liquid with the rise in capillary tubes of rectangular and elliptical cross-section. Comparison of theoretical with experimental values shows agreement within the limits of accuracy of the measurements. It is pointed out that the vapour pressure over the surface of a liquid is different for circular and non-circular capillaries of the same cross-sectional area.

H. INGLESON.

Surface tension of fused metals and alloys. III. **Gold, zinc, gold-copper, silver-copper, and iron alloys.** W. KRAUSE and F. SAUERWALD [with M. MICHALKE] (Z. anorg. Chem., 1929, 181, 353—371).—The surface tension of various gold-copper and silver-copper alloys, zinc, and alloys of iron with carbon, silicon, and phosphorus has been measured by the maximum bubble pressure method (cf. A., 1926, 790); in the case of zinc and the iron alloys the apparatus must be somewhat modified. The noble metals and their alloys and the above-mentioned iron alloys all exhibit a high surface tension in the fused state; a noteworthy feature of the iron alloys is their positive temperature coefficient. Some of the silver and gold alloys also show a maximum surface tension dependent on the temperature.

H. F. HARWOOD.

Dependence of surface tension and latent heat of vaporisation on the density and temperature up to the critical temperature. W. HERZ (Z. anorg. Chem., 1929, 181, 280—284).—Polemical against van Laar (this vol., 641).

A. R. POWELL.

Surface properties of soap solutions. W. C. PRESTON and A. S. RICHARDSON (J. Physical Chem., 1929, 33, 1142—1150).—Simultaneous measurements of surface viscosity (rotating-disc method), surface tension (drop method), and foaming power of soap solutions of distinct types, before and after exposure to air, have failed to reveal any simple correlation of these three properties. Low surface tension does not necessarily involve tendency to foam, and the combination of low surface tension with high surface viscosity or plasticity does not invariably confer high foaming power. Unknown factors determine this.

L. S. THEOBALD.

Surface varnishes on water and molecular dimensions. A. MARCELIN (Compt. rend., 1929, 189, 236—238).—If V is the volume of surface varnish on water in a state of maximum extension, S the area covered, l the length of the molecules, E the extension coefficient of the varnish, and C the coefficient of surface reduction necessary to compress the surface solution to the saturation point, then $l = VC/SE$. This formula gives results in good agreement with

X-ray spectrographic methods for oleic, myristic, palmitic, and stearic acids and for cetyl alcohol, whilst those obtained by Langmuir's method are low on account of decrease in the re-extension coefficient with increasing dilution of the benzene solution used for the production of the varnish. A surface film increases in solubility with increase in surface pressure and temperature (cf. following abstract).

J. GRANT.

Surface solutions and molecular varnishes. Determination of the lengths of their molecules. F. ÉMIR (Compt. rend., 1929, 189, 239—240; cf. this vol., 876).—Marcelin's formula (cf. preceding abstract) gives results in good agreement with X-ray spectrographic methods for palmitic and stearic acids and for cetyl alcohol.

J. GRANT.

Surface solutions of oleic acid. Measurement of very low pressures. J. GUASTALLA (Compt. rend., 1929, 189, 241—243; cf. preceding abstracts).—Marcelin's determinations of the pressure of surface solutions (A., 1926, 120) have been extended to very low pressures by means of a more sensitive modification of the apparatus used, a feature of which is the collection of impurities on the liquid surface by means of a jet of filtered compressed air, and their removal by aspiration. The extension curves of oleic acid on 0.01*N*-hydrochloric acid at 19° correspond with Mariotte's law for surface areas of 60—500 Å.², the value of the coefficient *K* being *R*/20. From 500 to 5000 Å.² the fall of pressure is only 0.007 dyne/cm., but beyond this it decreases considerably, and a Mariotte hyperbola in which *K*=*R* is obtained (cf. Adam and Jessop, A., 1926, 468).

J. GRANT.

Orientation of molecules at solid surfaces and the range of action of the orienting forces. D. TALMUD (Z. physikal. Chem., 1929, 142, 233—236).—When an aqueous suspension of a hydrophilic powder such as calcium carbonate or barium sulphate, containing a drop of oleic acid, is shaken with a liquid which is insoluble in and less dense than water, a considerable quantity of this liquid becomes adsorbed on the powder. Addition of an excess of oleic acid sets the liquid free. Further, a suspension in water of a hydrophobic powder such as lead sulphide will adsorb a considerable quantity of benzene which is set free on addition of one drop of oleic acid. In explanation, it is suggested that oleic acid is adsorbed on hydrophilic powders by its hydrophilic groups. The hydrophobic groups are free and able to attach benzene to themselves. With the hydrophobic lead sulphide, the hydrophilic groups of the oleic acid remain free and these are unable to adsorb benzene. Calculations made on the results of experiments with calcium carbonate suspensions and amyl alcohol show that the thickness of the adsorbed layer of amyl alcohol decreases with increase in the amount of oleic acid present.

F. J. WILKINS.

Optical investigation of metallic films rendered active and passive by electrochemical means. L. TRONSTAD (Z. physikal. Chem., 1929, 142, 241—281).—The nature of the polarisation of the light reflected from iron and nickel mirrors which have been rendered passive by various means has been investigated. The change of the optical properties of iron

and nickel films made passive in alkaline solution and of nickel films treated in acid solution resembles that which results when a clean iron surface is brought from vacuum into contact with air. Characteristic limiting values of the optical properties are exhibited in each case. Re-activation of a passive surface produces a reversion of its optical behaviour, but even on prolonged activation the initial state of the surface is never re-attained. Repeated changes from the active to the passive state, and *vice versa*, result in much greater changes taking place in the optical properties than result from passivity produced by one operation extending over a prolonged period. The passive state is regarded as being due to the presence of an unbroken surface of oxide film, which, on activation of the surface, is fractured and rendered porous, without, however, being destroyed. A theory of the passive state has been developed by consideration of the electric charge of the oxide film and the cataphoretic movement of the latter during the passage of the current. The theory is in close agreement with the observed behaviour of nickel film in acid solutions both at low and at relatively high current densities.

H. F. GILLBE.

Interference effect at the disturbed surface of a liquid and surface tension. Z. V. VOLKOVA and V. S. TIROV (Z. physikal. Chem., 1929, B, 4, 71—82).—The effect of variation of surface tension on the interference effect obtained with a beam of light at the disturbed surface of a liquid was studied by using solutions of inorganic substances which increase the surface tension of water. The substances used were such as to increase the surface tension according to a linear law, viz., calcium, magnesium, and lithium chlorides, and sodium and potassium hydroxides. The addition of these substances made the interference effect more stable and lasting. The concentration of the dissolved substance and the deviation of the rays are linearly connected. An attempt is made to explain this phenomenon on the hypothesis that there is a layer of particles which stands out a certain height from the level of the disturbed surface.

A. J. MEE.

Heat of wetting of powders by solutions of interfacially active substances, and heats of adsorption in solutions. Heat effect of the formation of dispersed systems. II. P. REHBINDER and L. KRAJUSCHKINA (Z. physikal. Chem., 1929, 142, 282—288; cf. A., 1927, 193).—Microcalorimetric measurements have been made of the heats of adsorption of isoamyl alcohol from aqueous solution by carbon, and of *n*-butyric acid from aqueous and *n*-hexane solutions by silica powder and by carbon. The heat of wetting of a hydrophilic powder (silica) by a solution increases with increase of dielectric constant of the pure solvent, whereas the reverse holds for hydrophobic powders. The heat of adsorption from a solution is, in accordance with theory, a minimum for those cases in which the heat of wetting is a maximum. The relationships between the differential and integral heats of adsorption and the concentration of the solution are discussed.

H. F. GILLBE.

Temperature at the liquid-solid interface during the crystallisation of supercooled sub-

stances. H. POLLATSCHER (Z. physikal. Chem., 1929, **142**, 289—300).—A method has been devised for the determination of the temperature prevailing at the liquid-solid interface of a crystallising super-cooled liquid. Measurements with salol indicate that, in contradiction to Tammann's assumption, the temperature at the boundary during the process of crystallisation does not reach the m. p. of the substance.

H. F. GILLBE.

Electrokinetic potential of gold in very dilute solutions of electrolytes. P. A. THIESSEN and J. HEUMANN (Z. anorg. Chem., 1929, **181**, 379—384).—The electrokinetic potential of gold in very dilute (10^{-8} to $10^{-5}N$) solutions of potassium sulphate and of the chlorides of potassium, caesium, and lithium has been investigated, using a modification of Coehn's apparatus (cf. A., 1927, 420). The negative electrokinetic potential exhibits a maximum value at a concentration of about $10^{-7}N$, and this result can be explained satisfactorily in terms of Debye's theory of a diffuse double layer.

H. F. HARWOOD.

Micelles and membrane equilibria. J. DUCLAUX and R. TITEICA (Compt. rend., 1929, **189**, 101—102).—The composition of the liquid removed by ultra-filtration of hydrosols of iron (produced by hydrolysis of ferric chloride at 100°), copper ferrocyanide, Congo-red, and caramel is independent of the nature of the membrane (cellulose, or its nitrate or acetate) and of the pressure employed, and does not change as the micelles become concentrated. Such equilibria are therefore heterogeneous and the intercellular liquid is that actually removed by ultra-filtration.

J. GRANT.

Polarisation of membranes due to metallic plates. J. LOISELEUR (Compt. rend., 1929, **189**, 170—171).—When a metal plate is placed in a solution of an electrolyte containing an animal membrane (bladder), the latter is polarised to an extent which depends on the nature of the metal and its surface, and also on the electrolyte. The effect decreases with time and with increase in concentration of the electrolyte. A modification of the ionic distribution in the different parts of the septum is suggested as an explanation.

J. GRANT.

Diffusion experiments with sugar-protein solutions. D. KRÜGER (Biochem. Z., 1929, **209**, 119—127; cf. Loeb and Krüger, A., 1928, 786).—Diffusion experiments carried out with the systems dextrose-egg-albumin, dextrose-caseinogen, dextrose-glycine, and dextrose-*D*-alanine indicate that, at neutral reaction, no appreciable condensation between the sugar and the protein or amino-acid takes place.

W. MCCARTNEY.

Preparation, analyses, and lead-ion concentration of solutions of colloidal lead. H. S. KEELAN, R. B. SMITH, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1929, **18**, 586—589).—The solutions were prepared by sparking lead electrodes dipped in a slowly agitated mixture of water containing gelatin, potassium chloride, and lead, covered with liquid paraffin. The materials used were oxygen-free. Such preparations are non-toxic. The amount of lead in the solution was determined

colorimetrically as lead sulphide. The lead-ion concentrations varied between 1.8×10^{-9} and 5.3×10^{-11} and were not altered by sterilisation. These values are probably due to a small amount of a very insoluble unidentified lead salt. The partition coefficient of lead acetate between water and liquid paraffin varies with the degree of agitation of the mixture.

C. C. N. VASS.

Tartaric acid method for the synthesis of electronegative sols. IV. A. DUMANSKI and A. JAKOVLEV (J. Russ. Phys. Chem. Soc., 1929, **61**, 213—215).—See A., 1928, 1321.

Molecularly dispersed silicic acid. H. BRINTZINGER and B. TROEMER (Z. anorg. Chem., 1929, **181**, 237—248).—The state of dispersion of silicic acid, prepared by the decomposition of alkali silicate with hydrochloric acid, by hydrolysis of silicon tetrachloride by ice-cold water alone and in the presence of silver oxide, by hydrolysis of methyl silicate by water and by $0.001N$ -, $0.01N$ -, and $0.1N$ -hydrochloric acid, and by hydrolysis of ethyl silicate by $0.01N$ -hydrochloric acid has been determined by measuring its rate of diffusion through parchment and cellophane. The results are expressed by plotting the logarithm of the concentration in the dialyser against the time; for an ionic or a molecularly dispersed substance this is a straight line inclined downwards, whereas for silicic acid solutions the line is curved more or less upwards from the ideal straight line, indicating a certain amount of polymerisation and the presence of two or more states of aggregation. Silicic acid produced by hydrolysis of alkyl silicates is in the most highly dispersed form, the $\log C_t-t$ curve approximating to a straight line; high acidity of the hydrolysing liquid favours polymerisation, whereas a small acidity favours the production of the molecularly dispersed form. The p_H value of both molecularly dispersed and colloidal dispersed silicic acid solutions is 4.7. The ageing of silicic acid solutions is accelerated by the absence of electrolytes and by the presence of alcohol; in feebly acid solutions the formation of di- and tetra-silicic acid may be detected during ageing, whereas the acid produced by hydrolysis of alkyl silicates rapidly condenses to large molecules.

A. R. POWELL.

Preparation of finely-dispersed colloidal gold. M. DOMANICKI (Ukraine Chem. J., 1929, **4**, 1—6).—Amylene, hexylene, diisobutylene, diallyl, and some other unsaturated hydrocarbons have been used in the preparation of colloidal gold sols from alkaline solutions of sodium and potassium aurate. The conditions to be observed and the properties of the sols are described. Although a colloidal palladium sol can be prepared by this method from an alkaline solution of palladium chloride, this is not the case for silver and platinum.

A. FREIMAN.

Germanate gels of the alkaline earths. J. H. MÜLLER and C. E. GULEZIN (J. Amer. Chem. Soc., 1929, **51**, 2029—2042).—Rapid and thorough mixing of a solution of germanic acid with suitable excess of calcium hydroxide solution produces precipitation of transparent (or translucent) homogeneous gels of calcium germanate of extremely high dispersion ("solid" gel). The acid and base concentrations

may vary between wide limits, but the temperature should be between 15° and 25°. The lime is responsible for the gelation phenomena. The gel is readily destroyed by mechanical means (agitation, suction-filtration), leaving practically pure calcium metagermanate; however, it is permanent if protected from dry air and carbon dioxide, and is not affected by temperatures up to 95°. The water present, which appears simply to be trapped in the form of lime water by minute fibres of the dispersed calcium salt, may be mechanically replaced by ethyl or methyl alcohol, ether, and benzene, usually with decrease in size and increase in firmness. Addition of lime water forms a characteristic test for germanium dioxide in solution, since the presence of the latter produces an extraordinarily bulky hydrogel.

Strontium gels, which are opaque, are obtained as above, but the reagents must be of higher concentration. Barium germanate forms octahedral, isotropic, crystals, soluble to the extent of 0.07536 g. in 100 g. of solution at 25°. S. K. TWEEDY.

Organo-gels. E. DA FANO (Giorn. Chim. Ind. Appl., 1929, 11, 199—203).—Confirmation is obtained of the fact that certain sodium soaps are dispersed by hot organic solvents, giving coherent gels on cooling. This phenomenon is general and many new gels have been prepared in this way. Small additions of certain substances, mostly fatty acids, act as protective colloids, facilitating the formation of sols and gels, for instance, with formates, acetates, propionates, butyrates, valerates, etc. in various organic solvents, and with other sodium soaps in dense mineral oils, tars, and bitumens. T. H. POPE.

Refractive index of colloidal solutions of sulphur. G. ROSSI and A. MARESCOTTI (Gazzetta, 1929, 59, 309—313).—The refractive index of a solution containing sulphuric acid and sodium sulphate is increased by the presence of sulphur in colloidal suspension. For a given concentration of electrolytes the increase in refractive index is proportional to the sulphur content, but the relative increase becomes smaller as the concentration of the electrolytes increases. F. G. TRYHORN.

Osmometer for measuring the osmotic pressure of colloids. A. GRIGAUT and A. BOUTROUX (J. Pharm. Chim., 1929, [viii], 10, 9—15).—See this vol., 761.

Structure and electrification of smoke particles. H. S. PATTERSON, R. WHYTLAW-GRAY, and W. CAWOOD (Proc. Roy. Soc., 1929, A, 124, 523—532).—The microscopic methods employed previously for large aggregates (cf. A., 1927, 17) have been improved so as to allow of the examination of the so-called ultramicroscopic particles present in dilute smokes. The type of particle appears to depend mainly on the method used to produce the smoke. High-temperature reactions and the arc discharge favour the formation of loose aggregates with a high degree of complexity, whilst volatilisation at a lower temperature gives rise to larger particles of a more compact structure composed of relatively few units. Of the former type the smokes of cadmium oxide, magnesium oxide, silver, and gold have been examined,

and of the latter arsenious oxide, mercuric chloride, and a number of organic substances. In the case of *m*-xyleneazo- β -naphthol a remarkable effect was observed after the particles had been deposited by sedimentation, some of the crystalline particles developing very long, hair-like tails of extreme tenuity; these grew at the expense of the crystal aggregates, until finally, in many cases, very long hairs only were left. Experiments were carried out to determine the influence of electrification on the rate of coagulation, a horizontal electric field being applied to the particles in a special ultramicroscopic cell and the proportion of electrified particles at different periods during the life of the smoke being obtained by direct counting. The results indicate that the electrification of a smoke depends largely on the way in which it is produced. The particles in smokes volatilised from a heater are initially but slightly charged, although the charge increases as the cloud ages; on the other hand, smokes made by the arc or by burning magnesium ribbon are highly charged. In smokes of ammonium chloride, about 70% of the particles finally become charged, the numbers of positively and negatively charged particles being equal, within the limits of error. Magnesium oxide smokes are also electrically neutral as a whole, about 90% of the particles being charged. No marked difference is observed in the coagulation rates of comparable smokes differing greatly in electrical character. L. L. BIRUMSHAW.

Structure of colloids. P. P. VON WEIMARN (Rev. gén. Colloid., 1929, 7, 153—158).—A reiteration of the author's views on the colloidal state.

E. S. HEDGES.

Pectography of colloidal solutions of metallic sulphides. P. BARY and J. V. RUBIO (Compt. rend., 1929, 189, 294—296).—Pectographs (patterns obtained by spontaneous evaporation of colloidal solutions in warm air or over sulphuric acid) of the sulphides of antimony, arsenic, zinc, mercury, cadmium, molybdenum, and copper are described. With the exception of copper sulphide the sulphides are deposited in thin layers of gel which gradually lose their imbibed water and crack in patterns.

J. GRANT.

Gel structure. Gels obtained with salts of quinine, optoquin, and eucupine. P. THOMAS and (Mlle.) M. SIBI (Compt. rend., 1929, 189, 292—294).—Gels prepared from mixtures of solutions of the hydrochlorides of quinine, optoquin, or eucupine (*isoamylhydrocupreine*) with saturated sodium acetate solution deposit long, fine, hair-like crystals after 15 min., several hrs., and some months, respectively. The mean diameters are 1—3 μ in all cases, including lithium urate, sodium oleate, and sorbitol acetal, and the mixtures rendered homogeneous by warming will redeposit gels with unchanged properties.

J. GRANT.

Chemistry of "tiles," and the plastic state. ZACHARIAS (Rev. gén. Colloid., 1929, 7, 201—205).—The nomenclature of colloid systems is discussed. The term "tile" (Gr. $\tau\iota\lambda\eta$) is introduced to designate an ultramicroscopic or microscopic particle. The term "solution" is used to comprise all liquid

mixtures, such as molecular solutions, "tilous" solutions, suspensions, and emulsions. "Absorption" denotes any penetration of one substance into another, such as a gas or other substance in a liquid, a jelly, or a porous body. It is pointed out that the idea of "tilous" solutions and jellies as two-phase systems is inconsistent, the notion of a surface of separation ceasing to be applicable below certain sizes of particles.

E. S. HEDGES.

Velocity function of the viscosity of disperse systems. G. W. S. BLAIR (*Kolloid-Z.*, 1929, 48, 283).—Polemical (cf. this vol., 262).

E. S. HEDGES.

Stability of colloidal solutions. A. BOUTARIC (*Rev. gén. Colloid.*, 1929, 7, 49—52).—Electrical charge is not the only factor determining the stability of a colloidal micelle. If the micelles are placed in a very feeble concentration of electrolyte, the ions cannot be adsorbed in sufficient numbers to neutralise the charge and those that are adsorbed will produce slow transformations within the micelle which may alter its whole character. Flocculation will take place only when so great a concentration of ions is present that they are adsorbed more quickly than the micelle can undergo the necessary transformations to resist their action.

E. S. HEDGES.

Factors of stability of colloidal systems. S. I. DIATSKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 423—440).—Two criteria for the stability of colloidal systems are assumed. First, their stability with time, *e.g.*, the persistence of the Brownian movement, the constancy of the electrical conductivity and of other physico-chemical properties, and, secondly, their stability towards electrolytes. The present investigation covers the negatively-charged sol of tungstic acid and positively-charged sol of ferric hydroxide, and the negatively-charged suspension of tungstic anhydride and positively-charged suspension of ferric hydroxide. To five separate quantities of 50 c.c. of a *N*-solution of sodium tungstate were added calculated amounts of hydrochloric acid, so that the solutions should contain $\text{Na}_2\text{O}, 2\text{WO}_3$, $\text{Na}_2\text{O}, 3\text{WO}_3$, $\text{Na}_2\text{O}, 4\text{WO}_3$, $\text{Na}_2\text{O}, 5\text{WO}_3$, and $\text{Na}_2\text{O}, 6\text{WO}_3$, respectively. To a further 100 c.c. of the sodium tungstate solution was added an excess of concentrated hydrochloric acid so that the solution should contain $\text{Na}_2\text{O}, 8\text{WO}_3$. A 0.1*N*-solution of potassium chloride was used as coagulator, and in each case the p_H , the velocity of coagulation, and the ultramicroscopic appearance were observed. The stabilising factors in this case are partly chemical and partly electrostatic in nature. So long as hydration of the colloidal particle continues the system is chemically unstable, but as soon as hydration is completed the system becomes chemically stable and stable towards electrolytes and the size of the electrical double layer becomes of the greatest importance. Since the presence of sodium and hydrogen ions affects the stability of the system the author investigated the effect of their removal on the stability, by determining the p_H of the suspension formed, its electrical conductivity, its ultramicroscopic appearance, the cataphoretic velocity of the particles, their rate of sedimentation, and from this, by applying Stokes' law, their radius, and,

finally, their density by several different methods. In this case the electrical double layer is of utmost importance. As soon as it becomes steady, the stability of the system and the degree of dispersion begin to increase and the system becomes chemically stable. The iron hydroxide sol was prepared by Graham's method, whilst the suspension was prepared by washing the iron hydroxide obtained by treating a ferric chloride solution with ammonia. The sol was dialysed for 150 days, when a shock was sufficient to gelatinise it. The p_H of the dialysed sol was determined by means of the quinhydrone electrode and its electrical conductivity was found to decrease continuously with dialysis. The suspension was decanted 20 times, when its electrical conductivity, its p_H , its cataphoretic velocity, and its coagulation velocity, both with a 0.1*N*-solution of potassium sulphate and with a 0.1*N*-solution of potassium chloride, and the rate of settling of the particles were determined. In contradistinction to the observation of other workers (*e.g.*, Handovsky, A., 1926, 23) it is found that the colloidal micelles of the iron hydroxide on prolonged dialysis do not show any trace of losing chlorine ions. It is concluded that the stability of the system is to a very large extent determined by its degree of hydration. Finally, the author points out that his results do not agree with von Weimarn's views.

A. FREIMAN.

Surface tension and stability of colloidal solutions. G. ROSSI and A. MARESCOTTI (*Gazzetta*, 1929, 59, 313—319).—The stability of arsenious sulphide sols is greatly enhanced by the addition of 0.6% of gelatin, although the surface tension, determined by the stalagmometric method, is unaltered. On the other hand, the surface tension and stability of ferric hydroxide sols are unaffected by the addition of 0.04% of gelatin.

F. G. TRYHORN.

Oxidation of colloidal arsenic, antimony, and copper sulphides. M. SWIDERSKA, W. KOSTANECKA, and P. WARSZAWSKA (*Rocz. Chem.*, 1929, 9, 411—417).—Colloidal arsenious sulphide undergoes oxidation in the presence of atmospheric oxygen, the products being arsenious oxide, free sulphur, and sulphuric acid. The last-named substance has a precipitative influence on the colloid present, and to this influence may be ascribed many of the apparently anomalous properties of arsenious sulphide sols. Oxygen has a similar effect on antimonious sulphide sols, but free sulphur is not formed in this case. With copper sulphide sols, the sulphuric acid, which is formed initially, disappears to some extent later, probably as a result of the formation of polythionic acids, and copper is not found in the filtrate until the excess of hydrogen sulphide has been expelled; at this point the sulphuric acid content of the suspension becomes constant.

R. TRUSZKOWSKI.

Emulsions: stability, area per molecule in the interfacial film, distribution of sizes, and the oriented wedge theory. W. D. HARKINS and N. BEEMAN (*J. Amer. Chem. Soc.*, 1929, 51, 1674—1694).—The size distribution of the oil droplets in liquid hydrocarbon emulsions produced by oleate soaps is the same for lithium, sodium, and caesium oleates. This result is independent of the viscosity

of the hydrocarbon, but the higher is this viscosity the greater is the diameter of the larger drops. The size distribution in fresh emulsions is independent of the soap concentration, but it varies on ageing. Emulsions made with soap solutions $>0.01M$ are stable over long periods of time; emulsions produced by very dilute soaps are unstable. The method of preparation has no influence on the maximum diameter of the drops. The presence of the corresponding hydroxide at a concentration above $1M$, or of oleic acid at $0.1M$, causes an increase in the number of small drops at the expense of the large drops. Variation in the hydrocarbon chains of the soaps has no effect on the size distribution, except in the case of potassium chaulmoograte, when the number of the smallest drops is greatly increased. The emulsions of water in oil produced by magnesium and aluminium soaps show a size distribution similar to that of the oil-in-water types; benzene-in-water emulsions also show the same size distribution. Calculation of the molar areas at the interfacial film in oil-in-water emulsions indicates that none of the soap films is thicker than unimolecular; it shows, indeed, that concentrated emulsions may be produced by means of an interfacial soap film in which the number of soap molecules is less than corresponds with a closely-packed unimolecular film.

S. K. TWEEDY.

Chemical effects of high-frequency sound waves. II. Emulsifying action. W. T. RICHARDS (J. Amer. Chem. Soc., 1929, 51, 1724—1729).—The emulsification of water and benzene and of water and mercury is due largely to action at the walls of the containing vessel. In the case of mercury the action depends on the amount of this metal present; an excess may arrest the emulsification, which is attributed to the damping action of the metal on the waves in the glass. Water is probably emulsified in the mercury; the action is accelerated by the presence of ammonium chloride. The walls of glass vessels are slightly emulsified in water when subjected to the action of high-frequency sound waves; small, uniform glass particles are not fractured by intense sound waves. A method of roughly estimating relative sound intensities by emulsifying action is described.

S. K. TWEEDY.

Certain phenomena in electric and magnetic fields. T. KUCZYŃSKI (Przemysł Chem., 1929, 13, 137—144, 161—167).—Microscopical examination of emulsions in high-frequency alternating fields shows that the drops of the dispersed phase first undergo deformation and then arrange themselves in chains along the lines of force. In emulsions of water in oil, coagulation then supervenes, the chains conducting the current, whilst in the case of oil in water coagulation does not occur, and the chains distribute themselves over the regions of least current density. In charging a condenser with an emulsion as dielectric, energy is absorbed, not only in polarising the dielectric, but also in the mechanical work associated with the deformation of the drops of dispersed phase, and changes in their distribution throughout the disperse phase. The dielectric constant of emulsions depends on the distribution of the dispersed phase. It is shown mathematically that, where the drops of the latter

are small in comparison with the condenser, the dielectric constant does not depend on their size, but is a function of their aggregate volume, provided that they are uniformly distributed throughout the medium.

R. TRUSZKOWSKI.

Influence of light on some colloids. (Miss) S. ROY (J. Indian Chem. Soc., 1929, 6, 431—440; cf. Ganguly and Dhar, A., 1922, ii, 604).—Observations on the coagulation, electric conductivity, and extinction coefficients of sols of stannic, aluminium, and thorium hydroxides, of antimony, arsenious, and mercuric sulphides, and of uranium and cupric ferrocyanides, when exposed to light, show that all, except the ferrocyanides, acquire increased conducting power after exposure. A short exposure increases the stability of arsenious and antimony sulphides and uranium and cupric ferrocyanides, but on longer exposure all become less stable, and sols of antimony sulphide, mercuric sulphide, and uranium ferrocyanide coagulate completely.

F. L. USHER.

Process of coagulation in smokes. H. S. PATTERSON, R. WHYTLAW-GRAY, and W. CAWOOD (Proc. Roy. Soc., 1929, A, 124, 502—522; cf. A., 1927, 9, 17).—Using an improved method of counting, the effect of particle size and the degree of heterogeneity on the rate of coagulation of ammonium chloride and resin smokes has been investigated. The particles are made brighter and more easily observable by introducing moisture into the cell. The series of particulate volume curves representing the results show that the process of coagulation in dilute clouds is not a simple linear function of the time, and that the average value of K in the equation $\sigma = \sigma_0 + Kt$ (cf. A., 1927, 1139) increases definitely with fall of weight concentration. From an estimate of the amount of solid matter present in the dispersed state it appears that the actual weight concentration of the smoke is invariably smaller than the weight volatilised, and that there is no constant proportionality between the two. If counting experiments are made with smokes of different concentrations in which the actual mass present in the particulate state is determined experimentally, then the previous haphazard variations disappear, and in all cases the change in form of the curves runs parallel to the mass of material in the smoke and the results are expressible by a comparatively simple formula. With a view to explore the early stages of coagulation the smoke was diluted immediately after formation by blowing a rapid stream of air over the volatilising material, and in this way evidence was obtained that the true initial number of particles was extremely high—probably of the order of 10^{12} per c.c. It is inferred that the smoke is formed initially by molecular collision, in contradistinction to the idea of condensation around nuclei already present. The results indicate why it is so difficult to obtain smokes of the same behaviour on different occasions, since reproducibility not only depends on following the same procedure for dispersal, but is also conditioned by the time at which the very rapid initial coagulation is slowed down by dilution. The collision theory of coagulation is discussed at length, and the underlying postulates of the Smoluchowski theory for systems originally homogeneous and the

modifications necessary to make it generally valid are considered. The course of coagulation may be expressed by the semi-empirical relation $\sigma = \sigma_0 + 2.20 \times 10^{-8}(1 + 9 \times 10^{-6}r^{-1})t$, where σ is the particulate volume of the smoke at time t , σ_0 the initial particulate volume, and r the average radius of the particles.

L. L. BIRCUMSHAW.

Coagulation of colloidal solutions. G. ROSSI and A. MARESCOTTI (*Gazzetta*, 1929, 59, 319—330).—Determinations have been made of the coagulating power of hydrochloric acid, sodium hydroxide, and magnesium sulphate for arsenious sulphide and ferric hydroxide sols of varying concentrations. By counting the particles at different dilutions it was found that both arsenious sulphide and ferric hydroxide sols increase in dispersion on dilution, but that the increase with the former sol is much greater than with the latter. As a consequence the ratio between the amount of electrolyte necessary for coagulation and the concentration of the sol increases with dilution much more for arsenious sulphide than for ferric hydroxide sol.

F. G. TRYHORN.

Coagulation of colloidal titanic hydroxide. S. K. MAJUMDAR (*J. Indian Chem. Soc.*, 1929, 6, 357—360).—A comparison of the flocculation values of various electrolytes for sols of titanic hydroxide has shown the latter to be a typical positive hydrosol. "Ageing" for three months made the sol considerably more stable to all electrolytes studied, without affecting the order of their coagulating power. The addition of methyl or ethyl alcohol produced sensitisation toward most electrolytes.

F. L. USHER.

Influence of dilution on the coagulation of certain colloids. A. F. GERASIMOV and A. S. URSHUMSKI (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 393—411).—The influence of dilution on the coagulation of certain colloids was determined by observing the direction of the change, if any, of the concentration of the coagulating agent in g. per c.c. on dilution and simultaneous addition of increasing amounts of coagulator. In the case of colloidal gold, using sodium chloride as the coagulator, an increasing stability was found with dilution. Colloidal silver, on the other hand, shows a decreasing stability with dilution independent of whether it has been dialysed or not or whether sodium or potassium nitrate has been used as the coagulator. This disagrees with the results obtained previously by Freundlich and Loening (*A.*, 1922, ii, 696). Adding ammonium sulphate or Paal's albuminous protective mixture to the silver colloid, then diluting, and adding the coagulator has no particular effect on the coagulation, and in the limit the coagulation tends to become equal to that in their absence. Colloidal arsenious sulphide was also investigated; using sodium chloride as coagulator the stability increases, with magnesium chloride the stability is unchanged, whilst with barium chloride it decreases quite rapidly. Also in this case addition of potassium sulphate and agar-agar leads finally to values equal to those for the chlorides alone. Attention is directed to the importance of the physico-chemical individuality of the coagulating cation quite independent of its valency. Thus in the coagulation of silver colloids the coagulation decreases

more rapidly with sodium nitrate as the coagulator than with potassium nitrate, and in the case of arsenious sulphide also the coagulation is quite different for magnesium chloride and barium chloride. Experiments with Prussian-blue in the presence of a constant or varying concentration of oxalic acid confirm the results obtained by Volshin (*A.*, 1910, ii, 1048) except that in the presence of a fixed concentration of oxalic acid the break in the curve is much less pronounced.

A. FREIMAN.

Influence of stirring on rate of coagulation of colloids. K. JABŁCZYŃSKI and (MLLE.) G. SZAMES (*Rocz. Chem.*, 1929, 9, 335—339).—See this vol., 761.

Coagulation of gelatin sols in alcohol-water mixture. S. GHOSH, S. N. BANERJEE, and N. R. DHAR (*J. Indian Chem. Soc.*, 1929, 6, 321—331).—Positively charged sols of gelatin (1%) in aqueous alcohol (about 87 vol.-%) become more stable on dilution when flocculated with hydrochloric acid and chlorides of potassium and magnesium, whereas with potassium sulphate and ferrocyanide the flocculation values decrease on dilution. Ionic antagonism was observed with mixtures of potassium chloride and sulphate, magnesium chloride and potassium sulphate, hydrochloric acid and potassium sulphate, and hydrochloric acid and potassium chloride. Positive acclimatisation was produced in flocculation by hydrochloric acid and potassium and magnesium chlorides. Negatively charged 0.1% gelatin sols show flocculation values which decrease with dilution in the case of hydrochloric acid and chlorides of potassium, magnesium, and barium, and increase in the case of potassium hydroxide, sulphate, and ferrocyanide. No marked ionic antagonism was observed, and there was negative acclimatisation during flocculation by hydrochloric acid, barium and magnesium chlorides, and aluminium nitrate, whereas positive acclimatisation was noticed with potassium hydroxide. The results are theoretically discussed.

F. L. USHER.

Protective action of colloids. S. OGATA (*Hokkaido J. Med.*, 1928, 6, 251—258).—Colloidal gold was precipitated by solutions more concentrated than 0.032*N*-sodium chloride, 0.001*N*-barium chloride, or 0.00124*N*-ferric chloride; protection was observed with glue solutions more concentrated than 0.00004, 0.00004, and 0.00029%, respectively. The larger threshold value with ferric chloride solution is due to hydrolysis, since with buffered solutions the results are identical. Similar results were obtained with colloidal copper ferrocyanide and mastic.

CHEMICAL ABSTRACTS.

Dissolution of albumin coagula by neutral salts. R. WILHEIM (*Kolloid-Z.*, 1929, 48, 217—231).—Serum-albumin which has been coagulated by heat can be brought into solution by treatment with concentrated solutions of certain salts (*e.g.*, thiocyanates, salicylates, and benzoates). After dialysing away the salt, the albumin is again coagulable. The salts concerned hinder the coagulation by heat. Two essential conditions for this dissolution are a minimal concentration of the salt and a sufficient amount of liquid, the latter depending on the amount of albumin coagulum. The dissolution is therefore supposed to occur in two stages: in the first stage the coagulated

albumin swells, this being controlled by the concentration of salt, and in the second stage the swollen albumin is dispersed, according to the amount of liquid available. Many other salts produce this effect when in sufficiently high concentration and the anions increase in effectiveness according to the order of the Hofmeister series. Since the process of dissolution appears to be definitely a swelling phenomenon, it would seem that the coagulation by heat is due to an energetic loss of water, and this view is supported by the fact that lithium halides, which have a strong swelling effect, also dissolve the albumin coagula. The solutions of albumin in alkali thiocyanates and salicylates are salted out with difficulty, even when the electrolyte has been dialysed away; such solutions are precipitated by acids. Measurements of the viscosity of the solutions with different concentrations of thiocyanate or salicylate in the cold show only a slight and variable increase in viscosity, but if the solution be boiled the viscosity-concentration curve rises very steeply, passes through a maximum, and then falls to the value for the unheated solution. This behaviour is probably connected with alterations in the degree of dispersion. The osmotic pressure is reduced after boiling the solutions.

E. S. HEDGES.

Changes in the viscosity and hydrogen-ion concentration of some inorganic substances during the process of jelly formation. S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 391—409; cf. Dhar and Chakravarti, A., 1928, 124).—The viscosities of a number of inorganic sols have been measured in a capillary viscosimeter during gelatinisation and found to increase exponentially with time. The behaviour of ferric and aluminium hydroxides is, however, exceptional. The hydrogen-ion concentration decreases during the first half hour, on the average by about 50% of the initial value. The results are discussed theoretically.

F. L. USHER.

Intensity of the Tyndall light in agar gels as a function of the degree of hydration. E. HATSCHEK (Kolloid-Z., 1929, 48, 246—248).—The curve connecting the intensity of light scattered by agar gels with the concentration of the gel is maximal at about 13% of agar. By comparing the values with those obtained by Krishnamurti (this vol., 260) for the intensity of scattered light in agar sols and gels of the same concentration and at the same temperature, it is concluded that the increase in the Tyndall light on setting to a gel is not caused by hydration alone, but may be caused by the increase in the size of the particles brought about by strong hydration. In the hydration of agar there is a reduction of the total volume of the system agar+water, which will have the effect of raising the refractive index.

E. S. HEDGES.

Reactions between silver nitrate or copper sulphate and potassium ferrocyanide in gelatin. M. S. DUNIN and F. M. SCHEMIKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 575—586).—Periodic precipitation of silver ferrocyanide, with the formation of a rosette-shaped figure, is observed when a drop of silver nitrate solution is placed on gelatin containing 0.01—0.05N-potassium ferrocyanide; this pheno-

menon does not take place if ferrocyanide is added to silver nitrate present in gelatin. At higher concentrations of ferrocyanide periodic precipitation takes place only beneath the drop of silver nitrate. A similar rosette is obtained when copper sulphate is substituted for silver nitrate in the above reaction; in the case of copper, at higher concentrations of ferrocyanide, a series of concentric rings forms around the drop. The actual shape of the figures obtained in the above experiments also depends on the kind of gelatin used.

R. TRUSZKOWSKI.

Influence of amount of surplus liquid on the swelling maximum of rubber jellies. C. M. BLOW and P. STAMBERGER (Rec. trav. chim., 1929, 48, 681—694).—The degree of swelling of a fixed quantity of rubber in varying amounts of benzene, toluene, and light petroleum has been measured and found to depend on the initial ratio of the solid and liquid phases, as shown by other workers with gelatin and water (cf. Ostwald and Köhler, A., 1928, 237). The liquid remaining unabsorbed after the completion of swelling always contained dissolved rubber, and when used to swell fresh rubber caused a lowering of the swelling maximum. The effect is reversible and is due, not to adsorbed impurities, but to the presence of dissolved rubber in the external liquid.

F. L. USHER.

Electrolysis in gels. II. P. HAPPEL, R. E. LIESEGANG, and O. MASTBAUM (Kolloid-Z., 1929, 48, 252—254).—A layer of gelatin containing dilute potassium nitrate is electrolysed between two platinum wires. Before passing the current, a drop of an electrolyte (e.g., calcium chloride) is placed in the field and after electrolysis the plate is placed in some reagent which will react with the electrolyte (e.g., silver nitrate for calcium chloride), so that the alteration in the shape of the drop becomes apparent. In the experiment described the drop spreads towards the anode.

E. S. HEDGES.

Mol. wt. of proteins, especially of the hæmocyannin of the blood of the snail (*Helix pomatia*). C. BAUMELER (Rev. gén. Colloid., 1929, 7, 145—152).—An account is given of Svedberg's work on the determination of the mol. wt. of proteins by sedimentation methods. The hæmocyannin of the snail has a remarkably high mol. wt., surpassing that of other proteins, but it may nevertheless be crystallised easily.

E. S. HEDGES.

Stability of humours, its causes, effects, and remedies. A. LUMIÈRE (Rev. gén. Colloid., 1929, 7, 158—165).—The principles of colloid chemistry are applied to the problem of the preservation of the normal colloidal state of humours.

General dilution law and mechanism of electrolytic dissociation. W. TRETJAKOV (Z. Elektrochem., 1929, 35, 440—451).—The fraction, F , of an electrolyte which on dissolution passes into free ions is connected with the degree of ionisation, α , given by conductivity measurements, by $F = \alpha / \sqrt{[1 + nD/V_1 \cdot \alpha^{3m/2n}]}$, D being the dielectric constant of the solvent, n the valency of the ions, m the number of ions into which an electrolyte dissociates, and V_1 the volume of solvent (litres) in which each g.-mol.

of electrolyte is dissolved. This value is substituted for α in the Ostwald dilution expression and numerous tables are given showing its applicability to various salts and acids. The values of K are considered to be more satisfactory than those calculated from the equations of Ostwald and Rudolphi. The deviations corresponding with concentrated solutions are attributed to the ions becoming solvated. A more general expression is developed using the relationship $\alpha = F + eA$ (e = ratio of the velocity of the free ions to that of the solvated ions; A = fraction of solvated ions). The values of e calculated for a series of electrolytes from conductivity data reveal that the expression $e = nKD/2$ is approximately valid. The validity of the above equations is also tested in the cases of a number of electrolytes in non-aqueous solvents. H. T. S. BRITTON.

Equilibrium law for electrolytes and ionic hydration. K. JABŁCZYŃSKI and C. SEIDENGART (Rocz. Chem., 1929, 9, 418—430).—Cryoscopic measurements of alkali chloride and hydrogen chloride solutions and of their mixtures, as well as of the mol. wt. of carbamide and of mannitol in solutions of these chlorides, give results in complete agreement with those calculated from the equation of Jabłczyński and Wiśniewski (A., 1922, ii, 190).

R. TRUSZKOWSKI.

Interionic forces and the ionisation of weak electrolytes. H. M. DAWSON (Proc. Leeds Phil. Soc., 1929, 1, 491—496).—A brief outline of the author's work on catalysis in solution in its bearing on the interionic force effects in solutions of weak electrolytes. This work affords new and independent evidence of the electrical field effects indicated by the Debye-Hückel theory, but it shows that the ionic strength hypothesis cannot be reconciled with the behaviour of acids in both salt-free and salt-containing solutions. L. S. THEOBALD.

B.-p. elevation of acetone solutions as related to the interionic attraction theory. A. L. ROBINSON (J. Physical Chem., 1929, 33, 1193—1199; cf. A., 1928, 944).—The b. p. of 0.001—0.3*M*-acetone solutions of anhydrous and hydrated sodium iodide, cobalt chloride, and lanthanum nitrate have been determined, and are in good agreement with the requirements of the Debye-Hückel theory. The results obtained with the hydrated salts indicate that definite ionic hydrates do not exist. L. S. THEOBALD.

Mutual salting-out of ions. J. A. V. BUTLER (J. Physical Chem., 1929, 33, 1015—1023).—Theoretical. The effect of the forces exerted by the electric field of an ion on the solvent molecules and on the distribution of the ions in its neighbourhood is discussed. An equation for the salting-out of a substance by an electrolyte is derived in a simple manner and is shown to be equivalent to the expression obtained by Debye and McAulay (A., 1925, ii, 171) using a different principle. The result is applied to the mutual salting-out of ions. L. S. THEOBALD.

Dissociation constants of organic acids. I. Primary dissociation constants of some alkylmalonic acids. II. Primary dissociation constants of some cyclic 1:1-dicarboxylic acids.

A. I. VOGEL (J.C.S., 1929, 1476—1487, 1487—1494).—I. From measurements of the conductivities of the free acids at concentrations between 0.0001*M* and 0.01*M* and of the disodium salts at concentrations between 0.0002*M* and 0.004*M* the following primary dissociation constants have been calculated: malonic 14.10×10^{-4} , methylmalonic 7.99×10^{-4} , ethylmalonic 10.30×10^{-4} , dimethylmalonic 6.57×10^{-4} , methylethylmalonic 13.94×10^{-4} , diethylmalonic 63.9×10^{-4} , ethyl-*n*-propylmalonic 73.7×10^{-4} , and di-*n*-propylmalonic acid about 90×10^{-4} . The last acid appears to behave as a strong electrolyte, since there is no evidence of a primary dissociation constant over the whole concentration range studied.

II. The following primary dissociation constants have been computed from accurate measurements of the conductivities of the free acids and of their disodium salts in aqueous solution over a fairly wide range of concentration: cyclobutane-1:1-dicarboxylic acid, 6.97×10^{-4} ; cyclopentane-1:1-dicarboxylic acid, 5.47×10^{-4} ; cyclohexane-1:1-dicarboxylic acid, 3.4×10^{-4} . cycloPropane-1:1-dicarboxylic acid is abnormal, inasmuch as it behaves as a strong electrolyte, giving a dissociation constant of about 0.14, which, however, is not constant over the concentration investigated. F. G. TRYHORN.

Ionisation constant of codeine. H. BAGGESGAARD-RASMUSSEN and I. MARTINS (Dansk Tidskr. Farm., 1929, 3, 197—207).—The acidity constant and the basicity constant for the ionisation of codeine, $R(\text{base}) + H^+ = RH^+(\text{acid})$ are found from electro-metric measurements to be 6.7×10^{-9} and 7.9×10^{-7} , respectively. The partition coefficient of codeine between chloroform and water is $83 \pm 10\%$. C. W. GIBBY.

Equilibria between hydroxy-acids and their anhydro-derivatives. M. GEHRKE and H. H. WILLRATH (Z. physikal. Chem., 1929, 142, 301—308).—A 0.1*N*-solution of lactic acid containing about 37% of lactide shows practically no change on keeping for 3 days at the ordinary temperature, but after boiling for about 20 hrs. complete conversion of the lactide into free acid takes place. A freshly-prepared glycollic acid solution is entirely free from glycollide. The hydrolysis curves of α - and β -hydroxybutyric acids indicate the existence, at equilibrium, of 4—5% of lactide derivative, assuming the latter to contain one free carboxyl group. H. F. GILLBE.

Esterification equilibrium and active molecules. S. POZNAŃSKI (Rocz. Chem., 1929, 9, 354—360).—A verification of Świątosławski's equation, $K_1 = KZ_3Z_4/Z_1Z_2$, where K is the equilibrium constant of the system ethyl alcohol-acetic acid-ethyl acetate-water, and Z_1, Z_2, Z_3, Z_4 are the deviations of the volatility of each of the components from that of the corresponding pure liquid. The value of K_1 is $14(\pm 10\%)$, and is independent of the proportions of the various components of the mixture. R. TRUSZKOWSKI.

Influence of salts on the activity of acetic acid molecules in aqueous solution. E. LARSSON (Svensk Kem. Tidskr., 1929, 41, 130—141).—The distribution of acetic acid between solutions of the chlorides of sodium, potassium, calcium, strontium,

and barium, on the one hand, and benzene, ether, or amyl alcohol on the other hand, has been determined. The activity coefficients of acetic acid in salt solutions of concentrations ranging from 0.125 to 3 mols. per litre have been calculated from the results. The values obtained for each salt with the different organic solvents agree satisfactorily, but differ from those derived from the distribution of acetic acid between salt solutions and the gaseous phase (cf. McBain and Kam, J.C.S., 1919, **115**, 1332); this may be due to the higher temperature (100°) employed in the latter case.

H. F. HARWOOD.

Tervalent carbon. VII. Accurate determination of dissociation equilibrium. Determination of heat of dissociation of hexaphenylethane. K. ZIEGLER and L. EWALD. **VIII. Molecular volume of hexaphenylethane and analogues.** K. ZIEGLER and F. DITZEL (Annalen, 1929, **473**, 163—193, 194—210).—VII. An apparatus in which dilution of a solution of hexaphenylethane is possible is described and the extinction coefficients of the solutions so obtained are measured in the visible spectrum. Extrapolation of the extinction coefficient, ϵ_v , to ϵ_∞ affords a measure of the degree of dissociation (α) which equals $\epsilon_v/\epsilon_\infty$. Application of Ostwald's dilution law gives the expression $K=4\alpha^2/(1-\alpha)v$, where v = volume in which 1 mol. of hexaphenylethane is dissolved. For hexaphenylethane in benzene solution at 20° the value of K is $4.1 \times 10^{-4} \pm 5\%$. The corresponding values for tetraphenyl- β -naphthylethane in cyclohexane at 20° and bis-2 : 3 : 4-triphenyl-6-methylchromenyl in benzene at 25° are $3.1-3.36 \times 10^{-1}$ and $1 \times 10^{-3} \pm 4\%$, respectively. Solutions of pentaphenylcyclopentadienyl (conveniently prepared by the action of potassium phenylisopropyl on bromopentaphenylcyclopentadiene) in various solvents show absorption maxima at about 5800—5900 Å. The values of ϵ fall into two groups, (a) light-stable solutions in cyclohexane, benzene, and ether, 6360—6720, (b) light-sensitive solutions in acetone, chloroform, and ethyl acetate, 5680—6000. The various results afford no evidence of the tautomerism of triarylmethyls. The extinction curve for pentaphenylcyclopentadienyl shows a decrease in the maximum value of ϵ for rise in temperature. The heat of dissociation of hexaphenylethane in various solvents is about 11.5 kg.-cals. This is a characteristic constant and is independent of the solvent.

VIII. To determine the mol. vol. of the C_6H_4 group density determinations of 38 solid substances have been carried out at 0°, and the values found vary from 53—54 to 66 (limits). The variations correspond with the differences in the values of the methylene group using Biltz's zero point volumes (A., 1927, 498). The values of $C_{\text{arom.}}$, $C_{\text{aliph.}}$, and H are calculated to be 5.86, 3.69, and 6.28 at 0° (cf. Biltz, *loc. cit.*). Using these values for the calculation of v_m it is found that 76% of the values for 34 substances examined agree within 3% and 94% within 4%. Compounds containing a relatively large number of aliphatic carbon atoms give values for v_m which are too low, but arylated hydrocarbons (not dissociable) give values usually of the order $+1-2\%$. The variation in the mol. vol. of hexaphenylethane,

crystallised from various solvents, is of the same order.

H. BURTON.

Hydrolysis of certain beryllium salts of strong acids. V. ČUPR (Coll. Czech. Chem. Comm., 1929, **1**, 377—386).—The hydrogen-ion concentration in N - to 0.001*N*-solutions of beryllium sulphate, chloride, bromide, chlorate, and perchlorate has been measured electrometrically and colorimetrically. The ratio $[H^+]/C$ varies with concentration in the same manner for all salts studied except beryllium sulphate. It falls on dilution as far as 0.1*N*, and then rises again to a constant value. The exceptional behaviour of beryllium sulphate is probably due to the formation of the ion HSO_4' .

C. W. GIBBY.

Partition of strong bases and strong acids in saturated aqueous solutions. V. I. NIKOLAIYEV (Z. anorg. Chem., 1929, **181**, 249—279).—The equilibria in the following four quaternary systems have been determined and are illustrated by space models based on the regular tetrahedron; (a) $Na_2O-N_2O_5-HCl-H_2O$, (b) $K_2O-N_2O_5-HCl-H_2O$, (c) $Na_2O-K_2O-N_2O_5-H_2O$, and (d) $Na_2O-K_2O-HCl-H_2O$. In system (a) at 15° the neutral saturated solution contains equal molecular proportions of sodium chloride and nitrate; with rising temperature the ratio $NaCl/NaNO_3$ falls rapidly to a minimum of 0.08 at 162°, then rises slightly to 0.13 at 210°. At 25° this ratio falls steadily with increasing concentration of sodium hydroxide to practically zero in a 40% solution of the alkali; at 100° in acid solution the ratio falls from 0.13 to zero with increase in the total acidity from 0 to 12%. In the corresponding potassium system (b) the saturated neutral solution contains an equimolecular mixture of chloride and nitrate at 50°; at 25° the equimolecular mixture is obtained only when 37.27% of free alkali is present or when the total free and combined nitric acid is 20.88%. In the nitrate system (c) addition of nitric acid decreases the combined solubility in such a way that the decrease in mol.-% of total nitrate is equal to the increase in mol.-% of nitric acid up to an addition of 10 mol.-% of acid. The ratio $NaNO_3/KNO_3$, originally 2.51 in neutral solution at 25° decreases with addition of nitric acid to a minimum of 0.51 with 0.62 mol. of acid, then increases again to 3.9 with 0.98 mol. of acid per mol. of salt. This behaviour is due to the formation of the additive compound $KNO_3 \cdot 2HNO_3$. Addition of sodium hydroxide increases the $NaNO_3/KNO_3$ ratio to a maximum of 4.41 with 0.369 mol. of alkali per mol. of salt; further addition of alkali decreases this ratio to 0.72 with 1 mol. of alkali per mol. of salt. Potassium hydroxide, on the other hand, decreases the solubility of potassium nitrate almost to zero with 0.19 mol. of alkali per mol. of salt without appreciably varying the solubility of the sodium salt. In the corresponding chloride system (d) the molecular solubilities are equal at 90°; below this temperature the ratio $KCl/NaCl$ is less than, and above 90° is greater than, unity. It is suggested that the influences controlling the partition of an acid between two bases or of a base between two acids are the heat of neutralisation, the heat of dissolution, and the heat of hydration.

A. R. POWELL.

Soluble lakes of aurintricarboxylic acid. W. E. THEBUN (J. Physical Chem., 1929, **33**, 977—983).—The equilibrium existing between alumina, aurintricarboxylic acid, and the resulting lake has been investigated colorimetrically. Values for the ratio (free alumina) (free aurin)/(total alumina)(lake) are fairly constant and give a mean of 1.41. With other oxides replacing alumina, the corresponding values are for ferric iron 0.15, chromium 1.41, ferrous iron 1.61, and beryllium 2.22. The existence of two kinds of lake is indicated, and the results show that lake formation depends on the insolubility of the hydrous oxide and that an excess of dye can counteract the solubility of the oxide. With alumina, the intensity of colour of the lake is the same when formed at the ordinary temperature during 24 hrs., at the b. p. during 1 min. followed by rapid cooling, or at 60° during 10 min. followed by rapid cooling. The addition of gum arabic prevents the flocculation of excess of alumina but does not alter the colour intensity of the lake. The volume and p_H value of acid solutions have no effect on the colour intensity provided that sufficient time is allowed or that lake formation is accelerated by rise of temperature.

L. S. THEOBALD.

Effect of neutral salts on p_H of phosphate buffer mixtures. H. W. ROBINSON (J. Biol. Chem., 1929, **82**, 775—802).—The effect of the presence of various neutral salts on the p_H of phosphate buffer solutions of different concentrations has been observed and the results are treated mathematically. The effects of potassium, sodium, and lithium salts are predominantly those of the cations and increase in the order mentioned; the effect depends on the total ionic strength of the buffer, which is not proportional to the total phosphate ion concentration owing to variations in the proportion of primary and secondary phosphate. From the results it is possible to calculate the p_H of a phosphate buffer containing known amounts of neutral salts, and also to deduce the amount of salt solution with which a phosphate buffer must be diluted in order that its p_H may remain unchanged.

C. R. HARRINGTON.

Oxidation-reduction systems of biological importance. IV. Cysteine complexes with metals of the iron group. L. MICHAELIS and E. S. G. BARRON (J. Biol. Chem., 1929, **83**, 191—210).—Cysteine gives a Bordeaux-red complex with nickel, the formation of which is independent of the presence of oxygen. With cobalt in the absence of oxygen a complex is formed which is green when viewed in bulk unless the cysteine be in large excess, when it is pink. This complex is a powerful reducing agent, its potential at p_H 7.5 matching that of the hydrogen electrode, and is converted in presence of an oxidant (ferricyanide, a dye, or even cystine) or by contact with atmospheric oxygen into a stable brown compound. The oxygen consumption increases with the amount of cobalt until the solution contains 1 atom of cobalt per 3 mols. of cysteine, such a solution absorbing 0.5 mol. of oxygen or reducing an equivalent amount of oxidant. The course of the reaction is not always the same, however, the oxidation by ferricyanide proceeding in two stages, and that by phenolindophenol following a smooth course.

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The violet complex of cysteine with iron is analogous to the stable brown complex with cobalt, and it is the instability of the former complex which renders iron a catalyst for the oxidation of cysteine, whilst cobalt has no such catalytic action.

C. R. HARRINGTON.

Chemical antagonism of ions. IV. Effect of salt mixtures on glycine activity. H. S. SIMMS (J. Gen. Physiol., 1929, **12**, 783—792).—The changes in p_H on adding sodium chloride, potassium chloride, magnesium chloride, and calcium chloride either singly or in pairs to a 0.01M-solution of glycine containing 0.5 equivalent of sodium hydroxide are shown to be analogous to the changes produced in a gelatin solution (cf. this vol., 140, 647). P. G. MARSHALL.

Influence of ethyl ether and of dimethylpyrone on the availability of hydrogen chloride in alcoholic solution. V. E. S. MITCHELL and J. R. PARTINGTON (J.C.S., 1929, 1562—1568).—The rate of esterification of phenylacetic acid in dry alcoholic solution under the influence of hydrogen chloride is accelerated in the presence of small amounts of ethyl ether, and is retarded by the addition of small amounts of water or of dimethylpyrone. The effect of dimethylpyrone becomes analogous to that of water if the former is regarded as dibasic, and therefore capable of uniting with 2 mols. of hydrogen ion, reducing thereby any catalytic action due to hydrogen ion. The slight accelerating effect of dry ether is due possibly to a solvent effect, or to the predominance of the solvent effect over retardation due to union with hydrogen ion. It is probable, however, that ethyl ether does not behave as a base under these conditions.

F. G. TRYHORN.

Hydrazine: solubility relations of hydrazine picrate, and the equilibrium $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$. E. C. GILBERT (J. Physical Chem., 1929, **33**, 1235—1246).—The solubility of hydrazine picrate in solutions of ammonium chloride and of ammonium chloride and ammonium picrate has been determined at 20°. The solubilities of the hydrazine and other picrates in salt solutions show a considerable deviation from the law of constancy of the ionic product where the solvents have a common ion. This effect is not noticeable except in homoionic solvents, and is specific, apparently, for the picrate ion. The solubility of hydrazine picrate in ammonium chloride solutions at 20° can be represented by the equation $\log s/s_0 = 0.5\mu^2 - 0.25\mu$ for values of μ , the ionic strength, up to 0.12. The coefficient at 20° of the equilibrium $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$ has been determined from the solubility data of hydrazine picrate in ammonium chloride-ammonia solutions and leads to a value of $5.3 - 6.5 \times 10^{-9}$ for the dissociation constant of the $N_2H_5^+$ ion. L. S. THEOBALD.

Existence of monocalcium aluminate in solution. A. TRAVERS and SCHNOUTKA (Compt. rend., 1929, **189**, 182—183).—Addition of lime water (or baryta) to a solution of an aluminium salt precipitates gelatinous hydrated alumina quantitatively when the ratio of CaO to Al_2O_3 reaches 3. When the ratio is increased to 4, the precipitate is dissolved. Hydrated monocalcium aluminate, however, cannot be crystallised from such solutions, as decomposition

occurs on evaporation, but after addition of an excess of lime water, crystals are obtained the form of which depends on the p_H of the solution. These phenomena are due to the low solubility product of the poly-calcium aluminates compared with the mono-compound.

J. GRANT.

Equilibrium between alcohols and salts. III. G. C. GIBSON, J. O. DRISCOLL, and W. J. JONES (J.C.S., 1929, 1440—1443).—The solubilities of the sulphates of magnesium, zinc, cadmium, manganese, cobalt, and zinc in methyl and ethyl alcohols have been measured at temperatures between 15° and 55°. The following alcoholates have been prepared by dissolving the metal in methyl alcohol containing 100% sulphuric acid: $MgSO_4 \cdot 3.5MeOH$; $ZnSO_4 \cdot 2.5MeOH$; $ZnSO_4 \cdot MeOH$; $FeSO_4 \cdot 1.5MeOH$. Between 15° and 55° cadmium, thorium, manganese, cobalt, and nickel sulphates exist in equilibrium with their respective saturated solutions as the non-alcoholated salts. The stabilities of the above methyl alcoholates, and the extent of the basic decomposition of copper and zinc sulphates by methyl alcohol, have been studied. In the case of copper basic decomposition is complete. F. G. TRYHORN.

System gold-mercury. I. I. PLAKSIN (J. Russ. Phys. Chem. Soc., 1929, 61, 521—534).—Thermal and micrographic methods indicate the formation of the compounds $AuHg_2$ and Au_2Hg . The former is stable below 310°; at higher temperatures it is converted into Au_2Hg with the liberation of mercury. At 420° the second compound forms a liquid alloy and a solid solution of mercury in gold. The maximum concentration of mercury in gold solid solutions is 16 at.-%. The compound $AuHg_2$ undergoes polymorphic changes at 122° and at -36°. A similar change occurs in the compound Au_2Hg at 402°. The liquidus curve thus consists of six sections, the transition points being at -36°, at 122° (1.3 at.-% Au), at 310° (13.5%), at 402° (50.3%), and at 420° (55.6%). The eutectic lies very close to the ordinate for pure mercury, and the eutectic temperature is practically the same as for mercury alone.

R. TRUSZKOWSKI.

Equilibrium diagram of the iron-vanadium system. S. OYA (J. Study Met., 1928, 5, 349—356).—By suitable adjustment of the proportion of aluminium and sodium carbonate employed, vanadium of 98.5% purity has been obtained from ammonium vanadate. The iron-vanadium alloys form solid solutions in all ranges of composition. The A4 point for iron is rapidly lowered by the addition of vanadium, whilst the A3 point is rapidly raised. The A2 point rises to 15% V, is slowly lowered at 20% V, and is rapidly lowered to the ordinary temperature at 35% V.

CHEMICAL ABSTRACTS.

System water-hexamethylenetetrammine. V. EVRARD (Natuurwetensch. Tijds., 1929, 11, 99—107).—The solubility diagram has been mapped from -10° to 165°. The curve consists of three parts: the first, the ice line, starts at 0° for pure water and ends at -10.3° and 29.8% of the solute; the second, corresponding with solubility of the hydrate (6 mols. H_2O), extends from the end of the first to the point 13°, 46.8% solute, and the third rises from this point

very steeply, almost parallel with the temperature axis. The solutions in pure water are very stable.

S. I. LEVY.

Effect of high temperatures on some metallic sulphides. PICON (Compt. rend., 1929, 189, 96—98; cf. A., 1927, 328).—The sulphides of chromium, molybdenum, tungsten, uranium, aluminium, and magnesium are volatilised or dissociated at 1200—1300° in a carbon resistance furnace. Dissociation occurs in all cases in a vacuum, although it is small for aluminium and magnesium sulphides.

J. GRANT.

Reduction equilibrium of lead sulphide and the chemical constants of sulphur and hydrogen sulphide. K. JELLINEK and A. DEUBEL (Z. Elektrochem., 1929, 35, 451—457).—The equilibrium $PbS + H_2 \rightleftharpoons Pb + H_2S$ was investigated at various temperatures between 655° and 1000° by passing hydrogen over the heated sulphide at definite rates and measuring the ratio of hydrogen to hydrogen sulphide in the issuing gases. From experiments at a fixed temperature and varying rates, it was possible to derive the equilibrium ratio (cf. Jellinek and Zakowski, A., 1925, ii, 401). From the published specific heats calculations have been made of the pressures of sulphur vapour existing in equilibrium at the different temperatures, of the heat of formation of crystalline lead sulphide (40.8 kg.-cal.), and the heat of transition from the form in which it is precipitated to the crystalline state (5.5 kg.-cal.). The chemical constants of sulphur vapour and hydrogen sulphide have also been derived.

H. T. S. BRITTON.

Equilibrium between molten metals and salts. XVII. Calcium and sodium and their chlorides. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, 181, 193—201).—The equilibria in the system $CaCl_2 + 2Na \rightleftharpoons 2NaCl + Ca$ have been investigated at 600—800°. When the salt phase contains 16—98.5 mol.-% of calcium chloride the metal phase has a constant composition, namely, 0.95 at.-% Ca and 99.05 at.-% Na. With lower concentrations of calcium chloride in the salt phase the calcium in the metal phase is a function of the composition of the salt phase, the equilibrium curve agreeing with that deduced from the phase rule in cases where there is only a limited solubility of the metals in one another. The equilibria in the system are independent of the temperature within the above limits and of the relative proportions of the salt and metal phases.

A. R. POWELL.

Double decomposition in the absence of a solvent. IX. System $AgCl + KI \rightarrow AgI + KCl$. A. P. ROSTKOWSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 595—605).—The existence of the compound $4AgI \cdot KI$ is indicated by the equilibrium data.

R. TRUSZKOWSKI.

Systems: borates and halides of sodium in the fused state. B. STÄLHANE (Z. Elektrochem., 1929, 35, 486—492).—Almost complete isotherms of the ternary systems $Na_2O - B_2O_3 - NaCl$ at 850° and $Na_2O - B_2O_3 - NaBr$ at 830° have been worked out. In each isotherm, two liquid phases coexist, the lighter one being rich in borate and the heavier rich in halide.

H. T. S. BRITTON.

Saturated solutions of salts having one common ion. E. V. KUKLIN (J. Russ. Phys. Chem. Soc., 1929, 61, 667—680).—The composition of the saturated solution is affected by double salt formation and by the relative solubilities of the simple and double salts. A. FREIMAN.

Equilibrium between two solids in a common solvent. V. K. PERSCHKE (J. Russ. Phys. Chem. Soc., 1929, 61, 441—444).—From the point of view of free-energy changes the author discusses the question of the solubilities of two solids which do not react with each other or with the common solvent. At a given temperature the simultaneous solubilities should be the same as when each dissolves separately. This is confirmed by investigations of the system azobenzene-carbamide-ethyl alcohol.

A. FREIMAN.

System $\text{NaNO}_3\text{-Na}_2\text{SO}_4\text{-MgCl}_2\text{-H}_2\text{O}$ at 0° , 10° , 25° , 50° , 75° , and 100° . G. LEIMBACH and A. PFEIFFENBERGER (Caliche, 1929, 11, 61—85).—Details are given of the phase relations at 0° , 10° , and 25° , and the results obtained are compared with those of other observers. H. F. GILLBE.

Mesophases. IV. Further examples of aqueous mesophases. V. Influence of electric and magnetic fields. H. ZOCHER and V. BIRSTEIN (Z. physikal. Chem., 1929, 142, 177—185, 186—194; cf. this vol., 876).—IV. Sodium and potassium palmitates, stearates, and oleates have been studied. Only sodium and potassium oleates form mesophases. Ammonium oleate solutions prepared by the action of concentrated ammonia on oleic acid gave no evidence of an aqueous mesophase. Sodium naphthenate forms a smectic mesophase in aqueous solution. Cetyl xanthate similarly forms a smectic phase in hot concentrated aqueous solution. The dispersion of the double refraction of this solution is anomalous. Sols of cetyl xanthate have been prepared in benzene, toluene, and xylene which show moderately strong negative stream double refraction. Friedel's observations (A., 1923, ii, 223) on the mesophase formed by bromophenanthrenesulphonic acid have been confirmed. It is further shown that the nematic phase formed at moderate concentrations, in contrast to the nematic phases already known, shows a negative stream double refraction and forms drops with optically positive radii. Commercial lecithin forms a mesophase; pure synthetic lecithin does not.

The structure of a smectic phase does not always make itself evident, since the diffuse double refraction obtained is also given by many gels and sols. In the latter cases the double refraction is to be ascribed to the anisotropic colloidal particles.

V. The dielectric and magnetic anisotropy of nematic phases is negative in the case of compounds such as *p*-azoxyanisole, for which the molecular structure is symmetrical. For nematic phases of substances of asymmetrical molecular structure, the magnetic and dielectric anisotropy is positive. By the use of strong fields (about 10,000 volts/cm.), it is shown that, contrary to Friedel's statement (A., 1923, ii, 223), nematic phases of the cholesterol type, such as that of optically active amyl ethoxybenzylidene-amino- α -methylcinnamate, are oriented and become

doubly refracting. The optical activity is decreased considerably by the field; removal of the field is accompanied by the disappearance of the double refraction and the restoration of the normal optical activity.

Smectic phases are also influenced by electric fields of suitable strength. In all the cases studied, the dielectric anisotropy is negative even when that of the corresponding nematic phase is positive. The magnetic anisotropy is positive. F. J. WILKINS.

Free energy charts for predicting equilibrium pressures and concentrations. R. F. NIELSEN (Ind. Eng. Chem., 1929, 21, 568—571).—A form of chart is suggested which admits the direct reading of physical and chemical equilibrium concentrations if a single chart be prepared for each pure substance concerned. The charts employ lines of constant pressure or concentration with temperatures as abscissæ and some function of free energy as ordinate. The methods of preparation are explained and an example of the use of the graphs is given. Problems involving electrolytes can be solved by the use of this type of graph. H. INGLESON.

Charts for predicting equilibria. M. RANDALL (Ind. Eng. Chem., 1929, 21, 571—572).—A method of preparing the charts which is a modification of that suggested by Nielsen (preceding abstract) is explained and examples of the use of the charts are given. H. INGLESON.

Extension of the Clausius-Maxwell criterion. L. SCHAMES (Helv. phys. Acta, 1928, 1, 417—420; Chem Zentr., 1929, i, 978).

Partial molal heat capacities and relative partial molal heat functions in solutions of molten metals. A. N. GUTHRIE and E. E. LIBMAN (J. Amer. Chem. Soc., 1929, 51, 1711—1715).—Calculations are made for solutions of lead and antimony and of bismuth and cadmium from previously published thermal data. The relative partial molal heat functions are zero for all temperatures and at all concentrations of these binary solutions. The partial molal heat capacities are constant, independent of concentration, and are equal to the molal heat capacities of the pure components in the liquid state. S. K. TWEEDY.

Heat of mixing of molten metals. IV. M. KAWAKAMI (J. Study Met., 1928, 5, 346—348).—It is deduced that $\Delta H = \Delta H' + RT\{y \log_e (x/y) + (1-y) \log_e (1-x)/(1-y) + yQ_A(T_{0A} - T)/T_{0A} + (1-y) \times Q_B(T_{0B} - T)/T_{0B}\}$, where $\Delta H' = y\bar{H}'_A + (1-y)\bar{H}'_B$ and ΔH is the heat of mixing A and B in the mol. proportion $y/(1-y)$ in the solid states to form a solid solution; y and x are the mol. fractions of A in equilibrium at T° Abs., Q_A and Q_B the heats of fusion, T_{0A} and T_{0B} the m. p., \bar{H}'_A the heat evolved when 1 mol. of the liquid A is mixed with an infinitely large quantity of the liquid mixture composed of x and $(1-x)$ mol. fraction of A and B, and \bar{H}'_B the heat evolved when B is mixed with an infinitely large quantity of that mixture. Values are recorded for bismuth-zinc, lead-cadmium, lead-tin, and tin-cadmium mixtures. When $y=1$, $RT \log_e x + Q_A(T_{0A} - T)/T_{0A} + \Delta \bar{H}'_A = 0$, where x is the solubility of A in B, applying to the binary system having no solid solubility. CHEMICAL ABSTRACTS.

Determination of the limiting heat of dissolution of some hydrated salts (direct method).

J. PERREU (Compt. rend., 1929, 189, 167—169).—The limiting heats of dissolution for various salts have been determined by extrapolation of the heat of dissolution-concentration curves to the saturation point. The data recorded are: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (—13.54), $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (—21.845), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (—16.83), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (—4.73), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (—2.44).

J. GRANT.

Measurement of the limiting heat of dissolution of hydrated salts (method of heats of dilution). J. PERREU (Compt. rend., 1929, 189, 285—287).—The heats of dilution of sodium carbonate and sulphate, barium chloride, copper sulphate, and disodium hydrogen phosphate (*L*) were measured at 11—12° by diluting in a calorimeter a known weight of standard solution with the amount of water necessary to lower the concentration to the same value as in the measurement of the initial molecular heat of dissolution (X_N) of the salt in a large volume of water. If Δ is the heat of molecular dilution and A the heat of addition, the modified Matignon formula $L = X_N - (\Delta + A)$ gives values of *L* in close agreement with those obtained by the direct method. *A* was determined directly by adding a small amount of water to a large excess of saturated solution (cf. preceding abstract).

J. GRANT.

Heat of solidification and heat of dissolution of sucrose. A. TIAN (Compt. rend., 1929, 189, 164—167).—A zero or compensation method is described for the determination of the heat of solidification of sucrose (*X*). This is based on the fact that the heat of dissolution of pure supercooled sucrose is positive (this vol., 1045), whilst that of crystalline sucrose is negative. If Q_s and Q_l are the molecular heats of dissolution of sucrose in the solid and liquid states, respectively, and α is the weight of crystalline sucrose which when mixed with unit weight of supercooled substance gives no thermal effect, $X = Q_l - Q_s = -(\alpha + 1)Q_s = 4595$ at 15.93°. The solubility curves of solid and liquid sucrose meet at the m. p.

J. GRANT.

Modification of the moving-boundary method for the determination of transference numbers. H. P. CADY and L. G. LONGSWORTH (J. Amer. Chem. Soc., 1929, 51, 1656—1664).—A metal anode soluble under the action of the current is used as the source of indicator ions, and a single ascending boundary only is observed, viz., that between the solution of electrolyte originally placed in the cell and the heavier electrolyte having a common anion and an unlike cation formed from the metal anode. This boundary starts at the anode. The transport numbers determined by this method are independent of the potential gradient over a wide range of the latter. Automatic adjustment of the concentration of the indicator ion occurs in accordance with Kohlrausch's relationship (Ann. Physik, 1897, 62, 209). The range of application of the method is briefly discussed.

S. K. TWEEDY.

Hittorf's explanation of electrolytic conduction. S. RAY (Z. Elektrochem., 1929, 35, 469—470).—It is suggested that the ionic velocity ordinarily measured

refers only to the final velocity of an ion, viz., in the vicinity of an electrode. Elsewhere, the velocity varies with the time the ion has been moving and its distance from the electrodes. The average velocities of anions and cations are stated to be equal, which therefore accounts for the amounts of ions discharged at the electrodes being proportional to the atomic or mol. wt.—a fact which cannot be explained on the Hittorf view.

H. T. S. BRITTON.

Inapplicability of Ohm's law to alternating-current circuits containing capacity and resistance. M. H. AHMADI and H. L. TANDON (Z. Elektrochem., 1929, 35, 471—473).—Theoretical; cf. Ray, this vol., 228.

H. T. S. BRITTON.

Frequency dependence of the electrical conductance of solutions of strong electrolytes. H. FALKENHAGEN and J. W. WILLIAMS (J. Physical Chem., 1929, 33, 1121—1134; cf. A., 1928, 596, 957, 1330).—Theoretical. The dispersion of electrical conductance consequent on the existence of a finite time of relaxation is further discussed together with the influence of concentration, ionic mobility, dielectric constant, temperature, and valency on this effect.

L. S. THEOBALD.

Dielectric loss in electrolyte solutions in high-frequency fields. W. T. RICHARDS and A. L. LOOMIS (Proc. Nat. Acad. Sci., 1929, 15, 587—593).—An expression is given connecting power loss in a liquid dielectric with its conductivity, dielectric constant, and the frequency of the field to which it is subjected. This is tested and verified over a considerable range of frequencies and conductivities for sodium chloride, lead acetate, mercuric chloride, and for some disperse and heterogeneous systems. Its application to physiological behaviour in high-frequency fields is discussed.

N. M. BLIGH.

Determination of conductivity of electrolytes with alternating current of low frequency. A. H. W. ATEN and (MISS) L. M. BOERLAGE (Rec. trav. chim., 1929, 48, 698—710; cf. A., 1921, ii, 159).—Comparative measurements of the resistance of electrolytes, using a galvanometer with alternating current of 50 cycles, and a telephone with frequencies of 1100 and 2300, have shown that the former arrangement can be used for resistances above 200 ohms with an accuracy of 0.01% if the liquid is contained in a cell of the Washburn type with well-platinised electrodes. For resistances above 10,000 ohms the galvanometer is always preferable to the telephone. Methods of dealing with capacity effects due to the cell and to the water in the thermostat are discussed.

F. L. USHER.

"Water correction" in the measurement of electrical conductivity of very dilute aqueous solutions of electrolytes. I. M. KOLTHOFF (Rec. trav. chim., 1929, 48, 664—680).—The conductivity of very dilute aqueous solutions of salts, acids, and bases has been studied in order to ascertain the best method of eliminating the uncertainty due to the conductivity of the water used in their preparation. A summary of previous work is given. In using "equilibrium water" (i.e., water saturated with and left exposed to the laboratory air) emphasis is laid on the importance of securing equilibrium with the air

at the temperature at which the measurements are made. Such water is suitable for neutral salts and strong acids down to a concentration $5 \times 10^{-5}N$. In the former case the results obtained by subtracting the total conductivity of the water from that of the solutions agreed within 0.5% with those obtained by using "ultra-pure" water (prepared by removing dissolved carbon dioxide from "equilibrium water" with purified air). The resistance of solutions of strong acids at concentrations $>10^{-4}N$ is the same whether they are made with "equilibrium water" or with "ultra-pure" water, and no correction for the conductivity of dissolved carbonic acid must be applied. At lower concentrations irregularities are encountered due to traces of alkaline impurities. Platinised electrodes give rise to slight adsorption effects with both salts and acids. In determining the conductivity of very dilute ($<10^{-4}N$) solutions of bases "ultra-pure" water must be substituted for "equilibrium water," the glass vessels must be paraffined, and blank platinum electrodes used in order to secure reproducible results. Equations have been derived for calculating the correction to be applied if "equilibrium water" is used for determining conductivities of slightly soluble hydroxides. The work of Remy and Kuhlmann (cf. A., 1925, ii, 30, 119, 299) is considered untrustworthy.

F. L. USHER.

Viscosity and conductance of mixed solutions of lead nitrate and ammonium nitrate. G. MALQUORI (Gazzetta, 1929, 59, 355—362).—The conductance and viscosity of solutions of lead nitrate, of ammonium nitrate, and of mixtures of these two salts have been measured between 15° and 60°. From the divergences shown by the conductances, corrected for viscosity, of the mixed solutions from those calculated from the mixture law, evidence is adduced for the existence of a complex of the type $Pb(NO_3)_2 \cdot 2NH_4NO_3$, giving rise probably to complex ions $Pb(NO_3)_4^{2-}$.

F. G. TRYHORN.

Great mobility of hydrogen and hydroxyl ions in aqueous solutions. M. SCANAVY-GRIGORIEVA (Z. anorg. Chem., 1929, 181, 337—346).—Conductivity measurements of aqueous solutions of potassium chloride, potassium hydroxide, and hydrochloric acid, ranging from 0.001M to M, and of similar solutions containing 50% of glycerol, show that the proportional decrease in conductivity due to the increased viscosity is no greater for the neutral salt than for the acid and alkali. The results consequently do not support the Danneel-Grotthus theory of conductivity.

H. F. HARWOOD.

Lead dioxide-lead sulphate electrode. W. C. VOSBURGH and D. N. CRAIG (J. Amer. Chem. Soc., 1929, 51, 2009—2019).—The *E.M.F.* of the cell $Hg|Hg_2SO_4, PbSO_4, H_2SO_4(c), H_2SO_4(c)|PbO_2, PbSO_4|Pt$ was measured at 20°, 25°, 30°, 35°, and 40°, *c* varying between 1M and 3.5M. The temperature coefficient varies with *c*. The effect of dissolved oxygen and of the method of preparation of the lead dioxide was also studied. The *E.M.F.* of the cell $H_2(Pt)|H_2SO_4(\text{unit activity})|H_2SO_4(\text{unit activity}), PbO_2, PbSO_4(Pt)$ was calculated to be 1.681 volts at 25°. From this the *E.M.F.* of the lead accumulator, assuming the double sulphate theory, is calculated as 2.03 volts, which result

is regarded as supporting this theory. Revised values for the activity coefficients of sulphuric acid are calculated from *E.M.F.* results here recorded. For the reaction $PbO_2 + 2Hg + 2H_2SO_4(1.036M) = Hg_2SO_4 + PbSO_4 + 2H_2O$, at 25°, the free energy change is $-43,960$ g.-cal., the entropy change -2.58 g.-cal./1°, and the heat of reaction $-44,730$ g.-cal. The last figure agrees with the value calculated from thermochemical data.

S. K. TWEEDY.

Polarographic studies with the dropping mercury cathode. III. Deposition of cadmium from cyanide solutions. I. PINES (Coll. Czech. Chem. Comm., 1929, 1, 387—391; cf. Nejedlý, this vol., 885).—The deposition potentials of cadmium in solutions containing cadmium salts only and in solutions containing potassium cyanide have been determined. The deposition potential in cyanide solutions agrees with the calculated reversible electrode potential. Cadmium can be deposited completely and reversibly at the dropping mercury cathode in any concentration of cyanide. In fairly dilute solutions, $Cd(CN)_3^-$ ions are formed; $[Cd(CN)_3^-]/[Cd^{2+}][CN^-]^3 = 8 \times 10^{18}$.

C. W. GIBBY.

Potential of an inert electrode in a solution of acetaldehyde. L. RAPKINE (Compt. rend., 1929, 189, 171—173).—The electrode potential of buffered 2% solutions of acetaldehyde at 40° varies linearly with the p_H up to p_H 10, at which point there is an inflexion towards the electronegative region, whilst at p_H 12 it cuts the co-ordinate of the limiting potential of dextrose. The potential is established more rapidly and becomes more negative in value as the alkalinity increases, and aldehyde-sugar condensation in alkaline media is therefore indicated. The irreversible nature of the potential was demonstrated by the addition of milk dehydrase and an acceptor (methylene-blue), and by titration with potassium ferricyanide.

J. GRANT.

Potential differences across the boundaries between solutions of mixed univalent chlorides. E. R. SMITH (Bur. Stand. J. Res., 1929, 2, 1137—1143).—Potential differences across the boundaries between solutions of mixed univalent chlorides (hydrogen chloride and sodium chloride) have been measured using a flowing junction and silver-silver chloride electrodes. There is no evidence of complex formation and potentials can be accurately computed from the formula $E = (RT/F) \log_e [(1 - N_{Na}) - x_2(N_H - N_{Na})] / [(1 - N_{Na}) - x_1(N_H - N_{Na})]$, where x_1 and x_2 represent molal proportions of sodium chloride to the total electrolyte concentration, and N_{Na} and N_H are the cation transference numbers in solutions of the pure electrolytes at the same concentration as the total concentration of the mixture.

C. J. SMITHELLS.

Ammonia-oxygen gas cell. C. MARIE and C. HAENNY (Compt. rend., 1929, 189, 149—150).—The system $air|Pt|pyrex\ glass|Pt|NH_3$ becomes a conductor above 480°, and the *E.M.F.* falls from 1.090 volts at 570° to 0.951 volt at 790°. The observed values correspond with those calculated from thermochemical data for the equation $4NH_3 + 3O_2 = 2N_2 + 6H_2O$.

J. GRANT.

Variation in the concentration of dilute amalgams of alkali and alkaline-earth metals caused by passing an electric current through them. M. LE BLANC and R. JACKH (*Z. Elektrochem.*, 1929, **35**, 395—409).—Dilute amalgams were electrolysed in glass tubes, straight and bent, for various periods of time with different current densities and the changes in concentration of alkali or alkaline-earth metal which occurred in the cathode, middle, and anode compartments were measured. With sodium amalgam the sodium travels to the anode, and the quotient of the difference in concentration of the sodium in the anode and cathode compartments and the current density gradually decreases as the temperature is raised from 25° to 75°, the maximum value of the quotient at any given temperature being attained after about 2000 hrs. The quotient is proportional to the original concentration of the amalgam, and when the electrolysis is carried out in a bent tube, instead of in a straight one, it is quadrupled. Similar increases in the difference between the concentration of the sodium in the amalgam at the two electrodes with increasing current density were found at other temperatures. In the case of barium amalgams the barium travels towards the anode, whereas the reverse is true of lithium and calcium amalgams. The cause of these changes in concentration cannot be traced back to thermoelectric effects. H. T. S. BRITTON.

Theory of passivity. R. MÜLLER (*Z. Elektrochem.*, 1929, **35**, 459—460).—The activation of iron is stated to be due to the equilibrium $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2e$, and passivation to $\text{Fe} \rightleftharpoons \text{Fe}^{3+} + 3e$, so that the change from the active to the passive state may be represented by $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e$. The activating effect of hydrogen and the passivating effect of oxygen are considered to be due to displacements of this equilibrium to the left and right respectively as the result of electron interchanges. H. T. S. BRITTON.

Passivity of metals. I. N. STRANSKI and Z. C. MUTAFSCHIEW (*Z. Elektrochem.*, 1929, **35**, 393—395).—The passivation of metals is discussed in relation to their crystal structure. The mode of dissolution of individual crystals is supposed to be due to the attack of the solvent being restricted to the corners and ultimately to the edges which happen to be exposed in the surfaces of the metals. If a relatively smaller network produced by the corners and edges should become exposed after the dissolution of a metal has been proceeding for some time, then anodic activity will become diminished, eventually giving rise to passivity. The superposition of oxide layers on metal surfaces and their effects are also discussed. H. T. S. BRITTON.

Unimolecular reactions. L. S. KASSEL (*Proc. Nat. Acad. Sci.*, 1929, **15**, 601—603).—Bourgoin's application of quantum mechanics to unimolecular reaction rates (cf. this vol., 771) is discussed critically. N. M. BLIGH.

Types of unimolecular reactions. O. K. RICE (*Proc. Nat. Acad. Sci.*, 1929, **15**, 459—462).—Since there is evidence that chemical reactions are to be explained on the basis of the quantum mechanical resonance phenomenon, relations between types of reactions which have been treated by quantum

methods are pointed out. The types considered are: predissociation, in which a molecule is excited by absorption of radiation of a given frequency in two different ways, unimolecular decompositions of complex organic compounds, in which activation must be assumed, and the more complicated case of photochemical decomposition. N. M. BLIGH.

Rate of recombination of atomic hydrogen. H. M. SMALLWOOD (*J. Amer. Chem. Soc.*, 1929, **51**, 1985—1999).—The rate of the reaction $2\text{H} = \text{H}_2$ was determined calorimetrically between 0.5 and 0.9 mm. The results show that the reaction proceeds according to the "three-body" mechanism. The reaction is catalysed by nitric oxide, perhaps owing to the formation of an intermediate molecule $\text{H}-\text{NO}$. One fifth to one sixth of the atomic hydrogen present will react with solid sulphur to form hydrogen sulphide. S. K. TWEEDY.

Ignition temperature of some gases. H. K. SEN and H. N. CHATTERJEE (*J. Indian Chem. Soc.*, 1929, **6**, 441—450; cf. McDavid, A., 1918, ii, 10).—The ignition temperature of mixtures of hydrogen and oxygen of varying composition has been determined in soap bubbles, ignition being produced by contact with an electrically heated platinum wire. The ignition temperature decreases with decreasing length of the wire, becoming lowest for a point source. It is lower for large than for small bubbles. When the wire is wound on different insulating materials the ignition temperature rises in the order mica, silica, porcelain, glass. F. L. USHER.

Formation and decomposition of ozone. E. H. RIESENFELD (*Z. angew. Chem.*, 1929, **42**, 729—734).—The decomposition of ozone at low concentrations is unimolecular, and at high concentrations bimolecular. The rate of the unimolecular reaction is depressed and the rate of the bimolecular decomposition accelerated in presence of inert gases. The decomposition apparently involves a series of chain reactions and the influence of the added gases is such that they break the chain by actual participation in one of the reactions involved. J. S. CARTER.

Rate of decomposition of nitrogen pentoxide at moderately low pressures. H. C. RAMSPERGER, M. E. NORDBERG, and R. C. TOLMAN (*Proc. Nat. Acad. Sci.*, 1929, **15**, 453—459).—In view of divergent results (cf. Hibben, A., 1928, 601; Loomis, *ibid.*, 961; Sprenger, *ibid.*, 1099; Rice, *ibid.*, 1193) experiments were made with special attention to the elimination of errors due to occlusion and adsorption. A reaction vessel of very large volume was used to minimise surface errors, and the reaction was followed by periodically freezing out the oxides of nitrogen and measuring the pressure of the residual oxygen. Data for a large number of experiments are tabulated; the pressure rates of decomposition are calculated and are found to agree within the limits of experimental error with those available for high pressures. It is concluded that, down to the pressures investigated, nitrogen pentoxide shows no change in its specific first-order rate of decomposition. N. M. BLIGH.

Velocity of reaction between iodide and persulphate ions. W. OOSTVEEN (*Rec. trav. chim.*,

1929, 48, 697).—A note on papers by King and Jette (this vol., 771), re-affirming the part played by the tri-iodide ion in the reaction between the iodide and persulphate ion.
F. L. USHER.

Kinetics of the oxidation of iodide ion by acid dichromate solutions in presence of a neutral salt. R. F. BEARD and N. W. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 1973—1985).—The above reaction was investigated at 25° in presence of sodium chloride and perchloric acid over a wide range of hydrogen-ion concentration. The reaction is of the first order with respect to potassium dichromate (DeLury, A., 1903, ii, 471), having a constant k . The graph of k against $\mu^{\frac{1}{2}}$, μ being the ionic strength of the solution, is very similar to the activity curves of strong acids when plotted as a function of $u^{\frac{1}{2}}$. A minimum occurs at $\mu=0.7$. Some theoretical justification for the shape of this curve in the region of dilute sodium chloride solutions is obtained on the ground of Brønsted's reaction-rate theory and Debye and Hückel's interionic attraction theory, provided the total reaction is regarded as being quinquemolecular. The reaction is not wholly bimolecular with respect to iodine; two simultaneous reactions occur, which the experiments in presence of 1.5*M*-sodium chloride indicate to be: $H^+ + I^- + Cr_2O_7^{2-} = HI, Cr_2O_7^{2-}$ and $2H^+ + 2I^- + Cr_2O_7^{2-} = (HI)_2, Cr_2O_7^{2-}$, the latter reaction accounting for the oxidation of about 65% of the iodine.

S. K. TWEEDY.

Rate of oxidation of hydrazine by ferricyanide. E. C. GILBERT (Z. physikal. Chem., 1929, 142, 139—150).—The rate of oxidation of hydrazine by ferricyanide in a buffer solution of p_H about 6 has been measured at 20°. The reaction is of the third order, being unimolecular in respect of the hydroxyl ion, ferricyanide ion, and $N_2H_5^+$ ion, *i.e.*, is equivalent to a reaction of the second order, unimolecular in respect of the hydrazine molecule and ferricyanide ion, so that under the experimental conditions the hydrazine molecule is more reactive than the $N_2H_5^+$ ion. This is interpreted as indicating the formation of an unstable complex of ferricyanide ion and hydrazine, $N_2H_4 + Fe(CN)_6^{3-} \rightleftharpoons [N_2H_4, Fe(CN)_6]^{3-} \rightarrow N_2H_3 + H^+ + Fe(CN)_6^{3-}$. The N_2H_3 then either decomposes quantitatively, or is oxidised to nitrogen and water, almost instantaneously, no ammonia being formed.

R. CUTHILL.

Thermodynamic relations in the hydrolysis of esters by alkali hydroxide and sodium carbonate. A. MUSIL (Monatsh., 1929, 52, 192—219).—Skrabal's thermodynamic considerations (cf. A., 1924, ii, 666, 667, 842) in statical systems have been extended to the effect of temperature on velocity coefficients in kinetic systems. Expressions are obtained for the velocity of hydrolysis of esters by alkali hydroxide and by sodium carbonate, for the heats of hydrolysis and dissociation, and for the temperature coefficients. The rate of hydrolysis of ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate (at 0.2°, 10°, 20°, and 30°) of *i*-amyl acetate (at 10°, 20°, and 30°) and of *n*-propyl acetate at 30° in the presence of sodium carbonate and 0.01*N*-potassium ferricyanide has been determined. An improved technique is described. These and related results together with those obtained by H.

Olsson ("Die Abhängigkeit der Hydrolysegeschwindigkeit der Ester von der Konstitution," Lund, 1927) on the hydrolysis by alkali hydroxide of these esters are in fair agreement with the calculated values.

A. I. VOGEL.

Kinetic salt effect. III. Influence of non-electrolytes on salt effect in ionic reactions. A. N. KAPPANNA (J. Indian Chem. Soc., 1929, 6, 419—430; cf. this vol., 516).—The reaction between monobromoacetate and thiosulphate ions has been further studied in order to determine the effect of altering the dielectric constant of the solvent, since this has a marked influence on the activity coefficients of the ions. The velocity coefficients were determined at ionic strengths varying from 0.0025 μ to 0.305 μ , in 20, 40, 60, and 80% solutions of alcohol and in 30% and 50% solutions of sucrose. The slopes $d \log k/d\sqrt{\mu}$ differ considerably from those required by the Debye-Hückel limiting equation in 20, 40, and 60% alcoholic solutions, but in the 30 and 50% sucrose solutions up to ionic strengths 0.015 and 0.010, respectively, the Debye-Hückel expression predicts the course of the reaction with fair accuracy. The temperature coefficients of the velocities have also been measured and found to remain constant for a given solvent over the entire range of ionic concentration. No general relationship could be traced between the percentage of alcohol and the velocity coefficient.

F. L. USHER.

Action of hydrochloric acid on alcohol. VI. Velocity coefficients. S. KILPI (Z. physikal. Chem., 1929, 142, 195—210).—Velocity measurements have been made of the reaction between hydrochloric acid and alcohol in various alcohol-water mixtures at 96.5° and 110°. A strict integration of the differential equation of reaction velocity has been carried out. The values of the velocity coefficients have been calculated from this equation and also from an approximate integrated form which assumes that the velocity coefficient of the reaction between alcohol and hydrogen chloride is constant during the course of the reaction. For alcohol-water mixtures containing less than 0.5*M*-alcohol the approximate equation is satisfactory. At higher concentrations the more accurate form has to be used.

F. J. WILKINS.

Velocity of saponification of methyl acetate by sodium hydroxide at 25°. W. T. GOOCH and (Miss) E. M. TERRY (J. Amer. Chem. Soc., 1929, 51, 1959—1965).—An exact measurement at 25° of the velocity coefficient of the hydrolysis of methyl acetate of 0.008*M* and 0.016*M* concentration in 0.01*M*- and 0.02*M*-aqueous sodium hydroxide solution gives 11.67 moles per min., independent of exposure to diffused daylight (cf. Walker, A., 1906, ii, 732). An apparatus for taking samples of the reaction mixture for analysis at noted times is described. A mechanical shaker in which the liquid is whirled within, but independent of, an open container is also described.

S. K. TWEEDY.

Stability of *tert*-amyl trichloroacetate in different solvents. L. M. ANDBEASOV (Ukraine Chem. J., 1928, 3, 467—470).—The decomposition of *tert*-amyl trichloroacetate at 25° and 50° in chloroform, carbon tetrachloride, benzene, acetone, nitro-

benzene, ether, ethyl acetate, and carbon disulphide solution and in presence of 1 c.c. of a 0.5% solution of trichloroacetic acid has been determined. The extreme slowness of the reaction rendered it impossible to calculate a reaction constant, but even after 200 hrs. equilibrium was not reached. The percentage decomposition is smallest at 25° in benzene solution and at 50° in nitrobenzene, whilst both at 25° and 50° it is highest in carbon disulphide. The percentage decomposition of the ester in ethyl benzoate solution at 50° is very high and is explained as being due to the decomposition of the complex formed between the ester and ethyl benzoate (cf. Konovalov, A., 1907, ii, 854).
A. FREIMAN.

Kinetics of the interaction of esters with potassium alkoxides. I. Reaction between potassium ethoxide and ethyl acetate in ethyl alcohol-water mixtures. R. F. W. SELMAN and P. B. FLETCHER (Trans. Faraday Soc., 1929, 25, 423—435).—The velocity of the reaction between potassium ethoxide and ethyl acetate depends on the amount of water present. Fractionation of the reaction products on a large scale by Cox's method (A., 1919, ii, 83) shows that no ether is produced. The solid residue consists mainly of potassium acetate. The reaction comprises: (i) the hydrolytic action of water on the potassium ethoxide, and (ii) the hydrolysis of the ester by the potassium hydroxide so formed. An expression corresponding with the dual reaction is derived; it involves the equilibrium relations of the first stage and the velocity equation of the second, assuming it to be bimolecular. The experimental values of the velocity coefficient thus found are composed of the equilibrium constant of the first reaction and the theoretical velocity coefficient of the hydrolysis. They, however, justify the assumption that the latter reaction is bimolecular.
H. T. S. BRITTON.

Thermal decomposition of methylisopropyl-di-imide, a homogeneous unimolecular reaction. Thermal decomposition of azoimide and methyl azide. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, 51, 2134—2143).—The thermal decomposition of methylisopropyl-di-imide is homogeneous and unimolecular over the range 250—332°, but the velocity coefficient falls at pressures below a few cm. (cf. A., 1927, 737). Analogous results were obtained with methyl azide. In the former case the reaction is explained by Rice and Ramsperger's second theory (*ibid.*, 833), the molecule being assumed to have 33 degrees of freedom. The reactions which occur are: $3\text{NMe}\cdot\text{NPr}^\beta \rightarrow 3\text{N}_2 + \text{C}_2\text{H}_6 + \text{C}_4\text{H}_{10} + \text{C}_6\text{H}_{14}$ and $\text{NMe}\cdot\text{NPr}^\beta \rightarrow \text{N}_2 + \text{CH}_4 + \text{C}_3\text{H}_6$. The two radicals in the compound are probably not combined at the instant of reaction, but are separately dislodged and combine at random later. The thermal decomposition of azoimide is not homogeneous.

S. K. TWEEDY.

Ketonic decomposition of β -ketocarboxylic acids. K. J. PEDERSEN (J. Amer. Chem. Soc., 1929, 51, 2098—2107).—The kinetics of the decomposition of α -dimethylacetoacetic acid were investigated at 18° in hydrochloric acid solution, in which the reaction is unimolecular, and in buffer solutions: $\text{CAcMe}_2\cdot\text{CO}_2\text{H} = \text{CHAcMe}_2 + \text{CO}_2$. The dissociation

constant of the acid is 3.14×10^{-4} . The reaction is accelerated by aniline. The acid is relatively unstable, whence it follows that the keto-form of the β -ketocarboxylic acids is unstable. It is suggested that only the keto-form undergoes ketonic decomposition, amines catalysing the reaction by producing an intermediate compound with this form, which compound yields carbon dioxide more rapidly than the free keto-form.
S. K. TWEEDY.

Velocity of oxidation of amines by potassium permanganate. B. V. TRONOV and L. S. NIKONOVA (J. Russ. Phys. Chem. Soc., 1929, 61, 541—549).—The relative velocities of oxidation of triethylamine by potassium permanganate in alkaline and in acid solutions are as $10^6 : 3.3$, of piperidine as $2.8 \times 10^5 : 92$, of quinoline as $5.2 \times 10^3 : 1.4 \times 10^5$, of isoquinoline as $9.5 \times 10^3 : 3.8 \times 10^4$, of pyridine as 1:74, and of 2-methylpyridine as 21:126. The values obtained for oxidation of these substances in neutral solution differ little from those in alkaline solution. It is concluded that pyridine is less resistant towards oxidation when present in the form of a salt.

R. TRUSZKOWSKI.

Velocity of oxidation of benzoic [and other] acids by potassium permanganate in alkaline solution. B. V. TRONOV and A. A. GRIGORIEVA (J. Russ. Phys. Chem. Soc., 1929, 61, 653—665).—The following acids were investigated in the form of their sodium salts: benzoic, *o*-chlorobenzoic, *p*-bromobenzoic, *o*-, *m*-, and *p*-nitrobenzoic, *o*-, *m*-, and *p*-toluic, salicylic, *m*- and *p*-hydroxybenzoic, anthranilic, *m*- and *p*-aminobenzoic, *o*-, *m*-, and *p*-phthalic, anisic, gallic, α - and β -naphthoic, phenylacetic, phenylpropionic, mandelic, benzilic, cinnamic, *o*-, *m*-, and *p*-nitrocinnamic, pyromucic, benzene-sulphonic, α - and β -naphthionic, and sulphanilic. The salts were treated with an equimolecular amount of sodium hydroxide (0.1*N* or *N*). The potassium permanganate was used in 5.5% solution, the temperature being kept at 18—20°. Except in the case of *o*-chlorobenzoic acid all substituents accelerate the reaction. Chlorine, bromine, a nitro-group, a carboxyl group, and a methoxy-group increase the rate of reaction from 2 to 100 times; the increase for a sulphonic group is of the order 10^4 times and for a hydroxyl or an amino-group of the order 10^5 times. The effect of position is not yet clear, although the position of the carboxyl group has some slight effect. The stability of the furan ring is much less than that of the benzene ring.
A. FREIMAN.

Velocity of dissolution of copper. R. GLAUNER (Z. physikal. Chem., 1929, 142, 67—91).—The velocity of dissolution of copper foil in various reagents was determined, the foils having different crystal layers exposed. The liquids used were hydrochloric, hydrobromic, nitric, sulphuric, perchloric, and acetic acids, ammonium persulphate, and ammonia, and mixtures of hydrochloric acid, sulphuric acid, acetic acid, and oxalic acid, respectively, with hydrogen peroxide. A mathematical expression for the velocity of dissolution is derived. It is a differential equation of one or two terms. The first term is dependent on the initial velocity of the reaction as conditioned by the nature and concentration of the

solvent. The second term accounts for the auto-catalytic effect of copper in the solution. The equation is tested for a series of solvents, and the agreement, in the majority of cases, is good. There are a few cases where the equation satisfies only the initial conditions, and others where the agreement is good only in the later stages of the reaction. The applicability of the Nernst-Brunner diffusion theory is discussed, and it is shown that the constants of the differential equation are proportional to the diffusion coefficients of the solvent and the copper salt formed. Opposed to this are the observed differences in dissolution velocity with different crystalline structure which cannot be accounted for by the original theory.

A. J. MEE.

Kinetics of dissolution of cadmium in hydrochloric acid. K. JABECZYŃSKI and H. WAJCHSELFISZ (Rocz. Chem., 1929, 9, 340—347).—The velocity of dissolution of cadmium in 5*N*-hydrochloric acid at 25° diminishes to zero within about 40 min., after which *K* rises gradually to a constant value 20 hrs. later. Subsequently a further slight progressive increase in velocity is found. The temperature coefficient of the reaction is 2.02, and it is concluded that the process of dissolution of cadmium in hydrochloric acid is one of a purely chemical nature, independent of diffusion.

R. TRUSZKOWSKI.

Oxidation of copper at high temperatures. F. J. WILKINS (Z. Elektrochem., 1929, 35, 500—501).—The data obtained by Feitknecht (this vol., 517) relating to the oxidation of copper between 600° and 1020° are shown to satisfy the equation $x^2 = kt + c$, *x* being the oxygen combined in time *t*, and *k* and *c* being constants. The diffusion occurring at the boundaries of crystals is held to be less than that at their lattices.

H. T. S. BRITTON.

Rate of dissolution of alloys in hydrochloric acid. P. FISCHER (Z. Elektrochem., 1929, 35, 502—505).—The rate of dissolution in 0.5*N*- and *N*-hydrochloric acid solution of zinc and of its alloys containing 2.5, 5, and 10% Pt; 10% Sb; 2.5, 5, and 10% Ag; arsenic; 5, 10, and 20% Pb; and 20% Hg was measured by revolving pieces of metal having the same surface area in the acid and measuring the volumes of hydrogen evolved after equal periods of time had elapsed. Pure zinc showed no signs of dissolving in 0.5*N*-hydrochloric acid after 2 days. The effects of the various metals in the alloys in accelerating dissolution showed no parallelism with their order in the electro-potential series, but seemed to be related with the hydrogen over-voltage; thus platinum with the lowest hydrogen over-voltage had the greatest influence, and mercury with the highest hydrogen over-voltage had an extremely small effect. Respecting the "theory of local action," it is emphasized that it is not only the magnitude of *E.M.F.* set up between the two metals, but it is essentially the magnitude of the current available, and this is determined also by the number of local elements actually present.

H. T. S. BRITTON.

Induced reactions. W. D. BANCROFT (J. Physical Chem., 1929, 33, 1184—1192).—Previous classifications of induced reactions are discussed and

a new one based on the induction factor, *i.e.*, the ratio of the amount of the actor reacting with the acceptor to the amount reacting with the inductor, is advanced. This eliminates the difficulty of interpreting reaction velocity experiments, but is liable to serious error if the actor reacts at an appreciable rate with the acceptor. All induced reactions can be arranged in three groups or combinations of these; the acceptor may react with a lower stage of the actor, or with a reaction product of the inductor, or the actor may react with a reaction product of the inductor and acceptor. Consecutive reactions are those in which the acceptor reacts with a stable oxidation or reduction product of the inductor and should be classed as induced reactions.

L. S. THEOBALD.

Homogeneous catalysis. N. A. MILAS (Proc. Nat. Acad. Sci., 1929, 15, 596—601; cf. this vol., 149).—To test the view that a negative catalyst for auto-oxidation should be a good reducing agent or easily oxidisable, quantitative experiments were made which showed that anthraquinone acts as a truly negative catalyst in the oxidation of anethole, but can be recovered quantitatively at the end of the reaction. The effect of anthraquinone and benzoquinone, which was the stronger inhibitor, on the maximum oxygen absorption rate of anethole was measured for several concentrations. This absorption rate is emphasised as a most characteristic property in all auto-oxidation reactions, and an equation is derived, and verified experimentally, connecting the maximum oxygen absorption rate, the concentration of the catalyst, and the time necessary for the oxidation rate to reach a maximum value.

N. M. BUGH.

Auto-oxidations. N. A. MILAS (J. Physical Chem., 1929, 33, 1204—1216).—The view is advanced that in all auto-oxidations the atoms to which the oxygen molecule is initially added make definite contributions of two electrons to it; metastable or dative peroxides (Menzies, A., 1928, 349), characterised by high instability and energy content, are formed and may either revert instantaneously to ordinary peroxides by transferring their excess energy to other molecules, or initiate the oxidation of other molecules. Various auto-oxidations, together with the inhibition and acceleration of such reactions, are discussed in the light of the above views.

L. S. THEOBALD.

Autocatalytic decomposition of thiosulphuric acid. K. JABECZYŃSKI and S. FRENKENBERG (Rocz. Chem., 1929, 9, 327—334).—See this vol., 772.

"Oxygen activation" or "induced oxidation." XIV. W. P. JORISSEN and A. H. BELINFANTE (Rec. trav. chim., 1929, 48, 711—725; cf. A., 1927, 326).—A summary of work on induced oxidation done since 1851 is given. Measurements of the absorption of oxygen by various mixtures containing sodium sulphite show that the following substances can act as "acceptors": indole, mannitol, *n*-propyl alcohol, glycol, *cis*- and *trans*-cyclohexane-1:2-diol, inositol, sodium potassium tartrate, glycerol, erythritol, lævulose, sucrose. In some instances the extent of the induced oxidation depends on the hydrogen-ion concentration in the solution.

F. L. USHER.

Rapid absorption of hydrogen by solutions of permanganate containing silver. F. HEIN and W. DANIEL (*Z. anorg. Chem.*, 1929, **181**, 78—82).—Absorption of hydrogen by aqueous solutions of permanganate is considerably accelerated in presence of silver salts, especially silver nitrate. There is apparently for each concentration of permanganate an optimum concentration of silver at which the rate of absorption is maximal. Under favourable conditions the whole of the hydrogen in appropriate gaseous mixtures can be absorbed. J. S. CARTER.

Oxidation of sodium sulphite by air in the presence of ferrous hydroxide and a theory of negative induced reaction. S. MIYAMOTO (*Bull. Chem. Soc. Japan*, 1929, **4**, 132—142, and *Sci. Papers Inst. Phys. Chem. Res.*, 1929, **11**, 81—92; cf. *A.*, 1926, 915).—The inhibiting effect of a primary on a secondary reaction is termed a negative induced reaction in which the activated molecules of the reactants of the secondary reaction lose their activity, before they can react, through the presence of the primary reaction. Three kinds of negative induced reactions can occur in which the active states of the molecules of the reactants of the secondary reaction can be transferred to the molecules of (i) the reactants, (ii) the reaction products, and (iii) to both reactants and reaction products of the primary reaction. The oxidation of sodium sulphite and stannous hydroxide in sodium hydroxide or carbonate solution (*A.*, 1928, 598) by air is an example of the first kind, whilst that of sodium sulphite and ferrous hydroxide in sodium hydroxide is now shown to be of the second kind. The velocity of oxidation of sodium sulphite in the presence of ferrous hydroxide by means of air decreases rapidly with time, a direct transference of activation taking place from sodium sulphite molecules to those of ferric hydroxide, the reaction product of the primary reaction. In confirmation, the velocity of oxidation of sodium sulphite in the presence of ferric hydroxide is shown to be small, and sodium sulphate is also without effect. L. S. THEOBALD.

Effect of neutral salts on the velocity of oxidation of organic compounds by potassium permanganate. B. V. TRONOV and A. A. LUKANIN (*J. Russ. Phys. Chem. Soc.*, 1929, **61**, 727—734).—The effect of sodium and potassium chloride and nitrate, potassium perchlorate, potassium sulphate, and of sodium carbonate on the oxidation of ethyl alcohol in an alkaline medium at temperatures of 16.8—26.8° was investigated. The addition of neutral salts increases the rate of reaction almost proportionally to the amount used. The nature of the cation or anion and variation of the concentration of the potassium permanganate used (0.0001—0.0004*M*) have no marked effect. The temperature coefficient calculated in terms of the percentage of active oxygen lost increases on addition of potassium chloride and still more on addition of potassium sulphate. The authors finally conclude that neutral potassium permanganate is a more effective oxidising agent than the permanganate ion. A. FREIMAN.

Catalysis by silver of the union of hydrogen and oxygen. D. L. CHAPMAN and W. K. HALL (*Proc. Roy. Soc.*, 1929, **A**, 124, 478—493).—The method

adopted by Hughes and Bevan for testing whether a nickel surface was covered with a layer of oxide (*A.*, 1928, 27) has been used in an investigation of the catalysis by silver of the reaction between hydrogen and oxygen. Determinations of the accommodation coefficients of hydrogen at silver surfaces support the assumption of Chapman, Ramsbottom, and Trotman (*A.*, 1925, ii, 310) that silver which has been heated to redness in oxygen and allowed to cool in the gas is covered with a film of oxide. At the same temperature and pressure hydrogen molecules remove less heat from a hot metallic surface than from one which has been subjected to the action of oxygen at a high temperature. A series of experiments is described which shows that when a surface of metallic silver is brought into contact with gaseous oxygen in sufficient quantity to form more than a complete unimolecular layer of oxide, it becomes coated almost immediately with a film of oxide, and that this oxide, formed at a low temperature, is a much more effective catalyst than that formed at a high temperature and is also more easily reduced by hydrogen. There appear therefore to be two forms of silver oxide, and it is assumed that in the active film, formed at a low temperature, some of the silver oxide molecules are in relatively unstable positions, but that on raising the temperature the arrangement becomes more stable and the film in consequence less active chemically. The mechanism of the catalysis is in both cases one of alternate oxidation and reduction. The accommodation coefficient of hydrogen (at 16° and 48810×10^{-6} mm.) at a silver surface heated at 100° is calculated to be 0.25; the corresponding value for an oxidised surface is 0.28. L. L. BIRCUMSHAW.

Influence of various salts on the dissolution of pure aluminium in hydrochloric acid. J. CALVET (*Compt. rend.*, 1929, **189**, 183—186; cf. *B.*, 1929, 438).—Platinic chloride (4×10^{-5} to 0.21 mg. per litre) hastens the action of 0.5*N*-hydrochloric acid on pure aluminium to an extent which increases with the amount present; the effect is greater than that produced by an equivalent amount of gold. Nickel and relatively large amounts of mercury have similar but less marked effects, whilst other metals have little or no influence. In 2.5*N*-acid, copper (5 mg. per litre) diminishes the period of induction, whilst mercuric chloride (20 mg. per 800 c.c.) produces a period of induction followed by attack more rapid than in the pure acid. Smaller quantities of mercury (1 mg. per 800 c.c.) give rise to irregularly alternating phases of activity and passivity. J. GRANT.

Catalysis of solids by solids. II. Catalytic decomposition of mercuric oxide. S. Z. ROGINSKI, L. M. SAPOSCHNIKOV, and N. A. KUTSCHERENKO (*Ukraine Chem. J.*, 1929, **4**, 99—119).—To discover the actual mechanism of the thermal decomposition of mercuric oxide crystals of the substance were placed in a tube which was heated electrically at 360—380° and was evacuated to 10^{-4} — 10^{-5} mm. after being closed by another tube, containing liquid air, which reached almost to the bottom of the first tube. After several hours' heating nothing but pure mercury was found to be condensed on the outside of the second tube. The authors therefore conclude

that the mercuric oxide decomposes directly into mercury and oxygen and that it does not vaporise and then decompose. They observed neither a period of induction nor an initial acceleration of the process of decomposition, but they found that the velocities of decomposition are different for the red and the yellow oxide. The yellow oxide decomposes about six times as fast as the red oxide, but by powdering the red oxide its rate of decomposition increases until, when the powder is very fine, the rate becomes almost equal to the rate for the yellow oxide. The catalytic effect of the following oxides on the rate of decomposition of mercuric oxide was also studied: nickel, ferric, manganese, manganese dioxide, cobaltocobaltic, cupric, stannic, lead, chromium, cadmium, zinc, magnesium, titanium, uranium, aluminium, and silica; also barium sulphate and barium carbonate. Silica and chromium oxide which react with mercuric oxide retard the decomposition; the others, particularly nickel oxide, accelerate it. It was also found that the catalytic effect for the same catalyst varies according to its mode of preparation. The theory of intermediate compound formation is criticised and is shown to be untenable in this case. The catalytic activity of a solid is assumed to be due to a large number of small electric fields covering the surface of the catalyst and the difference in the activity of different oxides to be due to differences in intensity, distribution, and distances apart of these fields.

A. FREIMAN.

Catalytic activity of molten tin. Relative efficiencies of tin and its oxides as catalysts for the reduction of nitrobenzene vapour. G. WILLIAMS (Trans. Faraday Soc., 1929, 25, 446—451).—Unlike Brown and Henke (A., 1924, ii, 31), the author observed that the reduction of stannic oxide by hydrogen is extremely slow at 300°, and that a temperature of about 500° is required for reduction to be complete within 1—2 hrs. (cf. Fink and Mantell, B., 1927, 369; A., 1928, 257). The author has obtained high yields of aniline by the reduction of nitrobenzene vapour with hydrogen at 310° with tin oxide catalysts. No evidence was obtained of the reduction of the oxide to the metal in the experiments, and it was, moreover, found that normal specimens of tin (contrary to Brown and Henke) do not catalyse this reaction at this temperature, which happens to be above the m. p. of tin.

H. T. S. BRITTON.

Electrolysis with diaphragm. (Formulae of Foerster and of Guye.) O. ESSIN (Z. Elektrochem., 1929, 35, 492—500).—From a consideration of the concentrations and conductivities of the electrolyte used (an alkali metal salt) and the alkali formed and the mobilities of the various ions involved, the author has derived an expression which is shown to lead to the theoretical formula of Foerster and Jorre (A., 1900, ii, 343) and to the empirical formula of Guye (A., 1903, ii, 586; 1904, ii, 29), relating to the current efficiency of the electrolytic production of alkali in a cell in which a diaphragm is interposed between the electrodes. Two series of experiments are described in which a perforated nickel anode, an iron net cathode, and potassium carbonate solutions of different concentrations as anolytes and catholytes were used.

The current efficiencies actually obtained are compared with the corresponding values calculated with the author's formula and those of Foerster and of Guye.

H. T. S. BRITTON.

Formation and properties of very thin electrolytic nickel films. K. M. OESTERLE (Z. Elektrochem., 1929, 35, 505—519).—The nickel deposits obtained from *N*-nickel chloride solution, buffered to various p_H -values with "acetate mixture," "acetate mixture" and gelatin, ammonium chloride, or boric acid, on platinum or silver cathodes, using a nickel anode and a cathodic current density of 2.5 amp./dm.², have been investigated by means of measurements (a) with the contractometer (Kohlschütter and Jakober, A., 1927, 1016), (b) with the Pendel magnetometer, (c) of the normal electrode potentials, and (d) with Debye and Scherrer's X-ray apparatus. The crystal structure, and consequently the physical properties, of the deposits depend on the p_H value of the electrolyte and also on the presence of gelatin, which in serving as a protective colloid of the dispersed nickel hydroxide, caused a bright smooth layer to be formed. The data corresponding with those deposits obtained from solutions of p_H 4.5—6.0 illustrate how great an effect a small change in p_H may have on the quality of the layer. It is within this range that the electrolyte becomes contaminated with small amounts of nickel hydroxide.

H. T. S. BRITTON.

Electrolytic zinc refining. II. Influence of foreign elements on the hydrogen overvoltage. H. SETO.—See B., 1929, 648.

Cataphoresis of lead sulphate. E. L. JEWETT (J. Physical Chem., 1929, 33, 1024—1026).—The part played by cataphoresis in a lead accumulator in the Luckow process for the electrolytic preparation of insoluble lead salts and in the electrolytic determination of lead is discussed.

L. S. THEOBALD.

Electrolytic preparation of iodoform without the use of platinum. A. VYSKOČIL (Chem. Listy, 1929, 23, 212—215, 249—251).—In the electrolytic preparation of iodoform from ethyl alcohol the platinum anode may be replaced by one of coinage nickel (25% Ni, 75% Cu) or of carbon, but not of chromium, nichrome, nickel, copper, or brass. The copper-nickel anode does not undergo corrosion in the presence of sodium carbonate.

R. TRUSZKOWSKI.

Connexion between absorbed energy and velocity in photochemical reactions of the $I^{0.5}$ type. A. J. ALLMAND (J.C.S., 1929, 1557—1560).—When the velocity of a photochemical reaction is proportional to the first power of the intensity, if reaction chains are not set up, the quantum efficiency γ is a characteristic for the reaction. For the $I^{0.5}$ type of reaction γ is not characteristic and is a function of intensity, thickness of the reaction vessel, and concentration of reactant. An attempt is made to derive a quantity which shall be as characteristic of the $I^{0.5}$ reactions as γ is of the $I^{1.0}$ reactions. It is suggested that the photochemical susceptibility σ (Henri and Wurmser, J. Physique, 1913, 3, 305) or the coefficient of utilisation Γ (Tian, Ann. Physique, 1916, 5, 248) fulfils this function. F. J. WILKINS.

Primary process of light absorption and activation in photochemical reactions. K. P. BASU (J. Physical Chem., 1929, 33, 1200—1203).—In photochemical reactions the abnormal yield per quantum of radiation absorbed is due partly to the activation of more than one molecule of the absorbing substance by one quantum of incident radiation. The increase in photochemical efficiency with an increase in frequency of the incident radiation is explained by the increase in scattering and the number of activated molecules which accompanies the greater frequency. L. S. THEOBALD.

Chemical reactions in infra-red radiations (7304 Å.). A. K. BHATTACHARYA and N. R. DEAR (J. Indian Chem. Soc., 1929, 6, 451—464; cf. this vol., 516).—Work previously described has been extended to 30 reactions which have been found to be accelerated by radiation of wave-length 7304 Å., and the general conclusions with regard to quantum efficiency and temperature coefficients previously arrived at are confirmed. F. L. USHER.

Extinction coefficient of Br₃' ions and its function in photochemical reactions. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1929, 6, 361—373).—In order to ascertain the function of tribromide ions in the photochemical oxidation of organic acids by bromine in the presence of potassium bromide, the extinction coefficient of this ion has been determined for 5360, 5460, and 5790 Å. The oxidation of mandelic and lactic acids by bromine, which has no appreciable velocity in darkness, is unimolecular in the absence of bromide, but when a bromide is added, or when the hydrobromic acid formed in the reaction is allowed to accumulate, it becomes zero-molecular, the velocity coefficient increasing with the ratio of free bromine to tribromide ion. The results are satisfactorily accounted for by assuming that only that fraction of the incident light which is absorbed by the bromine molecules is photochemically active. F. L. USHER.

Photochemical equilibrium in nitrogen peroxide. III. Comparison of the thermal, photochemical, and electrical decompositions, and a general theory of the change. IV. Relation between fluorescence and photochemical action. R. G. W. NORRISH (J.C.S., 1929, 1604—1611, 1611—1621).—III. The thermal decomposition of nitrogen peroxide possesses a heat of activation of 32,000 g.-cal. (this vol., 33). For the photochemical reaction, however, a minimum excitation to about 80,000 g.-cal. is required in order that reaction may follow at the next collision. It is thus necessary to distinguish between the two molecular conditions of excitation and activation. The former involves a partition of the absorbed energy between electronic, vibrational, and rotational degrees of freedom, whilst the latter occurs only when the vibrational and rotational energy is raised to a critical value. The earlier work (this vol., 893) on the relation between quantum efficiency and wave-length demonstrated that blue light of wave-length 4360 Å. is without photochemical activity, although it causes molecular excitation to the extent of 64,000 g.-cal. Such absorbed energy cannot be degraded to heat, for in that case sufficient

energy would be provided to cause decomposition. It must therefore be re-radiated, the de-excitation of the electronic degree of freedom being followed by fluorescence. Further, in light which is incompletely active photochemically the fluorescence will be restricted. For wave-lengths giving a quantum efficiency of two (complete photochemical activity) there will be no fluorescence.

It is suggested that the fluorescence observed by Zenneck and Strasser (A., 1912, ii, 127) when nitrogen peroxide is decomposed in an alternating discharge is capable of an analogous interpretation. The fluorescence is due to radiation from excited molecules which do not decompose, formed by collisions of the first kind with electrons.

IV. The relationship predicted between fluorescence and photochemical action in nitrogen peroxide has been verified experimentally. Light of wave-length 4360 Å. (photochemically inactive) produces an orange fluorescence and violet light (4050 Å., photochemically incompletely active) a greenish-yellow fluorescence. The spectra of the fluorescent radiations are identical, possessing two wide maxima at about 6400 and 5900 Å., different intensity distributions accounting for the colour difference. Addition of oxygen destroys the fluorescence. From the concentration required, it is estimated that the mean life of the excited molecule is 5×10^{-8} sec., a result which is supported by the observation that the fluorescence is unpolarised. In view of the comparatively long life of the excited molecule, it is possible that even for wave-lengths which are almost completely photochemically active a small fraction of excited molecules will fluoresce before reaction occurs. A very faint fluorescence of this nature has been observed at λ 3650 Å. It is shown that reaction follows when one of the reactant molecules possesses among its vibrational and rotational degrees of freedom 26,000 g.-cal. It is suggested that the energy of activation, 32,000 g.-cal., is just sufficient to stimulate the vibrational and rotational degrees of freedom to this extent. This conclusion is probably of general significance. F. J. WILKINS.

Photosensitised and photochemical decomposition of hydrazine. J. C. ELGIN and H. S. TAYLOR (J. Amer. Chem. Soc., 1929, 51, 2059—2082).—Gaseous hydrazine is completely decomposed by ultra-violet radiation at a rate which is independent of temperature (15—45°): (i) $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$; (ii) $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Reaction (i) has ten times the rate of (ii). As a whole, the reaction is unimolecular in character; this, however, is here meaningless. The rate is uninfluenced by addition of nitrogen, hydrogen, or ammonia.

The thermal decomposition of hydrazine in a quartz vessel commences at about 250°: (iii) $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$; a small quantity of hydrogen is also liberated, but not from the ammonia, which is stable even at 500°. The reaction is heterogeneous and of unimolecular character. On the surface of heated platinum or tungsten wire reaction (i) occurs.

The photochemical decomposition of hydrazine sensitised by mercury vapour to light of 2537 Å. was also investigated. Reaction (i) occurs with forty

times the speed of reaction (ii), so that the latter becomes negligible. The reaction, which proceeds chainwise, has a rate which is at least twice that of the sensitised reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ (which reaction was briefly examined) and is independent of the presence of nitrogen, ammonia, and hydrogen, but is proportional to the incident radiation intensity. The quantum efficiency of the sensitised hydrazine decomposition is about 13, which indicates an efficiency of 0.3 for the sensitised ammonia decomposition. The spectrum of gaseous hydrazine indicates that this substance offers another example of "pre-dissociation." The results as a whole are satisfactorily explained by a reaction mechanism based on a dissociation of primarily excited molecules into either $\text{N}_2\text{H}_3 + \text{H}$ or 2NH_2 as a primary process. The results show that hydrazine cannot form an intermediate product in ammonia decomposition, but the mechanism type proposed for the latter by Bates and Taylor (A., 1927, 1153) is favoured.

S. K. TWEEDY.

Photochemical oxidation with potassium dichromate. D. S. MORTON (J. Physical Chem., 1929, 33, 1135—1141).—Experiments on the light and dark reactions between ethyl alcohol and potassium dichromate in the presence of varying concentrations of sulphuric acid show that (i) under suitable conditions, dichromate solutions are photochemically active for light absorbed by dichromate, (ii) with increasing acidity the oxidising power of the dichromate solution increases and the apparent action of light decreases, and (iii) the light reaction can be varied from approximately zero to totality by varying the concentration of sulphuric acid. The general insensitivity of chromic acid to light implied by Luther and Forbes (A., 1909, ii, 632), although correct for the high acidity used in their experiments, is misleading.

L. S. THEOBALD.

Photolysis of potassium ferrioxalate solutions.

I. Experimental. II. Discussion. A. J. ALLMAND and W. W. WEBB (J.C.S., 1929, 1518—1531, 1531—1537).—I. The influence of concentration of photolyte, wave-length, added neutral salts, intensity, intermittent illumination, and inhomogeneous light have been studied on the quantum efficiency (γ) of the photolysis of potassium ferrioxalate solutions. Between the limits studied, 0.02*M* and 0.06*M*, γ is independent of the concentration of the photolyte. Increase of wave-length from 313 to 436 $\mu\mu$ causes a decrease in γ from 1.6 to 0.9. Addition of strong electrolytes increases γ . Potassium oxalate forms an exception in that it causes a slight decrease in γ . For the light used (wave-length 365 $\mu\mu$ together with some of 405 $\mu\mu$), γ is independent of the intensity and of whether the illumination is constant or intermittent. The use of light forming a continuous band between 390 and 460 $\mu\mu$ causes a degree of decomposition which is about 20% lower than that calculated on the assumption that the action of the rays is additive. Although these results agree with the work of Padoa and Vita (A., 1924, ii, 322) they cannot be regarded as definitive owing to the possibility of certain errors. Results not liable to these errors were obtained with light containing two or more of

the three mercury lines 365, 405, and 436 $\mu\mu$. They show that the degree of decomposition is 25—30% greater than that corresponding with an additive effect of the different wave-lengths.

II. It is suggested that the primary result of the absorption of a light quantum is the activation of the ferrioxalate ion, a process which is regarded as involving the partial dislocation of the union between the ferric ion and one of the attached oxalate ions. Reaction occurs following on the collision of a ferrioxalate ion so activated with a normal ion. On the basis of this theory it is possible to explain the influence of concentration of photolyte, wave-length, intensity, and intermittent illumination on the quantum efficiency γ of the photolysis. The influence of neutral salts is not understood. An explanation of the increase of γ obtained with inhomogeneous light which was suggested by the existence of the Raman effect is put forward.

F. J. WILKINS.

Physical development and nature of the latent image. R. E. OWEN.—See B., 1929, 623.

Technique of photographic measurement of absorption in the ultra-violet. V. HARDNUNG (Helv. phys. Acta, 1928, 1, 472—507; Chem. Zentr., 1929, i, 1130—1131).—Two methods are described and applied to the examination of glass. Experiments performed with betaine, glycine, and sarcosine, with a view to test Pfeiffer's theory of the structure of betaine, were inconclusive.

A. A. ELDRIDGE.

Decomposition of ethylene by ultra-violet light. R. B. MOONEY and E. B. LUDLAM (Trans. Faraday Soc., 1929, 25, 442—445).—The ultra-violet absorption spectrum of very pure ethylene has been investigated. Absorption is practically complete from 1850 to 1990 Å., about 75% at 2020 Å., and slight absorption at 2060—2110 Å. The long wave-length limit of absorption, viz., 2110—2130 Å., coincides with that calculated from the heat of dissociation of ethylene into acetylene and atomic hydrogen. Light radiations of wave-length shorter than 2110 Å. cause ethylene to decompose giving acetylene as one of the decomposition products. Contrary to the view of Bates and Taylor (A., 1927, 1153), the presence of mercury vapour is not essential for the decomposition.

H. T. S. BRITTON.

Photochemical reaction between cinnamic acid and chlorine in carbon tetrachloride solution. K. P. BASU (J. Indian Chem. Soc., 1929, 6, 341—352).—In the photochemical reaction between chlorine and cinnamic acid in carbon tetrachloride solution the quantum efficiency is 2 at 4360 Å., 4 at 4040 Å., and 7 at 3665 Å. A "chain" mechanism is therefore indicated, and the following scheme is suggested: (1) $\text{Cl}_2 + h\nu = \text{Cl}^* + \text{Cl}$, (2) $\text{R} + \text{Cl}^* = \text{RCl}^*$, (3) $\text{RCl}^* + \text{Cl}_2 = \text{RCl}_2 + \text{Cl}^*$. The increase of quantum efficiency with increase of frequency of the incident light is explained by assuming that the activated monochloride carries with it in the form of kinetic energy part of the higher energy content of the activated chlorine atom associated with light of higher frequency, and that the length of the "chain" is proportional to the energy associated with the monochloride formed. The temperature coefficient of the

reaction varies from 1.1 at 3665 Å. to 1.38 at 4360 Å. No fluorescence could be detected in a solution of chlorine in carbon tetrachloride. F. L. USHER.

Oxidation of some hydroxy-acids by bromine.

I. The light reaction. II. The dark reaction. R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1929, 6, 375—383, 385—390; cf. Ghosh and Basu, A., 1928, 970).—I. The photochemical oxidation of lactic, phenyl-lactic, mandelic, and citric acids by bromine has been studied with the object of elucidating the large increase in the unimolecular velocity coefficient with diminution of the concentration of bromine. The velocity coefficients are nearly proportional to the concentration of the organic acid, and inversely proportional to that of the bromine. There is an induction period which vanishes in the presence of potassium bromide. The quantum efficiency for light about 4700 Å. is 15, 13, 13, and 3 in the order in which the acids are named above. The experimental results, whilst supporting the view previously put forward, that the bromine atoms which are the primary products of the photochemical action become deactivated by collision with oxygen molecules, indicate that this view is incomplete, since the reaction velocity is determined solely by the ratio of bromine to tribromide ion, irrespective of the concentration of total bromine or free bromine. The induction period is probably due to the formation of complexes between bromine and the reacting acid.

II. The influence of various electrolytes on the rate of oxidation of phenyl-lactic acid and mandelic acid in the dark has been studied. Unimolecular velocity coefficients are obtained in the presence of potassium bromide and of hydrobromic acid. The velocity coefficient is lowered more by hydrobromic acid than by potassium bromide. The reaction is accelerated by hydrochloric acid and still more by potassium chloride, and is also catalysed by the sulphate ion. Addition of sodium hydroxide to the system containing potassium bromide increases the velocity coefficient regularly, whence it is inferred that the organic acid anion is alone reactive. When the hydrogen-ion concentration is maintained constant the reaction is due to free bromine molecules only.

F. L. USHER.

Effect of ultra-violet light on proteins. M. ARTHUS [with G. BOSHELL] (Arch. Int. Physiol., 1928, 30, 244—249; Chem. Zentr., 1929, i, 1083).—Fibrinogen of the citrate-plasma of rabbits and horses loses its coagulability at 56°; it is no longer precipitated by sodium chloride, nor does it afford fibrin with thrombin or calcium chloride. Fibrinogen solutions (Hammarsten) on irradiation deposit a precipitate and are no longer coagulated by the toxin of *Crotalus terrificus*. Caseinogen is converted into a substance which is not precipitated by acetic acid; gelatin in sodium fluoride solution exhibited a diminished solidifying power. A. A. ELDRIDGE.

Oxidising action of solar light on a solution of zymosterol in oil. E. ROUSSEAU (Compt. rend., 1929, 189, 173—174).—Solutions of zymosterol (m. p. 92.1°) in olive oil are slowly and progressively oxidised under the influence of solar radiation at 25°, although to a smaller extent than ergosterol or

cholesterol (this vol., 895). Strict comparison is not possible, as the cholesterol used (m. p. 146.3°) probably contained traces of ergosterol. J. GRANT.

Effect of ultra-violet light on some toxins and antitoxins. M. ARTHUS [with H. N. W. COLLINS] (Arch. Int. Physiol., 1928, 30, 250—266; Chem. Zentr., 1929, i, 1084).—The toxins of *Crotalus terrificus*, *Lachesis lanceolatus*, *Vipera Russellii*, and *Naja tripudians* are decomposed by irradiation with ultra-violet light. With cobra venom the coagulation-inhibiting action was sometimes replaced by a slightly accelerating action. Presence of horse-serum, egg-white, or Witte peptone protected the snake venoms from decomposition on irradiation. Anti-cobra, -dabaia, and -bothrops sera were little affected by irradiation unless diluted. A. A. ELDRIDGE.

Reduction of cuprous chloride. S. SEN (Z. anorg. Chem., 1929, 181, 427—428).—Cuprous chloride is readily reduced to metallic copper by warming its saturated ammoniacal solution with a little sodium potassium tartrate and 40% formaldehyde, care being taken to avoid excess of the latter, since otherwise cuprous oxide is precipitated.

H. F. HARWOOD.

Physical and chemical properties of beryllium. K. ILLIG (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 74—82).—A review of the literature dealing with the physical properties of beryllium and its behaviour towards acids, bases, gases, and various oxides.

A. R. POWELL.

Preparation of beryllium by thermal methods. K. ILLIG and M. HOSENFELD (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 26—29).—An historical survey of methods of producing beryllium by heating the oxide, chloride, fluoride, and various double salts with alkali or alkaline-earth metals.

A. R. POWELL.

Preparation of beryllium chloride from beryl. R. W. WINTERS and L. F. YNTEMA.—See B., 1929, 641.

Beryllium and its chloride. J. M. SCHMIDT (Ann. Chim., 1929, [x], 11, 351—446).—Beryllium chloride is obtained by heating a mixture of the oxide and sugar charcoal (the latter in 25% excess) in a current of chlorine at 900°, but is best prepared by heating the oxide (from the pure sulphate) contained in a silica tube, part of which is maintained electrically at 900°, in a current of dry carbonyl chloride, the beryllium chloride formed condensing in the cold posterior end of the tube. Beryllium chloride combines with dry ammonia to form the compound $\text{BeCl}_2 \cdot 2\text{NH}_3$; if the action of ammonia is prolonged the product contains other complexes. Similar results are obtained with sodamide. Dry ammonia and beryllium chloride dissolved in a mixture of anhydrous benzene and acetone give a complex containing some of the solvent. Attempts to prepare the bromide by heating the chloride in a mixture of hydrogen bromide and hydrogen were partly successful; the amounts of conversion into the bromide at 325° and 400° were 12% and 16%, respectively.

Thermal analyses of mixtures of anhydrous beryllium chloride and various metallic chlorides were made. It combines with the chlorides of lithium,

sodium, barium, and univalent thallium to give chloroberyllates of the type M_2BeCl_4 , and only the thallium salt is fusible without decomposition. Thermal analysis also indicated the existence of another compound, $TlBe_2Cl_5$. The presence of compounds $MBeCl_3$ was not detected. Very fusible mixtures are formed with some chlorides; e.g., a mixture of 41.3 parts of sodium chloride and 58.7 parts of beryllium chloride has m. p. 215° .

The conductivity of beryllium chloride in methyl, ethyl, or amyl alcohol, pyridine, and in ethyl bromide over a wide range of concentration has been measured. The conductivity-concentration curves are abnormal and do not obey Kohlrausch's square-root law in dilute solutions. This is probably due to complex formation with the solvent.

Attempts to prepare pure beryllium by reduction of the chloride with sodium, lithium, calcium, magnesium, or cerium gave a product containing at most 70–80% Be. Electrolysis of the chloride was abandoned owing to the difficulty of finding a sufficiently resistant anode. Reduction of the oxide with carbon gave only the carbide below 2000° ; above this temperature beryllium is obtained, but volatilises as formed. If the reduction is carried out above 2000° in a high-frequency electrical induction furnace in the presence of copper or iron, an alloy of beryllium and the metal from which beryllium cannot be easily separated is obtained. Electrolysis of a mixture of 2 parts of barium fluoride and 1 part of beryllium chloride placed in the cavity of a cylindrical block of graphite, the base of which contains a layer of the barium fluoride-iodide or calcium fluoride-chloride eutectics or of an equimolecular mixture of beryllium fluoride and sodium fluoride, the graphite serving as anode and the cathode consisting of a water-cooled iron cylinder, the latter being gradually raised as the electrolysis proceeds as in the preparation of calcium, gave beryllium in the form of rods weighing about 6 g. and of 99.5–99.8% purity.

The following m. p. of salts mixed with 5% of beryllium were obtained: sodium chloride, 822° ; potassium chloride, 800° ; calcium chloride, 788° ; barium chloride, 970° ; sodium fluoride, 1045° ; barium fluoride, 1050° ; beryllium fluoride (1 part) and barium fluoride (2 parts), 1075° . The result for calcium chloride is not in accord with that of Engle and Hopkins (B., 1924, 473), who found that the m. p. could be lowered to 650° .

Attempts to measure the electrolytic potential of beryllium in ethyl and amyl alcohols and in pyridine and also the decomposition potential of the chloride in these solvents are described. The anomalous results are due to interactions between the metal and solutions of its chloride in the organic solvents. Beryllium reacts with ethyl alcohol to form the ethoxide, a decomposition which is greatly accelerated by the presence of the chloride. Solutions of beryllium chloride in pyridine dissolve silver chloride very readily, the solubility of silver chloride in pyridine saturated with beryllium chloride being 22.5 times that in pure pyridine.

A. I. VOGEL.

Action of magnesium amalgam on nitrates, and its action on nitrous acid, and salts of the

oxy-acids of sulphur and the halogens. P. NEOGI and R. C. BHATTACHARYYA (J. Indian Chem. Soc., 1929, 6, 333–340; cf. A., 1928, 855).—The nitrates of beryllium, cerium, and uranium, on reduction with 5% magnesium amalgam, give hyponitrites, the solutions of which are decomposed during concentration. Aluminium, thallium, and thorium nitrates give the hydroxides only. Ammonia is formed in all cases, hydroxylamine only in the case of cerium nitrate. Free nitrous acid yields no hydroxylamine and very little ammonia, the main product being magnesium nitrite, which is not further reduced. Sulphates, sulphites, and dithionates are unaffected, whilst thiosulphates are reduced to a mixture of sulphite and sulphide with evolution of hydrogen sulphide. Persulphates are reduced to sulphates, bromates, iodates, and periodates to the corresponding halides, whilst chlorates and perchlorates are not reduced even at 50° .

F. L. USHER.

Preparation of fluorescent substances. I. Sulphides of calcium, strontium, and barium. N. F. SHIROV (Ukraine Chem. J., 1928, 3, 209–227).—The choice and preparation of the starting materials, the selection of apparatus and conditions to be observed, and the method of preparation of the above luminophores are discussed. The pure carbonates are mixed with sulphur, sugar (to reduce any sulphate formed to sulphide), a flux (which is usually a salt of sodium, potassium, or lithium, e.g., sodium borate, lithium phosphate), and with an activator (which is a nitrate of any metal, e.g., copper, caesium, lead, etc.). For the preparation of complex luminophores either magnesium oxide or calcium tungstate is also added. Lenard and Vanino's results were partly repeated. Barium sulphide with rubidium and calcium sulphide and strontium sulphide with manganese give very poor luminophores. The best red luminophores are those of barium sulphide with copper and rubidium, the best yellow luminophores are those of strontium and barium sulphides with lead, copper, antimony, and thallium. Indium and calcium sulphide give a bluish-green luminophore, whilst indium or zirconium in strontium sulphide gives yellowish-green luminophores and thorium in calcium sulphide a bluish-violet luminophore. Complex luminophores of composition strontium sulphide-copper, strontium sulphide-uranium, bismuth-strontium-barium sulphide-thorium, lead, copper, calcium sulphide-thallium, uranium, bismuth, and rubidium were prepared.

A. FREIMAN.

Hydrated polycalcium aluminates. A. TRAVERS and SCHNOUTKA (Compt. rend., 1929, 188, 1677–1679).—If the authors' method (A., 1928, 1104) for the preparation of hydrated tricalcium aluminate from solutions of calcium nitrate and potassium aluminate is carried out other than at p_H 11.57–11.62 the resulting crystals contain 3–4 parts of CaO to 1 part of Al_2O_3 . These have now been shown by selective dissolution of the free lime in hydrochloric acid to be solid solutions of calcium hydroxide and hydrated tricalcium aluminate, the actual composition being dependent on the p_H of the medium.

J. GRANT.

Use of barium perchlorate as a drying agent and ammonia absorbent. G. F. SMITH (Chemist-Analyst, 1929, 18, 18—24).—Directions for the preparation, and data concerning the use, of barium perchlorate are given. CHEMICAL ABSTRACTS.

Pure aluminium orthohydroxide. P. A. THIESSEN and K. L. THATER (Z. anorg. Chem., 1929, 181, 417—424).—Aluminium orthohydroxide, $\text{Al}(\text{OH})_3$, has been prepared by the careful decomposition of aluminium triethyl with water. By the action of water on a solution of aluminium triethyl in absolute alcohol the hydroxide is obtained as a gelatinous precipitate, whilst the passage of a stream of nitrogen charged with the vapour of aluminium triethyl through water yields a fine granular precipitate; both correspond with the formula $\text{Al}(\text{OH})_3$. The substance in suspension in water shows a weak positive charge, and must consequently be regarded as a base. H. F. HARWOOD.

Basic gallium acetate and [ammonium] sulphate and gallium oxalate. A. TCHAKIRIAN (Compt. rend., 1929, 189, 251—252).—*Basic gallium acetate*, $4\text{Ga}(\text{OAc})_3 \cdot 2\text{Ga}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is deposited slowly at the ordinary temperature as white, hygroscopic micro-crystals from a mixture of a solution of a gallium salt, neutralised with ammonium carbonate, with a 30% excess of acetic acid. *Basic gallium ammonium sulphate*,

$3(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{Ga}_2(\text{SO}_4)_3 \cdot 5\text{Ga}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$, is precipitated from a warm mixture of solutions of gallium and ammonium alums in the presence of less than 10% of sulphuric acid. *Gallium oxalate*, $\text{Ga}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, a hygroscopic, micro-crystalline powder which is easily hydrolysed, is prepared by boiling a solution of gallium nitrate with oxalic acid in the presence of sufficient concentrated nitric acid to destroy the excess of oxalic acid, which otherwise dissolves the oxalate. J. GRANT.

New type of rare-earth salts. G. A. BARRIERI (Atti R. Accad. Lincei, 1929, [vi], 9, 906—909).—Tervalent rare-earth metals of the cerium group form argentocyanides and aurocyanides, but it has not been found possible to obtain analogous salts of other trivalent metals. The following argentocyanides are described: *cerium*, $\text{Ce}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$; *lanthanum*, $(+ 3\text{H}_2\text{O})$; *neodymium*, $(+ 3\text{H}_2\text{O})$; *luteocobalt*, $[\text{Co}(\text{NH}_3)_6][\text{Ag}(\text{CN})_2]_3$; the three aurocyanides have analogous formulae. T. H. POPE.

Extraction of commercial rare-earth residues with a view to the concentration of illinium. R. W. BALL [with J. A. HARRIS] (J. Amer. Chem. Soc., 1929, 51, 2107—2112).—Efficient methods of extracting rare earths from double sulphate residues are described; they involve either fusion with sodium carbonate followed by evaporation with sulphuric acid and subsequent extraction with water, or digestion with hot, saturated sodium hydroxide solution and subsequent extraction of the residue with nitric acid. Commercial hydrated oxides of the rare earths are preferably extracted with nitric acid and hydrogen peroxide. S. K. TWEEDY.

Addition of ammonia to lead nitrate and lead sulphate. W. KRINGS (Z. anorg. Chem., 1929, 181, 309—336).—Lead nitrate forms three additive compounds with ammonia, the *hexammine*, *triammine* (m. p. 115°), and the *monoammine*. The hexammine is stable only below 0° , whereas the triammine not only has a more or less definite m. p., but also appears to form a eutectic with the monoammine, a preparation containing 2 mols. of ammonia to 1 mol. of nitrate becoming a viscous liquid at 99 — 100° . The vapour tension of the monoammine reaches 760 mm. at about 160° . At -70° lead nitrate absorbs more ammonia than corresponds with the hexammine, but the excess of ammonia appears to be retained in solid solution. Lead sulphate forms a diammine and a tetrammine, both of which are much less stable than the nitrate amines. The heat of formation of the nitrate hexammine is approximately the same as those of the halide hexammines, and that of the sulphate tetrammine approximately the same as those of the halide tetrammines. The densities and vapour pressures of the amines at various temperatures are tabulated. A. R. POWELL.

Dichloroamine. R. M. CHAPIN (J. Amer. Chem. Soc., 1929, 51, 2112—2117).—Chlorination of excess of ammonium ions at the ordinary temperature yields solely monochloroamine when the p_H of the solution exceeds 8.5, and nitrogen trichloride when the p_H is below 4.4. Dichloroamine is practically the sole product between p_H 4.5 and 5.0. It may also be produced by suitably acidifying a monochloroamine solution. S. K. TWEEDY.

Action of hydrazine on quinquevalent arsenic in weakly acid solution. II. H. KUBINA (Z. anal. Chem., 1929, 78, 1—36; cf. A., 1928, 972).—In the reduction of quinquevalent arsenic to the trivalent state by means of hydrazine salts in acid solution some elementary arsenic is always formed; the amount depends on the concentration of the acid, being a maximum when 1.5*N*-hydrochloric acid is used. With 5.5*N*-acid only minimal amounts of arsenic are produced, arsenic trichloride being practically the sole product. The arsenic results in consequence of the secondary reaction $\text{AsH}_3 + \text{AsCl}_3 = 2\text{As} + 3\text{HCl}$, which has been proved to be quantitative. It is suggested that its formation is due to the production of quadrivalent arsenic and di-imide as unstable intermediate compounds, and experiments showed that the addition of an arsenite to the original reaction mixture of arsenate, hydrazine salt, potassium bromide, and hydrochloric acid greatly increased the production of elementary arsenic, presumably by favouring the formation of the quadrivalent form. Napoli's statement that hydrogen arsenide in contact with boiling hydrochloric acid yields arsenic trichloride could not be confirmed. Further experiments on the decomposition of hydrogen arsenide which results when a mixture of the gas with hydrogen and a little air is heated in presence of hydrochloric acid showed that the formation of arsenic does not take place according to the equation $4\text{AsH}_3 = 4\text{As} + 6\text{H}_2$, but is due to the acceleration of the reaction $4\text{AsH}_3 + 3\text{O}_2 = 4\text{As} + 6\text{H}_2\text{O}$ by hydrochloric acid. H. F. HARWOOD.

Reduction of dichromates to basic chromium salts. G. GRATHER and T. NAGAHAMA (Hokkaido J. Agric., 1928, 24, 25—38).—Acid solutions of potassium dichromate are reduced, in order of decreasing effect, by lactic acid, tartaric acid, dextrose, tannin, glycerol, formaldehyde, sodium thiosulphate, sodium sulphite, sodium sulphide.

CHEMICAL ABSTRACTS.

Chromium ethoxides: preparation and properties. P. A. THIESSEN and B. KANDELAKY (Z. anorg. Chem., 1929, 181, 285—294).—Passage of dry hydrogen chloride into absolute alcohol containing small pieces of chromium results in the formation of a dark red solution which, after distilling off part of the alcohol and keeping for some weeks over sulphuric acid in a vacuum, deposits dark green, tetragonal crystals of the compound $\text{CrCl}_3 \cdot 4\text{EtOH}$, which loses 1 mol. of alcohol at 50° in a vacuum. When a 10% solution of either compound in absolute alcohol is treated with an equivalent quantity of sodium the chlorine is removed and the solution, after filtration and cooling, deposits short, green prisms of *chromium ethoxide monoalcoholate*, $\text{Cr}(\text{OEt})_3 \cdot \text{EtOH}$. Evaporation of the filtrate from the above compound affords an amorphous residue of *chromium ethoxide*, $\text{Cr}(\text{OEt})_3$.

A. R. POWELL.

Reduction of alkali tungstates by hydrogen. J. A. M. VAN LIEMPT (Z. anorg. Chem., 1929, 181, 425—426).—Polemical against Spitzin (cf. A., 1925, ii, 1191; this vol., 165). The reduction of sodium tungstate by hydrogen at 1100° is represented by the equation $\text{Na}_2\text{WO}_4 + 3\text{H}_2 = \text{W} + 2\text{NaOH} + 2\text{H}_2\text{O}$. Potassium tungstate is not reduced under these conditions, but volatilises unchanged.

H. F. HARWOOD.

Uranium tetroxide dihydrate. A. ROSENHEIM and H. DAEHR (Z. anorg. Chem., 1929, 181, 177—182).—Contrary to the statements of Hüttig and Schroeder (A., 1922, ii, 510) uranium tetroxide dihydrate exists and has been prepared in amorphous and crystalline forms.

J. S. CARTER.

Reactivity of iodine cyanide in different organic solvents. E. CHARGAFF (J. Amer. Chem. Soc., 1929, 51, 1999—2002).—The reactivity of iodine cyanide towards silver benzoisulphinide is independent of the solvent (ether, alcohol, carbon disulphide, etc.), contrary to the behaviour of iodine (A., 1928, 1131). Iodine cyanide, therefore, probably functions not as a mixed halogen but as a salt of hydrocyanic acid and iodine hydroxide. The results confirm the hypothesis that the iodine cyanide molecule differs in structure from the iodine molecule.

S. K. TWEEDY.

Oxygen compounds of rhenium. I. NODDACK and W. NODDACK (Z. anorg. Chem., 1929, 181, 1—37).—Mainly an amplification of work previously published (this vol., 411). The *potassium, silver, and neodymium* salts of per-rhenic acid are described.

J. S. CARTER.

Composition of iron fluoride. E. DEUSSEN (Monatsh., 1929, 52, 107—116).—Ferric hydroxide is dissolved in an excess of 40% hydrofluoric acid, evaporated, and allowed to crystallise in presence of nitric acid (cf. Peters, A., 1898, ii, 419). The salt obtained is stable in dry air, alters gradually when

exposed to the atmosphere, and has the composition $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (cf. Peters, *loc. cit.*). There are two hydrated ferric fluorides, the second crystallising with $4 \cdot 5\text{H}_2\text{O}$ (cf. Weinland, Lang, and Fikentscher, A., 1926, 136).

Krupp's steel V2A (Fe 70%; Cr 23%; Ni 7%) is acted on by aqueous hydrofluoric acid, rapidly with 20%, but less rapidly with 5%. Iron is the chief substance dissolved.

H. BURTON.

Iron tetranitrosyl. W. MANCHOT and E. ENK (Annalen, 1929, 470, 275—283).—When iron carbonyl is treated with nitric oxide under pressure, best at $44\text{--}45^\circ$, a violently exothermic reaction occurs, giving black crystals of *iron tetranitrosyl*, an unstable substance of which the dissociation pressure is variable. This when treated with dilute sulphuric acid gives the compound $\text{Fe}(\text{NO})\text{SO}_4$; with liquid ammonia a brown product is formed, for which the formula $\text{Fe}(\text{NO})_3 \cdot \text{NH}_3$ is tentatively suggested. The substance reacts with pyridine, aniline, pyrrole, and (violently) with hydrazine, and with the appropriate reagents gives rise to the compounds $\text{Fe}(\text{NO})_2 \cdot \text{S}_2\text{O}_3\text{K}$, $\text{Fe}_4(\text{NO})_7 \cdot \text{S}_3\text{K}$, $\text{Fe}(\text{NO})_2 \cdot \text{SEt}$, and $\text{Fe}(\text{NO})_2 \cdot (\text{S} \cdot \text{C} \cdot \text{OEt})_2$.

E. W. WIGNALL.

Methyl alcohol compound of iron nitrosyl. W. MANCHOT and H. GALL (Annalen, 1929, 470, 271—274).—In attempts to obtain from the compound $\text{Fe}(\text{NO})_3 \cdot 3\text{Fe}(\text{CO})_5$ a compound free from carbon monoxide, it was found that the replacement of carbon dioxide by nitric oxide was facilitated by the presence of methyl alcohol. When iron pentacarbonyl in methyl-alcoholic solution was treated with nitric oxide at the ordinary temperature, a black product was obtained, which was found to contain carbon, but did not give carbon monoxide when treated with acid; it actually contained methyl alcohol, retained up to 200° . The formula of the compound is probably $\text{Fe}(\text{NO})_2 \cdot 2\text{MeOH}$. No similar product was obtained when acetone, acetic acid, or chloroform was used as solvent.

E. W. WIGNALL.

Characterisation of sulphur-nitric oxide compounds of univalent iron, cobalt, and nickel. W. MANCHOT and G. LEHMANN (Annalen, 1929, 470, 255—261).—The sulphur-nitric oxide compounds of the above metals (this vol., 526) are compared with the hyponitrites. When the former are treated with dilute acid, they give rise to nitric oxide, and to nitrous oxide and nitrogen; these are presumably formed by the reduction of the nitric oxide by the univalent metal, which becomes oxidised to the bivalent, and, in the case of iron, to the trivalent state. Since the reducing action of hydrogen sulphide vitiates results, measurements of the amounts of the different gases produced were made after decomposing the compounds by silver sulphate, with or without added acid; it has not been found possible to relate the proportions of the gases to the extent of oxidation of the metal. When the decomposition was carried out in presence of ferric sulphate, the yield of nitric oxide was increased, owing to the hindering of the reduction process.

In contrast with the above results, the hyponitrites were found not to give nitric oxide, whether or not ferric sulphate was present. It is therefore concluded

that the sulphur-nitric oxide compounds do not contain a hyponitrite grouping, and that the nitric oxide is attached (co-ordinately) as a neutral molecule.

E. W. WIGNALL.

Constitution of sulphur-nitric oxide compounds of univalent iron, cobalt, and nickel. W. MANHOT (Annalen, 1929, 470, 261—270).—A theoretical discussion of the structure of these compounds on the basis of Sidgwick's co-ordination theory. A compound such as $\text{Fe}(\text{NO})_2\text{SEt}$, which is soluble in benzene and other organic solvents, and is thus homopolar, is considered to have the nitric oxide groupings attached to the iron atom by co-ordinated covalencies (donated by nitrogen), and the $\cdot\text{SEt}$ grouping attached by a normal (shared) covalency, which may also become an electrovalency, as is shown by the small but actual conductivity of the substances. The following new compounds are mentioned: $\text{Co}(\text{NO})_2\text{SEt}$; $\text{Co}(\text{NO})_2\text{SPh}$; $\text{Ni}(\text{NO})\text{SPh}$; $\text{Ni}(\text{NO})\text{SPh}, \text{C}_5\text{H}_5\text{N}$.

E. W. WIGNALL.

Cobalt oxides and systems with oxygen. M. LE BLANC and E. MÖRBS (Z. physikal. Chem., 1929, 142, 151—176).—Cobaltous oxide prepared by igniting the carbonate in a vacuum absorbs oxygen, the absorbent power being the greater the lower is the temperature of ignition; also the higher is the temperature at which the solid is brought in contact with the gas, the more is taken up. The oxygen absorbed is activated, reacting immediately with hydrogen iodide. Below about 100° , the absorption causes no change in the lattice, but the system $\text{CoO}, n\text{O}_2$ is unstable, and at higher temperatures is transformed into the system $\text{Co}_3\text{O}_4, m\text{O}_2$, the lattice being converted into that of cobaltocobaltic oxide. On thermal decomposition, this system proves to be bivariant, consisting of a single solid phase of variable composition. When treated with oxalic acid, the cobaltous salt is formed, and the excess of oxygen corresponding with the cobaltocobaltic oxide rapidly oxidises the acid, whilst the free oxygen reacts only slowly, thus proving that the solid is actually cobaltocobaltic oxide with absorbed oxygen, and not cobaltic oxide; the system $\text{CoO}, n\text{O}_2$ behaves similarly. Thermal decomposition of pure cobaltocobaltic oxide shows the existence of an equilibrium $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + 0.5\text{O}_2$, whereas with pure cobaltous oxide the decomposition pressure is less than 0.1 mm., even at 1250° . None of the experiments gives indication of the existence of any oxides other than cobaltous and cobaltocobaltic; the dry methods for the preparation of cobaltic oxide to be found in the literature actually give the system $\text{Co}_3\text{O}_4, m\text{O}_2$. Hydrated cobaltic oxide may, however, be prepared by precipitating an aqueous solution of cobaltic sulphate with alkali. Oxalic acid in aqueous solution is slowly oxidised at 100° by air, the reaction being catalytically accelerated by cobaltous ions.

R. CUTHILL.

Cobalt with a covalency of four: new series of complex compounds. E. G. V. PERCIVAL and W. WARDLAW (J.C.S., 1929, 1505—1512).—A new series of compounds of the formula $\text{R}_2[\text{CoX}_4]$, where $\text{R} = \text{C}_5\text{H}_5\text{N}$, $\text{C}_6\text{H}_5\text{N}$, or $\text{C}_{10}\text{H}_{10}\text{N}$ and X is a halogen, has been isolated by the addition of the appropriate base to a solution of the cobalt halide in solution in

the corresponding concentrated halogen acid. The complex chlorides were also prepared by the addition of the organic hydrochloride to an alcoholic solution of cobaltous chloride. Determinations of the mol. wt. and conductivities of these compounds indicate that they are not double salts of the type $2\text{RX}, \text{CoX}_2$, but complex salts of the formula $\text{R}_2[\text{CoX}_4]$. Definite evidence is therefore provided of the existence of the CoX_4^{2-} ions postulated by Donnan and Bassett (J.C.S., 1902, 81, 939) to account for the blue colour of solutions of cobalt halides in alcohol or concentrated halogen acids.

Cobaltous diquinolinium chloride has m. p. $170-171^\circ$; its *monohydrate* has also been isolated. The corresponding *dipyridinium* and *di-2-methylquinolinium* compounds have m. p. $169-170^\circ$ and $239-240^\circ$, respectively. *Cobaltous diquinolinium bromide* has m. p. $164-165^\circ$; the corresponding *dipyridinium* and *di-2-methylquinolinium* compounds, m. p. $165-166^\circ$ and $231-232^\circ$, respectively. *Cobaltous diquinolinium iodide* has m. p. $156-157^\circ$; the compound $\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ has m. p. $196-197^\circ$. F. J. WILKINS.

Colours of cobaltous hydroxide. C. W. STILLWELL (J. Physical Chem., 1929, 33, 1247—1271).—The colours obtained by the interaction between cobalt chloride and potassium hydroxide under various conditions have been investigated microscopically and also by means of X-ray analysis. Freshly-precipitated cobaltous hydroxide is green to yellowish-green by transmitted light, and is gelatinous, laminar, amorphous, and metastable. The blue colour is essentially a reflected colour; it is probably a Tyndall blue scattered by small crystal nuclei which form within the amorphous matrix as the gelatinous precipitate ages to the crystalline form. The freshly precipitated hydroxide tends to change to the rose-coloured hydroxide which is granular in appearance and is the stable, crystalline form. No other crystalline forms were produced; the light blue, aged precipitate is crystalline, but it has the same structure as the rose-coloured hydroxide. The blue of the aged precipitate is also structural. Adsorbed cobaltous chloride inhibits crystal growth, favours the formation of the green precipitate, and hinders that of the rose. Freshly-precipitated nickelous hydroxide is laminar and amorphous, and tends to stabilise the corresponding amorphous cobalt hydroxide. The change from green to blue of freshly-precipitated cobaltous hydroxide is not due to oxidation.

When cobaltous chloride solution is added to potassium hydroxide solution in amounts greater than the molecular ratio 1:1.5 and the precipitate is allowed to remain in contact with the mother-liquor, ageing occurs and the colour of the precipitate changes from green to blue to rose; the final rose-coloured precipitate is a basic salt of cobalt and is the only crystalline product formed under the experimental conditions; the blue is a mixture of the rose and the green; and the green is amorphous, containing small amounts of crystalline hydroxide and basic salt.

L. S. THEOBALD.

"Tartratecobaltinitrite" [existence of the cobaltyl group]. M. WIKUL (Z. anorg. Chem.,

1929, 181, 121—130).—The suggested formula of a complex salt used for the determination of potassium (A., 1928, 264) contains a cobaltyl (CoO) group. The plausibility of this assumption has been investigated and although no complete confirmation has resulted, a salt of composition corresponding approximately with the formula $(\text{CoO})_2\text{SO}_4 \cdot \text{NaHSO}_4$ has been isolated. J. S. CARTER.

Action of hydrogen at high pressures and at high temperatures on solutions of ruthenium salts. V. N. IPATIEV and O. E. ZVAGINCEV (J. Russ. Phys. Chem. Soc., 1929, 61, 823—825).—The reducing action of hydrogen at pressures of 60—150 atm. and from the ordinary temperature up to 350° has been studied for slightly acidified aqueous solutions of ammonium, potassium, and sodium pentachlororuthenates. With rising temperature and increasing pressure the product isolated varied from the hydrated oxides of ruthenium, $\text{Ru}(\text{OH})_3 \cdot \text{aq.}$ and $\text{Ru}(\text{OH})_3$, to Ru_2O_3 and metallic ruthenium. No intermediate oxides were formed, nor was a blue solution formed as by the reduction of ruthenium salts with zinc and hydrochloric acid. A. FREIMAN.

Indicators. N. A. ZAITZEV (J. Chem. Ind. Moscow, 1928, 5, 722—723).—Ammonium 5:5'-*p*-diphenylenebisazobis-8-anilino-1-naphthalenesulphonate (from tetrazotised benzidine and phenyl-peri-acid) is pink; with acids it becomes blue. 5-*p*-Acetamidophenylazo-8-anilino-1-naphthalenesulphonic acid (from diazotised acetyl-*p*-phenylenediamine and phenyl-peri-acid) is less sensitive to acids. Since it is insensitive to aniline hydrochloride it is suitable for the titration of aniline. 5-(4-Sulpho-1-naphthaleneazo)-8-anilino-1-naphthalenesulphonic acid and 4-(4-anilino-5-sulpho-1-naphthaleneazo)-5-hydroxynaphthalene-2:7-disulphonic acid are suitable for the titration of alkali hydroxides.

CHEMICAL ABSTRACTS.

Possible, ready replacement of the Zerewitinoff method. K. ZIEGLER and F. DERSCH (Ber., 1929, 62, [B], 1833—1834).—Intensely coloured organic compounds of the alkali metals (sodium triphenylmethyl; potassium phenylisopropyl) are suitable for titrimetric determination of active hydrogen. The substance is preferably weighed, without solvent, in a nitrogen-filled tube and titrated with the alkali compound until the colour persists. The titer of the solution is determined previously by addition of a dry aliphatic bromide (*n*-butyl bromide) and determination of bromine by Volhard's method after treatment with water. Alternatively, an excess of metallic derivative is used followed by addition of alkyl bromide until the colour is discharged and titration of bromine. H. WREN.

Determination of water in micas. K. I. VISKONT and I. P. ALIMARIN (Trans. Inst. Econ. Min. Met., Moscow, 1928, No. 40, 18 pp.).—To avoid evolution of hydrogen by interaction of water and ferrous oxide, the substance is heated with platinum-black, lead oxide, and sodium tungstate.

CHEMICAL ABSTRACTS.

Apparatus for the determination of water by the distillation method. J. PRITZKER and R. JUNGKUNZ (Chem.-Ztg., 1929, 53, 603).—A new

form of apparatus which permits of the employment of liquids of any sp. gr. for treating the substance under examination is described; the expelled water is collected in a graduated tube and measured directly. If the water content of the material does not exceed 25% the determination can be completed in 5 min., and the results compare satisfactorily with those obtained by other methods. H. F. HARWOOD.

Determination of chloride ion in reagents. A. FROST (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 35—37).—Addition of nitric acid first increases and then decreases the turbidity, the maximum effect being obtained with 13% acid; sulphuric acid behaves similarly. Ammonium or potassium nitrate, potassium or sodium sulphate, potassium chlorate, cadmium sulphate, and zinc acetate (1 g. per 20 c.c.) increase the turbidity by 20% and 40% when the chloride-ion concentration is 0.44—0.11 and 0.55—0.20 mg. per 20 c.c. respectively. CHEMICAL ABSTRACTS.

Gravimetric titration and micro-determination of hydrochloric and arsenic acids. B. ORMONT (J. Russ. Phys. Chem. Soc., 1929, 61, 355—362).—See this vol., 41.

Determination of bromine in sea-water and estuary waters. A. I. KOGAN (Ukraine Chem. J., 1928, 3, 131—137).—Methods of determination of small quantities of bromine in the presence of large quantities of chlorine are reviewed and the applicability to the determination of bromine in sea-water and estuary waters is considered. Vescelski's method (Z. anal. Chem., 1899, 39, 81) is inapplicable, whilst Berg's method (A., 1926, 1017) gives good results. Bromine is determined colorimetrically by adding 3 drops of 20% sulphuric acid to 10 c.c. of sea-water and then chlorine water until the maximum depth of colour is attained. The solution is then shaken with 5 c.c. of chloroform and the extract compared with a solution of a known weight of potassium bromide in estuary water from which the bromine has been previously entirely removed. With ordinary water as solvent for the potassium bromide the results are too low as compared with those found by Berg's method. A. FREIMAN.

Potentiometric determination of bromine, octovalent and quadrivalent osmium in hydrobromic acid solutions. W. R. CROWELL and H. D. KIRSCHMAN (J. Amer. Chem. Soc., 1929, 51, 1695—1702).—The above titration may be effected by means of tervalent titanium. Three inflexions in the titration curve correspond respectively with the reduction of bromine to bromide ion, the reduction of octovalent osmium to quadrivalent osmium, and the reduction of quadrivalent osmium to the tervalent state. This last inflexion is unsuitable for quantitative work. Some results of Hendrixson (A., 1923, ii, 781) are confirmed. S. K. TWEEDY.

Determination of sulphur in steels etc. K. SWOBODA.—See B., 1929, 601.

Determination of sulphur in antimony. C. G. SNYDER.—See B., 1929, 603.

Determination of sulphuric acid in presence of chromic acid. D. TARASENKOV (Trans. Inst.

Pure Chem. Reagents, Moscow, 1927, No. 6, 31—34).—Excess of sodium hydroxide is added and titrated back with sulphuric acid to sodium dichromate and sulphate, using Congo-red as indicator. The chromic acid is determined iodometrically in a strongly acid solution. CHEMICAL ABSTRACTS.

Iodometric determination of a mixture of sulphide, sulphite, and thiosulphate. R. WOLLAK (Z. anal. Chem., 1929, 77, 401—406).—The procedure is identical with that of Kurtenacker and Bittner (A., 1925, ii, 239) save for the determination of thiosulphate. This constituent is determined by addition of an excess of iodine to an acidified aliquot portion and titration back with sodium sulphite, the resulting tetrathionate being determined by the cyanide method of Kurtenacker and Fritsch (A., 1921, ii, 502). J. S. CARTER.

Volumetric determination of polysulphides. P. SZEBERÉNYI (Z. anal. Chem., 1929, 78, 36—40).—A portion of the polysulphide solution is boiled for 2—3 min. with an excess of a standardised solution of sodium sulphite, whereby all polysulphide is converted into thiosulphate. The cooled solution is titrated with 0.1*N*-iodine after addition of sodium hydrogen carbonate. Another portion of the original solution is titrated in the cold with 0.1*N*-iodine, and this figure, together with the iodine value corresponding with the sodium sulphite added, subtracted from the first. The difference corresponds with the sulphur present as polysulphides, each c.c. of 0.1*N*-iodine representing 0.0032 g. of sulphur. An alternative method is based on the change in alkalinity when a polysulphide is oxidised with an alkaline solution of hydrogen peroxide. A portion of the solution is titrated with *N*-acid, using methyl-orange as indicator. A second portion is treated with zinc sulphate to remove sulphides, filtered, and the thiosulphate in the filtrate titrated with iodine solution. A third portion is treated with a known volume of *N*-sodium hydroxide and 10—20 c.c. of 30% hydrogen peroxide until oxidation is complete, and the residual alkalinity found by titration. The decrease in total alkalinity, less twice the titration corresponding with the thiosulphate present in the oxidised portion, gives the amount of polysulphide present, each c.c. of *N*-acid corresponding with 0.016 g. of sulphur.

H. F. HARWOOD.

Analytical applications of sodium hyposulphite. B. S. EVANS (Analyst, 1929, 54, 395—405).—Sodium hyposulphite reduces salts of copper, silver, mercury, bismuth, selenium, lead, arsenic, and antimony to the elementary state in alkaline solutions and the reduction is not obstructed by many oxidising agents which would react in an acid medium. Potassium cyanide prevents the precipitation of copper but favours that of antimony, and the separation, at least in the case of lead, antimony, and bismuth, is rapid and complete. The following processes have been worked out in detail: determination of antimony in high-antimony copper alloys; small amounts of bismuth in tin-zinc alloys; small amounts (0.01—0.2%) of antimony in lead and lead alloys; separation of cadmium from bismuth; and lead from antimony. D. G. HEWER.

Determination of selenium dioxide in sulphuric acid. T. RAIKHINSTEIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 27—30).—For 0.01—0.00005% SeO_2 , 0.1 c.c. of a 4% aqueous solution of codeine phosphate is added to 10 c.c. of the solution in concentrated sulphuric acid, and the selenium is determined colorimetrically. Arsenic acid, if below 1%, gives no coloration; ferric iron, if present in excess of 0.0015% (or, if phosphoric acid is also present, 0.0074%), also gives a blue coloration.

CHEMICAL ABSTRACTS.

Rapid determination of nitrogen by Kjeldahl's method. H. LUNDIN and J. ELLBURG.—See B., 1929, 596.

Determination of nitric nitrogen by alkaline reduction with powdered aluminium. A. SEYEWETZ (Bull. Soc. chim., 1929, [iv], 45, 463—465).—Sodium hydroxide solution is added at the rate of 2—3 drops per sec. to 150 c.c. of water, 10 g. of powdered aluminium, and an amount of nitrate equivalent to about 1 g. of potassium nitrate, at 50°. When the reaction has ceased, the liquid is distilled into *N*-sulphuric acid. C. W. GIBBY.

Jena glass filtering crucibles. [Determination of phosphorus and potassium.] R. H. SIMON.—See B., 1929, 625.

Electrometric titration of boric acid. I. V. GREBENSCHTSCHIKOV and T. A. FAVORSKAIA (J. Russ. Phys. Chem. Soc., 1929, 61, 561—574).—The titration curves of boric acid solutions exhibit a series of breaks, the number and position of which depend on the previous history of the solution. Further, cryoscopic measurements show that the mol. wt. of boric acid in aqueous solution falls on keeping from 72 in a fresh solution to a limiting value of 59. This transformation is accelerated by heat, the equilibrium mixture probably containing a series of variously hydrated and associated acids. In titrating boric acid solutions in the presence of indicators the result will depend on the method of preparation of the solution and on its age.

R. TRUSZKOWSKI.

Oxidisability of silicon and of Moissan and Siemens' allotropic modification. A. SANFOURCHE (Compt. rend., 1929, 188, 1672—1675; cf. Bedel, this vol., 756, 997).—Silicon may be gradually but completely converted into silica by successive treatments with hydrofluoric acid followed by ignition at 150°, the silica produced at each stage being determined from the percentage loss in weight. The rate of conversion depends on the method of production and state of division of the silicon, and it is concluded that an allotropic modification of silicon partly soluble in hydrofluoric acid (Moissan and Siemens) does not exist. There is also evidence of lower oxides (Si_3O_2 and Si_3O_4) which impart a brown colour to the supposed allotropic form and liberate hydrogen on addition of the acid. J. GRANT.

Determination of small amounts of potassium in presence of much sodium by a direct, gasometric method. G. JANDER and H. FABER (Z. anorg. Chem., 1929, 181, 189—192).—A micro-

modification of the method previously described (A., 1928, 980).

J. S. CARTER.

Qualitative reagent for sodium. E. R. CALEY (J. Amer. Chem. Soc., 1929, 51, 1965—1969).—A saturated solution of uranyl acetate and cobalt acetate in 6% acetic acid, when added in large volume, favours the precipitation from solution of sodium uranyl cobalt acetate in preference to the corresponding potassium compound. The precipitate approximates to the composition

$3\text{UO}_2(\text{OAc})_2 \cdot \text{Co}(\text{OAc})_2 \cdot \text{NaOAc} \cdot 6\text{H}_2\text{O}$. The presence of potassium does not appreciably influence the detection of sodium by means of the reagent. The reagent is only moderately sensitive to lithium, and is unaffected by heavy metals. However, phosphates must always be absent. The use of the reagent in Noyes' scheme of qualitative analysis is described.

S. K. TWEEDY.

Determination of hardness in water by means of soap solution. G. BRUHNS.—See B., 1929, 662.

Analytical chemistry of beryllium. H. FISCHER (Wiss. Veröff. Siemens-Konz., 1929, 8, [1], 9—20).—Iron in quantity exceeding that of the beryllium interferes with the quinalizarin colorimetric titration of beryllium (A., 1928, 385). To separate beryllium from large quantities of iron both metals are precipitated with ammonia from a cold solution, the precipitate is collected, washed, dried, and ignited over a blast, the mixed oxides are reduced in hydrogen, and the metallic iron is extracted with hydrochloric acid. Strongly ignited beryllia is insoluble in all acids except hydrofluoric; the residue is therefore dissolved in warm hydrofluoric acid, the solution treated with sodium hydroxide to 0.25*N*, and titrated colorimetrically with quinalizarin. To determine beryllium in copper, nickel, or zinc alloys, 0.5 g. is dissolved in concentrated hydrochloric acid and a little hydrogen peroxide, the solution evaporated to dryness on the water-bath, the residue dissolved in water, and 10% potassium cyanide solution added until the precipitate ceases to dissolve; after addition of 50 c.c. of *N*-sodium hydroxide the solution is diluted to 200 c.c. and the beryllium titrated. For the determination of beryllium in beryl and similar minerals 1 g. of the finely-ground substance is intimately mixed with 1 g. of sodium fluosilicate and the mixture heated at 680—710° in a porcelain crucible. The aqueous extract of the product is treated with sodium hydroxide etc., as described above. Ammonia does not precipitate beryllia completely from fluoride solutions; they must therefore be evaporated with sulphuric acid before addition of ammonia for the gravimetric determination of beryllia.

A. R. POWELL.

Simple qualitative analysis of alloys. D. SCRUTO (Notiz. chim.-ind., 1928, 3, 698—701; Chem. Zentr., 1929, i, 1029—1030).—Methods suitable for instructional purposes are described.

A. A. ELDRIDGE.

Solubility influences and quantitative analysis. L. DEDE (Z. angew. Chem., 1929, 42, 723).—Polemical against Wendehorst (A., 1928, 726). Cadmium is not completely precipitated as carbonate by an excess of ammonium carbonate, but good results

are obtained by precipitation with potassium carbonate, even in presence of potassium chloride, and ignition to oxide at 900°; ignition at 1000° results in loss by volatilisation.

A. R. POWELL.

[Solubility influences and quantitative analysis.] E. WENDEHORST (Z. angew. Chem., 1929, 42, 723—724).—The author reaffirms the interference of potassium chloride in the carbonate precipitation of cadmium and considers that Dede's precipitate contained sulphate or alkali salt (cf. preceding abstract).

A. R. POWELL.

Spectroscopic detection of lead in gold-copper-silver alloys. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1929, 181, 101—102).—The method previously described (A., 1928, 859) is applicable only to specimens of gold of low silver content. For the detection and approximate determination of small quantities of lead in gold alloys containing appreciable amounts of copper and silver the lead line 4057.8 appears to be suitable.

J. S. CARTER.

Spacu's sensitive reaction for copper and thiocyanate. Reagent for polysulphides. A. J. FOLCINI (Rev. Centro Estud. Farm. Bioquim., 1928, 17, 305—309; Chem. Zentr., 1929, i, 562).—Spacu's and Fleming's reactions are not specific for thiocyanate. Spacu's reaction for copper is improved by the substitution of polysulphide for thiocyanate. Dianisidine and diaminofluorene behave similarly to toluidine and benzidine (cf. A., 1924, ii, 502; 1925, ii, 1003).

A. A. ELDRIDGE.

Action of complex halides and cyanides on certain aromatic diamines. A. J. FOLCINI (Rev. Centr. Estud. Farm. Bioquim., 1928, 17, 413—417; Chem. Zentr., 1929, i, 1132).—The blue precipitate produced in presence of copper by iodides with diamines of the diphenyl series is not produced by other halides, but the reaction is given by cyanides as well as by thiocyanates (cf. preceding abstract).

A. A. ELDRIDGE.

Volumetric determination of mercury. H. B. DUNNICLIFF and H. D. SURI (Analyst, 1929, 54, 405—410).—The mercury is first converted into chloride. Equal volumes of a 25% sodium tartrate solution and stannous chloride solution are mixed in the presence of a constant current of carbon dioxide, the hydrochloric acid is neutralised with sodium hydrogen carbonate, the solution diluted to 80—90 c.c., stirred (still in presence of carbon dioxide), and standardised by the ferric alum and titanous chloride method. The above process is repeated, but before dilution 10 c.c. of the mercuric chloride solution are added; after quickly filtering through a Gooch crucible with a double layer of barium sulphate filter-paper and asbestos into a burette in an atmosphere of carbon dioxide, 10 c.c. of the filtrate are added to an excess of a hot solution of standard ferric alum, acidified with hydrochloric acid, and the excess is titrated against titanous chloride. The percentage error in 15 determinations varied from +0.55 to -0.22. In an alternative method, the stannous chloride solution is neutralised as before, mercuric chloride solution added, and after complete reduction diluted to known volume and filtered. A

known volume of filtrate is added to standard iodine solution more than sufficient for oxidation of the stannous chloride in the filtrate, and the excess titrated against 0.05*N*-sodium thiosulphate. The degree of accuracy is much the same as in the first method, and the method should not be relied on for concentrations below 0.025*N*. D. G. HEWER.

Volumetric determination of mercury. M. L. COLOMBIER (*J. Pharm. Chim.*, 1929, [viii], 10, 15—24).—Methods described in the literature are examined experimentally; the method of Denigès (*Bull. Soc. chim.*, 1895, 15, 862) receives special attention and slight improvements of it are suggested.

R. J. W. LE FÈVRE.

Determination of minute quantities of mercury. J. BODNÁR (*Z. angew. Chem.*, 1929, 42, 826; cf. Thilenius and Winzer, this vol., 531; Stock and Zimmerman, *ibid.*, 784).—Attention is directed to a previous publication (*ibid.*, 614). J. S. CARTER.

Potentiometric standardisation of ceric sulphate [solutions]. K. SOMEYA (*Z. anorg. Chem.*, 1929, 181, 183—188).—In presence of sulphuric acid solutions of ceric sulphate may be titrated potentiometrically using potassium ferrocyanide and *vice versa*. In presence of hydrochloric acid, solutions of alkali iodides may be similarly titrated with ceric sulphate solutions. The end-point in the latter case is more marked in presence of potassium cyanide.

J. S. CARTER.

Separation of aluminium as hydroxide from steels. W. J. SHANEMAN and J. J. GALLAGHER.—See B., 1929, 601.

Volumetric determination of manganese as manganic salt. R. LANG and F. KURTZ (*Z. anorg. Chem.*, 1929, 181, 111—120).—The method is based on the induced oxidation of manganous to manganic salts in presence of dichromate and arsenite (A., 1928, 600). The neutral or slightly acid solution of manganous salt, which should contain not more than 0.2 g. of manganese, is acidified with 25 c.c. of 5*N*-sulphuric acid; 5 g. of sodium fluoride and 5—10 c.c. of syrupy phosphoric acid are then added and the whole is treated with 45 c.c. of a solution of potassium dichromate containing 15 g. per litre and 50 c.c. of a solution containing 15 g. of arsenious oxide and 10 g. of sodium carbonate per litre. After addition of 3 drops of a solution of 1 g. of diphenylamine in 100 c.c. of phosphoric acid the manganic salt is titrated with a solution of ferrous sulphate until the colour changes from blue to green. Mercuric, aluminium, calcium, and (when present in appreciable amounts) ammonium salts interfere. If it is desired to determine iron in presence of manganese, the former may be determined by Knop's method (A., 1924, ii, 351) and the latter, after addition of sodium fluoride etc., by the present method.

J. S. CARTER.

Decomposition of potassium permanganate to solid manganese oxides in oxidation reactions. [Determination of manganese and arsenic.] B. REINITZER and F. HOFFMANN (*Z. anal. Chem.*, 1929, 77, 407—441).—An examination of the constitution of the precipitates obtained at various stages in titrations with permanganate involving

complete eventual precipitation of manganese as dioxide shows that only in the Volhard process for the determination of manganese is the precipitate always free from lower oxides. In all other cases the initial precipitates contain lower oxides which are finally converted into the dioxide. Conversion into dioxide is complete only when the titrated solution is maintained at 95—100° and when the acidity is low. Manganese may be titrated in a manner similar to that previously described (A., 1926, 705) in media made alkaline with sodium phosphate and containing potassium chloride. Flocculation of manganese dioxide is assisted by addition of barium chloride towards the end of the titration. In boiling solutions containing acetic acid and sodium acetate arsenites are quantitatively oxidised to arsenates according to the equation $3As_2O_3 + 2Mn_2O_7 = 3As_2O_5 + 4MnO_2$. Analysis of a precipitate which had deposited in a stock solution of potassium permanganate showed the presence of both manganese dioxide and manganic oxide. J. S. CARTER.

Determination of ferrous iron in silicate rocks.

II. Electrometric. B. A. SOULE (*J. Amer. Chem. Soc.*, 1929, 51, 2117—2120).—A warm solution of the ore in mixed hydrochloric and hydrofluoric acids, prepared and maintained in an atmosphere of carbon dioxide, is titrated electrometrically with ceric sulphate. The titration is rapid and accurate, arsenic from the glass vessels having no disturbing effect (A., 1928, 725, 861). S. K. TWEEDY.

Determination of bi- and ter-valent cobalt.

V. CUVELIER (*Natuurwetensch. Tijds.*, 1929, 11, 123—130).—Cobalt in the bi- and ter-valent states may be differentiated and determined by titrations based on successive oxidations and reductions. Hydrogen peroxide or sodium perborate in sodium hydroxide solution oxidises both cobalt and iron; the excess of oxidising agent is removed by boiling, and the solution reduced by means of a known excess of stannous chloride. The excess and the ferrous salt are then oxidised by means of a known excess of potassium dichromate, and this excess is in turn reduced by titration with a standardised ferrous sulphate solution. By this method of analysis, the formula determined for the black colloidal mineral from the Star of the Congo mine at Katanga, which contains finely disseminated malachite and chrysocolla, was $3Co_2O_3 \cdot 2CuO \cdot 10H_2O$; this mineral has recently been described as heterogenite, for which the formula $CoO \cdot 2Co_2O_3 \cdot 6H_2O$ was originally put forward. S. I. LEVY.

Drop method of detecting molybdenum. N. A. TANANAEV and G. A. PANTSCHENKO (*Ukraine Chem. J.*, 1929, 4, 121—122).—A method is described which allows of the detection of 0.001 mg. of molybdenum in a drop of solution (0.02 c.c.). A drop each of hydrochloric acid, of the solution to be tested, again of hydrochloric acid, and finally of a potassium thiocyanate solution are placed in turn on a filter-paper. A drop of a stannous chloride solution is then added, when any red colour due to iron disappears and the crimson colour due to the presence of molybdenum appears. The test can be employed in the presence

of titanium, uranium, tungsten, or vanadium, and is applicable in the analysis of steel and minerals.

A. FREEMAN.

Determination of molybdenum in steel. W. F. MURRAY.—See B., 1929, 601.

Rapid detection of tungsten in ores. A. PETROVSKY.—See B., 1929, 603.

Rapid determination of tin in lead-base alloys containing antimony. T. B. DIANA.—See B., 1929, 647.

Rapid determination of vanadium in ferro-vanadium. J. SILBERSTEIN.—See B., 1929, 647.

Determination of vanadium in steel. J. KASSLER.—See B., 1929, 601.

Colorimetric determination of bismuth. FRICK and ENGEMANN (Chem.-Ztg., 1929, 53, 505—507).—A review of the various modifications of the iodide method for the colorimetric determination of bismuth.

A. R. POWELL.

Separation of bismuth from lead. I. FRICK and ENGEMANN (Chem.-Ztg., 1929, 53, 601—602).—The usual methods for the separation of small amounts of bismuth from lead are too tedious for technical purposes, and a new method has been devised, which is both rapid and exact. The nitric acid solution of the two metals, containing up to 0.2% of bismuth, is diluted to 300 c.c., and a few drops of Congo-red are added. Sodium hydroxide is added until the p_{H} value of the solution is between 3 and 5.2, as shown by the bluish-red colour of the indicator, whereupon 20 c.c. of a 0.7% solution of cinchonine hydrochloride are introduced, and the liquid is set aside for 30 min. The precipitate is collected, washed with a cold, very dilute solution of the precipitant until free from lead, redissolved in nitric acid, and the bismuth in solution determined colorimetrically.

H. F. HARWOOD.

Separation of bismuth by rapid electrolysis in acid solution. A. JILEK and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 369—376).—Satisfactory deposits of bismuth can be obtained by electrolysis after the following treatment: after slight acidification with nitric acid, sucrose and a considerable excess of hydrofluoboric acid are added, giving rise to a complex salt. To obviate the disturbing action of the nitric acid, the acidity is first reduced by adding potassium hydroxide, and the resultant precipitate redissolved by sucrose and hydrofluoboric acid. Electrolysis is carried out in hot solution with a small current. A similar procedure can be used for sulphate solutions. For bismuth chloride solutions containing hydrochloric acid, potassium citrate is used for neutralising the acid instead of potassium hydroxide.

C. W. GIBBY.

Micro-determination of bismuth. P. DUMONT and M. BOUILLENNE (Compt. rend. Soc. Biol., 1928, 99, 1247—1248; Chem. Zentr., 1929, i, 562).—The colour reaction with an excess of potassium iodide is employed (cf. A., 1928, 1348).

A. A. ELDRIDGE.

Spectro-analytical method for the rapid determination of iridium, rhodium, and palladium in platinum. W. GERLACH and E. SCHWEITZER (Z. anorg. Chem., 1929, 181, 103—110; cf. A., 1927,

845).—Observation lines are tabulated for the determination of quantities of rhodium and iridium in platinum of the order 10—0.1% with an accuracy of $\pm 10\%$. No such data are given for palladium, but suitable lines are indicated.

J. S. CARTER.

Benzidine reaction in mineralogical analysis. M. DOMINIKIEWICZ (Przemysł Chem., 1929, 13, 233—236).—The benzidine reaction is not given by ozone. The reaction is positive for pyrolusite, manganite, hausmannite, psilomelane, and ilmenite, and is negative for chromite and cassiterite.

R. TRUSZKOWSKI.

Apparatus for strong ultra-violet and infra-red light and photography with heat rays. J. PLOTNIKOV (Z. Elektrochem., 1929, 35, 434—438).

—Three types of apparatus, involving a carbon arc, strong sunlight, or magnesium light, for the production of strong ultra-violet or strong infra-red radiations are described.

H. T. S. BRITTON.

Small gas muffle oven. F. W. HORST (Chem. Fabr., 1929, 280—281).—A small muffle oven with diatomite insulation is described.

J. S. CARTER.

Apparatus for determination of m. p. W. FRIEDEL (Biochem. Z., 1929, 209, 65—73).—The apparatus consists of a suitably bored copper cylinder in which are placed a thermometer and a capillary tube containing the substance under examination. A highly-magnified image of the tube can be thrown on an attached screen so that the behaviour of small amounts of substance when heated can be watched with ease.

W. MCCARTNEY.

Apparatus for demonstration [by projection on a screen] of m.-p. and f.-p. determinations. W. SCHMIDT (Chem. Fabr., 1929, 279).

Influence of time of outflow and subsequent drainage on burette measurements. J. LINDNER and F. HASLWANTER (Z. angew. Chem., 1929, 42, 821—825).—Burettes were emptied at various rates and the subsequent drainage was measured after various time intervals. The data are discussed in their bearing on errors introduced into volumetric determinations.

J. S. CARTER.

Rapid calibration of pipettes and burettes. A. T. SHOHL (Ind. Eng. Chem. [Anal.], 1929, 1, 152—153).—The required weights and one of a pair of tared flasks are placed on the pan of a rough balance. The other tared flask is placed on the other pan. Mercury, covered by a layer of water to obtain a suitable meniscus, is run from the apparatus to be calibrated into the second flask until the balance just turns.

J. S. CARTER.

Volumeter using water as the measuring medium. J. A. FRIES (Ind. Eng. Chem. [Anal.], 1929, 1, 123—125).—The volume of flasks etc. is determined by connecting them to a burette filled with water and observing the change in the water level when the stop-cock is opened. The procedure and the method of calculation are described.

J. S. CARTER.

Nitrometer without rubber connexions for semi-micro-chemical work. E. BERL, K. HOFMANN, and R. BEMMANN (Chem. Fabr., 1929, 359—360).—The apparatus described presents certain new

features in control by manipulation of suitably pierced stop-cocks. The customary arrangement of nitrometer and levelling tube is replaced by a gas burette sealed within a glass jacket; the burette and jacket may be connected by manipulation of a stop-cock at the base.

J. S. CARTER.

Stopcock [for vacuum work] in which contamination by grease is prevented, and its application to a problem in gas technique. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, 51, 2132—2134).—The lowest edge only of the cock is lubricated; an annular "washer" of mercury prevents access of gas to the grease. The use of such a tap constructed to work also as a McLeod gauge in measuring velocities of gaseous reactions is indicated.

S. K. TWEEDY.

Vacuum contraction of density bulbs. M. BECKERS (J. Amer. Chem. Soc., 1929, 51, 2042—2051).—An investigation of the contraction of density globes on evacuation by the hydrostatic and by Travers' method confirms the validity of Moles and Miravalles' empirical formula for the contraction of such globes (A., 1924, ii, 451). The contraction appears to be a linear function of the pressure difference to which the bulb is submitted.

S. K. TWEEDY.

Pyrex glass as a radium container. S. C. LIND (Science, 1928, 68, 643—644).—Longitudinal and transverse cracks developed in 1 year in a 250-c.c. pyrex flask half-filled with 265 mg. of radium chloride solution (cf. Curtis, Nature, 1927, 120, 406). Incipient scaling accompanied by interference colours was also noted.

L. S. THEOBALD.

Simple apparatus for direct reading of corrosion of metals, formation of incrustations, and the oxidising power of solutions (Tödt oxidimeter). L. KÖHLER (Chem.-Ztg., 1929, 53, 567; cf. Tödt, this vol., 145, 270).—The apparatus consists of electrodes of a noble metal and the metal under examination immersed in the corrosive liquid and connected to a recording instrument.

J. S. CARTER.

Portable apparatus for p_H determination. A. ITANO (Ber. Ohara Inst. landw. Forsch., 1929, 4, 19—26).—A simple and inexpensive type of portable potentiometer which has been designed for p_H determinations with quinhydrone and calomel electrodes, together with a form of quinhydrone electrode suitable for p_H determinations with volumes of solution of the order of 0.02 c.c., are described. Data which are thought to establish that the error of the instrument is of the order of 1% are given.

E. A. LUNT.

Apparatus for hydrogen-ion determinations. H. K. MULFORD and F. R. GREENBAUM (J. Amer. Pharm. Assoc., 1929, 18, 564—568).—An apparatus based on the Hildebrand arrangement, and reading to an accuracy of 0.01 is described. The p_H values of 49 medicinal solutions are recorded. The apparatus is unsuitable for the determination of the hydrogen-ion concentration of solutions containing copper, arsenic, bismuth, antimony, and mercury when a quinhydrone electrode is employed.

C. C. N. VASS.

Bimetallic electrodes for titrations involving a change of hydrogen-ion concentration. R. M. FUOSS (Ind. Eng. Chem. [Anal.], 1929, 1, 125—128; cf. Furman and Wilson, A., 1928, 382).—The electrode pairs, antimony-lead, antimony-amalgamated copper, bismuth-silver, and copper-copper oxide, have all given satisfactory results when used for potentiometric titrations involving changes in hydrogen-ion concentration. For general acidimetric work the antimony-amalgamated copper pair is preferred.

J. S. CARTER.

Flexible seal for electrodes. M. C. MARSH (J. Sci. Instr., 1929, 6, 234—235).—A flexible seal for electrodes through metal or thick glass walls is described. A short length of tightly-fitting rubber tubing is placed on the rod forming the lead, and is splayed out on each side of the wall by tightening two nuts threaded on to the rod.

C. W. GIBBY.

Electrolytic conductivity bridge. D. C. GALL (J. Sci. Instr., 1929, 6, 231—233).—A substitution method of measuring electrolytic conductivities, involving only the accuracy of the resistance box, is described.

C. W. GIBBY.

Electrically-heated thermostats. L. HOCK and C. L. NOTTEBOHM (Z. Elektrochem., 1929, 35, 458; cf. van Campen, this vol., 786).—The ordinary electrical control of a thermostat can be greatly improved by placing a 4-microfarad condenser in parallel with the mercury contact which is connected to a 2-volt accumulator (cf. Nottebohm, Diss., Giessen, 1929).

H. T. S. BRITTON.

Thermostat constant to 0.001°. F. R. WINTON (J. Sci. Instr., 1929, 6, 214—217).—A sensitive toluene-mercury thermoregulator has as contact at the open end a wire having the tip covered with burnt sealing wax. The variations in this resistance control the grid bias of a thermionic valve, the anode current of which passes through the heating resistance. Numerous essential precautions are described.

C. W. GIBBY.

Pyknometer for viscous substances. E. H. RIESENFELD and T. HAMBURGER (Chem.-Ztg., 1929, 53, 547).—The apparatus comprises a thick-walled cylindrical vessel 10 mm. high and 16 mm. internal diameter covered with a cover-glass 2 mm. thick. The cylinder is filled with the oil or other viscous liquid to be examined, so that the surface of the liquid is just above the upper edges and the cover is then pressed down without including any air bubbles, after which the determination is made as with the ordinary pyknometer.

A. R. POWELL.

Large-capacity laboratory condensers. D. F. OTHEMER (Ind. Eng. Chem. [Anal.], 1929, 1, 153).—Two double-coil jacketed condensers are described. In one water flows inside the coils and in the other water flows outside the coils.

J. S. CARTER.

Modification of the Kjeldahl trap. G. H. W. LUCAS (Ind. Eng. Chem. [Anal.], 1929, 1, 140).—The usual bulb trap is replaced by an arrangement in which vapours leave the Kjeldahl flask through a 1-cm. tube fused into a distillation flask. Spray etc. is returned to the Kjeldahl flask by means of a

3-mm. tube sealed to the bottom of the distillation flask. As an extra precaution a small funnel packed with glass wool is suspended in the neck of the distillation flask just below the side arm.

J. S. CARTER.

Simple extraction apparatus for liquids. H. BACH (Chem.-Ztg., 1929, 53, 517).—The apparatus of Baas and Bosmann (Pharm. Weekblad, 1893, No. 9) for the extraction of liquids with ether has been modified by providing a separate overflow tube from the extraction vessel back to the ether distillation flask and sealing the delivery tube for the ether vapour into the upper part of the extraction flask well above the surface of the liquid being extracted. The extraction flask is also provided with a stopcock at its lower end for withdrawing the spent liquid.

A. R. POWELL.

Colour measurement by means of Moll's extinctions. M. J. VAN TUSSENBOEK (Chem. Weekblad, 1929, 26, 374—381; cf. A., 1927, 537).—The radiant energy transmitted by standard baths of oil coloured by addition of selected yellow and red dyes is balanced against that transmitted by selected filters of which the permeability for given wave-lengths is known. In order to make the

apparatus sensitive to rays in the visible spectrum, infra-red rays are suppressed by means of copper sulphate solution. The effect of bleaching oils by various refining methods is determined by measuring the amounts of energy transmitted for the range of visible light, the results being mapped on a curve relating wave-length to transmitted energy.

S. I. LEVY.

Spinning target X-ray generator. A. MÜLLER (Nature, 1929, 124, 128).

Production of high Lo Surdo fields. Y. ISHIDA and S. HIYAMA (Nature, 1929, 124, 129).

Alcoholometric tables. A. V. RAKOVSKI (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 5, 5—112).—New tables have been prepared by critical use of published data.

CHEMICAL ABSTRACTS.

Nomography. XV. Electrometric determination of p_H . O. LIESCHE (Chem. Fabr., 1929, 279—280).—A nomogram for the derivation of p_H values from the observed *E.M.F.* is given.

J. S. CARTER.

Nomography. O. LIESCHE (Chem. Fabr., 1929, 373—374).—Charts for converting pycnometer weighings (water and liquid both at 20°) into d_4^{20} are given.

Geochemistry.

Atmospheric precipitations. II. III. W. LIESEGANG (K. Mitt. Ver. Wasserversorg., 1928, 4, 178—182, 261—265; Chem. Zentr., 1929, i, 1208).—A discussion of the composition of rain and snow.

A. A. ELDRIDGE.

Differences in the condition of sea-water at the margins of two opposing tidal currents. T. G. THOMPSON and R. C. MILLER (Science, 1928, 68, 517—518).—Analysis of two samples of water taken from opposing currents in the channel north of San Juan island and within a few feet of each other show differences of 2.4° in temperature, 0.22 in p_H , and of 2.8 parts Cl per 1000 parts of water. Colour, sp. gr., and carbon dioxide content also differed considerably. Such changes are suggested to be of marked biological importance.

L. S. THEOBALD.

Alkaline reserve of sea-water. R. MARGARIA (Atti R. Accad. Lincei, 1929, [vi], 9, 816—820).—The absorption of carbon dioxide by sea-water is approximately proportional to the pressure of the gas up to 51.6 mm., at which pressure 13.3 c.c. of carbon dioxide (at 0° and 760 mm.) are absorbed per 100 c.c. of sea-water. From these data, and from the known solubility of carbon dioxide in a prepared water of salinity equal to that of sea-water, the amounts of carbon dioxide simply dissolved and combined as hydrogen carbonate in the latter are computed, and hence by Hasselbach's modification of Henderson's formula the p_H value of the sea-water is derived. The bearing of these data on the dependence of the p_H value of sea-water on the tension of carbon dioxide in contact with it is discussed and its physiological importance indicated.

F. G. TRYHORN.

Meteorite from Ballinger, Texas. H. H. NININGER (J. Geol., 1929, 37, 88—90).—The meteorite contained Fe 91.48, Ni 6.54, Co 0.48, Cu 0.07, P 0.26, S 0.01, SiO₂ 0.12, C 0.09, O 1.03%, with traces of chromium and magnesium. Platinum (0.19 oz. per ton) was also present.

CHEMICAL ABSTRACTS.

Origin of moldavite. J. CHLOUPEK (Naturwiss., 1929, 17, 598—600).—A summary of a paper by F. Hanus (Abh. Prag. Akad. Wiss., 1928, 37, [24]). Moldavites are aluminium silicates (90%) occurring as greenish glassy solids with a rounded appearance. The material is not readily fusible (m. p. 1300—1400°). The evidence points to a meteoritic origin.

R. A. MORTON.

Synthesis of kaolin. R. SCHWARZ (Rec. trav. chim., 1929, 48, 695—696).—Explanatory. The author regards the synthesis of kaolin by van Nieuwenburg and Pieters (cf. this vol., 280) as a further proof of the correctness of his theory of the formation of kaolin in nature.

F. L. USHER.

Blue rock salt. C. DOELTER (Monatsh., 1929, 52, 241—252).—A discussion of the distribution and of the origin of the colour in blue rock salt. Siedentopf's hypothesis that the colour is due to the presence of sodium of ultramicroscopic dimensions, the view that the colour is induced by exposure to radium, and also other theories are considered to be improbable. The author's view is that a pigment containing iron and manganese, and possibly organic substances or sulphur, is responsible for the blue colour.

A. I. VOGEL.

Radium in rocks. I. Radium content of some representative granites of the eastern

seaboard of the United States. C. S. PIGGOT (Amer. J. Sci., 1929, [v], 17, 13—34).—A detailed account is given of the experimental procedure to be used in the determination of the radium content of rocks. The main results obtained have been described already (this vol., 163). It is further stated that part of the radioactive material may be leached out of a granite by hot water. Apparently some of this material is associated with the interstices between the grains and with the surfaces of the grains rather than with their interiors. F. J. WILKINS.

Formation of cupriferous "black earths" in Niari (French Congo). R. BURKHARDT (Arch. Sci. Phys. Nat., 1929, [v], 11, 163—183; cf. this vol., 788).—Analyses of "black earths" and limestones from various parts of Niari are given.

C. W. GIBBY.

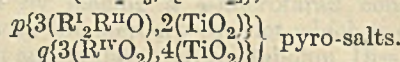
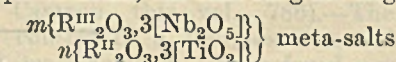
Niobium : tantalum ratios of titanium minerals. G. VON HEVESY, E. ALEXANDER, and K. WÜRSTLIN (Z. anorg. Chem., 1929, 181, 95—100).—The niobium and tantalum contents of a number of titanium minerals have been determined by a combination of chemical and X-ray spectroscopic methods. The average atomic ratio of titanium to niobium for rutile, titanite, and perovskite is about 3000 and the titanium : tantalum ratio is about 7000. The corresponding values for ilmenite are about 100 times as great. J. S. CARTER.

Composition of apophyllite. B. GOSSNER and O. KRAUS (Z. Krist., 1928, 68, 595—615; Chem. Zentr., 1929, i, 496—497).—The fluorine content of apophyllite varies between 1.2 and 1.5%; the formula $4[\text{H}_2\text{Si}_2\text{O}_5, \text{Ca}(\text{OH})_2], \text{KF}$ is proposed. Analysis shows that 28—44 mol.-% of the potassium fluoride has been replaced by hydroxide without marked disturbance of the atomic lattice. X-Ray investigation gave: a 12.73, c 15.84 Å.; $a:c=1:1.244$; the unit cell contains 4 mols.; space-group D_{2h}^{14} .

A. A. ELDRIDGE.

Analyses of echenite. Echenite-blomstrandite-priorite series. G. P. TSCHERNIK (J. Russ. Phys. Chem. Soc., 1929, 61, 735—770).—The results obtained by previous workers from the analyses of echenite and blomstrandite are discussed and the methods used by the author described. Typical Ural echenite had d 5.00—5.36; that of blomstrandite was 4.97, and of priorite 4.67. Uranium is absent from typical Ural echenites, but is an essential constituent of both blomstrandite and priorite, although echenites having an abnormally high radioactivity were assumed to contain uranium. Lead is always found in blomstrandite but not in echenite, whilst thorium is

found in all minerals of the echenite-blomstrandite-priorite series. In echenites of maximal d 11—12% Th, in blomstrandite 8.5% Th, and in priorite 0.5—0.75% Th is present. With respect to their rare-earth content the minerals of the echenite series can be divided into two groups. In the typical echenites the cerites exceed the yttrites, whilst in blomstrandite the relation is reversed. The author assumes that the actual proportions in which the separate component elements of the cerite group are found is the same as found in monazite, i.e., Ce_2O_3 20, La_2O_3 15, Nd_2O_3 3, and Pr_2O_3 1. Zirconium dioxide is not a component of the Ural echenites, but is found to an extent of about 0.5—1.5% in some blomstrandites, whilst it is absent from others. Tin is always found in the minerals of this family and so is silicon, which replaces titanium. There are also present small quantities of alkaline earths, lime, of bivalent iron, and magnesium. Iron is found to the extent of 2.3% in echenites, 1.5—2% in blomstrandite, and 5% in priorite. 1—2% of lime are found in blomstrandite and 4% in priorite. Traces of fluorine are also found and so are traces (1%) of water and gases which escape on heating. Although the composition is not fixed and cannot be expressed by a simple formula, the following are suggested:



A. FREIMAN.

Theory of the formation of fusain. R. LIESKE (Brennstoff-Chem., 1929, 10, 185—191).—Study of the mode of occurrence of fusain has established the following facts: (1) the deposits are usually lenticular in shape, (2) the fusain has been formed in hollow spaces containing a greater or smaller amount of gas, (3) the fusain has not been subjected to direct earth pressure in the same way as has the surrounding bright or dull coal, (4) the fusain has not been subjected to the infiltration of finely-divided or colloidal humin substances. These observations, for which previous theories fail to account, lead to the assumption that fusain has been formed by the coalification of coarser particles of plant material which have collected in the lenticular spaces filled with gas produced by the decomposition of the surrounding material. The differences in the conditions to which the plant material within these hollow spaces and that in the surrounding mass are subjected account fully for the observed differences in the final products. A. B. MANNING.

Organic Chemistry.

Isomerism and configuration. A. C. LUNN and J. K. SENIOR (J. Physical Chem., 1929, 33, 1027—1079).—A theoretical paper in which a mathematical treatment is developed. L. S. THEOBALD.

Vapour-phase oxidation of isomeric octanes. II. Octanes with branched chains. III. Effect

of lead tetraethyl; relation of oxidation to engine detonation. J. C. POPE, F. J. DYKSTRA, and G. EDGAR (J. Amer. Chem. Soc., 1929, 51, 2203—2213, 2213—2220).—The oxidation of γ -methylheptane, γ -ethylhexane, β -methyl- γ -ethylpentane, β -dimethylhexane, and $\beta\beta$ -trimethylpentane has been studied by the methods previously described for

n-octane (this vol., 906). The effect of temperature on the oxygen consumed, and on the amounts of carbon monoxide and dioxide produced from mixtures of hydrocarbon with oxygen sufficient for complete combustion, is shown graphically for each isomeride. The onset of the "low-temperature disturbance" (the "aldehyde oxidation"), involving a large increase in the production of carbon monoxide, is observed only with γ -methylheptane (280—305°) and γ -ethylhexane (285—302°). The "high-temperature disturbance," accompanied by complete combustion, begins in the three cases examined, namely, γ -ethylhexane, β -methyl- γ -ethylpentane, and $\beta\beta\beta$ -trimethylpentane, at 560°, 520°, and 515°, respectively. The curves for the low-temperature oxidation of all the isomerides except $\beta\beta\beta$ -trimethylpentane are similar in general nature. When allowance is made for the formation of small amounts of unsaturated hydrocarbons, the oxygen consumption agrees closely with that calculated from the amounts of oxides of carbon formed, by means of the equations used in the case of *n*-octane. The results are in accordance with the view that oxidation begins at the methyl group at the end of the longest unbranched chain in the molecule and continues along the chain, giving aldehydes of successively lower mol. wt., until a branch is reached. The resulting ketone is more resistant, and little further oxidation takes place until the temperature of complete combustion is reached. This temperature becomes higher as the amount of oxygen consumed in the low-temperature oxidation increases, being highest with *n*-octane. The oxidation of $\beta\beta\beta$ -trimethylpentane begins at 515° and goes directly to completion. In general, the temperature of initial attack rises with the degree of branching of the molecule. The probable behaviour of other hydrocarbons is discussed.

Curves are given for the consumption of oxygen by, and production of oxides of carbon from, *n*-octane, alone and with 0.3 vol.-% and 1.07 vol.-% of lead tetraethyl, and from heptaldehyde, alone and with 1% of lead tetraethyl, under the conditions described above. With *n*-heptaldehyde the presence of lead tetraethyl greatly retards the aldehyde oxidation and raises its temperature of onset from 235° to 270°. The production of carbon dioxide remains unaffected. With *n*-octane the initial oxidation to octaldehyde and, in consequence, the subsequent formation of carbon dioxide is slightly retarded, and the aldehyde oxidation much retarded. The tendencies of 10% solutions of each of the above isomeric octanes in a "standard gasoline" to produce engine detonation have been compared. The order of decreasing ease of detonation is *n*-octane, γ -methylheptane, γ -ethylhexane, β -methyl- γ -ethylpentane, $\beta\epsilon$ -dimethylhexane, and $\beta\beta\beta$ -trimethylpentane. This is also the order of the extents to which these hydrocarbons undergo low-temperature oxidation, as found experimentally, and as given by the length of the longest unbranched carbon chain. Thus a repression of the aldehyde oxidation, whether by the presence of lead tetraethyl or by a change in structure, is accompanied by a decreasing tendency to detonate. The behaviour of other paraffins and the mechanism of detonation are discussed in view of this generalis-

ation. Much detailed matter is presented for which the original papers must be consulted.

H. E. F. NOTTON.

Polymerisation of ethylene by the electric discharge. Synthesis of butene and hexene. G. MIGNONAC and R. V. DE SAINT-AUNAY (Compt. rend., 1929, 189, 106—108; cf. this vol., 537).—Ethylene was submitted to an electric discharge, using a current of high frequency (d'Arsonval apparatus) in a closed circuit containing a circulating pump, and condensers at -60° ; 80—90% of the ethylene was transformed into Δ^1 -butene and Δ^1 -hexene, identified by their ozonides. The authors' theory that, under the influence of the discharge, certain ethylene molecules are activated and link with unactivated molecules to form butene, which can then link with further activated ethylene to form hexene, is supported by the fact that, when the circulation of the gas is accelerated and the temperature of the condensers lowered to -80° , butene is the main product, whereas with less vigorous condensation mostly hexene is produced.

B. W. ANDERSON.

Aliphatic diolefines. II. Preparation and physical constants of Δ^1 -hexadiene. F. CORTESE (J. Amer. Chem. Soc., 1929, 51, 2266—2269).—Pure diallyl, obtained in good yield from allyl bromide, or chloride, and magnesium in ether (cf. Lespieau, A., 1912, i, 934), has b. p. 59.57°/760.0 mm., f. p. -140.9° , d_4^{25} 0.6863, n_D^{25} 1.4012.

H. E. F. NOTTON.

Contact isomerisation of an aliphatic hydroterpene. N. D. ZELINSKI and R. J. LEVINA (Ber., 1929, 62, [B], 1861—1863).— $\gamma\eta$ -Dimethyl- Δ^1 -octene, b. p. 154°/753 mm., d_4^{25} 0.7396, n_D^{25} 1.4212, is isomerised by passage in a current of carbon dioxide over palladised asbestos at 200°/1 atm. to $\gamma\eta$ -dimethyl- Δ^2 -octene, b. p. 161°/744 mm., d_4^{25} 0.7458, n_D^{25} 1.4259. The intermediate production of $\gamma\eta$ -dimethyl- $\Delta^1\Delta^2$ -octadiene is postulated.

H. WREN.

Thermochemical investigation of petroleum. Thermochemical change in squalene. R. ABE and G. SHOBAYASHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 496—501).—On heating squalene, exothermic reaction sets in at 300°. Probably, preliminary polymerisation is followed by the formation of volatile hydrocarbons from the unstable polymerisation products. The favourable action of aluminium chloride on cracking is thus explained.

B. W. ANDERSON.

Ozonisation of unsaturated gaseous hydrocarbons. IV. Ozonisation of acetylene. E. BRINER and R. WUNENBURGER (Helv. Chim. Acta, 1929, 12, 786—790).—When acetylene and ozonised oxygen (7% O₃) were passed alternately through liquid methyl chloride and the apparatus was swept out by a stream of dry air after each saturation the residue after removing the solvent contained glyoxal (81%), formic acid (5.6%), and traces of formaldehyde.

R. J. W. LE FÈVRE.

Trichloronitrosomethane, dichloroformoxime (phosgene oxime), and their derivatives. W. PRANDTL and K. SENNEWALD (Ber., 1929, 62, [B], 1754—1768).—Carbon disulphide is converted by

potassium dichromate and hydrochloric acid into trichloromethylsulphonyl chloride, transformed by hydrogen sulphide and anhydrous sodium carbonate in presence of absolute alcohol into sodium trichloromethylsulphinate. The last-named substance is converted into *trichloronitrosomethane*, b. p. 5.0° to 5.5°/70 mm., d_4^{20} 1.50, either by cautious warming with 10% nitric acid or by regulated addition of 68% nitric acid to its aqueous solution. The compound decomposes slowly when preserved, rapidly when heated, into nitrosyl chloride, nitric oxide, trichloronitromethane, and *trichloromethyldichloromethyleneamine*, $\text{CCl}_2 \cdot \text{N} \cdot \text{CCl}_2$. It is slowly hydrolysed by water or aqueous alkalis, of which 3 mols. are required for complete decomposition, dichloronitromethane being apparently produced. It reacts slowly with oxygen at the ordinary temperature or its b. p., but is converted at 120° into nitrogen peroxide, trichloronitromethane, and hexachloroethane. Chromic acid oxidises it to trichloronitromethane. It appears to be reduced quantitatively to methylamine by iron filings and acetic acid, whereas hydrogen sulphide or aluminium amalgam in alcohol converts it into *dichloro-oximinomethane* (phosgene oxime). Trichloromethyldichloromethyleneamine, b. p. 170°/1 atm., 77°/30 mm., d_4^{20} 1.698, is a colourless, stable liquid reduced by iron filings in acetic acid to ammonia. Dichloro-oximinomethane has m. p. 39—40° after softening at 38—39°, b. p. 129°/1 atm., 53—54°/28 mm. It is stable at the atmospheric temperature, slowly hydrolysed by cold water to carbon dioxide, hydrogen chloride, and hydroxylamine. It is vigorously decomposed by aqueous alkalis without yielding well-defined products. Under definite conditions, trichloronitrosomethane and aniline afford *chloroanilobenzeneazomethane*, $\text{NPh} \cdot \text{CCl} \cdot \text{N} \cdot \text{NPh}$, m. p. 208° (decomp.). H. WREN.

[Preparation of] **methylene bromide**. W. W. HARTMAN and E. E. DREGER (*Organic Syntheses*, 1929, 9, 56—57).

[Preparation of] **pentamethylene bromide**. J. VON BRAUN (*Organic Synthesis*, 1929, 9, 70—71).

Reaction between nitrobenzene and secondary alcohols. R. E. LYONS and M. E. PLEASANT (*Ber.*, 1929, 62, [B], 1723—1727; cf. A., 1927, 234).—The action of nitrobenzene on isopropyl alcohol in the presence of sodium hydroxide follows the course: $3\text{CHMe}_2 \cdot \text{OH} + \text{SNO}_2\text{Ph} \longrightarrow 6\text{NH}_2\text{Ph} + \begin{matrix} \text{NPh} \\ | \\ \text{NPh} \end{matrix} \text{O} + 3(\text{CO}_2\text{H})_2 + 3\text{H} \cdot \text{CO}_2\text{H}$. Under similar conditions, acetone is readily oxidised to the same products. Azoxybenzene is not reduced by isopropyl alcohol or acetone under these conditions. Benzoin is transformed into benzoic acid and azoxybenzene with a little azobenzene; benzil and aniline do not appear to be formed. H. WREN.

Configurative relationship of ζ -methylheptan- β -ol with lactic acid. Effect of unsaturation on optical activity. P. A. LEVENE and H. L. HALLER (*J. Biol. Chem.*, 1929, 83, 177—183).— ζ -Methyl- Δ^c -hepten- β -ol was resolved by the phthalate method; the insoluble *brucine* salt had $[\alpha]_D^{25}$ -4.2° , and gave a *hydrogen phthalate*, $[\alpha]_D^{25}$ $+60.3^\circ$, which yielded the *d*-carbinol, b. p. 60—61°/4 mm., $[\alpha]_D^{25}$ $+19.0^\circ$ in ether

(*α -naphthylcarbamate*, m. p. 64—66°, $[\alpha]_D^{25}$ $+32.8^\circ$); the mother-liquors yielded a carbinol, b. p. 87°/22 mm., $[\alpha]_D^{25}$ -16.2° in ether. The *d*-carbinol, with ozone, gave *l- γ -hydroxyvaleraldehyde*, b. p. 43—46°/1—2 mm., $[\alpha]_D^{25}$ -7.8° in ether; this, when oxidised with silver oxide, yielded *d- γ -hydroxyvaleric acid*, $[\alpha]_D^{25}$ $+18.8^\circ$ (silver salt, $[\alpha]_D^{25}$ $+5.4^\circ$). The *d*-methylheptenol, when reduced with hydrogen and palladium, gave *d- ζ -methylheptan- β -ol*, b. p. 61—63°/4 mm., $[\alpha]_D^{25}$ $+13.0^\circ$ in ether (*α -naphthylcarbamate*, m. p. 75—77°, $[\alpha]_D^{25}$ $+16.4^\circ$ in alcohol); the latter carbinol is therefore configuratively related to *d*-lactic acid. The statement of Pickard and Kenyon (*J.C.S.*, 1911, 99, 47) that unsaturation increases the magnitude of rotation does not hold universally; such increase is, however, constantly observed when the double linking is situated in the γ -position to the asymmetric carbon atom. C. R. HARRINGTON.

***r*-Citronellol**. J. DŒUVRE (*Bull. Soc. chim.*, 1929, [iv], 45, 403—412).—Magnesium methylheptenylbromide with magnesium β -chloroethoxybromide yields β -methyl- Δ^{β} -heptene, b. p. 115—120° (*dibromo-derivative*, b. p. 108—110°/15 mm.), and *r*-citronellol, b. p. 115—117°/15 mm., d_4^{20} 0.863, n_D^{20} 1.4588 [allophanate, m. p. 105—106° (cf. A., 1928, 1113)]. On ozonisation *r*-citronellol yields 8% of formaldehyde, 17% of formic acid, and 76% of acetone, indicating 22% of α - and 76% of β -form, and hence the condensation has produced no appreciable isomerisation. With ethylene oxide, magnesium methylheptenyl bromide yields a little β -methyl- Δ^c -heptene, ethylene bromohydrin, and a small amount of *r*-citronellol and polymerisation products. Repetition of the process of G.P. 423,544 (B., 1926, 771) afforded 60% of β -methyl- Δ^c -heptene, b. p. 120—121°, d_4^{20} 0.728, and ethylene bromohydrin, b. p. 61—62°/23 mm., with only a very small amount of citronellol. With trioxymethylene in a hydrogen atmosphere, magnesium methylheptenyl bromide affords in 3 days 15% of a mixture, b. p. 121°, of β -methyl- Δ^{β} -heptene and β -methyl- $\Delta^{\beta c}$ -heptadiene and 45% of $\beta\zeta$ -*dimethyl- Δ^c -hepten- α -ol*, b. p. 105—106°/18 mm., d_4^{25} 0.859, n_D^{25} 1.4547. $\beta\zeta$ -*Dimethyl- Δ^c -heptenyl bromide*, b. p. 99—100°/18 mm., d_4^{25} 1.123, n_D^{25} 1.4749 (yield 45%), gives a magnesium derivative which with trioxymethylene similarly affords about 40% of a mixture of 28% of the α - and 72% of the β -forms of *r*-citronellol, together with $\beta\zeta$ -*dimethyl- Δ^c -heptene*, b. p. 142—143°, d_4^{25} 0.768, n_D^{25} 1.4321. This preparation of *r*-citronellol confirms the constitution of *d*-citronellol and *l*-rhodinol, the difference between the latter consisting in the different proportions of the α - and β -forms present (cf. this vol., 907).

R. BRIGHTMAN.

Partial esterification of polyhydric alcohols. VIII. Proposed standards in work on configuration of glycerol derivatives. A. FAIRBOURNE (*J.C.S.*, 1929, 1151—1153; cf. A., 1927, 131; this vol., 292).—The " $\alpha\beta$ "- and " $\alpha\gamma$ "-dimethyl ethers of glycerol prepared as described by Gilchrist and Purves (A., 1926, 153) and Zunino (A., 1899, i, 410), which were proposed as reference compounds by Hibbert, Whelen, and Carter (this vol., 292), have been shown to be identical. The products show the

same characteristic properties and yield the same *p*-nitrobenzoyloxydimethoxypropane, m. p. 43°.

R. K. CALLOW.

[Preparation of] chloromethyl ether. C. S. MARVEL and P. K. PORTER (Organic Syntheses, 1929, 9, 58—59).

Preparation of boric esters. E. KHOTINSKY and S. POUPKO (Ukraine Chem. J., 1929, 4, 13—18).—In the preparation of the esters of boric acid by the action of fused borax on primary alcohols in the presence of gaseous hydrogen chloride, in equivalent amounts, the reaction appears to stop half-way, since the yield of ester never exceeds 48% and only half of the hydrogen chloride is used. The methyl, b. p. 63—65°, ethyl, b. p. 120°, propyl, b. p. 175—177°, *iso*-butyl, b. p. 210—211°, and *iso*amyl, b. p. 254—255°, esters were obtained.

M. ZVEGINTZOV.

Diethyl pentasulphides. I. and II. G. R. LEVI and A. BARONI (Atti R. Accad. Lincei, 1929, [vi], 9, 772—778, 903—906).—Treatment of ethyl mercaptan with sulphur chloride and sulphur yields ethyl tri- and tetra-sulphides, together with an ethyl pentasulphide, probably $S \begin{matrix} \leftarrow S:SEt \\ S:SEt \end{matrix}$, b. p. 119°/26 mm., d_{20}^{20} 1.1687, n_D^{20} 1.60269, and an isomeric pentasulphide, b. p. 130°/26 mm., d_{20}^{20} 1.1620, n_D^{20} 1.59517. The latter is transformed into the former when heated above 200°.

T. H. POPE.

Action of niobium and tantalum pentachloride on organic compounds. III. H. FUNK and K. NIEDERLÄNDER (Ber., 1929, 62, [B], 1688—1691; cf. A., 1928, 876).—The action of cold glacial acetic acid on tantalum pentachloride affords the tetra-acetate, $TaCl(OAc)_4$, occasionally as the additive compound, $TaCl(OAc)_4 \cdot 4CH_3 \cdot CO_2H$. At a higher temperature the substance $Ta_2O_3Cl(OAc)_3$ is produced. The various acetates are hydrolysed by water to the compound $TaO_2(OAc)$. Niobium pentachloride yields the substance $Nb_2O_3Cl(OAc)_3$. With methyl and ethyl alcohol, tantalum pentachloride affords the compounds $TaCl_2(OMe)_3$ and $TaCl_2(OEt)_3$. Niobium pentachloride yields ill-defined products with these alcohols.

H. WREN.

Titration of acetic anhydride in mixtures of ethyl or methyl alcohol and water. J. F. M. CAUDRI (Rec. trav. chim., 1929, 48, 778—792).—The anomalous results of Lumière and Barbier (A., 1906, i, 791) for the titration of acetic anhydride with sodium hydroxide in dilute aqueous-alcoholic solution are explained by the partial esterification of the anhydride. The amount of ester formed is considerable even in very dilute solutions and is greater in dilute methyl alcohol than in dilute ethyl alcohol. In agreement with deductions made from Wegscheider's theory (A., 1918, ii, 394), it is found that the amount of acetic anhydride converted into the ester during titration with sodium hydroxide in aqueous-alcoholic solution depends chiefly on the temperature (the higher the temperature the lower is the yield of ester) and on the alcohol concentration, but is independent of the initial concentrations of the anhydride and alkali except when these are very small. This type of reaction is shown to be general for the interaction of esters of organic and inorganic

acids, acid anhydrides, and chlorides with organic compounds containing the $\cdot ONa$ group. Thus by the interaction of sodium hydroxide and benzoyl chloride or benzoic anhydride in aqueous acetone solution, ester formation is shown to occur, although the isolation of the ester-like compound was not possible in this case. On the basis of these results it was found that acetic anhydride may be accurately determined in dilute aqueous-alcoholic solution by the potentiometric method, using a standard solution of ammonia in the burette.

J. W. BAKER.

Interaction of bromine with acetic anhydride. V. Bromination and chlorination compared. Some properties of acetic chloroacetic anhydride. H. B. WATSON and C. E. GREGORY (J.C.S., 1929, 1373—1375).—Acetic chloroacetic anhydride (Anthonine, Jahresber., 1883, 1032) decomposes when heated into acetic anhydride and chloroacetic anhydride. When refluxed with chloroacetic acid (1 mol.), acetic acid and chloroacetic anhydride are formed. It reacts with hydrogen chloride at the ordinary temperature to give acetyl chloride and chloroacetic acid. When acetic acid and chloroacetyl chloride are heated together, hydrogen chloride is evolved, and from the product are separated acetyl chloride, acetic acid, and chloroacetic anhydride, with relatively small amounts of chloroacetic acid and acetic anhydride. One stage of the scheme proposed for the halogenation of acetic acid (A., 1925, i, 1232; 1928, 716), which is further discussed, therefore occurs as (a) $CH_3X \cdot COX + AcOH = CH_2X \cdot CO \cdot OAc + HX$, and (b) $CH_2X \cdot CO \cdot OAc + HX = CH_2X \cdot CO_2H + AcX$.

R. K. CALLOW.

Activity of the halogens in halogen-substituted esters. B. V. TRONOV, A. I. AKIVIS, and V. N. ORLOV (J. Russ. Phys. Chem. Soc., 1929, 61, 345—353).—The activity of the halogens in the ethyl esters of a number of aliphatic halogeno-acids was investigated. The degree of activity of the halogen in a particular ester was found by measuring its velocity of reaction with pyridine, piperidine, quinoline, and metallic sodium. Experiments with the amines were carried out without a solvent, those with sodium methoxide in a methyl-alcoholic solution. The reagents were mixed in equimolecular proportions, the temperature being kept at 18—20°. The amount of halogen which had reacted in a given time was determined either gravimetrically or by Volhard's method. The degree of activity was determined by calculating the times necessary for an equal percentage of halogen to react in the different compounds. It was found that bromine reacts with the amines several hundred times as fast as chlorine, that the activity of the halogens decreases with an increase in the number of halogens in the chain, that bromine shows an activity with quinoline and pyridine about 3 times as high when in the α -position as when in the β -position and about 10—12 times as high as when in the γ -position. Also that the substitution of a hydrogen atom in a halogen-substituted acetate or propionate by a carbethoxy-group decreases the activity of both chlorine and bromine, whilst a substitution of an acetyl group increases the activity quite considerably, and finally that pyridines acts about 2.7—4.3 times as rapidly as

quinoline. The results with sodium methoxide are less trustworthy, since it can react, not only with the halogen, but also with the carbonyl group.

A. FREIMAN.

Cadmium, manganous, and cobaltous chloroacetates. L. FOGEL, T. RUBINSZTEIN, and A. TAUMAN (Rocz. Chem., 1929, 9, 348—353).—The preparation and crystalline form of the following salts are described: $(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Cd}\cdot 6\text{H}_2\text{O}$;

$(\text{CHCl}_2\cdot\text{CO}_2)_2\text{Cd}\cdot\text{H}_2\text{O}$; $(\text{CCl}_3\cdot\text{CO}_2)_2\text{Cd}\cdot 1.5\text{H}_2\text{O}$;

$(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Co}\cdot 6\text{H}_2\text{O}$; $(\text{CHCl}_2\cdot\text{CO}_2)_2\text{Co}\cdot 3\text{H}_2\text{O}$;

$(\text{CCl}_3\cdot\text{CO}_2)_2\text{Co}\cdot 3.5\text{H}_2\text{O}$; $(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Mn}\cdot 1.5\text{H}_2\text{O}$;

$3(\text{CHCl}_2\cdot\text{CO}_2)_2\text{Mn}\cdot 2\text{CHCl}_2\cdot\text{CO}_2\cdot\text{H}\cdot 6\text{H}_2\text{O}$;

$(\text{CCl}_3\cdot\text{CO}_2)_2\text{Mn}\cdot 3.5\text{H}_2\text{O}$. R. TRUSZKOWSKI.

Reaction between amylene and dichloroacetic acid. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 93—94).—The rate of reaction between amylene and dichloroacetic acid was investigated in benzene, chloroform, carbon disulphide, ethyl alcohol, and ether, in order to compare the reactivities of dichloroacetic and trichloroacetic acids. It is very slow, and in the order benzene > chloroform > carbon disulphide. In the so-called "active" solvents (ethyl alcohol and ether) the reaction does not take place at all, due, probably, to the formation of inert solvation complexes by the two reacting substances.

M. ZVEGINTZOV.

Reaction limits in the formation of amyl trichloroacetate in mixtures of solvents. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 89—92).—The reaction limits between amylene and trichloroacetic acid were investigated in the mixtures of inert solvents: benzene-carbon tetrachloride and carbon tetrachloride-carbon disulphide. Although the limits in the pure solvents were similar, a simple straight-line relation could be expected in mixtures, but the graphs were very complex, being, in the case of the system carbon tetrachloride-benzene, convex and showing pronounced maxima, the position of which depended in the concentration of the reacting substances, whilst on the system carbon tetrachloride-carbon disulphide they were convex for a concentration of 0.75 mol./litre and concave for 0.375 mol.

M. ZVEGINTZOV.

[Preparation of] *n*-butyryl chloride. B. HELFERICH and W. SCHAEFFER (Organic Syntheses, 1929, 9, 32—33).—Butyric acid is treated with thionyl chloride.

A. A. ELDRIDGE.

Oxidation of simple and complex unsaturated fatty acids and hydrocarbons with perbenzoic acid. K. H. BAUER and O. BÄHR (J. pr. Chem., 1929, [ii], 122, 201—213).—Unsaturated acids are primarily oxidised by perbenzoic acid to oxido-acids, $\text{CH}_3\cdot[\text{CH}_2]_n\cdot\text{CH}=\text{CH}\cdot[\text{CH}_2]_m\cdot\text{CO}_2\text{H}$, which by hydro-

—O—

lysis with aqueous potassium hydroxide form the corresponding polyhydroxy-fatty acid. The following examples are given: oleic acid, oxido-oleic acid, m. p. 52°, dihydroxystearic acid, m. p. 96°; elaidic acid, oxidoelaidic acid, m. p. 57.5—58.5° (methyl ester, m. p. 32—33.5°), dihydroxystearic acid, m. p. 132°; erucic acid, oxidoerucic acid, m. p. 67.5° (from which, by treatment with hydrazine hydrate, hydrazinoerucic acid, m. p. 94.5°, is obtained), dihydroxybehenic acid, m. p. 133°; ricinoleic acid, hydroxy-

oxidoricinoleic acid, an oil, trihydroxystearic acid, m. p. 110°; ricinelaic acid, hydroxyoxidoricinelaic acid, trihydroxystearic acid, m. p. 110°; linoleic acid, dioxidolinoleic acid, an oil, tetrahydroxystearic acid, m. p. 175°.

Dicyclopentadiene yields mono- and di-oxido-derivatives. The last gives a mercurichloride, m. p. 154°. Indene with perbenzoic acid gives an oily oxidation product, from which β -hydrindone is isolated.

R. J. W. LE FÈVRE.

Fatty acids associated with rice starch. L. LEHRMANN (J. Amer. Chem. Soc., 1929, 51, 2185—2188).—Hydrolysis of rice starch with dilute hydrochloric acid gives about 0.6% by weight of a mixture of palmitic (36%), oleic (35%), and linoleic (29%) acids, approximately in the proportions named. The mixture does not contain compounds of nitrogen, sulphur, phosphorus, and halogens and no glycerol or phytosterol is liberated during the hydrolysis. The acyl residues must be combined with the carbohydrate molecule (cf. B., 1926, 686).

H. E. F. NOTTON.

Composition of α -elæostearic acid, the most important component of Chinese wood (tung) oil. J. BÖESEKEN.—See B., 1929, 607.

Oleosylvic acid. F. BALÁŠ and R. HAZUKOVÁ (Coll. Czech. Chem. Comm., 1929, 1, 401—410).—Oleosylvic acid can be separated by fractional crystallisation of its di-*d*-amylamine salt into abietic acid and *d*-pimaric acid, m. p. 212—213°, $[\alpha]_D + 78.4^\circ$ in alcohol. The following salts of *d*-pimaric acid are also described: propylamine, m. p. 158°, $[\alpha]_D + 79.7^\circ$ in chloroform; dipropylamine, m. p. 112°, $[\alpha]_D + 72.2^\circ$ in alcohol; tetramethylammonium, m. p. 230° (decomp.); di- α -amylamine, m. p. 113°, $[\alpha]_D + 42.5^\circ$ in alcohol; piperidine, m. p. 133°, $[\alpha]_D + 61.6^\circ$ in alcohol; quinine, m. p. 195°, $[\alpha]_D + 57.8^\circ$ in alcohol; quinidine, m. p. 90°, cinchonidine, m. p. 175°, $[\alpha]_D - 30.5^\circ$ in chloroform. Abietic acid forms the following salts: dipropylamine, m. p. 160°, di-*d*-amylamine, m. p. 133°, $[\alpha]_D - 17.1^\circ$ in alcohol; piperidine, m. p. 114°, quinine, m. p. 180°; quinidine, m. p. 198°, cinchonidine, m. p. 178°. Di-*d*-amylammonium dihydro-*d*-pimarate has m. p. 120° and $[\alpha]_D + 16.2^\circ$ in chloroform.

R. J. W. LE FÈVRE.

Constitution of linoleic acid. R. D. HAWORTH (J.C.S., 1929, 1456—1461).—Contrary to the statement of Takahashi (cf. A., 1919, i, 468; 1921, i, 303) it has been found that linoleic acid isolated from soya bean is identical with that obtained from poppy-seed oil. Goldsobel's conclusions (J. Russ. Phys. Chem. Soc., 1906, 38, 904) that linoleic acid is octadeca- Δ^w -dienic acid have been confirmed by oxidation experiments. Oxidation with potassium permanganate in alkaline solution gave *n*-hexoic, azelaic, and oxalic acids in 80% of the theoretical yield, whilst traces of malonic acid were detected by the formation of hydrogen formazyl. Satiivic acid yielded mainly *n*-valeric, suberic, and oxalic acids when oxidised with potassium permanganate in cold alkaline solution, but in warm solution increasing amounts of azelaic and *n*-hexoic acids were obtained. The existence of various tetrabromo- and tetrahydroxy-additive products of linoleic acid is explained on steric grounds.

A. A. GOLDBERG.

Syntheses of ethyl acetoacetate and malonate. H. LUX (Ber., 1929, 62, [B], 1824—1827).—Powdered sodium is covered with a boiling mixture of ether and ethyl carbonate to which acetone is gradually added. After treatment with acetic acid, ethyl acetoacetate is obtained in 38—41% yield (calculated on sodium or acetone). Ether may be replaced by benzene. Ethyl malonate is prepared in 18% yield by the addition of ethyl acetate to sodium and boiling ethyl carbonate and benzene; ethyl acetoacetate is obtained simultaneously.

H. WREN.

[Preparation of] **lævulic acid.** B. F. MCKENZIE (Organic Syntheses, 1929, 9, 50—51).

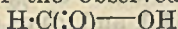
Preparation of tertiary α -hydroxy-acids. R. HELLMANN (Bull. Soc. chim., 1929, [iv], 45, 412—414).—Methyl α -hydroxy-ketones, $\text{OH}\cdot\text{CRR}'\cdot\text{COMe}$, obtained by hydration of dialkylethinylcarbinols (Locquin and Wouseng, A., 1923, i, 302; 1924, i, 822) in presence of acid mercuric sulphate, are oxidised by alkaline hypochlorite or hypobromite. α -Hydroxy- α -propylvaleric acid, m. p. 80° (methyl ester, b. p. 83—84°/10 mm.), α -hydroxy- α - β -trimethylbutyric acid, m. p. 141°, and α -hydroxy- α -methylvaleric acid (yield 70%), b. p. 127—128°/10 mm. (methyl ester, b. p. 65—66°/15 mm., ethyl ester, b. p. 68°/9 mm.), have been thus prepared.

R. BRIGHTMAN.

Existence of an isomeride of oxalic acid. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1929, 61, 607—612).—The theoretical possibility of the existence of *cis-trans*-isomerism of oxalic acid is considered and certain results obtained by earlier workers are reviewed in the light of this possibility.

R. TRUSZKOWSKI.

Constitution of maleic acid. K. VON AUWERS and L. HARRES (Ber., 1929, 62, [B], 1678—1688).—Spectroscopic examination of a series of compounds of the fumaric acid group in many of which the methyl group or halogen atom is present as substituent shows certain peculiarities as a consequence of the individual nature of its conjugated system which do not fall outside the limits of the usual spectrochemical laws. In the case of the corresponding derivatives of maleic acid the exaltations in refractive power and index of dispersion caused by the introduction of a methyl group or halogen atom into the parent molecule are inexplicable if the open-chain structure is assumed, but are expected if Anschütz' cyclic structure is adopted. The latter conception is supported by the optical behaviour of anhydrides of the maleic acid group. The spectrochemical properties of the maleic series show that some type of equilibration of valency exists between the neighbouring carboxyl groups. The Anschütz formulation represents the extreme expression of the observed



facts for which possibly the scheme

$$\begin{array}{ccc} \dots & \dots & \dots \\ & \text{::} & \\ \text{H}\cdot\text{C}(\text{OH})\text{=O} & & \end{array}$$

(I.)

suffices. The following data, amongst others, are recorded. Ethyl fumarate, d_4^{20} 1.0522, n_{D}^{20} 1.43957; propyl fumarate, d_4^{20} 1.0120, n_{D}^{20} 1.44278; methyl mesaconate, d_4^{24} 1.1266, n_{D}^{24} 1.45789; ethyl mesaconate, d_4^{27} 1.0516, n_{D}^{27} 1.45130; α -methyl β -ethyl mesaconate, d_4^{28} 1.0821, n_{D}^{28} 1.45345; β -methyl α -ethyl mesaconate,

d_4^{28} 1.0851, n_{D}^{28} 1.45470; β -methyl ester α -chloride, d_4^{27} 1.2368, n_{D}^{27} 1.47775, β -ethyl ester α -chloride, d_4^{28} 1.1823, n_{D}^{28} 1.47521, and α -ethyl ester β -chloride of mesaconic acid, d_4^{25} 1.1777, n_{D}^{25} 1.47325; methyl dimethylfumarate, m. p. 41°, d_4^{26} 1.0494, n_{D}^{26} 1.43688; ethyl dimethylfumarate, d_4^{24} 1.0244, n_{D}^{24} 1.44570; methyl chlorofumarate, b. p. 108°/15 mm., d_4^{27} 1.3028, n_{D}^{27} 1.44570; ethyl chlorofumarate, b. p. 119°/12 mm., d_4^{28} 1.1822, n_{D}^{28} 1.45979; methyl bromofumarate, m. p. 27.5—28.5°, b. p. 115°/9 mm., d_4^{26} 1.5381, n_{D}^{26} 1.47935; ethyl bromofumarate, b. p. 135—136°/12 mm., d_4^{28} 1.4174, n_{D}^{28} 1.48194; propyl maleate, d_4^{26} 1.0271, n_{D}^{26} 1.44329; methyl citraconate, d_4^{27} 1.1097, n_{D}^{27} 1.44710; ethyl citraconate, d_4^{29} 1.0420, n_{D}^{29} 1.44269; methyl chloromaleate, b. p. 100°/17 mm., d_4^{28} 1.2775, n_{D}^{28} 1.46170; ethyl chloromaleate, d_4^{30} 1.1754, n_{D}^{30} 1.45532; methyl bromomaleate, b. p. 105°/10 mm., d_4^{29} 1.5497, n_{D}^{29} 1.48756; methyl pyrocinchonate, d_4^{30} 1.0997, n_{D}^{30} 1.45552; ethyl pyrocinchonate, d_4^{30} 1.0434, n_{D}^{30} 1.45262; maleic anhydride, d_4^{28} 1.3001, n_{D}^{28} 1.45135; citraconic anhydride, d_4^{27} 1.2469, n_{D}^{27} 1.47070; chloromaleic anhydride, d_4^{29} 1.5455, n_{D}^{29} 1.50933; bromomaleic anhydride, d_4^{28} 1.9642, n_{D}^{28} 1.54236; pyrocinchonic anhydride, d_4^{29} 1.1070, n_{D}^{29} 1.43842. H. WREN.

Configurative relationship of chlorosuccinic acid to chloropropionic and lactic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 185—190).— $\Delta^{\alpha\epsilon}$ -Hexadien- γ -ol, b. p. 133—134°, d_4^{25} 0.8596, n_{D}^{25} 1.4464, obtained from acraldehyde and allyl bromide with zinc, was converted into the hydrogen phthalate. From the insoluble brucine salt was obtained a product with $[\alpha]_{\text{D}}^{25} +18.0$, which yielded a carbinol, b. p. 133—134°, $[\alpha]_{\text{D}}^{24} +12.9$ in ether; this, with phosphorus trichloride, gave 1- γ -chloro- $\Delta^{\alpha\epsilon}$ -hexadiene, $[\alpha]_{\text{D}}^{25} -13.2$ in ether, which, with ozone, yielded *d*-chlorosuccinic acid, m. p. 168—171°, $[\alpha]_{\text{D}}^{25} +18.9$ in water. 1- $\Delta^{\alpha\epsilon}$ -Hexadien- γ -ol, $[\alpha]_{\text{D}}^{25} -6.2$ in ether, was reduced with hydrogen and palladium to *d*-hexan- γ -ol. *l*-Chlorosuccinic acid is therefore configuratively related to *d*-malic, *l*-lactic, and *l*- α -chloropropionic acids. C. R. HARRINGTON.

Walden inversion. II. H. N. K. RÖRDAM (J.C.S., 1929, 1282—1290; cf. A., 1928, 1215).—Two types of Walden inversion are distinguished, viz., (a) reactions in which the fission of the active molecule is spontaneous or caused by some molecule which is neither identical with nor contains the entering radical, including replacement of halogen by hydroxyl ions or of hydroxyl by halogen ions, and (b) reactions in which the course of inversion is the result of propinquity of radicals in an additive phase, and to which the author's theory does not apply. Further data on a reaction of type (a), between sodium *l*-bromosuccinate and potassium xanthate in presence of sodium nitrate, have now been obtained. The simplified expression $n = kc_x F$ deduced from the theory (*loc. cit.*) indicates a linear relation between n , the fraction of the product with the original configuration, and c_x , the mean concentration of the entering radical. Such a relation is actually found within limits where the simplified equation may be expected to apply, and the derived values of F are in fair agreement with values from other sources. R. K. CALLOW.

Action of piperidine on ethyl $\alpha\alpha'$ -dibromo-adipate. J. VON BRAUN (Ber., 1929, 62, [B], 1694).—If piperidine is allowed to act on the ester without initial cooling so that a sudden, very marked heating of the reactants occurs, ethyl β -piperidino-propionate is formed in amount not exceeding 40% (cf. Fuson and Bradley, this vol., 425); if reaction occurs slowly, the amount of piperidinopropionic ester is very small in comparison with that of ethyl dipiperidinoadipate (cf. von Braun, A., 1926, 1128).

H. WREN.

Production of kojic acid from pentoses by *Aspergillus oryzae*. F. CHALLENGER, L. KLEIN, and T. K. WALKER (J.C.S., 1929, 1498—1505).—The investigation of the growth of *Aspergillus oryzae* diastase on arabinose and xylose showed that kojic acid is formed and not pyromeconic acid as would be expected from analogy with the behaviour of dextrose. The formation of kojic acid involves the breakdown of the pentose molecule and the synthesis of a six-carbon compound. This is similar to the formation of citric acid by the growth of *A. niger* on arabinose and xylose. The mould grows well on glycuronic acid, but neither comenic acid nor kojic acid nor any hydroxypyrene derivative could be detected. Both pyromeconic and comenic acids were found to be toxic to *A. oryzae*.

A. A. GOLDBERG.

Polygalacturonic acid. W. WŁOSTOWSKA (Roczn. Chem., 1929, 9, 371—389).—Polygalacturonic acid, $[\alpha]_D^{20} +279.5^\circ$, prepared from beet pectic acid, contains 94.2% of hexuronide groups and 93.2% of galacturonide groups. The product examined contains 7% of araban; 100 g. of polygalacturonic acid neutralise 543.1 c.c. of *N*-sodium hydroxide. Its empirical formula is $[C_6H_8O_6]_n$, and it appears to be a condensation product of galacturonic acid. It has no action on Fehling's solution. On the addition of sodium hydroxide to polygalacturonic acid solution a transient green coloration appears at p_H 9; sodium polygalacturonate is precipitated when the concentration of alkali attains 10%. Vitreous or gelatinous precipitates are formed on addition of alkaline-earth salts to solutions of the sodium salt. The p_H of 0.1% solutions of polygalacturonic acid is 3.1. The electro-titration curve of this acid shows that it behaves as a monobasic acid, *i.e.*, the carboxyl groups are all dissociated to the same extent, the dissociation constant being 0.8×10^{-4} . The viscosity of polygalacturonic acid solution is highest at p_H 1.5, least at p_H 2.1, and rises to a second maximum at p_H 6.3. The surface tension of 0.1% solutions varies from 80 to 90, according to the age of the solution and its previous treatment. The particles of the acid are charged negatively, the isoelectric point being at p_H 2.2. More than 80% of the particles have a magnitude less than 5μ . Sodium polygalacturonate may be obtained in 3—5% solutions; at higher concentrations, the solutions gelatinise. Cryoscopic measurements of the sodium salt solution show that the mol. wt. of polygalacturonic acid is not less than 594.

R. TRUSZKOWSKI.

Preparation of allomucic acid and derivatives. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1929, 51, 2167—2170).—Mucic acid is epimerised

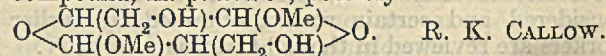
by prolonged heating with 10% aqueous pyridine (cf. A., 1927, 340; Fischer, A., 1891, 1193) to allomucic acid (33% yield). This is converted through the syrupy monolactone into the *monoamide*, m. p. 175—176°, and esterified by a large excess of alcohol and sulphuric acid to *ethyl allomucate*, m. p. 138°, converted by ammonia into *allomucodiamide*, m. p. 209° (decomp.), darkening from 185°. Although allomucic acid resembles mannosaccharic acid (A., 1928, 741) in having two *cis*-hydroxyl groups adjacent to each carboxyl, it does not (a) reduce Fehling's solution, (b) form a dilactone, or (c) give coloured products when boiled with 10% sodium hydroxide.

H. E. F. NOTTON.

Precipitant for aldehydes. H. LEEFMANN and C. C. PINES (Bull. Wagner Free Inst., 1929, 4, 15—16).—Photomicrographs are given of the distinctive precipitates produced by dimethyldihydroresorcinol with formaldehyde and acetaldehyde (cf. Stepp, A., 1922, i, 300; Vorländer, this vol., 949).

R. K. CALLOW.

Methylation of *dl*-glyceraldehyde. H. G. REEVES (J.C.S., 1929, 1327—1329).—An attempt has been made to methylate *dl*-glyceraldehyde in the hope of determining its structure by conversion into a methylglycerol. The action of methyl sulphate and alkali, or of methyl alcohol at 100° yielded non-reducing oils. Treatment with methyl-alcoholic hydrogen chloride at the ordinary temperature gave a 5% yield of a non-reducing bimolecular *monomethyl* compound, m. p. 204.5°, possibly



R. K. CALLOW.

Isomeric trithioacetaldehydes. E. V. BELL, G. M. BENNETT, and F. G. MANN (J.C.S., 1929, 1462—1465).—The supposed γ -isomeride of the α - and β -trithioacetaldehydes (Mann and Pope, *ibid.*, 1923, 123, 1178) is shown by m. p. evidence to be identical with the eutectic mixture of these two isomerides (60% α and 40% β). The explanation of its formation and of other peculiarities of the case is discussed. A crystallographic examination of the two isomerides is recorded.

A. A. GOLDBERG.

Cyclic acetals. II. R. DWORZAK and K. HERRMANN (Monatsh., 1929, 52, 83—106; cf. this vol., 421).—Cyclic acetals have been prepared from glycols and various aliphatic ketones or aromatic aldehydes by (a) condensation of equimolecular quantities of the reactants at 0° with hydrogen chloride (Franke and Gigerl, A., 1928, 759), (b) using excess of ketone containing 1% of hydrogen chloride in presence of anhydrous sodium sulphate at the ordinary temperature (Fischer and Pfähler, A., 1920, i, 807), (c) as *b* but in presence of 0.25—0.5% of sulphuric acid (Böeseken, A., 1923, i, 86), and (d) as *a* but with 40% sulphuric acid as condensing agent (Hibbert and Timm, A., 1924, i, 710). The yields are essentially the same by any of the methods. Acetone does not condense with trimethylene glycol, but with ethylene glycol and glycerol there are obtained 7.6—8.0 and 74—77% of the corresponding *isopropylidene* derivatives, respectively. Methyl ethyl ketone does not condense with trimethylene glycol; with ethylene glycol and glycerol the cyclic *methylethylmethylene* derivatives, b. p. 113.5°

and 150°, respectively, are obtained in yields of 11—15 and 60%. The following cyclic acetals are obtained using the requisite aldehyde or ketone: *dipropylmethylene* derivatives of ethylene glycol (28—30%), b. p. 172.5—174°/760 mm., trimethylene glycol (0—2.7%), b. p. 187°, and glycerol (10%), b. p. 160°; *benzylidene* derivatives of ethylene glycol (28%), b. p. 223—225° (cf. Hibbert and Timm, *loc. cit.*), trimethylene glycol (32—38.5%), m. p. 41—41.5°, and glycerol (50—52%); *m-toluylidene* derivatives of trimethylene glycol (23—24.7%), b. p. 140°/12 mm. (ethylene glycol does not react), and glycerol (5—6%), b. p. 158°/11 mm., and *anisylidene* derivatives of trimethylene glycol (30%), b. p. 164—165°/11 mm. (ethylene glycol does not react), and glycerol (13%), b. p. 163.5—165°/10 mm., m. p. 20°. The above glycerol ethers are formulated as $\alpha\beta$ - or $\alpha\gamma$ -derivatives. In general, ketones give rise to five-membered ring acetals, whilst aldehydes favour the formation of six-ring compounds; this is explained by the Ingold-Thorpe strain theory. The presence of methyl groups in the aldehyde or ketone results in a distinct lowering of the amount of acetal produced. The factors governing the formation of acetals are "tendency of formation" and the overcoming of ring tension; these are approximately equal.

H. BURTON.

Rate of ring-closure of the $\alpha\delta$ -diketones. I. A. TREFILIEV and RAZUMOV (Ukraine Chem. J., 1929, 4, 19—35, and J. Russ. Phys. Chem. Soc., 1929, 61, 699—712).—The mechanism of the formation of the monoethyl ester of carbopyrotritaric acid by the action of hydrogen halides on ethyl diacetylsuccinate was investigated, with a view to elucidate whether a rapid ring closure of the $\alpha\delta$ -diketone, with the formation of a furan derivative, occurs first, followed by a partial hydrolysis of the di-ester to the mono-ester. Since the bromo-derivatives of ethyl carbopyrotritarate are insoluble in hydrobromic acid, the reaction mixture of ethyl diacetylsuccinate and hydrobromic acid was treated with bromine, to remove the furan derivative as soon as it was formed. A canary-yellow solid was obtained, which was very unstable, hydrolysing in air with loss of bromine, first with the formation of a ruby-red solid and then with separation of ethyl carbopyrotritarate, b. p. 275—278°. The yellow and red solids were found by analysis to be the *hexa*- and *tetra*-bromo-derivatives of the ethyl ester. Treatment of ethyl acetylsuccinate under the same conditions with iodine in concentrated hydriodic acid yielded a green *tetra*- and brown *di*-iodide. All these halogen derivatives were very unstable, and decomposed completely into the halogen and original ester in moist air, so that they were considered to be oxonium compounds of the furan ring. Attempts to prepare similar products from ethyl metronate proved unsuccessful, whilst with furan itself a complex mixture of condensation products was obtained, which could not be analysed. M. ZVEGINTZOV.

Rotatory power and structure in the sugar group. XIX. Preparation of aldonic acids. C. S. HUDSON and H. S. ISBELL (J. Amer. Chem. Soc., 1929, 51, 2225—2229, and Bur. Stand. J. Res., 1929,

3, 57—62).—Aldoses are oxidised almost quantitatively by bromine water in presence of calcium or barium benzoate to the corresponding aldonic acids. The removal by the benzoate of the hydrogen bromide formed accelerates the reaction and prevents the hydrolysis of compound sugars, such as lactose and maltose (cf. Fischer and Meyer, A., 1889, 485, 1132). The preparation of calcium gluconate, of the double cadmium xylostate and bromide, $[\alpha]_D^{20} +8.8^\circ$, and of calcium lactobionate, and the hydrolysis of the last to galactose and gluconic acid, are described in detail.

H. E. F. NOTTON.

Decomposition of sugars by alkalis. F. FISCHLER (Z. angew. Chem., 1929, 42, 682—684).—Dilute solutions of most sugars, admixed with 50% potassium hydroxide solution, give definite rings of iodoform crystals when a dilute solution of iodine in potassium iodide is poured carefully on the surface and the whole cooled; with laevulose, very little iodoform only is obtained, even with concentrated solutions. Sucrose gives a positive result, although on distillation no methylglyoxal is obtained. The behaviour of dihydroxyacetone and methylglyoxal towards Ost's solution in presence of sulphites is compared with that of sucrose, to show that the latter is in fact decomposed by alkalis with formation of trioses.

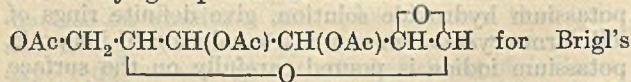
S. I. LEVY.

Acetate of free aldehydic form of dextrose. M. L. WOLFROM (J. Amer. Chem. Soc., 1929, 51, 2188—2193).—Careful treatment of the penta-acetate, m. p. 45—47°, of glucose ethyl mercaptal (cf. Schneider and Sepp, A., 1918, i, 252), prepared by an improved method, with cadmium carbonate and mercuric chloride in aqueous acetone gives *glucose* $\beta\gamma\delta\epsilon\zeta$ -*penta*-acetate, m. p. 116—118°, $[\alpha]_D^{20} +2.7^\circ$ in *s*-tetrachloroethane (optical and crystallographic properties; *semicarbazone*, m. p. 150—151°), which gives a positive Schiff's reaction. H. E. F. NOTTON.

Reactivity of dextrose in presence of hydrochloric acid. II. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, 25, 435—442).—Polarimetric evidence of the formation of diglucose shows that dextrose and glucoside-glucose kept in *N*-hydrochloric acid solutions at the same temperature reach the same equilibrium, which is dependent on the total dextrose content of the solution and not on its origin. Nascent dextrose, *i.e.*, immediately after its liberation from a glucoside, is considered to be straight-chained and does not accelerate diglucose formation. The rate of transformation of reactive dextrose in *N*-hydrochloric acid solutions containing salicin indicates that the change is unimolecular. The author (A., 1928, 374) has shown that the nascent dextrose molecule is energised, and the inference now made is that it is not sufficiently activated for condensation purposes. In view of the large value of the energy of activation of the condensation process and the fact that normal tetramethylglucose condenses to octamethyldiglucose, it is considered that diglucose formation is brought about by thermal activation, and not by the interposition of a structurally active form of dextrose having a definite chemical existence. H. T. S. BRITTON.

Carbohydrates. VIII. $\alpha\beta$ -Derivatives of dextrose. P. BRIGL and R. SCHINLE (Ber., 1929,

62, [B], 1716—1723).— α -Chloro- $\gamma\delta\zeta$ -triacetylglucose is converted by silver carbonate in aqueous acetone into $\gamma\delta\zeta$ -triacetylglucose, m. p. 110—112°, $[\alpha]_D^{25} +139.1^\circ$ in ethyl acetate, transformed by silver oxide and methyl iodide into $\gamma\delta\zeta$ -triacetyl- $\alpha\beta$ -dimethylglucose, m. p. 74—75°, $[\alpha]_D^{25} +6.28^\circ$ in chloroform, $[\alpha]_D^{25} +5.88^\circ$ in alcohol. The last-named compound is hydrolysed by methyl-alcoholic ammonia to $\alpha\beta$ -dimethylglucose, m. p. 95—97°, $[\alpha]_D^{25} -23.90^\circ$ in alcohol, and by 0.2*N*-sulphuric acid into β -methylglucose, characterised as the phenylhydrazone, m. p. 178°, $[\alpha]_D^{25} -12.31^\circ$ in pyridine. Treatment of the methylglucose with an excess of phenylhydrazine affords solely glucosazone, thus establishing the β -position of the methyl group and the constitution

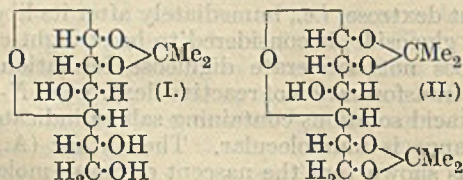


glucose anhydride triacetate (cf. Hickinbottom, this vol., 174). The structure of Pictet's glucosan therefore becomes uncertain.

Tribenzoylglucose is converted by thionyl chloride in carbon tetrachloride into the cyclic sulphite, $\text{C}_{27}\text{H}_{22}\text{O}_{10}\text{S}$, m. p. 139—140°, $[\alpha]_D^{25} -136.7^\circ$ in chloroform. H. WREN.

Derivatives of isopropylidene-glucose. Rearrangement reactions in carbohydrate group. I. K. JOSEPHSON (Annalen, 1929, 472, 217—229).—Mainly an account of work already reviewed (this vol., 912). The following is new. γ -Acetyl- $\alpha\beta$ -isopropylidene-glucose reacts with triphenylmethyl chloride in presence of pyridine at the ordinary temperature, yielding γ -acetyl- ζ -triphenylmethyl- $\alpha\beta$ -isopropylidene-glucose, sinters at 55°, $[\alpha]_{D, \text{yellow}}^{20} -16^\circ$ in chloroform, acetylated by acetic anhydride in pyridine solution to $\gamma\epsilon$ -diacetyl- ζ -triphenylmethyl- $\alpha\beta$ -isopropylidene-glucose, sinters at 64°, $[\alpha]_{D, \text{yellow}}^{20}$ about $+5^\circ$ in chloroform. H. BURTON.

Constitution of glucose-monoacetone and -diacetone, and of the derived $\gamma\epsilon\zeta$ -trimethylglucose and γ -monomethylglucose. C. G. ANDERSON, W. CHARLTON, and W. N. HAWORTH (J.C.S., 1929, 1329—1337).—Direct evidence has now been obtained in favour of the butylene-oxide ring structure for diisopropylidene-glucoses (I and II) and against the



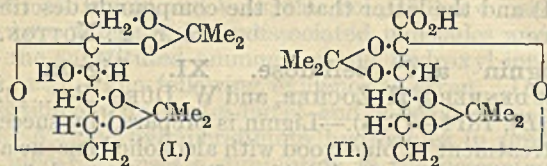
propylene- or ethylene-oxide structures proposed by Irvine and others (J.C.S., 1913, 103, 573; 1915, 107, 1710; 1922, 121, 2146). Consideration of the space formulæ of the glucofuranose and glucopyranose forms of dextrose shows that the former alone provides favourable *cis*-positions for condensation with acetone groups. Moreover, the former, with substitution in the $\alpha\beta$ - or $\alpha\beta\epsilon\zeta$ -positions, respectively, is alone consistent with recent work and with the isolation of γ -methylglucose from diisopropylidene-glucose and of $\gamma\epsilon\zeta$ -trimethylglucose of glucofuranose structure from

isopropylidene-glucose by methylation, followed by hydrolysis. The preparation and determination of the constitution of these products are now described.

γ -Methylglucose, m. p. 160—161°, prepared from diisopropylidene-glucose, is converted into the methylglucoside, and this is methylated with methyl iodide and silver oxide. The oil obtained is hydrolysed with 5% hydrochloric acid and yields $\beta\gamma\delta\zeta$ -tetramethylglucose. γ -Methylglucosephenylosazone has m. p. 178—179° (Irvine and Scott, J.C.S., 1913, 103, 575, give 164—165°) and is shown to be identical with γ -methylfructosephenylosazone (cf. following abstract) both by mixed m. p. determinations and by the identity of the rate of mutarotation and the initial and final values of $[\alpha]_D$ ($-109^\circ \rightarrow -9^\circ$) in alcohol. *iso*Propylidene-glucose is best methylated by treatment with methyl sulphate and alkali. Conversion of the product into the trimethyl methylglucoside and hydrolysis by dilute hydrochloric acid yields $\gamma\epsilon\zeta$ -trimethylglucose (phenylosazone, m. p. 70—72°), which is converted into tetramethyl-methylglucoside by methyl sulphate and alkali. Hydrolysis yields $\beta\gamma\epsilon\zeta$ -tetramethylglucose and a *by-product*, m. p. 97—98°. Oxidation of the former with bromine water yields a product identical with $\beta\gamma\epsilon\zeta$ -tetramethyl- γ -gluconolactone from other sources and yielding an identical phenylhydrazide. R. K. CALLOW.

Constitution of α - and β -fructosediacetones. Alleged oxidative degradation of the derived monomethyl- and tetramethyl-fructoses. C. G. ANDERSON, W. CHARLTON, W. N. HAWORTH, and V. S. NICHOLSON (J.C.S., 1929, 1337—1346).—3-Methylfructose, obtained from diisopropylidene-fructose by methylation and removal of the acetone residues, has, when adequately purified, m. p. 128—130°, $[\alpha]_D^{20} -84.1^\circ \rightarrow -53.5^\circ$, and yields a phenylosazone, m. p. 177—179° (cf. Irvine and Hynd, J.C.S., 1909, 95, 1220; Irvine and Scott, *ibid.*, 1913, 103, 573). The reported oxidation to $\alpha\beta$ -dihydroxy- γ -methoxybutyric acid (Irvine and Hynd, *loc. cit.*) is erroneous. The sugar is recovered unchanged after treatment with bromine water, and itself has the properties, such as formation of a compound with barium hydroxide, attributed to the acid. The "diethyl dimethoxyhydroxyglutarate" obtained by Irvine and Patterson (J.C.S., 1922, 121, 2146) from α -diisopropylidene-fructose by alternate hydrolysis and methylation and subsequent oxidation of the tetramethylfructose with nitric acid has previously (Haworth, Hirst, and Learner, A., 1927, 649) been assigned the constitution of ethyl trimethylfructuronate, and this is now confirmed by its oxidation with permanganate to yield d-2 : 3 : 4-trimethyl- δ -arabonolactone, m. p. 44°, $[\alpha]_D^{18} -177.3^\circ \rightarrow -10.2^\circ$, which has properties similar to those of the *l*-lactone (Drew, Goodyear, and Haworth, A., 1927, 750). The conclusions that the tetramethyl fructose is 1 : 3 : 4 : 5-tetramethylfructopyranose and that the monomethylfructose is γ -methylfructose (cf. preceding abstract) are thus confirmed, and the formula I for α -diisopropylidene-fructose is supported. Another example of this attack by oxidising agents on the $\text{CH}_2\cdot\text{OMe}$ group in position 1 is provided by the oxidation of β -diisopropylidene-fructose to a diisopropylidene-

fructuronic acid (II) (Ohle, A., 1926, 150). This is converted by simultaneous methylation and hydrolysis



with methyl sulphate and sodium hydroxide, and final methylation with Purdie's reagents, into methyl tetramethylfructuronate (Haworth, Hirst, and Learner, *loc. cit.*) which yields the amide, m. p. 118—119°. Hydrolysis of the fructuronic acid with dilute sulphuric acid and subsequent methylation gives an isomeric product which yields an amide, m. p. 100—101°, identical with that from the oxidation of tetramethyl- γ -fructose (Haworth, Hirst, and Nicholson, A., 1927, 859). The formula II for Ohle's acid is thus confirmed, and it is demonstrated that its ring structure is displaced in contact with sulphuric acid to give a five-membered ring acid.

R. K. CALLOW.

Volumetric determination of invert sugar by reduction in solutions containing sucrose. IV. Influence of calcium salts on the reduction. A. A. GABREËLS and A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1929, 26, 394—398).—At low sucrose concentrations calcium salts exert considerable inhibitory influence on the reduction of copper in alkaline solution. The determination of invert-sugar in alkaline tartrate solutions containing sucrose may be effected normally if the tartrate concentration is about 69.2 g. per litre. The phenomenon of acid adsorption on the walls of glass apparatus has been shown to be due principally to a permutit type of reaction.

H. F. GILLBE.

Solidification of sucrose. Catalysis by water. A. TIAN (*Compt. rend.*, 1929, 188, 1675—1677).—Sucrose, fused rapidly at about 100° to avoid decomposition, remains in the colourless, vitreous, super-cooled state indefinitely in the absence of moisture, or for 5 months in an atmosphere having a water-vapour pressure less than 5 mm. of mercury at 16°. With vapour pressures of 5—11 mm. it absorbs water until a maximum is reached, when the sugar crystallises, after which water is slowly lost. Micro-calorimetric measurements show the catalytic effect of water as a function of time, viz., heat absorption for 1 hr. due to dissociation, followed by liberation of heat of crystallisation which rises to a maximum and slowly falls to zero after a few days.

J. GRANT.

Crystalline turanose. C. S. HUDSON and E. PACSU (*Science*, 1929, 69, 278).—Crystals of turanose formed from a syrup of hydrolysed melezitose after keeping for several years have been successfully used to seed fresh syrups and obtain rapid crystallisation. The crystals are moderately soluble in methyl alcohol, from which they can be easily recrystallised in prisms, m. p. 157°, $[\alpha]_D^{20} + 43.5$ to 75.6° (const.) in 3—20 min. in water.

L. S. THEOBALD.

Triphenylmethyl ethers of di- and tri-saccharides. Constitution of maltose, sucrose, and raffinose. K. JOSEPHSON (*Annalen*, 1929, 472,

230—240).—Treatment of di- and tri-saccharides with triphenylmethyl chloride in pyridine solution at the ordinary temperature gives ethers in which primary alcoholic hydrogen atoms are replaced by the triphenylmethyl group. Thus, maltose yields a *di*(tri-

phenylmethyl) derivative [6-triphenylmethylglucosido(1:5)-1:6-di(triphenylmethyl)fructosido(2:5)] (II), m. p. 127—129° (corr.), $[\alpha]_D^{25} + 44.3^\circ$ in alcohol, and raffinose gives a *tri*(triphenylmethyl) derivative

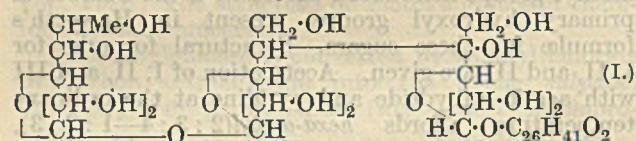
[6-triphenylmethylgalactosido(1:5)-glucosido(1:5)-1:6-

di(triphenylmethyl)fructosido(2:5)] (III), m. p. about 130°, $[\alpha]_D^{25} + 79^\circ$ in alcohol. The number of triphenylmethyl groups introduced agrees with the number of primary hydroxyl groups present in Haworth's formulæ for these sugars. Structural formulæ for I, II, and III are given. Acetylation of I, II, and III with acetic anhydride and pyridine at the ordinary temperature affords *hexa-acetyl*(2:3:4—1:2:3), m. p. 116—119° (corr.), $[\alpha]_D^{25} + 91^\circ$ in chloroform, *penta-acetyl*(2:3:4—3:4), sinters at 125—126°, $[\alpha]_D^{25} + 57^\circ$ in chloroform, and *octa-acetyl* derivatives (2:3:4—2:3:4—3:4), m. p. 123—125° after sintering at 118—120°, $[\alpha]_D^{25} + 66^\circ$ in chloroform, respectively. The sets of numbers in parentheses indicate the positions of the acetyl groups in the sugar units. Treatment of these acetyl derivatives with hydrogen bromide in acetic acid solution effects almost quantitative fission into triphenylmethyl bromide.

H. BURTON.

Saponins and related compounds. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1929, 48, 726—742).—Exhaustive extraction of the powdered root of Honduras sarsaparilla with light petroleum yields sitosterol, subsequent extraction with ether yielding the sitosterol glucoside, m. p. 290—295°, isolated by Power and Salway (*J.C.S.*, 1914, 105, 201), which is not identical with the parillin obtained by Schulz (*Arb. pharmakol. Inst. Dorpat*, 1896, xiv., since it gives a positive Liebermann cholesterol test and yields sitosterol on hydrolysis. Renewed extraction of the residue with 99% methyl alcohol and precipitation of the extract with ether yields a mixture of sarsasaponin and parillin, which is thus separated from the calcium and magnesium derivatives of the polysaccharides. This mixture dissolved in water and precipitated with 30% alcohol yields pure crystalline parillin (+4H₂O and anhydrous), m. p. 238—240°, $[\alpha]_D^{20} - 63.7^\circ$, although a large quantity of this product remains in pseudo-solution with the soluble amorphous sarsasaponin. The latter cannot be separated from the residual parillin and thus cannot be isolated as a chemical individual. Hydrolysis of this mixture (containing 9.6% of water) with 5% sulphuric acid followed by aqueous-alcoholic sulphuric and hydrochloric acid hydrolysis yields dextrose (30.85%), rhamnose (8.8%), and sapogenin (41%). The final residue insoluble in light petroleum, ether, and methyl alcohol, when heated with 45% alcohol and dialysed

yields the calcium and magnesium compounds of polysaccharides which are precipitated with alcohol and ether. On hydrolysis these yield 7.4% of insoluble matter but no saponin, their composition being: water 8.2%, ash 1%, pentoses 5.1%, methylpentoses 2.95%, aldehydic acids 3%, and fermentable hexoses 42.5%. Hydrolysis of pure parillin also yields parigenin, m. p. 203°, $[\alpha]_D -69.6^\circ$ (48.56%) (acetyl derivative, m. p. 130°), dextrose (41.84%), and rhamnose (15.8%), these results corresponding almost exactly with the decomposition $C_{44}H_{72}O_{17} + 3H_2O = C_{26}H_{42}O_3 + 2C_6H_{12}O_6 + C_6H_{12}O_5$. The composition thus assigned to parillin and parigenin agrees with the analysis and mol. wt. determinations of these compounds. By distillation with zinc dust in a current of hydrogen parigenin yields a sesquiterpene (probably a mixture) and not a monoterpene as stated by Kaufmann and Fuchs (A., 1924, i, 196). On the basis of these results coupled with the observation that whilst



parigenin contains only one hydroxyl group, parillin possesses no reducing properties, the structure I is assigned to the latter compound. By the interaction of tetra-acetylglucosidyl bromide and parigenin in the presence of quinoline in boiling toluene, and deacetylation of the product, a small yield of an artificial saponin, m. p. 225—230°, is obtained.

J. W. BAKER.

Diffusion of high-molecular substances into very thin layers on a water surface and its use as a method of determining the form and size of the molecule and micelle. I. Application to polysaccharides. J. R. KATZ and P. J. P. SAMWELL (Annalen, 1929, 472, 241—267).—A more detailed account of work previously reviewed (A., 1928, 937).

H. BURTON.

Molecular structure of inulin; new anhydrofructose. J. C. IRVINE and J. W. STEVENSON (J. Amer. Chem. Soc., 1929, 51, 2197—2203).—Inulin triacetate is converted by nitric acid in chloroform into a mixture of fructose triacetate dinitrate with 20% of anhydrofructose triacetate ($+0.5C_2H_4O_2$), m. p. 123°, $[\alpha]_D +1.5^\circ$ in chloroform (cf. this vol., 683), which is separated by means of boiling alcohol. This is obtained in approximately the same yield by hydrolysing inulin triacetate with acetic acid containing 0.03% of sulphuric acid, and from the insoluble residue left when inulin is subjected to graded acetolysis (Barnett, A., 1921, i, 164). It is converted by dimethylamine in methyl alcohol into an anhydrofructose, m. p. 143—145°, $[\alpha]_D +30.17^\circ$ in water, which does not reduce Fehling's solution and is quantitatively hydrolysed to lævulose by dilute acids. Methylation with methyl sulphate and alkali, and finally with silver oxide and methyl iodide, gives a dimeride of trimethylanhydrofructose, b. p. 166°/0.1 mm., $n_D 1.4730$, $[\alpha]_D +23.8^\circ$, which is partly depolymerised by hydrogen chloride in methyl alcohol to the monomeric form, $n_D 1.4610$. These results indicate that inulin contains anhydrofructose residues of two different types in the ratio of

4:1, the former being the source of the γ -fructose derivatives previously isolated (cf. J.C.S., 1920, 117, 1474) and the latter that of the compounds described above.

H. E. F. NOTTON.

Lignin and cellulose. XI. Lignin. K. FREUDENBERG, H. ZOCHER, and W. DÜRR (Ber., 1929, 62, [B], 1814—1823).—Lignin is prepared by successive treatment of pine wood with alcoholic benzene and cold 5% sodium hydroxide. Pentosans and hemicelluloses are removed by boiling 1% sulphuric acid and the residue is treated with Schweizer's solution. The product has a pale yellowish-brown colour and contains 16% of methoxyl and 1.1—1.4% of formaldehyde. After treatment with syrupy phosphoric acid and hydrochloric acid ($d 1.19$) the methoxyl content has increased to 17%. Treatment with alkali increases the resistance of lignin to attack by calcium hydrogen sulphite and the effect is enhanced by the following boiling with dilute acid. There does not appear to be any chemical difference between lignin from spring and autumn wood, although the morphological distinction is very marked. Histological investigation suggests that the lignin permeates the membrane like a network which remains intact after removal of nearly three fourths of the tissue substance. The surface is very markedly developed. Methylene-blue is adsorbed in large amount and water and alcohols are tenaciously retained. The behaviour towards benzyl alcohol and aniline indicates the saturation of a network which resists extension. Lignin appears to be wetted by all types of liquid and to retain its form when dried.

Treatment of lignin, obtained from wood by alcoholic benzene followed by hydrochloric and phosphoric acids, with *p*-toluenesulphonyl chloride followed by hydrazine indicates the presence of 5—6 secondary alcoholic hydroxyl groups and 1 phenolic hydroxyl group. If a treatment with alkali hydroxide is interspersed, the action of *p*-toluenesulphonyl chloride remains unchanged, but sulphinic acid is not produced by hydrazine, so that phenolic hydroxyl groups do not appear present. Possible structures of the lignin molecule are discussed in detail.

H. WREN.

Genuine lignin. III. Action of diazomethane on pine wood. W. FUCHS and O. HORN (Ber., 1929, 62, [B], 1691—1693).—Treatment of pine wood with diazomethane ultimately yields a product containing about 16% of methoxyl, from which a lignin with 19.7% of methoxyl can be isolated. Since the original lignin, isolated by treatment with hydrochloric acid, contains 15.4% of methoxyl, it follows that one hydroxyl group susceptible to diazomethane is present in a molecule of mol. wt. about 800. The methylated lignin exhibits double refraction. Willstätter lignin resembles lignin in wood, since it gives a methylated product with 20.8% of methoxyl. Cotton-wool and filter-paper are methylated with greater difficulty than the cellulose in wood by ethereal diazomethane; under similar conditions, dextrose is unaffected.

H. WREN.

Decomposition of quaternary ammonium and sulphonium hydroxides. IV. J. VON BRAUN, W. TEUFFERT, and K. WEISSBACH (Annalen, 1929, 472, 121—142).—The decomposition of quaternary

ammonium hydroxides into an alcohol and tertiary amine (reaction *B* of Hanhart and Ingold, A., 1927, 650; cf. Ingold and Vass, this vol., 175) is considered to be a function of undissociated molecules and not of the substituted ammonium and hydroxyl ions (cf. *loc. cit.*). The following evidence is given. Decomposition of trimethyl-*n*-butyl- and -*n*-decyl-ammonium and *N*-dimethylpiperidinium hydroxides in presence of glycerol causes a diminution in the percentage of olefine formed (Hanhart and Ingold's reaction *A*), with a corresponding increase in the amount of tertiary amine produced by reaction *B* (the possible intermediate formation of glycerolates is noted). In presence of potassium hydroxide an increase in the amount of olefine is obtained. Decomposition of trimethyl-*n*-decylammonium hydroxide in aqueous solution (2–16%) at 200° also results in a preponderance of dimethyldecylamine; the ratio of this and decylene produced is essentially the same at all the concentrations studied.

With sulphonium hydroxides the percentage of olefine produced is diminished in presence of glycerol and increased in presence of potassium hydroxide. Decomposition of dimethyl- β -phenylethylsulphonium hydroxide results essentially in the production of styrene (cf. A., 1924, i, 632). The yields of olefines previously reported (A., 1911, i, 610; 1912, i, 165) are too low. The error is due to contamination of the quaternary ammonium hydroxides by carbonates (produced during evaporation of the hydroxide solutions in the atmosphere). The following compounds were prepared during the investigation: *docosyl bromide*, b. p. 225°/0.6 mm., m. p. 44°; *trimethyldocosylammonium bromide*, decomp. about 240°; *dimethyldocosylamine*, b. p. about 190°/0.6 mm. (*hydrochloride*, m. p. 180°; *picrate*, m. p. 84°); Δ° -*docosylene*, b. p. 174–178°/0.6 mm., m. p. 41°. *n*-Hexyl bromide and ammonium dithiocarbamate react in warm alcoholic solution yielding *hexyl dithiocarbamate*, m. p. 50°, converted by potassium hydroxide solution into hexyl mercaptan. Treatment of this with methyl iodide and methyl-alcoholic sodium methoxide gives *methyl n-hexyl sulphide*, b. p. 61–62°/15 mm. (*methiodide*, m. p. 68°). *n*-Decyl dithiocarbamate, m. p. 76°; *n*-decyl mercaptan, b. p. 114–115°/13 mm.; *methyl n-decyl sulphide*, b. p. 125°/13 mm. (*methiodide*), and *methyl β -phenylethyl sulphide*, b. p. 111°/12 mm. [*methiodide*, m. p. 130° (decomp.)], are obtained similarly. A small amount of decyl alcohol is produced together with decylene and dimethyldecylamine during the decomposition of trimethyldecylammonium hydroxide.

Treatment of an aqueous-alcoholic solution of sodium hydrogen selenide with decyl bromide in an atmosphere of hydrogen affords *decyl hydrogen selenide*, b. p. 128–129°/13 mm., methylated in the usual way to *methyl decyl selenide*, b. p. 137–138°/14 mm. When this is treated with methyl iodide *trimethylselenonium iodide*, decomp. 173°, results.

H. BURTON.

Poly-acid amines and diamines containing sulphur. Z. FÖLDI (Ber., 1929, 62, [B], 1700–1709).—Pentamethylenediamine is converted by phenyl ϵ -bromoamyl ether in boiling alcohol into NN'-*di- ϵ -phenoxyamylpentamethylenediamine hydro-*

bromide, m. p. 275–276° (corresponding *picrate*, m. p. 162–163°), converted by hydrobromic acid (*d* 1.72) into NN'-*di- ϵ -bromoamylpentamethylenediamine hydrobromide*, m. p. 260–263° (decomp.) (corresponding *picrate*, m. p. 162–163°). The di-bromo-compound is transformed by alcoholic ammonia into *pentamethylenedipiperidine* [CH₂]₅(NC₅H₁₀)₂, m. p. 237° (*picrate*, m. p. 193–195°), whereas its *dibenzene-sulphonyl* derivative is converted by successive treatment with alcoholic ammonia and fuming hydrobromic acid into NN'-*di- ϵ -aminoamylpentamethylenediamine hydrobromide* (corresponding *picrate*, m. p. 195–196°). ϵ -Chloroamylbenzamide and pentamethylenediamine in boiling alcohol give NN'-*di- ϵ -benzamidoamylpentamethylenediamine hydrochloride*, m. p. 252–254° (corresponding *picrate*, m. p. about 110°), which is hydrolysed to NN'-*di- ϵ -aminoamylpentamethylenediamine hydrochloride*, not molten below 300°. The *monoguanidine* derivative of the free base, its *picrate*, m. p. 170°, non-crystalline *hydrochloride*, and *tetra-nitrate*, m. p. 150°, are described.

ϵ -Chloroamylbenzamide is converted by alcoholic ammonia into *di- ϵ -benzamidoamylamine*, m. p. 68–72°, rising to 93–96° after preservation over sodium hydroxide; the non-crystalline *picrate* and *tribenzoyl* derivative and the *hydrochloride*, C₂₄H₃₃O₂N₃·HCl, m. p. 200°, are described. Hydrolysis of the dibenzoyl derivative affords *di- ϵ -aminoamylamine*, b. p. 129°/0.1 mm. [*hydrochloride*, m. p. about 285° (decomp.); *picrate*, m. p. 200°; *picrate*, m. p. 156–158°, and *nitrate*, m. p. 162°, of the diguanidine derivative]. ϵ -Iodoamylbenzamide and alcoholic ammonia afford *monobenzoylcadaverine hydriodide*, m. p. 175°. *Diisomyltrimethylenediamine* and thiocarbamide *S*-ethyl ether hydrobromide afford the monoguanidine derivative of the diamine, isolated as the *dihydrobromide*, not molten below 300°, and *sulphate*, m. p. about 255°.

ϵ -Chloroamylbenzamide and sodium sulphide in boiling alcohol afford *di- ϵ -benzamidoamyl sulphide*, m. p. 96°, whereas with sodium disulphide the product is *di- ϵ -benzamidoamyl disulphide*, m. p. 132–133°. *Di- ϵ -aminoamyl sulphide*, b. p. 141–143°/1 mm., its *hydrochloride*, m. p. about 240–245° (decomp.), *picrate*, m. p. 179°, *diguanidine* derivative (*hydrobromide*, m. p. 123–125°; *picrate* m. p. 148–150°) are described. *Di- ϵ -aminoamyl disulphide*, b. p. 135–140°/1 mm. (decomp.), yields a *diguanidine* derivative (*dipicrate*, m. p. about 162–165°). H. WREN.

Decomposition of α -amino-alcohols and their salts on heating. K. A. KRASUSKI (Ukraine Chem. J., 1929, 4, 61–74; cf. this vol., 1078).—The behaviour of α -amino-alcohols on heating and the formation of halogen derivatives from them, were investigated. Dimethylaminoethylcarbinol when heated for 3 hrs. in a sealed tube at 100° with excess of fuming hydrobromic acid charred, with the separation of ammonium bromide. A similar result was obtained with aminotrimethylcarbinol, although traces of isobutaldehyde were also detected. The hydrochloride of dimethylaminoethylcarbinol when heated gave methyl isopropyl ketone, b. p. 94–96°, together with condensation products. With the hydrochloride of dimethylethylaminoethylcarbinol the products were the same, together with traces of tri-

methylethylene oxide, which may be regarded as the first stage of the reaction. Aminotrimethylcarbinol hydrochloride gave isobutaldehyde and its polymeride, m. p. 60—61°.

The same products were obtained if the phosphate of the aminocarbinol was employed. The hydrochlorides of the primary hydroxy-amine of hexylene oxide and dimethylaminoisopropylcarbinol yielded the corresponding ketones, a ketone, b. p. 121—128°, and pinacolin. The hydrochlorides of these two aminocarbinols decomposed so readily that on diazotisation and hydrolysis only small quantities of the glycols were obtained, the main products being the ketones. Only those aminocarbinols decomposed easily of which the corresponding glycols readily formed aldehydes and ketones, since aminodimethylcarbinol hydrochloride on heating gave only traces of the aldehyde.

The decomposition of the aminocarbinols was found to take place, under certain conditions, in alkaline solution, and to be favoured by the introduction of alkyl groups into the amino-group. The formation of the α -oxide was an intermediate stage. The mechanism of the decomposition of choline and its derivatives, and the reaction between piperazine and trimethylethylene oxide, are discussed.

M. ZVEGINTZOV.

Action of ammonia on isopropylethylene oxide. K. A. KRASUSKI and F. F. KRIVONOS (Ukraine Chem. J., 1929, 4, 79—84).—*iso*Propylethylene oxide was obtained by treating *iso*propylethylene with hypochlorous acid or perbenzoic acid, the yields in either case not exceeding 30%. With excess of ammonia the oxide yielded α -amino- γ -methylbutan- β -ol, b. p. 174°/754 mm., whilst with smaller quantities of ammonia the corresponding secondary amine, $[\text{CHMe}_2\text{CH}(\text{OH})\text{CH}_2]_2\text{NH}$, b. p. 265—268°, was obtained. The rate of the reaction is in accordance with the authors' rule, that the rate of the action of ammonia on the α -oxides decreases with increase of mol. wt., and is greater for oxides containing a primary carbon atom than for those containing a secondary one, since ammonia reacts with *isopropylethylene oxide* more slowly than with *isobutylene oxide*, but faster than with trimethylethylene oxide.

M. ZVEGINTZOV.

Action of ethylamine on isobutylene oxide and isobutylene chlorohydrin. K. A. KRASUSKI and V. D. KUCENOS (Ukraine Chem. J., 1929, 4, 75—77).—Equimolecular amounts of ethylamine and *isobutylene oxide* in aqueous solution when heated in a sealed tube for 8 hrs. at 100° furnished almost pure ethylaminotrimethylcarbinol, b. p. 156°, which yielded with dry gaseous hydrogen chloride a hydrochloride, m. p. 153°. The aminocarbinol can likewise be obtained by treating *isobutylene chlorohydrin* with ethylamine under the same conditions. With ammonia instead of ethylamine, the primary, secondary, and tertiary aminocarbinols resulted, the proportion depending on the concentration of ammonia. With diethylamine, the corresponding diethylaminotrimethylcarbinol was obtained. M. ZVEGINTZOV.

Reaction between nitrous acid and certain amino-acids at 45°. C. L. A. SCHMIDT (J. Biol.

Chem., 1929, 82, 587—594).—Prolonged action of nitrous acid at 45° yielded more nitrogen than corresponded with the free amino-groups in arginine, cysteine, cystine, glycine, tryptophan, and glycyglycine; β -(α -oxindole)propionic acid yielded the whole of its nitrogen, whilst the corresponding tetrahydro-compound failed to react; other amino-acids tested reacted normally. The excess liberation of nitrogen in the anomalous cases is apparently due to secondary oxidative reactions. C. R. HARRINGTON.

Preparation of the glyceryl esters of the aliphatic amino-acids. WEIZMANN and L. HASKELBERG (Compt. rend., 1929, 189, 104—108; cf. A., 1926, 716).—*Glycine glyceryl ester*, m. p. 160—170°, and *dl-alanine glyceryl ester*, m. p. 219°, were obtained by heating the sodium salts of the respective acids with glycerol α -monochlorohydrin. They are hygroscopic compounds, almost insoluble in the usual organic solvents except methyl alcohol. Similarly, by the use of $\alpha\beta$ -*distearyl α -iodohydrin*, m. p. 52·5°, and $\alpha\beta$ -*dipalmityl α -iodohydrin*, m. p. 43·6°, prepared by Fischer's method (A., 1920, i, 807), the following were obtained: α -*glycyl- α' β -dipalmitylglyceride*, m. p. 215°; α -*glycyl- α' β -distearylglyceride*, m. p. 170°; α -*dl-alanyl- α' β -dipalmitylglyceride*, m. p. 216°; α -*dl-alanyl- α' β -distearylglyceride*, m. p. 233°; α -*dl-leucyl- α' β -dipalmitylglyceride*, m. p. 219°, and α -*dl-leucyl- α' β -distearylglyceride*, m. p. 150°. These compounds are soluble in hot water (cloudy solution) and in hot methyl and ethyl alcohols, but insoluble in most of the usual solvents. B. W. ANDERSON.

Use of aniline in preparing amino-acids. H. C. BENEDICT (J. Amer. Chem. Soc., 1929, 51, 2277).—Glycine, alanine, α -aminoisobutyric acid, and α -amino-*n*-valeric acid are conveniently isolated by adding aniline to alcoholic solutions of their hydrochlorides (cf. Cox, A., 1928, 993). H. E. F. NOTTON.

Influence of glycine on f.-p. depression. K. OGURA, T. SHIRO, and S. YAMANO (Hokkaido J. Med., 1928, 6, 421—424).—F.-p. determinations indicate combination between potassium chloride and boric acid or glycine in aqueous solution.

CHEMICAL ABSTRACTS.

[Preparation of] *dl*-alanine. E. C. KENDALL and B. F. MCKENZIE (Organic Syntheses, 1929, 9, 4—7).

Specific rotatory power of *d*-arginine. A. HUNTER (J. Biol. Chem., 1929, 82, 731—736).—*d*-Arginine has $[\alpha]_D^{20} +21\cdot94^\circ$ in presence of 1 mol. and $[\alpha]_D^{20} +26\cdot54^\circ$ in presence of 8 mols. of hydrochloric acid. Treatment of arginine in the Van Slyke apparatus with nitrous acid liberates one fourth of the total nitrogen in 5 min. C. R. HARRINGTON.

Synthesis of optically active, substituted asparagines. I. O. LUTZ (Ber., 1929, 62, [B], 1879—1884).—*l*-Bromosuccinmonoamide dissolved in water is converted by a methyl-alcoholic solution of *o*-toluidine at the atmospheric temperature into *d*-*o*-*toluidinosuccinmonoamide*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 164—166°, $[\alpha]_D^{20} -70\cdot7^\circ$ in *N*-hydrochloric acid. The following substituted *succinmonoamides* have been prepared: *d*-*p*-*toluidino*-, m. p. 100—101°, $[\alpha]_D^{20}$

—55·8° in *N*-hydrochloric acid; *d*-*o*-anisidino-, m. p. 153—154°, $[\alpha]_D^{25}$ —72·2° in 0·5*N*-hydrochloric acid; *d*-*m*-phenetidino-, $[\alpha]_D^{25}$ —71·3° in *N*-hydrochloric acid; *d*-*p*-phenetidino-, m. p. 139—140°, $[\alpha]_D^{25}$ —43·6° in 0·2*N*-hydrochloric acid; *d*-xylydino-(1:2:4-), m. p. 145—146°, $[\alpha]_D^{25}$ —67·8° in 0·2*N*-hydrochloric acid; *d*-*p*-xylydino-(1:2:5-), m. p. (indef.) 138—139°, $[\alpha]_D^{25}$ —48·2° in 3*N*-hydrochloric acid. H. WREN.

[Preparation of] cyanoacetamide. B. B. CORSON, R. W. SCOTT, and C. E. VOSE (Organic Syntheses, 1929, 9, 36—37).

[Preparation of] *n*-butyl carbamate. T. L. DAVIS and S. C. LANE (Organic Syntheses, 1929, 9, 24—26).

Ureides of brominated valeric acids. S. WEIL, J. LANGIERT, and A. KASSUR (Rocz. Chem., 1929, 9, 464—470).—The following substances have been prepared: *methylisopropylbromoacetyl bromide*, b. p. 130°/15 mm., *ethylisopropylbromoacetyl bromide*, b. p. 145°/20 mm., *menthyl methyl- and ethyl-isopropylbromoacetates*, b. p. 173—175°/20 mm., and 161°/11 mm., respectively, *bornyl methyl- and ethyl-isopropylbromoacetates*, b. p. 170°/11 mm., and 178°/10 mm., respectively, and *methyl- and ethyl-isopropylbromoacetylcarbamides*, m. p. 177—179° and 197°, respectively. The narcotic action of these ureides is no greater than that of α -bromoisovalerylcarbamide.

R. TRUSZKOWSKI.

Methylcrotononitriles. F. DE LAET (Bull. Soc. chim. Belg., 1929, 38, 163—167).— β -Methylcrotononitrile, prepared by dehydration of the cyanohydrin of isobutaldehyde, has d_4^{20} 0·83136, n_D^{20} 1·43720. This nitrile was also prepared in a less pure state by dehydration of γ -hydroxyisovaleronitrile. By the action of sulphuric acid on the nitrile the corresponding *amide*, m. p. 107—108°, was obtained. Dehydration of the cyanohydrin of methyl isopropyl ketone yielded $\alpha\beta$ -dimethylcrotononitrile, d_4^{20} 0·84321, n_D^{20} 1·44554, from which the corresponding *amide*, m. p. 130·5°, was prepared.

B. W. ANDERSON.

Tertiary phosphines containing higher alkyl radicals. W. C. DAVIES, P. L. PEARSE, and W. J. JONES (J.C.S., 1929, 1262—1268).—Tertiary phosphines have been prepared by the interaction of Grignard reagents with phosphorus trichloride (cf. Davies and Jones, this vol., 303) and with aryl-dichlorophosphines. The method is restricted by the yield of Grignard reagent and by side reactions in the case of magnesium *sec.*- and *tert.*-alkyl halides. Tri-isoalkylphosphines are more readily converted into the oxides in air than the *n*-compounds, whilst aryl derivatives are unaffected. The following are described: *Tri-n-propylphosphine*, b. p. 103·5°/50 mm., 187·5°/760 mm., d_4^{25} 0·807 (carbon disulphide compound, m. p. 108°; *mercurichloride*, m. p. 137°); *methyltri-n-propylphosphonium iodide*, m. p. 212·5°; *tetra-n-propylphosphonium bromide*, decomp. 200°; *phenyl-di-n-propylphosphine*, b. p. 159°/50 mm., d_4^{25} 0·925 (*mercurichloride*, m. p. 192·5°); *phenylmethyl-di-n-propylphosphonium iodide*, m. p. 137°; *phenyltri-n-propylphosphonium bromide*, m. p. 131·5°; *p-tolyldi-n-propylphosphine*, b. p. 174°/50 mm., d_4^{25} 0·921 (*mercurichloride*, m. p. 129·5°); *p-tolylmethyl-di-n-propylphosphonium iodide*, m. p. 81·5°; *p-tolyldi-n-propyl-*

phosphonium bromide, m. p. 125·5°; *triisobutylphosphine*, b. p. 126°/50 mm. (carbon disulphide compound; *mercurichloride*, m. p. 191·5°; *methyltriisobutylphosphonium iodide*, m. p. 287°); *phenyl-diisobutylphosphine*, b. p. 168°/50 mm., d_4^{25} 0·910 (*mercurichloride*, m. p. 158·5°); *phenylmethyl-diisobutylphosphonium iodide*, m. p. 166·5°; *p-tolyldiisobutylphosphine*, b. p. 182·5—184·5°/50 mm., d_4^{25} 0·915 (*mercurichloride*; *methiodide*); *tri-n-amylyphosphine*, b. p. 185·5°/50 mm., d_4^{25} 0·820 (carbon disulphide compound, m. p. 55°); *phenyl-di-n-amylyphosphine*, b. p. 210°/50 mm., d_4^{25} 0·902 (*mercurichloride*, m. p. 108°; *methiodide*, m. p. 90·5°); *p-tolyldi-n-amylyphosphine*, b. p. 220°/50 mm., d_4^{25} 0·898 (*mercurichloride*, m. p. 112°; *methiodide*); *tri-(dl- β -methylbutyl)phosphine*, b. p. 113—117°/10 mm.; *phenyl-di-(dl- β -methylbutyl)phosphine*, b. p. 198°/50 mm., d_4^{25} 0·906 (*mercurichloride*, m. p. 120°; *methiodide*, m. p. 150°); *p-tolyldi-(dl- β -methylbutyl)phosphine*, b. p. 210—211°/50 mm., d_4^{25} 0·902 (*mercurichloride*, m. p. 99°; *methiodide*, m. p. 131°); *tri-(γ -methylbutyl)phosphine*, b. p. 131°/11 mm. (carbon disulphide compound, m. p. 79·5°; *methiodide*); *phenyl-di-(γ -methylbutyl)phosphine*, b. p. 198·5°/50 mm., d_4^{25} 0·900 (*mercurichloride*, m. p. 152°; *methiodide*, m. p. 181·5°); *p-tolyldiisooamylyphosphine*, b. p. 210°/50 mm., d_4^{25} 0·894 (*mercurichloride*, m. p. 107°; *methiodide*, m. p. 150°); *phenyl-di-(δ -methylamyl)phosphine*, b. p. 219°/50 mm. (*methiodide*, m. p. 146°; *ethiodide*, m. p. 115·5°); *p-tolyldi-(δ -methylamyl)phosphine*, b. p. 234—235°/50 mm., d_4^{25} 0·888 (*mercurichloride*, m. p. 110·5°; *methiodide*). Where attempts were made to use magnesium isopropyl and *sec.*-butyl bromides no tertiary phosphine could be obtained. R. K. CALLOW.

Conductivity of magnesium ethyl iodide in ethereal solution. N. V. KONDYREV and A. K. SUST (Ber., 1929, 62, [B], 1856—1861).—The proportion of magnesium iodide formed during the preparation of magnesium ethyl iodide increases with diminution of the amount of ether. The equivalent conductivity of magnesium ethyl iodide in ether has been determined at 0°, 5°, 10°, 15°, and 20°. The maximal conductivity is observed at different temperatures for different concentrations; every concentration of magnesium ethyl iodide in ether corresponds with a definite degree of association of the complex. Magnesium iodide is not a component of the organometallic complex; its presence increases the conductivity additively. H. WREN.

True mixed organomagnesium carbonates. D. IVANOV (Compt. rend., 1929, 189, 51—53).—The following true mixed organomagnesium carbonates, $RO\cdot CO\cdot OMgBr$ (as distinct from mixed magnesium carboxylates, $R\cdot CO\cdot OMgBr$), have been prepared from the appropriate mixed organomagnesium alcoholate shaken with carbon dioxide in a closed flask: *ethyl*, *propyl*, *isopropyl*, *butyl*, *isobutyl*, *isoamyl*, and *cyclohexyl bromomagnesium carbonates*, also *butyl* and *benzyl chloromagnesium carbonates*. These mixed carbonates are sparingly soluble in ether, but soluble in alcohols, pyridine, etc.; when treated with water they give the corresponding alcohol and a basic of magnesium carbonate, whilst with acid they form the alcohol with evolution of carbon dioxide.

B. W. ANDERSON.

Lead tetramethyl and the application of magnesium alkyl chlorides in the preparation of organometallic compounds. E. KRAUSE (Ber., 1929, 62, [B], 1877—1878).—Apart from the question of economy, magnesium alkyl iodides are unsuitable for the preparation of organometallic compounds on account of the pronounced side reactions, the higher b. p. of the alkyl iodide residues, and the specific affinity of iodine for the metallic atom. There is no general objection to the use of bromides; with the chlorides the yields are particularly good. Lack of activity towards magnesium is overcome by the use of finely-divided metal. Lead tetramethyl is readily prepared by use of magnesium methyl chloride (the initial lead trimethyl decomposing during distillation of the ether into lead and lead tetramethyl) or from lead trimethyl bromide. During the sealing of lead tetramethyl in glass tubes, violent explosions may occur. H. WREN.

Photochemical and oxidative degradation of carbonyls. H. REIHLEN, A. GRUHL, and G. VON HESSLING (Annalen, 1929, 472, 268—287).—There is practically no reaction between ethyl mercaptan and iron penta- or nona-carbonyl in the dark at the ordinary temperature, but with an excess of the pentacarbonyl at 60° slow formation of carbon monoxide, hydrogen, and bisironmercaptotricarbonyl (I), $[\text{Fe}_2(\text{SEt})_2(\text{C}_3\text{O}_3)_2]$, m. p. 75.5° (cf. A., 1928, 1114), occurs. Irradiation of the mixture with light from a mercury-vapour lamp causes the reaction to proceed 30—50 times as fast. A mixture of the pentacarbonyl (1 vol.) and mercaptan (5 vols.) reacts at 38° according to the scheme: $2\text{Fe}(\text{CO})_5 + 2\text{EtSH} = (\text{I}) + 4\text{CO} + \text{H}_2$; a secondary reaction also occurs, probably the slow decomposition of I to iron mercaptide. With a mixture of equal vols. of the reactants at 3—5° the ratio hydrogen : carbon monoxide evolved is 1 : 9.2. This is due to the reaction $2\text{Fe}(\text{CO})_5 + 2\text{EtSH} = (\text{I}) + 3\text{CO} + \text{H}\cdot\text{CHO}$; the formaldehyde liberated is polymerised during irradiation. In both the above cases the reactions taking place are: (a) $2\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}_2(\text{CO})_9 + \text{CO}$; (b) $\text{Fe}_2(\text{CO})_9 + 2\text{EtSH} \rightarrow (\text{I}) + \text{H}_2\text{C}_3\text{O}_3$; (c) $n\text{H}_2\text{C}_3\text{O}_3 \rightarrow 3n\text{CO} + n\text{H}_2$ at the higher temperature and $\rightarrow 2n\text{CO} + n(\text{H}_2\text{CO})_n$ at the lower temperature. When a mixture of iron pentacarbonyl (1 vol.) and acetylacetone (5 mols.) is irradiated at about 130° until evolution of gas ceases, the products formed are hydrogen, carbon monoxide, ferric acetylacetone, m. p. 180°, and a substance (probably an impure peroxide of ferrous acetylacetone); 20—25% of the carbonyl is unchanged. Nickel carbonyl and acetyl chloride react at 50—55° thus: $\text{Ni}(\text{CO})_4 + 2\text{AcCl} = 4\text{CO} + \text{NiCl}_2 + \text{Ac}\cdot\text{Ac}$. The additive compound, $\text{NiCl}_2\cdot\text{C}_4\text{H}_6\text{O}_2$, is isolated; decomposition of this with water gives diacetyl. Irradiation has no influence on the reaction. In presence of oxygen about 25% of the carbon monoxide is oxidised to carbon dioxide, and acetic acid and anhydride are also produced. H. BURTON.

Spatial models of aromatic compounds and the interpretation of isomerism. S. HAECKEL (J. pr. Chem., 1929, [ii], 122, 182—200).—With the usual model of the carbon atom consisting of a ball with four stiff wires representing valencies, a model of

benzene is constructed in which the valencies form the edges of a thin hexagonal prism with carbon atoms at alternate corners; this resembles Sachse's model. The sides represent six similar parallelograms of forces. This model accounts for various properties of benzene, its hydro-derivatives, and of benzoquinone. In polycyclic compounds the analogous models, by consideration of the parallelograms of force involved, enable the positions of reactivity to be deduced in a manner resembling that of Thiele's theory. The configurations are in agreement with the results of X-ray analysis. An explanation is afforded of the existence of stereoisomeric forms of 2 : 3-diphenylindone and of 9 : 10-dihydroanthracene derivatives (Schlenk, A., 1928, 1031). R. K. CALLOW.

Atom models of aromatic compounds. H. MARK (J. pr. Chem., 1929, [ii], 122, 349).—An acknowledgment to Haackel (preceding abstract) in connexion with the work of Bergmann and Mark (this vol., 689), with whose views the latter authors are in agreement. J. W. BAKER.

Action of cyclohexene and its derivatives on organic compounds in the presence of aluminium chloride. M. D. BODROUX (Ann. Chim., 1929, [x], 11, 511—582).—Interaction of cyclohexene, b. p. 83—84°, d^{20}_4 0.809, n^{20}_D 1.445, with benzene and aluminium chloride gave chiefly phenylcyclohexane, b. p. 240°/743 mm., d^{20}_4 0.947, n^{20}_D 1.528, and a small quantity of 1 : 2-diphenylcyclohexane, m. p. 169—170°; naphthalene furnished two cyclohexylnaphthalenes, a liquid, b. p. 341—347°/747 mm., d^{20}_4 1.021, n^{20}_D 1.597, and a solid, m. p. 31° (picrate, m. p. 100—101°), which was the 2-compound, since dehydrogenation with sulphur gave 2-phenylnaphthalene, m. p. 101—102°, together with a dicyclohexylnaphthalene, m. p. 151—152°; tetrahydronaphthalene yielded a mixture of cyclohexyltetrahydronaphthalenes, b. p. 329—335°/768 mm., d^{20}_4 0.9855, n^{20}_D 1.5498, containing some of the 2-compound, since a poor yield of 2-phenylnaphthalene was obtained by dehydrogenation with sulphur at 230—250°. The following condensations were carried out in the presence of carbon disulphide and aluminium chloride: cyclohexene and diphenyl gave a mixture of two cyclohexyldiphenyls, a solid, m. p. 75—76°, and a liquid, b. p. 238—240°/30 mm., d^{20}_4 1.028, n^{20}_D 1.598, together with a little dicyclohexyldiphenyl, m. p. 205—206°; cyclohexene and diphenylmethane yielded diphenylcyclohexylmethane, b. p. 252—257°/35 mm., d^{20}_4 1.005, n^{20}_D 1.571, and *p*-benzyl-diphenyl, m. p. 85°; cyclohexene and dibenzyl furnished two cyclohexyldibenzyls, a solid, m. p. 68—69°, and a liquid, b. p. 240—244°/25 mm., d^{20}_4 0.994, n^{20}_D 1.564.

The interaction between bromine and the following hydroaromatic hydrocarbons in the presence of a small quantity of aluminium bromide has been studied: cyclohexylbenzene gave hexabromobenzene, m. p. 315—316°; cyclohexyltoluene and cyclohexylcymene gave pentabromotoluene, m. p. 281—282°; cyclohexylmesitylene yielded tribromomesitylene, m. p. 223—224°; 2-cyclohexylnaphthalene and also its liquid isomeride gave a hexabromonaphthalene, m. p. 250—252°.

cycloHexene condenses with the following phenols

in the presence of aluminium chloride and usually in carbon disulphide solution: phenol gave chlorocyclohexane, *phenyl cyclohexyl ether*, b. p. 247—249°/756 mm., d^{25} 0.999, n_D^{25} 1.527, *p*-cyclohexylphenol, m. p. 130—131° (*methyl ether*, b. p. 275.5—276.5°/748 mm., m. p. 57—58°; *ethyl ether*, m. p. 41—42°; *n*-propyl ether, m. p. 36°; *n*-butyl ether, m. p. 29°), and *o*-cyclohexylphenol, m. p. 56—57° (*methyl ether*, b. p. 267—268°/749 mm., d^{18} 1.007, n_D^{18} 1.5365; *ethyl ether*, b. p. 276—278°/750 mm., d^{21} 0.976, n_D^{21} 1.5223; *n*-propyl ether, b. p. 292—294.5°/758 mm., d^{21} 0.966, n_D^{21} 1.5198; *n*-butyl ether, b. p. 305—307°/756 mm., d^{23} 0.955, n_D^{23} 1.5137); anisole yielded cyclohexylanisole (mixture of 2- and 4-compounds, since demethylation with hydrobromic acid yielded 2- and 4-cyclohexylphenols); carvacrol gave *carvacryl cyclohexyl ether*, b. p. 305—310°, d^{19} 0.966, n_D^{19} 1.5215, and a cyclohexylcarvacrol, b. p. 315—325° (mixture of two isomerides).

I-Methyl- Δ^4 -cyclohexene, b. p. 104—105°/762 mm., d^{17} 0.804, n_D^{17} 1.442 (prepared by dehydration of 1-methyl-4-cyclohexanol with orthophosphoric acid), condenses in the presence of aluminium chloride with benzene to form dimethyldicyclohexylbenzene, b. p. 230—235°, d^{22} 0.962, n_D^{22} 1.533, and a methylcyclohexylbenzene, b. p. 247—251°/759 mm., d^{21} 0.918, n_D^{21} 1.512 (treatment of the latter with bromine and aluminium bromide afforded penta- and hexa-bromobenzenes); *p*-xylene yielded methylcyclohexyl-*p*-xylene, b. p. 275—285°, d^{24} 0.927, n_D^{24} 1.522, whilst diphenylmethane furnished methylcyclohexyldiphenylmethane, b. p. 238—248°, d^{23} 1.01, n_D^{23} 1.574 (slightly impure). In the presence of aluminium chloride menthene, b. p. 165—167°/763 mm., d^{18} 0.807, n_D^{18} 1.451 (prepared in 92% yield from menthol and orthophosphoric acid), condenses with benzene with the formation of menthylbenzene, b. p. 194—210°, d^{24} 0.9145, n_D^{24} 1.5068 (mixture of isomerides), whilst Δ^1 phenylcyclohexene condenses similarly with benzene to give a product, b. p. 267—300°, the exact nature of which was not ascertained.

A. I. VOGEL.

[Preparation of] iodobenzene. F. B. DAINS and R. Q. BREWSTER (Organic Syntheses, 1929, 9, 46—48).

I. Nitro- and halogenonitro-benzenesulphonic acids. II. Preparation and solubility in water of some salts of nitro- and halogenonitro-benzenesulphonic acids. III. Nitro- and halogenonitro-benzenesulphonic acids. J. N. ELGERSMA (Rec. trav. chim., 1929, 48, 752—764, 765—769, 770—777).—I. The following have been prepared by Blanksmä's method (A., 1901, i, 460) by oxidation of the corresponding disulphides and their properties investigated: *o*- and *p*-nitro-, 2:4-dinitro-, 4- and 5-chloro-2-nitro-, 6-chloro-3-nitro-, and 4-bromo-2-nitro-benzenesulphonic acids, all of which are found to contain varying amounts of water of crystallisation. In agreement with Hodgson and Wilson (A., 1925, i, 532), 4:4-dinitrodiphenyl disulphide can be separated by boiling alcohol into two forms, m. p. 170° (most soluble) and 181°, respectively, a small quantity of a substance, m. p. 139°, also being obtained. When equivalent quantities of 4-chloro-2-nitrobenzenesulphonic acid and aniline are heated at 185° the aniline salt, m. p. 207°, is obtained, whilst reduction

of its sodium salt with zinc dust in boiling aqueous solution yields the corresponding 2-amino-acid, converted by bromine water into 3-chloro-2:4:6-tri-bromoaniline with elimination of the sulphonic group. Fischer's proof (A., 1892, 182) of the structure of 6-chloro-3-nitrobenzenesulphonic acid is invalid, since the same *p*-phenylenediaminesulphonic acid would be obtained by treatment with alcoholic ammonia and reduction if the sulphonic group were in position 2 instead of 1. Rigid proof of the correctness of the structure assigned is, however, furnished by the following reactions. By boiling with aqueous sodium hydroxide the corresponding nitrophenolsulphonic acid, which is converted by bromine water into 2:6-dibromo-*p*-nitrophenol, is obtained, whilst by heating in a sealed tube with alcoholic ammonia the original sulphonic acid yields 3-nitro-6-aminobenzenesulphonic acid, similarly converted into 2:6-dibromo-*p*-nitroaniline, or, by elimination of the amino-group by diazotisation, into pure *m*-nitrobenzenesulphonic acid.

II. The solubilities of the alkali salts of various nitro- and halogenonitro-benzenesulphonic acids in water at 25° have been determined. The solubility of the potassium salts of *o*-, *m*-, and *p*-nitro-, 2:4-dinitro-, 4-chloro-2-nitro-, 5-chloro-2-nitro-, 6-chloro-3-nitro-, and the 4-bromo-2-nitro-acids are, respectively, 9.63, 3.04, 5.95, 4.70, 0.87, 1.59, 2.83, and 1.68 g. of anhydrous salt/100 g. of water; those of the corresponding rubidium salts are, respectively, 16.08, 6.09, 5.80, 3.90, 1.93, 1.07, 1.32, and 1.80, and of the caesium salts 20.74, >37, 5.46, 2.50, 6.98, 1.51, and 6.09 g. of anhydrous salt/100 g. of water, respectively. Although no general rule can be formulated, the introduction of a nitro-group into benzenesulphonic acid decreases the solubility of the salts investigated, a further decrease being caused by the introduction of a halogen atom or a second nitro-group independently of the positions of these groups in the benzene ring. The very sparing solubility of the potassium salt of 4-chloro-2-nitrobenzenesulphonic acid renders this acid a suitable reagent for the detection of potassium even in the presence of other metallic ions except caesium and rubidium, a concentration of 1 in 360 yielding a crystalline precipitate within 4 min. Most of the salts are anhydrous, but a few contain water of crystallisation the amount of which was determined.

III. The equivalent conductivity of the various nitro- and halogenonitro-benzenesulphonic acids and some of their salts has been determined in aqueous solution at various dilutions at 25° by the usual method. The value of λ_{∞} is almost constant for the whole series (376—378) and agrees well with the value of Rimbach or Walden for an acid composed of 18 atoms, but is in disagreement with the value of Wightman and Jones (A., 1911, ii, 689) for *m*-nitrobenzenesulphonic acid. All are strong acids and are almost completely ionised at $v=64$.

J. W. BAKER.

[Preparation of] *o*-bromotoluene. L. A. BIGELOW (Organic Syntheses, 1929, 9, 22—23).

Aromatic compounds of fluorine. III. Nitration of fluorotoluenes. G. SCHIEMANN (Ber., 1929, 62, [B], 1794—1805; cf. A., 1927, 654).—*o*-Fluoro-

toluene, b. p. 30°/26 mm., loses hydrogen fluoride with somewhat greater readiness than its isomerides. Diazotisation of *m*-toluidine and treatment of the product with hydrofluoboric acid affords *m*-tolyl-diazonium fluoborate, $C_7H_7N_2BF_4$, decomp. 108°, converted when heated into *m*-fluorotoluene, b. p. 114—115°/758 mm., in 87% yield. Nitric acid (d 1.51) is added gradually to *m*-fluorotoluene at -15° to +20° and the mixture is ultimately heated to 55°. Fractional distillation of the product combined with suitable cooling of the individual fractions gives 3-fluoro-4-nitrotoluene, m. p. 53.2° (corr.) [crystallographical data] (identified by conversion into 4-nitro-3-methoxytoluene, m. p. 60—61°), 3-fluoro-2-nitrotoluene, b. p. 92.2—92.6° (corr.)/11 mm., m. p. 17.5—18°, and, mainly, 3-fluoro-6-nitrotoluene, b. p. 97—98°/10 mm., m. p. 27—28° [oriented by transformation into 6-nitro-3-methoxytoluene, m. p. 52° (corr.)]. Reduction of 3-fluoro-6-nitrotoluene with tin and hydrochloric acid affords 5-fluoro-*o*-toluidine, b. p. 92—94°/15 mm., [picrate, m. p. 199° (decomp.) after softening and darkening at 192°; benzoyl derivative, m. p. 166°; *p*-nitrobenzoyl compound, m. p. 168°]. The amine is converted through the diazonium fluoborate, decomp. 114—115°, into 2:5-difluorotoluene, b. p. 117°/775 mm. *o*-Fluorotoluene when treated similarly to the *m*-compound (see above) yields unchanged material, 2-fluoro-5-nitrotoluene, b. p. 99.4—99.6° (corr.)/13 mm., m. p. 41.5° (oriented by conversion into 5-nitro-2-methoxytoluene, m. p. 62—63°, and 5-nitro-2-methoxybenzoic acid, m. p. 150°), and 2-fluoro-6-nitrotoluene, b. p. 97—97.2° (corr.)/11 mm., m. p. -2°. Partial nitration of *p*-fluorotoluene with nitric acid (d 1.51) at -10° to -15° affords 4-fluoro-3-nitrotoluene, b. p. 104.2° (corr.)/9 mm., m. p. +1° to +2°, and 2:6-dinitro-*p*-cresol, m. p. 81°.

H. WREN.

Chromic *p*-toluenesulphonates. G. JANTSCH and K. MECKENSTOCK (Monatsh., 1929, 52, 169—184).—Treatment of green chromic chloride with silver *p*-toluenesulphonate followed by concentration of the aqueous solution gave hydrated chromic *p*-toluenesulphonate. Crystallisation below 12° afforded a bluish-violet hydrate containing 16H₂O; vapour-pressure measurements showed that this hydrate is stable between -0.5° and +12°. The hydrate content could not be determined directly, owing to hydrolysis at about 50°; mixtures of hydrates with 8 to 12H₂O were obtained by crystallisation at ordinary temperatures. Isothermal decomposition of the bluish-violet salt at 10° and of the greyish-green mixed hydrate at 30°, over sulphuric acid established the existence of a hydrate, $[Cr(OH)_6][SO_3 \cdot C_6H_4Me, H_2O]_3$; tensimetric measurements indicated that this hydrate is stable at 61°/10 mm. Further dehydration over sulphuric acid gave a green tetrahydrate, sparingly soluble in water. Attempts to isolate the lower hydrates by crystallisation at 76° were unsuccessful, mixtures being obtained. Transport number experiments for these complexes at temperatures from 0° to 95° are described.

A. I. VOGEL.

[Preparation of] *n*-butyl *p*-toluenesulphonate. A. T. ROOS, H. GILMAN, and N. J. BEABER (Organic Syntheses, 1929, 9, 28—30).

[Preparation of] ω -nitrostyrene. D. E. WORRALL (Organic Syntheses, 1929, 9, 66—68).

Electrochemical oxidation of *m*-xylene-4-sulphonic acid. M. YOKOYAMA (Helv. Chim. Acta, 1929, 12, 756—785).—Oxidation of the above acid at a lead dioxide anode (*M*-solution, 0.04 amp./cm.² at 75—80°, 10 farad./mol.) gave as principal products: dimethylmaleic anhydride, 6-sulpho-4:5-dihydroxy-*m*-toluic acid (I), and 6-sulpho-*m*-toluic acid. By electrolysis at a lower temperature (40—50°), another product, probably sulphoisophthalic acid, was formed, and possibly fumaric acid. Using a platinum anode (*M*-solution, 0.03 amp./cm.², 50 farad./mol. at 25—35°) there were obtained (traces of) a quinone, m. p. 143—160°, the sulphonic acid I, and *m*-tolualdehyde-6-sulphonic acid (phenylhydrazone). Electrolytic oxidation of *o*-xyloquinone dissolved and suspended in sulphuric acid afforded dimethylmaleic anhydride and maleic acid, whilst that of *m*-6-xylene-4-sulphonic acid gave the sulphonic acid I accompanied by dimethylmaleic anhydride. These observations accord with the author's interpretation of the mechanism of the electrolytic oxidation of *m*-xylene-4-sulphonic acid.

R. J. W. LE FEVRE.

Aromatic compounds of fluorine. IV. Fluorine derivatives of diphenyl. G. SCHIEMANN and W. ROSELUS (Ber., 1929, 62, [B], 1805—1814; cf. this vol., 1051).—2-Aminodiphenyl is converted into the corresponding diazonium fluoborate, decomp. 80.5—81°, and thence into 2-fluorodiphenyl, m. p. 71—72°, d_4^{25} 1.2452. Diphenyl-4-diazonium fluoborate, decomp. 115.5—116°, d_4^{25} 1.430, 4-fluorodiphenyl, m. p. 74—75°, d_4^{25} 1.247, diphenyl-3-diazonium fluoborate, decomp. 90.5—91°, and 3-fluorodiphenyl, m. p. 26—27° (corr.), d_4^{25} 1.2874, are described. Treatment of 4:4'-difluorodiphenyl with nitric acid affords 4:4'-difluoro-3-nitrodiphenyl, m. p. 94.5—95°. 3:4:4'-Trifluorodiphenyl, m. p. 83°, d_4^{25} 1.481, when slowly warmed with nitric acid (d 1.40) to 100—105° gives 3:4:4'-trifluoro-5-nitrodiphenyl, m. p. 103.8° (corr.), in 88.5% yield. 3:4:4'-Trifluoro-5-aminodiphenyl, m. p. 71.5° (corr.), from the nitro-compound, tin, and hydrochloric acid, is transformed through the diazonium fluoborate, decomp. 102—102.5°, into 3:4:4:5-tetrafluorodiphenyl, m. p. 138.5—139° (corr.), d_4^{25} 1.708. 4:4'-Difluorodiphenyl is oxidised by chromic acid in presence of glacial acetic acid and vanadium pentoxide to 4-fluorobenzoic acid. This acid is also obtained when 3:4:4'-trifluoro- or 3:4:4':5-tetrafluoro-diphenyl is treated similarly.

H. WREN.

Existence and stability of free radicals. H. BURTON and C. K. INGOLD (Proc. Leeds Phil. Soc., 1929, 1, 421—431).—Theoretical. The application by Flürscheim (A., 1905, i, 614; cf. Ziegler, A., 1924, i, 308, 850) of his theory of the alternately large and small affinity-content of a consecutive series of linkings, to explain the tendency of dissociation of hexa-arylethanes, is held to be invalid, since it does not explain the dissociation of tetra-arylhydrazines, decaphenyl-*n*-butane, and hexa-*p*-nitrophenylethane. An alternative explanation is advanced, based on the observations that aryl groups are able to activate both anionotropic and prototropic systems (Burton and

Ingold, A., 1928, 634; Burton, *ibid.*, 880; this vol., 554; Ingold and Shoppee, this vol., 556, 927), and hence confer on an attached atom the power of tolerating an electric charge of either sign. The occurrence of three distinct forms of triphenylmethyl, namely, the neutral radical (electron septet), the anion, and the cation, is thus readily explained. The hypothesis predicts or interprets (where known) that (a) the dissociation of hexa-arylethanes is promoted to a greater extent by polynuclear aromatic systems than by phenyl, (b) introduction of substituents to increase the stability of the anion should also increase the stability of the free radical, (c) a similar increase in the stability of the cation should inhibit radical formation. The addition of alkali metals to olefinic hydrocarbons (Schlenk and Bergmann, A., 1928, 1031) is known to proceed only when at least one aryl group is attached to the carbon atom at which the addition of the metal occurs. A free radical is then produced (electron septet on the adjacent carbon atom) and its ultimate behaviour depends on the presence (further addition, cf. triphenylmethyl) or absence (polymerisation) of aryl groups. The production of a similar additive compound by the attachment of a conjugated, unsaturated aliphatic group indicates the possibility of existence of aliphatic free radicals. The stability of the free radicals from tetra-arylhazines and diaryl peroxides should increase with the stability of the cation, whilst a similar condition for free hydrazyls is obtained by introducing both electron-releasing and -restraining groups.

H. BURTON.

Preparation of free radicals of the triaryl-methyl series. A. E. ARBUSOV and B. A. ARBUSOV (Ber., 1929, 62, [B], 1871—1877).—Diethyl hydrogen phosphite, b. p. 72°/11 mm., prepared from phosphorus trichloride and ethyl alcohol, is converted by sodium in ether into sodium diethyl phosphite, which with triphenylmethyl chloride in benzene and ether affords diethyl triphenylmethylphosphinate, m. p. 119.5—120.5°. Triphenylmethyl bromide and sodium diethyl phosphite, in presence and absence of air, respectively, afford triphenylmethyl peroxide and triphenylmethyl; the fate of the phosphorus residue is obscure. In the presence of anhydrous alcohol the reactants give triphenylmethyl ethyl ether. In air and nitrogen, respectively, diphenyl- α -naphthylmethyl bromide and sodium diethyl phosphite in ether give diphenyl- α -naphthylmethyl peroxide and diphenyl- α -naphthylmethyl, respectively.

H. WREN.

Triphenylmethane derivatives. H. WIELAND and H. KLOSS (Annalen, 1929, 470, 201—223).—When dimagnesium acetylene bromide is treated with triphenylmethyl chloride in ether, an intensely violet product is obtained, decomposed by water to the colourless, stable *hexaphenylbutinene*, $\text{CPh}_3\text{:C:C:CPh}_3$ (I), m. p. 260°. With fuming nitric acid this gives a *hexanitro-derivative*, m. p. above 300°. The formation of the last, and the stability of the hydrocarbon towards oxidising agents, support the formula I. The formula I is also confirmed by the preparation of a tri-*p*-tolyl compound (see below). Dimagnesium phenylacetylene bromide similarly gives rise to stable *alpha-gamma-tetraphenylpropinene*, CPh:C:CPh_3 (II), m. p.

139°, which gives a *tetranitro-derivative*, m. p. 182° (decomp.), and can be reduced in presence of platinic oxide (although not of palladium-black) to *alpha-gamma-tetraphenylpropane*, m. p. 126°; using tri-*p*-tolylmethyl chloride as reagent, the product is *alpha-phenyl-gamma-tri-p-tolylpropinene* (III), m. p. 141°, which is reduced catalytically to *alpha-cyclohexyl-gamma-tri-p-tolylpropane*, m. p. 126°. During the preparation of II an intense greenish-blue halochromic effect is observed; no such effect occurs in the preparation of III.

Unsuccessful attempts were made to bring triphenylethyl chloride into reaction with a magnesium derivative. The action of diphenylmethyl chloride, however, on the derivative from acetylene gives *alpha-delta-tetraphenyl-Delta-beta-butinene* (cf. Brand, A., 1921, i, 784), a reactive substance catalytically reduced, in presence of palladium-black, to the saturated compound. From phenylacetylene, *alpha-gamma-triphenyl-Delta-beta-propinene* (IV), m. p. 79°, is formed, catalytically hydrogenated, in presence of palladium-black, to *alpha-gamma-triphenylpropane*, (V), m. p. 46°, and in presence of platinic oxide to *alpha-cyclohexyl-gamma-diphenylpropane* (VI), b. p. 160—170°/1 mm. The compound V is also prepared by reducing *alpha-gamma-triphenylpropyl alcohol* (VII) (cf. Ziegler, A., 1925, i, 131) by phosphorus and hydriodic acid. Attempted oxidation of VII to a bimolecular product, using potassium permanganate in acetone, gave instead *alpha-gamma-delta-hexaphenyl-Delta-epsilon-hexadiene* (VIII) (cf. Moureu, A., 1927, 355), which is also formed by reduction of VII, using titanium chloride. The compound VIII is analogous in structure to hexaphenylethane, and it is found that solutions of the compound, colourless below 100°, become orange-red at high temperatures, and that the mass (above 174°) is intensely red; the compound is stable towards oxygen, and a further difference from hexaphenylethane is that coloured solutions which have been cooled revert very slowly to the colourless state at 20°, although more rapidly at 80°. It is considered that the phenylacetylene group has a smaller valency requirement than phenyl.

Treatment of *alpha-delta-tetraphenyl-Delta-beta-butinene-alpha-diol* with phosphorus pentachloride in ethereal solution gave *2-chloro-3-phenyl-1-diphenylmethyleindene*, m. p. 158°, a red compound, of which the structure was determined by oxidation to benzophenone and *o*-benzoylbenzoic acid, and by reduction. Gentle reduction by hydriodic acid leads to *3-phenyl-1-diphenylmethyleindene* (cf. Brand, A., 1924, i, 720); more energetic reduction, or catalytic hydrogenation, leads to *1-phenyl-3-diphenylmethyldihydroindene*, m. p. 133° (cf. Salkind, this vol., 56); moderate reduction by hydriodic acid gives *3-phenyl-1-diphenylmethylenedihydroindene*, m. p. 115°, which can be catalytically reduced to the preceding compound.

In addition to the above, the question of hexaphenylacetone is also investigated. The interaction of sodium triphenylmethyl (Schlenk, A., 1916, i, 380) and triphenylacetyl chloride gives a *sodium ketyl* which is decomposed by water to a *ketone*, $\text{C}_{30}\text{H}_{30}\text{O}$ (IX), m. p. 183—184° (without decomp.); since this is hydrolysed to triphenylmethane and triphenylmethane-*p*-carboxylic acid, and reduced by zinc and hydrochloric acid to the *hydrocarbon*,

$\text{CHPh}_2 \cdot \text{C}_6\text{H}_4(p) \cdot \text{CH}_2 \cdot \text{CPh}_3$, m. p. 177° (different from Schlenk's hexaphenylpropane, A., 1913, i, 34), it is considered to have the structure $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4(p) \cdot \text{CO} \cdot \text{CPh}_3$. During the formation of the original ketyl, carbon monoxide was evolved, and a considerable quantity of triphenylmethyl was formed. The hexaphenylacetone of Schlenk and Bergmann (A., 1928, 1040), m. p. $80-81^\circ$, is not obtained.

Sodium triphenylmethyl and diphenylacetyl chloride give pentaphenylacetone. E. W. WIGNALL.

Bromination of *as*-diphenyldimethylethylene. K. ZIEGLER and K. BÄHR (Ber., 1929, 62, [B], 1695—1697).—*as*-Diphenyldimethylethylene is converted by cautious treatment with bromine in carbon disulphide into the very unstable *dibromide*, m. p. 57° (decomp.), transformed when heated on the water-bath into *γ -phenyl- β -methylallyl bromide*, m. p. $57-58^\circ$, identical with the product derived from *γ -phenyl- β -methylcinnamyl alcohol* and hydrogen bromide in glacial acetic acid. The bromination of $\alpha\beta$ -triphenyl- β -methylethylene therefore follows the course $\text{CPh}_2 \cdot \text{CMePh} \rightarrow \text{CPh}_2 \cdot \text{Br} \cdot \text{CBrPhMe} \rightarrow \text{CPh}_2 \cdot \text{Br} \cdot \text{CPh} \cdot \text{CH}_2 \rightarrow \text{CPh}_2 \cdot \text{CPh} \cdot \text{CH}_2 \cdot \text{Br}$. H. WREN.

Supposed "ring-inclination isomerism" with derivatives of indene. K. ZIEGLER and F. GRÖSSMANN (Ber., 1929, 62, [B], 1768—1770).—The action of sodium on 1:1:3-triphenylindene is accompanied by wandering of a phenyl group and leads to a derivative of 1:2:3-triphenylindene. The "*dihydro-1:1:3-triphenylindene*" of Schlenk and Bergmann (A., 1928, 1031) is 1:2:3-triphenylindene, reduced by sodium and amyl alcohol to *dihydro-1:2:3-triphenylidene*, m. p. 153° . H. WREN.

1-Chloronaphthalene. Chlorination of naphthalene in solution. P. FERRERO and M. FEHLMANN (Helv. Chim. Acta, 1929, 12, 583—603, and J. pr. Chem., 1929, [ii], 122, 340—343; cf. A., 1928, 627; Traubenberg and Wassermann, A., 1928, 1365).—Chlorination of naphthalene dissolved in solvents which are themselves inert to chlorine (*e.g.*, carbon tetrachloride or 1-chloronaphthalene) gives results inferior to those obtained by direct chlorination of molten naphthalene. The reverse is true of benzene and particularly of chlorobenzene. These solvents are protected from chlorination by the naphthalene even in the presence of iodine; the solvents selected must always possess considerable stability to chlorine, otherwise they protect the naphthalene. Iodine, as a catalyst, favours monohalogenation, ferric chloride promotes polyhalogenation.

Under the optimum conditions (2 mols. of naphthalene, 0.5% of iodine, 450 g. of chlorobenzene, temp. $126-128^\circ$, increase in weight 66—68 g.), the yield of 1-chloronaphthalene on the naphthalene taken is 81% and on the naphthalene consumed 92%; 6—7% of polychloronaphthalenes are also produced. R. J. W. LE FÈVRE.

peri-Dibenzyl-naphthalene and two other isomeric hydrocarbons. K. DZIEWONSKI and J. MOSZEW (Rocz. Chem., 1929, 9, 361—370).—The main

products of the reaction between benzyl chloride and naphthalene in the presence of aluminium chloride are 1- and 2-benzyl-naphthalenes. In addition, in the presence of excess of naphthalene, α - and β -*dibenzyl-naphthalenes*, m. p. 146.5° and 88° , are formed (yield 3—5%), whilst in the presence of excess of benzyl chloride γ -*dibenzyl-naphthalene*, m. p. 132° (yield 1%), is obtained. The α - and γ -isomerides do not yield picrates; that of the β -compound melts at 107° . The α -isomeride yields 1:8-dibenzoylnaphthalene (*diphenylhydrazone*, m. p. $270-271^\circ$) on oxidation with nitric acid. The following derivatives of 1:8-dibenzyl-naphthalene are prepared: 4-*nitro*-derivative, m. p. 141° , 1:8-*dibenzyl-naphthalenesulphonic acid* (aniline salt, m. p. $252-253^\circ$; chloride, m. p. 151° ; amide, m. p. 167°), and 1-benzoyl-8-benzyl-naphthalene, m. p. 113° . R. TRUSZKOWSKI.

Question of isomerism in the case of 9-phenyl-9-benzylfluorene. R. E. SCHMIDT, B. STEIN, and C. BAMBERGER (Ber., 1929, 62, [B], 1890—1891).—Attempts to repeat the preparation of the isomeric 9-phenyl-9-benzylfluorene, m. p. $125-126^\circ$, from sodium 9-phenylfluorene and benzyl chloride according to Schlenk and Bergmann (this vol., 688) gave only the previously described compound, m. p. $136-136.5^\circ$. H. WREN.

Question of instances of "non-classical" isomerism among derivatives of anthracene. E. HAACK (Ber., 1929, 62, [B], 1771—1783).—According to Schlenk and Bergmann (A., 1928, 1031), successive treatment of 9-hydroxy-9:10-diphenyl-9:10-dihydroanthracene with potassium and an alkyl halide results in the formation of a colourless, "isomeric diphenylanthracene," m. p. 214° . This product is readily obtained when the hydroxy-compound is boiled with xylene containing a little potassium or solid potassium hydroxide or by gradual addition of ethyl alcohol to a boiling solution of diphenylanthracene in xylene in presence of potassium. When heated with sulphur at 180° it evolves hydrogen sulphide and yields diphenylanthracene, m. p. 247° . Reduction of diphenylanthracene with sodium and amyl alcohol gives a *dihydrodiphenylanthracene*, m. p. $227-228^\circ$ (corr.), in addition to the previously isolated dihydro-compound, m. p. $198.5-199.5^\circ$ (corr.); either compound depresses the m. p. of the product, m. p. 214° . Schlenk's product is an additive compound of molar proportions of diphenylanthracene, m. p. 247° , and dihydrodiphenylanthracene, m. p. $227-228^\circ$ (corr.), since (1) it crystallises from arbitrary mixtures of its two components in addition to one component, (2) its spectrochemical behaviour is in harmony with this conception, (3) it is unchanged by crystallisation from ethyl acetate, acetic acid, carbon tetrachloride, toluene, and alcohol or xylene and alcohol, and (4) the f.-p. diagram indicates very clearly the existence of such a compound.

10-Hydroxy-9-phenyl-10-*o*-tolyl-9:10-dihydroanthracene is converted by potassium hydroxide and boiling xylene into 9-phenyl-10-*o*-tolylanthracene, m. p. 257° , which, with potassium and ethyl alcohol in presence of xylene, affords unchanged material and a product, m. p. $170-173^\circ$ after crystallisation from amyl alcohol. Further purification of this product

from acetic anhydride and xylene results in the isolation of 9-phenyl-10-*o*-tolyl-9:10-dihydroanthracene, m. p. 186—187°. Reduction of phenyltolylanthracene with sodium and amyl alcohol gives a somewhat ill-defined product from which the dihydro-product is separated by means of acetic anhydride and xylene but not of amyl alcohol. An additive compound of phenyltolylanthracene and its dihydro-derivative does not appear to exist. Schlenk's "isomeric phenyltolylanthracene, m. p. 172—173°," is regarded as non-homogeneous phenyltolylidihydroanthracene, probably mixed with phenyltolylanthracene, m. p. 257°, and possibly with the isomeric dihydro-derivative.

Complete reduction of 9-phenylanthracene with sodium and amyl alcohol invariably yields a product, m. p. 87°, which evolves 1 mol. of hydrogen sulphide and yields 9-phenylanthracene when heated with sulphur, and hence is regarded as 9-phenyl-9:10-dihydroanthracene. Incomplete reduction affords mixtures, m. p. 87—151° of the two compounds. This behaviour is readily explained from the m.-p. diagram, which also discloses the existence of an additive compound (1:1), m. p. 119—120°. The corresponding synthetic mixture is non-separable when crystallised from a small quantity of methyl or ethyl alcohol, but separable from larger volumes of these solvents. Baeyer's phenyldihydroanthracene, m. p. 120—120.5°, and the analogous product, m. p. 123°, of Schlenk and Bergmann are regarded as equimolecular mixtures of phenylanthracene and 9-phenyl-9:10-dihydroanthracene, m. p. 87°.

H. WREN.

Syntheses of polynuclear anthracenes. L. F. FIESER and E. M. DIETZ (Ber., 1929, 62, [B], 1827—1833; cf. Clar, this vol., 689).—2-Methyl-1:1-dinaphthyl ketone and 2-methyl-1:2'-dinaphthyl ketone have m. p. 171° and 142—143°, respectively. A methyl-1:2-dinaphthyl ketone, m. p. 154.5°, is described. Benzoyl chloride and 2-methylnaphthalene afford phenyl 2-methylnaphthyl ketone, m. p. 71°. Phenanthrene-9-carboxyl chloride and 2-methylnaphthalene give 2-methylnaphthyl 9-phenanthryl ketone, m. p. 170°, passing when heated into 1:2:3:4:5:6-tribenzanthracene, m. p. 224°; 1:2:3:4:5:6-tribenzanthraquinone has m. p. 244°. 2-Naphthoyl chloride and 2:6-dimethylnaphthalene afford 2:6-dimethyl-1:2'-dinaphthyl ketone, m. p. 111°, yielding 3'-methyl-1:2:5:6-dibenzanthracene, m. p. 244—245°, and thence 3'-methyl-1:2:5:6-dibenzanthraquinone, m. p. 223°. 1:5-Di-2'-naphthoyl-2:6-dimethylnaphthalene, m. p. 278°, from 2-naphthoyl chloride and 2:6-dimethylnaphthalene, affords 2:3:8:9-dinaphtho-1:2'-chrysene, m. p. 500°.

H. WREN.

Reduction of aromatic nitro-compounds by hydrogen in presence of platinum-black. V. VESELY and E. REIN (Coll. Czech. Chem. Comm., 1929, 1, 360—367).—See A., 1927, 757.

Aniline-*o*-sulphonic acid (orthanilic acid). H. E. FIERZ, E. SCHLITTLER, and H. WALDMANN (Helv. Chim. Acta, 1929, 12, 663—668).—A mixture of 2:2'-dinitrodiphenyl sulphide with hydrochloric and nitric acids, at 70°, is treated with chlorine. The

resulting *o*-nitrobenzenesulphonyl chloride may be hydrolysed and reduced to aniline-*o*-sulphonic acid (yield 92%) or treated with aqueous ammonia to produce *o*-aminobenzenesulphonamide, m. p. 150° (crystallographic properties described). With amyl nitrite and hydrochloric acid in ethyl alcohol it yields the diazo-anhydride, $C_6H_4 \left\langle \begin{matrix} N(N) \\ SO_2 \end{matrix} \right\rangle NH$, which is intensely sweet.

The nitrobenzenesulphonic acids obtained by nitration of benzenesulphonic acid can be separated through their ferrous salts, that of the *m*-compound being very sparingly soluble, that of the *o*-compound the most soluble.

R. J. W. LE FÈVRE.

Action of phosphoric oxide on β -anilino-butyral. F. A. MASON (J.C.S., 1929, 1560—1562; cf. A., 1925, i, 834; *ibid.*, 1926, 735).—The action of phosphoric oxide on β -anilino-butyral, in benzene at 15—100°, affords 2-methylquinoline, b. p. 244—247° (picrate, m. p. 196—197°), accompanied by aniline formed as a by-product of hydrolysis; neither di- nor tetra-hydro-2-methylquinoline is produced. An improved preparation of β -anilino-butyral is described. Attempts to condense β -chlorobutyral with toluene-*p*-sulphonamide in the presence of sodium ethoxide or amyloxide were unsuccessful.

C. W. SHOPPEE.

[Preparation of] *o*-nitroaniline. L. EHRENFELD and M. PUTERBAUGH (Organic Syntheses, 1929, 9, 64—65).

New class of organic sulphur bases. T. G. LEVI (Atti R. Accad. Lincei, 1929, [vi], 9, 790—796).

—The interaction of an aromatic amine, formaldehyde, and hydrogen sulphide proceeds differently from that occurring with aliphatic amines (this vol., 707), bases containing two aromatic amine residues to one sulphur atom being obtained: $2NH_2Ph + 3CH_2O + H_2S = C_{15}H_{16}N_2S + 3H_2O$, although possibly the arylthioformaldines are formed simultaneously. These new basic compounds apparently contain no tertiary nitrogen, as they give no methiodides, but they react with nitrous acid to form dinitroso-derivatives; their structure is to be discussed later.

Aniline yields the base $C_{15}H_{16}N_2S$, m. p. 107°; *p*-toluidine, the base, $C_{17}H_{20}N_2S$, m. p. 103°; benzylamine, the base, $C_{17}H_{20}N_2S$, m. p. 93° [hydrochloride (+2HCl), m. p. 144°; nitroso-derivative, $C_{17}H_{18}O_2N_2S$, m. p. 75°]. From the xylylides, no such bases were obtainable, but *p*-xylylidine gives *p*-xylylformothialdine,

$C_6H_3Me_2 \cdot N \left\langle \begin{matrix} CH_2 \cdot S \\ CH_2 \cdot S \end{matrix} \right\rangle CH_2$, m. p. 89—90°.

Corresponding selenium bases are obtained in a similar manner, aniline giving a base, $C_{15}H_{16}N_2Se$, b. p. 116°; *p*-toluidine, a base, m. p. 114°; benzylamine, a base, m. p. 123°; *p*-xylylidine, a base, $C_{19}H_{24}N_2Se$, m. p. 100°.

T. H. POPE.

Action of phenylcarbimide on urethanes, carbamides, and thiocarbamides. H. LAKRA and F. B. DAINS (J. Amer. Chem. Soc., 1929, 51, 2220—2225).—The following reaction products are mentioned and the mechanism of their formation is discussed: from urethane at 140—160°, ethyl phenylalophanate, phenylurethane, phenylisocyanuric acid

(I), and ethyl α -phenylbiuret- ϵ -carboxylate; from phenylurethane at 200—250°, and from ethylurethane at 175°, *s*-diphenylcarbamide (II); from ethyl allophanate at 160°, II and isocyanuric acid (III), and at 170—178°, also I; from carbamide at 100°, mainly α -phenylbiuret; at 120°, also ammonia, biuret, I, II, and III, and at 140°, mainly II; from acetylcarbamide at 130—160°, α -acetyl- γ -phenylcarbamide and III, from benzoylcarbamide at 150°, α -benzoyl- γ -phenylcarbamide; from phenylcarbamide (cf. Kuhn and Henschel, A., 1888, 474) at 100°, II, α -phenylbiuret and $\alpha\epsilon$ -diphenylbiuret; from carbanilide at 150°, $\alpha\gamma\epsilon$ -triphenylbiuret; from phenylmethylcarbamide at 135—140°, and from acetylphenylcarbamide at 200°, only II; from thiocarbamide at 100°, α -phenyl- δ -thiobiuret, m. p. 186°, which is converted by methyl iodide at 100° into the *hydriodide* of α -phenyl- δ -methylisothiobiuret (IV), $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\cdot\text{NH})\cdot\text{SMe}$, m. p. 147—148°. Mono- and di-substituted thiocarbamides give no additive products, but only II, and the corresponding alkylthiocarbimide. Methylisothiocarbamide gives at the ordinary temperature the triuret *derivative*, $\text{NPh}\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}$ (V), m. p. 142°, which is also formed from IV and phenylcarbamide, and is hydrolysed by potassium hydrogen sulphide to $\alpha\eta$ -diphenyl- δ -thiotriuret. Ethylisothiocarbamide and phenylcarbamide give an *ethyl thioether*, m. p. 145°, analogous to V. α -Phenyl- β -methylisothiocarbamide gives $\alpha\epsilon$ -diphenyl- δ -methylisothiobiuret, m. p. 108°, but $\alpha\gamma$ -diphenyl- β -methylisothiocarbamide gives at 160—170° only II, phenylthiocarbimide, and triphenylecyanuric acid, and at 200°, methyl mercaptan, II, and carbodiphenylimide. Alkylisothiocarbamides and guanidine (cf. Michael, A., 1905, i, 195) combine with 2 mols. of phenylcarbamide, but with only 1 mol. of phenylthiocarbimide (cf. Johnson, A., 1903, i, 751).

H. E. F. NOTTON.

Forced reaction of phenylcarbamide, phenylthiocarbimide, and benzophenoneanil with magnesium phenyl bromide: unusual type of $\alpha\delta$ -addition. H. GILMAN, J. E. KIRBY, and C. R. KINNEY (J. Amer. Chem. Soc., 1929, 51, 2252—2261).—Prolonged refluxing of phenylcarbamide, phenylthiocarbimide, or the intermediately formed benzophenoneanil with excess of magnesium phenyl bromide in ether and toluene gives, instead of the expected triphenylmethylaniline, mainly *o*-phenylbenzhydrilaniline (I), $\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{NPh}$, m. p. 144° [*hydrochloride*, m. p. 182.5°; (?)*benzoyl derivative*, m. p. 155—156°]. Triphenylmethylaniline does not react with the Grignard reagent under these conditions. The amine, I, is identified by its synthesis from magnesium *o*-diphenyl iodide and benzylidencaniline. *o*-Iododiphenyl, b. p. 158°/6 mm., d_4^{25} 1.6038, is prepared from *o*-aminodiphenyl (Scarborough and Waters, A., 1927, 236). The benzhydrilamine is converted by aqueous or alcoholic hydrochloric acid into 9-phenylfluorene. Attempts to prepare *o*-phenylaminotriphenylmethane by reducing *o*-phenylaminotriphenylcarbinol were unsuccessful. The action of magnesium phenyl bromide on benzophenoneanil involves a new type of $\alpha\delta$ -addition in which the reacting conjugated system is partly in the aromatic nucleus and partly in the side-chain.

H. E. F. NOTTON.

Rubrene. Nitrogenous substances from α -chloro- $\alpha\gamma$ -triphenylallylene. J. ROBIN (Compt. rend., 1929, 189, 252—254).—By the action of aniline on α -chloro- $\alpha\gamma$ -triphenylallylene a 95—100% yield of a *substance*, m. p. 199—200°, is obtained, which cannot be converted into rubrene by heating either alone or with hydrogen chloride. Since this compound is yellow (which eliminates the possible allene structure) and is not an acetylene derivative, since it is also obtained by the action of aniline and zinc chloride on phenyl β -phenylstyryl ketone (I) (into which it is converted by acid hydrolysis), it is probably γ -phenylimino- $\alpha\gamma$ -triphenyl- Δ^{α} -propylene, $\text{CPh}_2\cdot\text{CH}\cdot\text{CPh}\cdot\text{NPh}$. Similar action of ammonia yields a series of derivatives, depending mainly on temperature conditions, from which was isolated a 45—50% yield of a colourless *substance*, $\text{C}_{21}\text{H}_{17}\text{N}$, m. p. 95—96° (*hydrochloride*, m. p. 166—167°, converted into rubrene by heating), which also hydrolyses to I and is probably $\alpha\gamma$ -amino- $\alpha\gamma$ -triphenylallylene.

J. W. BAKER.

Influence of the acylating component on chlorination of the basic residue of arylsulphonylarylates. R. SCHULOFF, R. POLLAK, and E. RIESZ [with I. EISNER, G. HITSCHMANN, and M. HOPMEIER] (Ber., 1929, 62, [B], 1846—1855).—Substitution in aromatic amines generally becomes more difficult with increasing strength of the acid used in acylation of the amino-group. The preparation of homogeneous, monochlorinated amines is frequently facilitated by replacement of acetyl by aromatic sulphonyl, particularly nitrosulphonyl groups. Ease of hydrolysis of the arylsulphonylarylates is increased by diminution of the acidity of the sulphonyl component or of the basicity of the amino-component. In the case of the nitrotoluenesulphonyl derivatives it is therefore advantageous to reduce the nitro- to the amino-group previously to hydrolysis.

Chlorination of *p*-toluenesulphon-*p'*-toluidide in ethereal suspension affords *p*-toluenesulphon-2'-chloro-*p'*-toluidide, m. p. 103°, in 60—65% yield, hydrolysed to 3-chloro-*p*-toluidine. A by-product, m. p. 176°, is hydrolysed to a *trichloro-p-toluidine*, m. p. 59—60°. *o*-Nitro-*p*-toluenesulphon-*p*-toluidide, m. p. 130°, is transformed by chlorine in tetrachloroethane at 50° into the corresponding 2'-chloro-compound, m. p. 152°, in 80% yield. *o*-Amino-*p*-toluenesulphon-2'-chloro-4'-methylanilide, m. p. 123°, is described. *p*-Nitro-*o*-toluenesulphon-*p*-toluidide, m. p. 127°, gives the corresponding *monochloro-derivative*, m. p. 154°; homogeneous chlorinated products could not be obtained from β -naphthalenesulphon-*p*-toluidide, m. p. 123°. *p*-Toluenesulphon-*o*-toluidide yields *p*-toluenesulphon-4'-chloro-2'-methylanilide, m. p. 143°, whence 5-chloro-*o*-toluidine, m. p. 29—30°. *o*-Nitro-*p*-toluenesulphon-*o*-toluidide, m. p. 128°, its *monochloro-derivative*, m. p. 139°, and the corresponding *amino-compound*, m. p. 167°, are described. *o*-Toluenesulphon-*o'*-toluidide gives the corresponding *monochlorotoluidide*, m. p. 154°, whereas chlorine could not be introduced into *p*-nitro-*o*-toluenesulphon-*o*-toluidide, m. p. 177°. β -Naphthalenesulphon-*o*-toluidide, m. p. 136°, and its *monochloro-derivative*, m. p. 179°, are described. *p*-Toluenesulphon-, *o*-nitro-*p*-toluenesulphon-, *p*-nitro-*o*-toluenesulphon-, and β -naph-

thalenesulphon-anilides gave, respectively, *p*-toluenesulphon-2':4'-dichloroanilide, a non-homogeneous product, *p*-nitro-*o*-toluenesulphon-*p*'-chloroanilide, m. p. 176°, and β -naphthalenesulphon-*p*'-chloroanilide, m. p. 94°. *p*-Toluenesulphon-2':4'-dichloro-1'-naphthalide, m. p. 188°, is prepared by chlorination of *p*-toluenesulphon- α -naphthalide or *p*-toluenesulphon-4'-chloro-1'-naphthalide, m. p. 161°. *p*-Nitro-*o*-toluenesulphon- α -naphthalide, m. p. 151°, and *p*-nitro-*o*-toluenesulphon-4'-chloro-1'-naphthalide, m. p. 177°, are described. β -Naphthalenesulphon-4'-chloro-1'-naphthalide and *p*-toluenesulphon-1'-chloro-2'-naphthalide have m. p. 160° and 112—114°, respectively. Homogeneous chlorinated compounds could not be prepared from the *p*-toluenesulphon-, *o*-nitro-*p*-toluenesulphon-, *p*-nitro-*o*-toluenesulphon-, and β -naphthalenesulphon-*p*-phenetidides, m. p. 106—107°, 128°, 127°, and 97°, respectively. Di-*p*-toluenesulphonylbenzidine yields successively 3:3'-dichloro-NN'-di-*p*-toluenesulphonylbenzidine, m. p. 194°, and 3:3'-dichlorobenzidine. Di- β -naphthalenesulphonylbenzidine, m. p. 257°, and 3:3'-dichloro-NN'-di- β -naphthalenesulphonylbenzidine, m. p. 237°, are described. *p*-Toluenesulphon-2'-chloro-4'-methylanilide gives a nitro-derivative, $C_{14}H_{13}O_4N_2Cl_2$, m. p. 197°. *p*-Toluenesulphon-4'-chloro-6'-nitro-2'-methylanilide, m. p. 145°, and *p*-nitro-*o*-toluenesulphon-2'-nitro-4'-methylanilide, m. p. 189°, have been prepared. *p*-Toluenesulphon-*p*'-toluidide is converted by chlorosulphonic acid at the atmospheric temperature into *p*-toluenesulphonyl chloride and a toluidinesulphonic acid.

H. WREN.

3:5:6-Trichloro-2-amino-*p*-xylene and some derivatives. E. BUREŠ and T. RUBEŠ (Časopis Českoslov. Lék., 1928, 8, 225—231; Chem. Zentr., 1929, i, 506—507).—Acet-*p*-xylylide on chlorination, e.g., with dry chlorine in acetic acid, affords as the most highly chlorinated product 3:5:6-trichloro-2-acetamido-*p*-xylene, m. p. 222°, from which 3:5:6-trichloro-2-amino-*p*-xylene, m. p. 206° [picrate, bluish-red, m. p. 100° (decomp.); benzoyl derivative, pink, m. p. 223°], is obtained after boiling for several days with alcoholic potash. The *N*-methyl compound has m. p. 62°. Diazotisation of the amino-compound is effected with difficulty; the diazo-group is most readily replaced by chlorine and least readily by cyano- or hydroxyl groups. 3:5:6-Trichloro-2-hydroxy-*p*-xylene, m. p. 175°, is obtained by adding the corresponding diazonium sulphate to a mixture of sodium sulphate, sulphuric acid, and water at 140° (basic mercury and bismuth salts); 3:5:6-trichloro-2-methoxy-*p*-xylene has m. p. 91°, the corresponding ethoxy-compound m. p. 79°, phenoxy-compound, m. p. 101°, and acetoxy-compound, m. p. 103°. 3:5:6-Trichloro-*p*-xylene has m. p. 96°, 2:3:5:6-tetrachloro-*p*-xylene, m. p. 223°, and 3:4:6-trichloro-2:5-dimethylbenzotrile, m. p. 213°.

A. A. ELDRIDGE.

[Preparation of] **ac-tetrahydro- β -naphthylamine.** E. B. H. WASER and H. MÖLLER (Organic Syntheses, 1929, 9, 84—89).

Influence of various alcohols in the preparation of cyclic thiocarbamides. E. MARANGONI and M. J. LAMORT (Rev. Centr. Estud. Farm. Bioquim., 1928, 17, 21—26, 64—70; Chem. Zentr., 1929,

i, 503—504).—Of the alcohols used as solvents (methyl, ethyl, propyl, isobutyl, isoamyl, allyl, benzyl, and cyclohexanol; phenol was also employed) for the interaction of α -naphthylamine and carbon disulphide, ethyl and allyl alcohols gave the best yields; the presence of sulphur or xanthate is necessary, except with technical methyl alcohol, which contains acetone. Reaction did not take place when phenol, cyclohexanol, or benzyl alcohol was used.

A. A. ELDRIDGE.

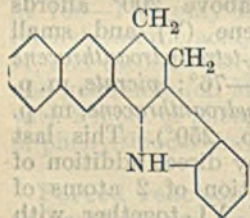
Catalytic hydrogenation under pressure in presence of nickel salts. XIII. α - and β -Hydroxy- and -amino-anthracenes. J. VON BRAUN and O. BAYER (Annalen, 1929, 472, 90—121; cf. A., 1926, 172).—When 1-hydroxyanthracene (I) is reduced with 2 atoms of hydrogen the products formed are 1-hydroxy-9:10-dihydroanthracene (II) (improved method of preparation given), 1-keto-1:2:3:4-tetrahydroanthracene (III) (semicarbazone, m. p. 250°), and an amorphous condensation product of I. Further reduction of II in decahydronaphthalene solution at 210° affords impure 1-hydroxy-1:2:3:4-tetrahydroanthracene, m. p. 109—110° (phenylcarbamide derivative, m. p. 153—154°) (readily converted by atmospheric oxygen into III), tetrahydroanthracene, and 1-keto-1:2:3:4:5:6:7:8-octahydroanthracene. The last two compounds are also obtained during the reduction of I and III. Complete reduction of I gives octahydroanthracene. Reduction of 2-hydroxyanthracene (IV), m. p. 255° (lit. 200°), with 2 atoms of hydrogen above 200° affords 2-hydroxy-9:10-dihydroanthracene (V) and small amounts of 2-hydroxy-1:2:3:4-tetrahydroanthracene (VI), m. p. 148° (acetate, m. p. 75—76°; picrate, m. p. 142°), and 2-keto-1:2:3:4-tetrahydroanthracene, m. p. 148—150° (semicarbazone, m. p. 250°). This last compound is probably formed by direct addition of hydrogen to IV. Further addition of 2 atoms of hydrogen to V yields 40% of VI together with 2-hydroxy-1:2:3:4:5:6:7:8-octahydroanthracene (VII), m. p. 122°, also formed by the addition of 4 atoms of hydrogen to VI. There is a marked tendency in these series of reductions for the replacement of hydroxyl by hydrogen.

Reduction of 1-aminoanthraquinone with zinc dust and ammonia in presence of small amounts of copper powder and potassium hydroxide gives 1-amino-9:10-dihydroanthracene (VIII), m. p. 85° (lit. 60—70°), which when heated at about 240° yields 1-aminoanthracene (IX), m. p. 127°. Treatment of this with boiling acetic acid furnishes the acetyl derivative, m. p. 212° (lit. 198°), of IX and di- α -anthrylamine, m. p. 252°. Catalytic reduction of IX in decahydronaphthalene solution at 200° results in the addition of 8 atoms of hydrogen, and the products formed are octahydroanthracene, 1-amino-1:2:3:4:5:6:7:8-octahydroanthracene, b. p. 188—193°/15 mm. (picrate, decomp. 255° after sintering at 220°; acetyl derivative, m. p. 185°), and 1-amino-5:6:7:8-tetrahydroanthracene (X), m. p. 97° (picrate, decomp. 180°; acetyl derivative, m. p. 190°). Benzenediazonium chloride converts X into the corresponding aminoazo-compound, $C_{20}H_{19}N_3$, m. p. 170°. When reduction of IX is effected with 4 atoms of hydrogen a mixture of VIII and X results; small amounts of tetrahydro-

anthracene and III are also produced. The formation of III is presumably due to the action of water (from nickel oxide and hydrogen) on IX, whereby I and ammonia are obtained. 2-Aminoanthracene (XI) is converted by reduction with 2 atoms of hydrogen chiefly into its 9:10-dihydro-derivative (XII). With 4 atoms of hydrogen the basic products are 2-amino-5:6:7:8-tetrahydroanthracene, m. p. 154° (picrate, decomp. 215° after darkening at 200°; acetyl derivative, m. p. 159—160°; phenylthiocarbimide derivative, m. p. 127°; aminoazobenzene derivative, m. p. 174°) (also obtained by reduction of XII with 2 atoms of hydrogen), and 2-amino-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 69—70° (picrate, m. p. 245° after darkening at 230°; acetyl derivative, m. p. 165°), formed also during the complete reduction of XI.

Thermal decomposition of the phenylcarbimide derivatives of VI and VII, m. p. 150° and 183°, respectively (cf. Straus and Rohrbacker, A., 1921, i, 172), affords 1:2-dihydroanthracene [1:2-diacene], m. p. 150° (picrate, m. p. 115°; dibromide, m. p. 102°), and 1:2:5:6:7:8-hexahydroanthracene [hexacene], m. p. 70°, respectively.

Reduction of III with sodium and alcohol affords no individual substance, whilst oxidation with permanganate gives phthalic and not naphthalene-2:3-dicarboxylic acid. When III is heated for a short time at its b. p. conversion into anthracene results. The phenylhydrazone, m. p. 116°, of III is converted by heating with concentrated hydrochloric acid into the dihydrocarbazole derivative (annexed formula), m. p. 245°, dehydrogenated by distillation with lead oxide or boiling with nitrobenzene into the corresponding carbazole, m. p. 325°, and oxidised by chromic and acetic acids to the corresponding o-quinone, not melted at 360°.



H. BURTON.

Thermal and hydrolytic decomposition of basic and phenolic diphenylmethane derivatives and synthesis of optically active aromatic compounds. J. VON BRAUN [with E. ANTON, W. HAENSEL, and G. WERNER] (Annalen, 1929, 472, 1—89).—Ketones condense with aromatic primary, secondary, and tertiary amines in presence of concentrated hydrochloric acid (cf. Döbner, A., 1879, 786; 1888, i, 278; also B.P. 204,722; B., 1924, 412) to give the corresponding diaminodiphenylmethane derivatives, $R' \cdot CH_2 \cdot CO \cdot R + 2C_6H_5 \cdot NR''_2 \longrightarrow R' \cdot CH_2 \cdot CR(C_6H_4 \cdot NR''_2)_2$, but a small amount of the unsaturated base, $R' \cdot CH:CR \cdot C_6H_4 \cdot NR''_2$, is also formed. This does not arise by thermal decomposition of the diamine, but can readily be obtained by heating the diamine with a small amount of hydrochloric or sulphuric acid (0.02—0.01 mol.) with subsequent distillation in a vacuum. The unsaturated base reacts with the original amine in presence of hydrochloric acid to give the diamine. Condensation occurs also with cyclic ketones, and the mechanism of the reaction is: $R' \cdot CH_2 \cdot CO \cdot R + C_6H_5 \cdot NR''_2 \longrightarrow R' \cdot CH_2 \cdot CR(OH) \cdot C_6H_4 \cdot NR''_2 \rightleftharpoons H_2O +$

$R' \cdot CH:CR \cdot C_6H_4 \cdot NR''_2 \xrightarrow{C_6H_5 \cdot NR''_2} R' \cdot CH_2 \cdot CR(C_6H_4 \cdot NR''_2)_2$. Thus, cyclohexanone (1 mol.), aniline (2 mols.), and aqueous-alcoholic hydrochloric acid (2 mols.) yield after several days at 100°, 1:1-pp'-diaminodiphenyl-cyclohexane (I), b. p. 248°/0.1 mm., m. p. 114° (hydrochloride, m. p. 235°; acetyl derivative, m. p. 266°; phenylthiocarbimide derivative, m. p. 163°), and a small amount of p-Δ¹-cyclohexenylaniline (II), b. p. 175°/14 mm. (hydrochloride, m. p. 228°; picrate, decomp. 170°; acetyl derivative, m. p. 152°; benzoyl derivative, m. p. 177°; phenylthiocarbimide derivative, m. p. 144°; benzylidene derivative, m. p. 82°). When I is heated for a short time at 100° with hydrochloric acid no change occurs, but after several days an appreciable amount of II results. Distillation of I under ordinary pressure effects little change, but conversion into II proceeds readily by the above acid-distillation treatment (general method of preparation). Reduction of II with a large excess of sodium and alcohol gives p-cyclohexylaniline, and conversion into I is effected by heating with aniline and hydrochloric acid or, better, with dry aniline hydrochloride. cycloHexanone and methylaniline afford 1:1-pp'-dimethyldiaminodiphenylcyclohexane, b. p. 250—252°/0.3 mm., m. p. 124° (hydrochloride, m. p. 220°; picrate, m. p. 105°; diacetyl derivative, m. p. 185°; bisphenylthiocarbimide derivative, m. p. 165°), and p-Δ¹-cyclohexenylmethylaniline, b. p. 184°/14 mm. (hydrochloride, m. p. 212°; picrate, m. p. 114°; acetyl derivative, m. p. 85°; nitroso-derivative, m. p. 89°). 1:1-p:p'-Tetramethyldiaminodiphenylcyclohexane, b. p. 282—283°/12 mm., m. p. 164° (hydrochloride, m. p. 180°; picrate, m. p. 148°; dimethiodide, m. p. 178°), and p-Δ¹-cyclohexenyldimethylaniline (III), b. p. 190°/14 mm., m. p. 56° (hydrochloride, m. p. 195°; picrate, m. p. 162°; methiodide, m. p. 190°), are obtained similarly from dimethylaniline. Treatment of III with aniline, diethylaniline, and α-naphthylamine hydrochlorides gives 1-p-aminophenyl-1-p-dimethylaminophenylcyclohexane, b. p. 250—255°/0.3 mm., m. p. 101° (hydrochloride, m. p. 195°; acetyl derivative, m. p. 115°), decomposed by the acid-distillation treatment into dimethylaniline and II, 1-p-dimethylaminophenyl-1-p-diethylaminophenylcyclohexane, b. p. 260—265°/0.1 mm., m. p. 108° (hydrochloride, m. p. 141—142°), and the compound C₂₄H₂₈N₂, b. p. 270—280°/0.1 mm., m. p. 152°, respectively. Treatment of III with cold, fuming hydrobromic acid during several days yields about 10% of a difficultly isolated additive compound (probably a tertiary bromide), C₁₄H₂₀NBr, m. p. 95°, which when warmed with water and magnesium carbonate yields a halogen-free substance, m. p. 45—48°, readily converted by dilute acid into III. Tetrahydroquinoline and cyclohexanone yield 1:1-ditetrahydroquinolylcyclohexane, b. p. 265—267°/0.1 mm., m. p. 114° (dinitroso-derivative, m. p. 85°; dibenzoyl derivative, m. p. 154°; bisphenylthiocarbimide derivative, m. p. 92°), and 6-Δ¹-cyclohexenyltetrahydroquinoline, b. p. 163—165°/0.1 mm. (hydrochloride, m. p. 120°; picrate, m. p. 90°), m-Toluidine and cyclohexanone do not condense in the above manner, but at 160° form a small amount of 4:6-di-Δ¹-cyclohexenyl-m-toluidine, b. p. 230—235°/12 mm. (picrate, m. p. 176—177°). Similarly, p-toluidine

yields 2:6-di- Δ^1 -cyclohexenyl-p-toluidine, m. p. 60° (picrate, m. p. 192°; benzoyl derivative, m. p. 69°), whilst small amounts of the compounds $C_{24}H_{25}N$ and $C_{18}H_{22}N_2Cl$, b. p. 200—205°/1 mm., and about 180°/1 mm., respectively, are formed from p-cyclohexyl- and p-chloro-anilines. 3-Methylcyclohexanone and aniline yield a mixture of 1:1-pp'-diaminodiphenyl-3-methylcyclohexane (IV), b. p. 285—290°/14 mm. (hydrochloride, m. p. 214°; bisphenylthiocarbimide derivative, m. p. 127°), and p- Δ^1 -3(or 5)-methylcyclohexenylaniline (V), b. p. 187—190°/14 mm. (acetyl derivative, m. p. 127°; benzoyl derivative, m. p. 178°; phenylthiocarbimide derivative, m. p. 143°). The amount of V produced is about ten times as great as of the corresponding base from cyclohexanone. Treatment of V with aniline gives IV. Dimethylaniline and 3-methylcyclohexanone afford 1:1-pp'-tetramethyldiaminodiphenyl-3-methylcyclohexane, b. p. 295°/13 mm., m. p. 109° (picrate, m. p. 164°; dimethiodide, m. p. 186°), and p-3-methylcyclohexenyldimethylaniline, b. p. 194—196°/14 mm., m. p. 38° (picrate, m. p. 162°; methiodide, m. p. 159°). 2-Methylcyclohexanone and aniline condense with difficulty, yielding a small amount of p-2-methylcyclohexenylaniline, b. p. 160°/14 mm. [chloroplatinate (?), m. p. 211—212°]. cyclopentanone and dimethylaniline at 150° furnish p-cyclopentenyldimethylaniline, b. p. 160°/12 mm., m. p. 10° (hydrochloride, m. p. 170°; picrate, m. p. 129°; methiodide, decomp. 180°) [reduced by sodium and alcohol to p-cyclopentylidimethylaniline, b. p. 156°/12 mm. (hydrochloride, m. p. 175°; picrate, m. p. 134°; methiodide, m. p. 179°)], and 1:1-p:p'-tetramethyldiaminodiphenylcyclopentane, m. p. 128° (hydrochloride, m. p. 213°; picrate, m. p. 181°; dimethiodide, decomp. 195°).

When aniline is heated with acetone in hydrochloric acid solution at 150° (B., 1924, 412) the main product is $\beta\beta$ -pp'-diaminodiphenylpropane (VI); a very small amount of p-isopropenylaniline (VII), b. p. 125—130°/vac., d_4^{20} 1.0320 (hydrochloride, m. p. 230—235°; picrate, m. p. 180°; acetyl derivative, m. p. 110—111°; phenylthiocarbimide derivative, m. p. 137°), is produced at the same time. Conversion of VI into VII is effected by the acid-distillation treatment. Polymerisation of VII occurs very readily at the ordinary temperature, forming a dimeride (VIII), probably

$NH_2 \cdot C_6H_4 \cdot CMe \cdot CH \cdot CH_2 \cdot CHMe \cdot C_6H_4 \cdot NH_2$, m. p. 173° (hydrochloride, m. p. 228°; picrate, m. p. 172°; phenylthiocarbimide derivative, m. p. 117°). Reduction of the diacetyl derivative, m. p. 205°, of VIII with hydrogen in presence of palladium and methyl alcohol gives the diacetyl derivative, m. p. 121—123°, of the base, $C_{18}H_{24}N_2$, b. p. 205—210°/0.1 mm., m. p. 50—52° (picrate, m. p. 213°; hydrochloride, not melted at 275°; bisphenylthiocarbimide derivative, m. p. 178°), converted by the usual method into the diphenol, $C_{18}H_{22}O_2$, m. p. 106—107° (dibenzoate, m. p. 117°; dimethyl ether, b. p. 192°/1.5 mm.). Acetone and methylaniline afford about 50% of $\beta\beta$ -pp'-dimethyldiaminodiphenylpropane, b. p. 190°/1.5 mm., m. p. 138° (hydrochloride, m. p. 218°; acetyl derivative, m. p. 139°; bisphenylthiocarbimide derivative, m. p. 170°), converted into p-isopropenylmethylaniline, b. p. 123—125°/14 mm., d 0.9675 (picrate, m. p. 147°),

which does not polymerise readily even at 100°. isoPropenyldimethylaniline (hydrochloride, m. p. 122°; picrate, m. p. 96°) has b. p. 120—122°/15 mm., m. p. 74°. Acetone and m-toluidine at 150—160° yield small amounts of 4:6-diisopropenyl-m-toluidine, b. p. 225—230°/8 mm. (hydrochloride, m. p. 218°; picrate, m. p. 204°), and 4-isopropenyl-m-toluidine, b. p. 150—155°/8 mm. (hydrochloride, m. p. 217°; picrate, m. p. 224°), reduced by Ladenburg's method to 4-isopropyl-m-toluidine, b. p. 141—145°/13 mm. (hydrochloride, m. p. 211°). Methyl ethyl ketone condenses with aniline, methyl- and dimethylanilines forming $\beta\beta$ -pp'-diaminodiphenyl-, b. p. 210°/3 mm., $\beta\beta$ -pp'-dimethyldiaminodiphenyl-, b. p. 240°/4 mm., m. p. 98° (bisphenylthiocarbimide derivative, m. p. 142°; diacetyl derivative, m. p. 121°), and $\beta\beta$ -p:p'-tetramethyldiaminodiphenyl-n-butane, b. p. 210—212°/0.8 mm. (hydrochloride, m. p. 125°; picrate, m. p. 80—90°; methiodide, m. p. 202°), respectively. These are converted into p-isobutenylaniline, b. p. 140—145°/14 mm. (?), d_4^{20} 0.9899 (hydrochloride, m. p. 238°; picrate, m. p. 196°; phenylthiocarbimide derivative, m. p. 131°; acetyl derivative, m. p. 121°), p-isobutenylmethylaniline, b. p. 145—150°/14 mm., and p-isobutenyldimethylaniline, b. p. 138—142°/14 mm., d_4^{20} 0.9561 (picrate, m. p. 125°; methiodide, m. p. 175°), respectively. Methyl n-butyl ketone and dimethylaniline afford 15% of $\beta\beta$ -pp'-tetramethyldiaminodiphenyl-n-hexane, b. p. 230—234°/4 mm. (dimethiodide, m. p. 196°), and 5% of p-isohexenyldimethylaniline, b. p. 160—162°/12 mm. (methiodide, m. p. 175°); with acetophenone, 20% of pp'-tetramethyldiaminotriphenylethane, m. p. 134° (dimethiodide, m. p. 188°), and 7—8% of p- α -phenylvinylidimethylaniline, b. p. 208—211°/13 mm., d^{20} 1.0409 (hydrochloride, m. p. 144°; methiodide, m. p. 170°), result. n-Butaldehyde and dimethylaniline yield $\alpha\alpha$ -p:p'-tetramethyldiaminodiphenyl-n-butane, b. p. 225—227°/0.3 mm., convertible into p-n-butenyldimethylaniline, b. p. 140—142°/12 mm., d_4^{20} 0.9395 (picrate, m. p. 99—100°), which on treatment with aniline hydrochloride gives some α -p-aminophenyl- α -p-dimethylaminophenyl-n-butane, b. p. 205—210°/0.2 mm.

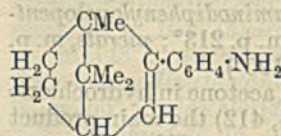
When aromatic aldehydes (1 mol.) are treated with aromatic bases (2 mols.) in presence of hydrochloric acid (2 mols.) the triphenylmethane derivative is generally formed considerably faster than from the amine (1 mol.) and the diphenylcarbinol (1 mol.), indicating in the first change an active intermediate. The change is formulated $C_6H_5 \cdot NR_2 \cdot HCl + R' \cdot CHO \rightarrow C_6H_5 \cdot NR_2 \cdot Cl \cdot CHR' \cdot OH \rightarrow CHR' \cdot C_6H_4 \cdot NR_2 \cdot Cl \rightarrow CHR'(C_6H_4 \cdot NR_2, HCl)_2$.

The condensation of ketones and phenols is best carried out in presence of hydrochloric acid (cf. Schmidlin and Lang, A., 1910, i, 836), but at a lower temperature than with amines. When the pp'-dihydroxydiphenylmethane derivatives are distilled under ordinary pressure decomposition into phenol and an unsaturated phenol usually occurs. Thus, cyclohexanone (1 mol.) and phenol (2 mols.) yield after 60 hrs. at 36°, 65% of the theoretical amount of 1:1-pp'-dihydroxydiphenylcyclohexane (IX) (dimethyl ether, b. p. 260—263°/16 mm., m. p. 82°; diacetate, m. p. 122°), which when distilled under

ordinary pressure decomposes into phenol, *p*-cyclohexylphenol (X) (methyl ether, m. p. 58°; acetate, b. p. 170°/15 mm., m. p. 35°), *p*-cyclohexenylphenol (XI), m. p. 123° (methyl ether, b. p. 155°/14 mm., m. p. 35°; acetate, m. p. 52°), and resinous products. Treatment of XI with hydrochloric acid at 100° gives X and resinous material. Hydrogenation of IX in presence of a nickel catalyst at 230—250° affords cyclohexanol, a substance, C₁₃H₂₆O₂ (probably 1-*p*-hydroxyphenyl-1-4-hydroxycyclohexylcyclohexane), and a mixture, b. p. 155—156°/15 mm., m. p. 92—93°, of *cis*- and *trans*-4-cyclohexylcyclohexanols (cf. Schrauth and Görig, A., 1923, i, 1084) (acetate, b. p. 158—160°/15 mm.). This mixture yields two phenylcarbimide derivatives, m. p. 156° and 105°, respectively, and is oxidised by chromic acid to 4-cyclohexylcyclohexanone, b. p. 145°/14 mm., m. p. 31° (lit. 28—29°) [semicarbazone, m. p. 216° (lit. 206°)]. *m*-Cresol and cyclohexanone afford a small amount of 4-cyclohexenyl-*m*-cresol, b. p. 175°/12 mm., converted by hot hydrochloric acid into 4-cyclohexyl-*m*-cresol and resinous material. 2-Methylcyclohexanone and phenol yield small amounts of methylcyclohexenylphenol, b. p. 173—175°/12 mm., and 1:1-*pp'*-dihydroxydiphenyl-2-methylcyclohexane, b. p. 280°/12 mm., m. p. 135—137°. 1:1-*pp'*-Dihydroxydiphenylcyclopentane (XII), b. p. 270°/12 mm., m. p. 155—156° (dimethyl ether, b. p. 240—245°/12 mm., m. p. 115°; diacetate, m. p. 79°), is decomposed by hydrochloric acid at 100° yielding *p*-cyclopentylphenol (XIII), b. p. 155°/12 mm., m. p. 63—65° (methyl ether, b. p. 143°/12 mm.; acetate, b. p. 150—152°/12 mm.), and thermally giving *p*-cyclopentenylphenol (XIV), m. p. 148—150° (methyl ether, m. p. 90°; acetate, m. p. 72°). Catalytic hydrogenation of XIII and XIV affords a mixture of 4-cyclopentylcyclohexanols, b. p. 135°/12 mm., oxidised to 4-cyclopentylcyclohexanone, b. p. 125°/12 mm., *n*_D²⁰ 1.4860 (semicarbazone, m. p. 195—197°). Acetone and phenol give a quantitative yield of $\beta\beta$ -*pp'*-dihydroxydiphenylpropame (XV), b. p. 250—252°/13 mm., which on thermal decomposition yields phenol, *p*-isopropylphenol, b. p. 112—115°/12 mm., m. p. 61°, and a dimeride, C₁₈H₂₀O₂ (probably a cyclobutane derivative), b. p. 255—256°/14 mm., m. p. 181° (diacetate, m. p. 165°; dimethyl ether, m. p. 115°), of *p*-isopropenylphenol. The same compound is obtained by treatment of XV with hydrochloric acid. Reduction of XV in presence of an active nickel catalyst at 260° affords cyclohexanol, 4-isopropylcyclohexanol, β -*p*-hydroxyphenyl- β -4-hydroxycyclohexylpropane, b. p. 244—248°/12 mm. [diacetate, b. p. 234—237°/16 mm.; monomethyl ether (XVI), b. p. 170—175°/1 mm.], and $\beta\beta$ -4:4'-dihydroxydicyclohexylpropane, b. p. 230—234°/14 mm. Oxidation of the last-named compound with chromic and acetic acids yields the diketone, C₁₅H₂₁O₂, m. p. 158—160° (disemicarbazone, m. p. 222°), whilst XVI furnishes the ketone, C₁₆H₂₂O₂, b. p. 205—210°/15 mm. (semicarbazone, m. p. 184°). Oxidation of XVI with cold alkaline permanganate gives 45% of β -(α -*p*-methoxyphenyl- α -methyl)ethyladipic acid, m. p. 116°. $\beta\beta$ -4:4'-Dihydroxy-di-*o*-tolylpropane has b. p. 230—235°/12 mm. $\beta\beta$ -*pp'*-Dihydroxydiphenyl-*n*-butane, b. p. 250—253°/12 mm. (cf. Zincke and Goldemann, A., 1908, i, 780), is decomposed to a mixture of phenol, *p*-isobutyl- and *p*-isobutenyl-

phenol, m. p. 86° (acetate, b. p. 148°/15 mm.). Catalytic reduction of the last-named substance yields 4-isobutylcyclohexanol, b. p. 128°/20 mm., oxidised by chromic and acetic acids to 4-isobutylcyclohexanone, b. p. 104—106°/13 mm. (semicarbazone, m. p. 190°). α -*pp'*-Dihydroxydiphenyl-*n*-butane (XVII), b. p. 270°/12 mm., on thermal decomposition yields *p*-*n*-butylphenol, b. p. 138—141°/15 mm. (acetate, b. p. 138—141°/15 mm.). Catalytic hydrogenation of XVII at 220° affords the substance, C₁₃H₂₄O₂, b. p. 235—240°/15 mm. (diacetate, b. p. 230—234°/15 mm.), and small amounts of cyclohexanol and 4-*n*-butylcyclohexanol, b. p. 120—122°/15 mm., *d*²⁰ 0.9106, *n*_D²⁰ 1.4691 (phenylcarbimide derivatives, m. p. 124° and 42°). 4-*n*-Butylcyclohexanone (semicarbazone, m. p. 175°) has b. p. 101—102°/15 mm. (?). *n*-Butaldehyde and *m*-cresol afford 4-butenyl-*m*-cresol, b. p. 150°/12 mm. (methyl ether, b. p. 130—133°/12 mm.; acetate, b. p. 140°/12 mm.), and α -4:4'-dihydroxy-di-*o*-tolyl-*n*-butane, b. p. 250°/12 mm. (diacetate, b. p. 230—235°/11 mm.), converted by treatment with hydrochloric acid into 4-*n*-butyl-*m*-cresol, b. p. 140—145°/14 mm. Catalytic hydrogenation of α -*pp'*-dihydroxydiphenylethane gives a small amount of α -*p*-hydroxyphenyl- α -4-hydroxycyclohexylethane, b. p. 240°/12 mm. (monomethyl ether, b. p. 175—178°/0.2 mm.), and α -4:4'-dihydroxydicyclohexylethane, b. p. 230°/12 mm., m. p. 140—146°, oxidised to the corresponding diketone, C₁₄H₂₂O₂, b. p. 225—230°/16 mm., m. p. 55—56° (semicarbazone, m. p. 215—217°).

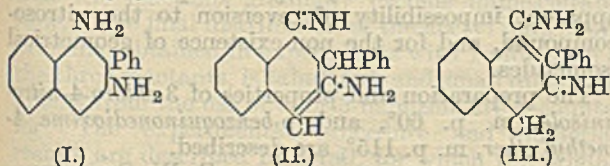
Camphor condenses with aniline in presence of 20% hydrochloric acid at 100° after 14 days yielding the compound C₁₆H₂₀N (annexed structure), b. p. 140°/0.8 mm., [α]_D²⁰ +9.49° in alcohol, whilst menthone and dimethylaniline give after 10 hrs. at 180° 1-*p*-dimethylaminophenyl-5-methyl-2-isopropyl- Δ^1 -cyclohexene, b. p. 195—205°/12 mm., [α]_D²⁰ +13° in chloroform. From *d*-3-methylcyclopentanone and -cyclohexanone and the appropriate base or phenol the following are prepared: 1:1-*pp'*-tetramethyldiaminodiphenyl-3-methylcyclopentane, m. p. 95°, [α]_D²⁰ +22.5° in chloroform; *p*-3-methylcyclopentenyl-dimethylaniline, m. p. 64°; 1:1-*pp'*-dihydroxydiphenyl-3-methylcyclohexane, b. p. 235—236°/2 mm., m. p. 153—155°, [α]_D²⁰ -18.74° in alcohol, converted by concentrated hydrochloric acid at 100° into phenol and *p*-3-methylcyclohexenylphenol, b. p. 170°/14 mm., m. p. 60—75°, [α]_D²⁰ -6.94° in benzene; 1:1-*pp'*-diaminodiphenyl-3-methylcyclohexane, [α]_D²⁰ -11.78° in chloroform; *p*-3-methylcyclohexenylaniline, [α]_D²⁰ +54.21° in alcohol, reduced by sodium and alcohol to *p*-3-methylcyclohexylaniline (XVIII), b. p. 176—178°/18 mm., [α]_D²⁰ -4.78° in alcohol; *p*-3-methylcyclohexenylmethylaniline, b. p. 192—195°/15 mm., m. p. 33°, [α]_D²⁰ +47.63° in chloroform [hydrochloride, m. p. 180°; nitroso-derivative (XIX), m. p. 50°]; 1:1-*pp'*-dimethyldiaminodiphenyl-3-methylcyclohexane, b. p. 260—265°/1.5 mm., [α]_D²⁰ -15.26° in chloroform (hydrochloride, m. p. 185°; bisphenylthiocarbimide derivative, m. p. 105°); *p*-3-methylcyclohexenyl-dimethylaniline, m. p. 48°, [α]_D²⁰ -46.69° in chloroform, and 1:1-*pp'*-tetramethyldiaminodi-



phenyl-3-methylcyclohexane, $[\alpha]_D^{20}$ -20.94° in chloroform. There are obtained from XVIII, by the usual methods, *p-3-methylcyclohexyl-phenol*, $[\alpha]_D^{20}$ -6.9° in benzene; *-benzene* (XX), b. p. 123—124°/14 mm., d_4^{20} 0.9304, n_D^{20} 1.5176, $[\alpha]_D^{20}$ -5.26° (cf. Kursanov, A., 1907, i, 600); *-bromobenzene*, b. p. 165—167°/14 mm., d_4^{20} 1.210, $[\alpha]_D^{20}$ -2.23° ; *-benzonitrile*, b. p. 166—168°/14 mm., d_4^{20} 1.0058, $[\alpha]_D^{20}$ -1.62° , and *-phenylhydrazine*, m. p. 84—85°, $[\alpha]_D^{20}$ -4.99° in alcohol (*hydrochloride*, m. p. 210°; *phenylcarbimide* derivative, m. p. 217—218°; *phenylthiocarbimide* derivative, m. p. 175°). Reduction of XIX with zinc dust and aqueous-alcoholic acetic acid gives *p-3-methylcyclohexenyl-phenylmethylhydrazine*, $\text{Me}\cdot\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}_2$, b. p. 174—176°/1 mm., m. p. 34°, $[\alpha]_D^{20}$ $+39.12^\circ$ in alcohol (*phenylthiocarbimide* derivative, m. p. 181°; *methylene* derivative, m. p. 121°; *benzylidene* derivative, m. p. 108°), whilst XX is converted by acetyl chloride in presence of aluminium chloride and carbon disulphide into *p-3-methylcyclohexylacetophenone*, b. p. 182—185°/14 mm., d_4^{20} 0.9986, $[\alpha]_D^{20}$ -3° (*semicarbazone*, m. p. 211°; *oxime*, m. p. 96—98°).

H. BURTON.

Isomerism of derivatives of 2-phenyl-naphthyl-ene-1 : 3-diamine. M. S. LESSLIE and E. E. TURNER (J.C.S., 1929, 1512—1517).—Previous work on the derivatives of 2-phenyl-naphthyl-ene-1 : 3-diamine (I) (Lees and Thorpe, J.C.S., 1907, 91, 1282; Gibson, Kentish, and Simonsen, A., 1928, 1128) is reviewed. The authors consider that the isomerism is structural in character and not stereochemical (cf. Gibson, Kentish, and Simonsen, *loc. cit.*), and it is shown that 2-phenyl-naphthyl-ene-1 : 3-diamine probably has the structure II, containing an asymmetric carbon atom, since it has been resolved. When an aqueous solution of the diamine (1 mol.) in *d*-camphorsulphonic acid (2.2 mols.) was kept, *d-2-phenyl-naphthyl-ene-1 : 3-diamine di-d-camphorsulphonate*, $[\alpha]_{D_{5461}}^{20} +40.5^\circ$, $[M]_{D_{5461}}^{20} +282.9^\circ$ (in alcohol), separated, from which dilute aqueous ammonia liberated the free *d*-base, m. p. 109—111°, $[\alpha]_{D_{5461}}^{20} +14.8^\circ$ in alcohol. By using *l*-camphorsulphonic acid, *l-2-phenyl-naphthyl-ene-1 : 3-diamine di-l-camphorsulphonate*, $[\alpha]_{D_{5461}}^{20} -40.7^\circ$, $[M]_{D_{5461}}^{20} -284.3^\circ$, was obtained.



It is suggested that on the basis of the tautomeric forms I, II, and III, by assuming that in hot acid media the diamine behaves as I, and that in cold alkaline media it behaves as III, the chemistry of the substance receives a simple and satisfactory explanation.

An improved preparation of I, m. p. 112.5—113.5°, is described.

C. W. SHOPPEE.

Derivatives of 2 : 4-dichloro-, 2 : 4 : 6-trichloro-, and 2-chloro-4-nitro-phenylhydrazines with aldehydes and ketones, particularly sugars. E. VOTOČEK and L. RYS (Coll. Czech. Chem. Comm., 1929, 1, 346—351).—2 : 4 : 6-Trichlorophenylhydrazine, m. p. 143°, and 2-chloro-4-nitrophenylhydrazine, m. p.

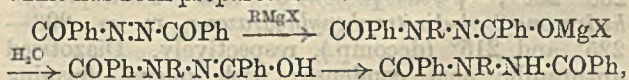
144°, are obtained by reduction of the requisite diazonium compound with stannous chloride and hydrochloric acid. 2 : 4-Dichlorophenylhydrazones, the following are described: arabinose, m. p. 161°; galactose, m. p. 181°; laevulose, m. p. 120°; acetone, m. p. 44°; benzaldehyde, m. p. 107°; salicylaldehyde, m. p. 148°; rhamnose and dextrose (gelatinous products). 2 : 4 : 6-Trichlorophenylhydrazones of rhamnose, m. p. 87—88°; dextrose, m. p. 174°; galactose, m. p. 135°; laevulose, m. p. 155°; benzaldehyde, m. p. 90°; acetone, m. p. 58° (formed in dilute aqueous solution), and 2-chloro-4-nitrophenylhydrazones of rhamnose, m. p. 135°; dextrose, m. p. 130°; galactose, m. p. 194°; laevulose, m. p. 185.5°; acetone, m. p. 121.5° (also obtained with dilute solutions), and benzaldehyde, m. p. 156°, are described. The 2 : 4-dichlorophenylsazones of rhamnose, m. p. 155°; dextrose, m. p. 209°; galactose, m. p. 150°; laevulose, m. p. 209°, and the 2-chloro-4-nitrophenylsazones of rhamnose, m. p. 190°; dextrose, m. p. 210°; galactose, m. p. 205°, and laevulose, m. p. 210°, are obtained in presence of 30% acetic acid. 2 : 4 : 6-Trichlorophenylsazones could not be obtained.

H. BURTON.

Preparation of organic reagents in the analytical laboratory. I. Diphenylcarbazine and diphenylcarbazone. K. H. ŠLOTTA and K. R. JACOBI (Z. anal. Chem., 1929, 77, 344—348).—To prepare diphenylcarbazine, 14 g. of finely-divided carbamide and 40 g. of freshly-distilled phenylhydrazine are heated at 155° for 2-25 hrs.; 250 c.c. of hot 96% alcohol are then added and the solution is boiled for about 15 min. After filtering and cooling in a freezing mixture the crystalline mass is collected, washed with ether, and air-dried. By evaporation of the mother-liquor a further yield may be obtained, bringing the total yield to 89%, calculated on the phenylhydrazine used. Diphenylcarbazone is prepared by rapidly adding, with stirring, 20 g. of finely-powdered potassium hydroxide, followed by 20 c.c. of 3% hydrogen peroxide solution, to 200 c.c. of a boiling alcoholic solution of 24 g. of diphenylcarbazine. After 5 min., 250 c.c. of 2*N*-sulphuric acid solution are added and the resulting pasty mass is diluted with 1500 c.c. of water, cooled, and filtered. The material should be recrystallised from 70—75 c.c. of alcohol, giving a yield of 50% of the theoretical.

H. F. GILLBE.

Action of magnesium alkyl and aryl halogen compounds on azodibenzoyl and benzoylazo-benzene. R. STOLLÉ and W. REICHERT (J. pr. Chem., 1929, [ii], 122, 344—349).—By the action of the appropriate Grignard reagent on azodibenzoyl a series of substituted derivatives of *s*-dibenzoylhydrazine has been prepared in accordance with the scheme



where R is ethyl, *n*-propyl (30% yield), isopropyl (poor yield), isobutyl, isoamyl (40%), phenyl (30%), and benzyl (30%). Similarly, from benzoylazo-benzene a 50% yield of *NN*-diphenyl-*N'*-benzoylhydrazine is obtained, whilst the action of magnesium phenyl bromide on methyl azodicarboxylate furnishes a poor yield of methyl phenylhydrazine-

s-dicarboxylate, m. p. 116°, identical with a specimen obtained in a similar manner to that previously used for the ethyl ester (Rupe and Labhardt, A., 1899, i, 356).

J. W. BAKER.

Relationship between quinonehydrazones and *p*-hydroxyazo-compounds. VI. *p*-Quinonedihydrazones from *p*-hydroxyazo-compounds. W. BORSCHÉ, W. MÜLLER, and C. A. BODENSTEIN (Annalen, 1929, 472, 201—216).—Oxidation of *p*-anisylsemicarbazide with chromic oxide in acetic acid solution gives 4-methoxybenzeneazofornamide (I), $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$, m. p. 157° (decomp.), which on treatment with semicarbazide hydrochloride in aqueous methyl alcohol affords *p*-benzoquinonedisemicarbazone, m. p. 251° (decomp.) (cf. A., 1904, i, 1056). With 2:4-dinitro- and 2-nitro-4-cyanophenylhydrazines in presence of methyl-alcoholic hydrochloric acid I furnishes *p*-benzoquinonesemicarbazone-2:4-dinitrophenylhydrazone (II), m. p. 242° (decomp.), and *p*-benzoquinonesemicarbazone-2-nitro-4-cyanophenylhydrazone, decomp. about 240°, respectively. Treatment of I with *p*-nitrophenylhydrazine in absence of hydrochloric acid causes reduction to *p*-anisylhydrazofornamide, and similar treatment of *p*-bromobenzeneazofornamide gives *p*-bromophenylsemicarbazide. 4-Phenoxybenzeneazofornamide has m. p. 165°. 2:4:6-Trinitro-4'-hydroxyazobenzene and 2:4-dinitrophenylhydrazine (III) react in aqueous methyl-alcoholic hydrochloric acid solution yielding *p*-benzoquinone-2:4-dinitrophenylhydrazone-2:4:6-trinitrophenylhydrazone, m. p. 204—206°. Similarly, 2:4-dinitro-4'-hydroxyazobenzene (IV) and III give *p*-benzoquinonebis-2:4-dinitrophenylhydrazone, m. p. 267—268° (decomp.), also formed from *p*-benzoquinone and III, by the action of hot, dilute hydrochloric acid on IV, and by the action of III on the benzoate, m. p. 164°, and methyl ether, m. p. 177—178°, of IV in presence of hydrochloric acid. Semicarbazide hydrochloride and phenylsemicarbazide hydrochloride convert IV into II and *p*-benzoquinonephenylsemicarbazone-2:4-dinitrophenylhydrazone, m. p. 248—250° (decomp.) (obtained also from 4-hydroxybenzeneazofornamide and III), respectively, whilst with 2-nitrophenylhydrazine hydrochloride *p*-benzoquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 236—238° (decomp.) (formed also from 2-nitro-4'-hydroxyazobenzene and III), results. From the appropriate 4-hydroxyazobenzene derivative and the hydrochloride of III the following were prepared: *p*-toluquinonebis-2:4-dinitrophenylhydrazone, m. p. 269°; *p*-toluquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 246—247° (decomp.); thymoquinone-2-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 258—260°; *p*-benzoquinone-3- and -4-nitrophenylhydrazone-2:4-dinitrophenylhydrazone, m. p. 223—225° and 215° (decomp.), respectively. Diazotised anthranilic acid condenses with phenol forming 4-hydroxyazobenzene-2'-carboxylic acid, m. p. 206—207°, which with methyl sulphate gives 4-methoxyazobenzene-2'-carboxylic acid, m. p. 170—172° (methyl ester, m. p. 105—106°). Both these acids react with III in methyl-alcoholic hydrochloric acid solution yielding *p*-benzoquinone-2:4-dinitrophenylhydrazone-2-carboxyphenylhydrazone, m. p. 226—228°.

4-Hydroxyazobenzenes react, therefore, as *p*-benzoquinonehydrazones. Elimination of the methyl group from the 4-methoxy-derivatives occurs presumably through an intermediate of the type $\text{NHR}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{OMeCl}$; this loses methyl chloride, yielding a *p*-benzoquinonehydrazone. *p*-Benzoquinonedihydrazones are formulated with a symmetrical structure (cf. Thiele and Barlow, A., 1899, i, 47).

H. BURTON.

Manufacture of water-insoluble azo-dyes [from new 6-acylamino-*m*-4-xylidines]. I. G. FARBENIND. A.-G.—See B., 1929, 637.

Nitrosation of phenols. VI. *m*-Chlorophenol. H. H. HODGSON and A. KERSHAW (J.C.S., 1929, 1553—1557).—The reported existence of 3-chlorobenzoquinone-4-oxime in stereoisomeric forms (Hodgson and Moore, *ibid.*, 1923, 123, 2499) is fallacious, and differences described are due to impurity.

The mechanism of the conversion of 3-chloro-4-nitrosophenol, m. p. 133°, into 3-chlorobenzoquinone-4-oxime is discussed from the point of view of electronic theory, the efficiency of both hydrogen and hydroxyl ions in promoting the change being satisfactorily accounted for. The action of hydriodic acid on nitroso-compounds (cf. Earl, Ellsworth, Jones, and Kenner, A., 1928, 1352) is also considered. The 3-chlorobenzoquinone-4-oxime has m. p. 184° (decomp.) (cf. Hodgson and Moore, *loc. cit.*) when obtained in either acid or alkaline media; the mol. wts. of the products and the parent nitrosophenol, determined cryoscopically in phenol and in naphthalene, are normal; the benzoate, m. p. 189·5°, and the methyl ether, m. p. 113°, are described.

The effect of the 3-chlorine atom is probably responsible for the slowness of the change of 3-chloro-4-nitrosophenol into the corresponding oxime, which is in striking contrast to the rapid action of hot acids on *p*-nitrosophenol; the behaviour of 3-bromo- and 3-iodo-nitrosophenols is similar. It is suggested that co-ordination of the chlorine atom, or its direct electronic effect, or steric hindrance, or some association of these influences, may be responsible for the apparent impossibility of reversion to the nitroso-compound, and for the non-existence of geometrical isomerides.

The preparation and properties of 3-chloro-4-nitroanisole, m. p. 60°, and *p*-benzoquinonedioxime 4-methyl ether, m. p. 115°, are described.

C. W. SHOPPEE.

[Preparation of] anisole. G. S. HIERS and F. D. HAGER (Organic Syntheses, 1929, 9, 12—14).

[Preparation of] γ -phenoxypropyl bromide. C. S. MARVEL and A. L. TANENBAUM (Organic Syntheses, 1929, 9, 72—73).

Substitution in the benzene ring. 3:4-Dibromo-*o*-anisidine and some of its derivatives. E. BUREŠ and M. SOUČEK (Časopis Českoslov. Lék., 1928, 8, 295—299, 317—325; Chem. Zentr., 1929, i, 1098—1099).—Bromination of *o*-acetanisidine in acetic acid affords 3:4-dibromo-*o*-acetanisidine, m. p. 146°, hydrolysed by potassium hydroxide at 100° in 4 days to 3:4-dibromo-*o*-anisidine, m. p. 103° (hydro-

chloride, decomp. 192°; sulphate, decomp. 159—160°). 3:4-Dibromo-*N*-methyl-*o*-anisidine has b. p. 162°, and the 2-benzamido-compound has m. p. 137—138°. 3:4-Dibromo-2-hydroxyanisole has m. p. 94° (*O*-benzoyl derivative, m. p. 114°; *O*-acetyl derivative, m. p. 90°); 3:4-dibromoanisole, b. p. 127°, 2-chloro-3:4-dibromoanisole, m. p. 98°, 2:3:4-tribromoanisole, m. p. 101°, 3:4-dibromo-2-iodoanisole, m. p. 94°.

A. A. ELDRIDGE.

Chaulmoogryl-aminophenols and -benzylamine. I. DE SANTOS and A. P. WEST (Phil. J. Sci., 1929, 38, 445—449).—Treatment of chaulmoogrylamine with appropriate chlorophenols or benzyl chloride in the presence of metallic copper gave: *chaulmoogryl-o*-, m. p. 104.9—105.9°; -*m*-, m. p. 105.9—108°; and -*p*-aminophenol, m. p. 97.8—101.9°; *chaulmoogrylbenzylamine*, m. p. 92.7—95.8°.

R. J. W. LE FÈVRE.

Reactions of a mixture of ethyl ether, acetyl bromide, and naphthol. H. L. BASSETT and K. F. TAYLOR (J.C.S., 1929, 1568—1578).—The reaction between acetyl chloride and various alcohols in ethereal solution has been examined, and found to be bimolecular, the values obtained for the velocity coefficients agreeing with the known order of reactivity of the alcohols used. With the naphthols, acetyl chloride reacted too slowly, and acetyl bromide, which was shown not to react with the solvent under the conditions used, gave the following results. The primary and most rapid reaction consists in the formation of naphthyl acetate, but secondary reactions quickly set in, which involve the solvent, and decompose the naphthyl acetate first formed. The reactions taking place may be represented by the equations: (1) $C_{10}H_7 \cdot OH + AcBr = C_{10}H_7 \cdot OAc + HBr$; (2) $2HBr + Et_2O = 2EtBr + H_2O$; (3) $2HBr + Et_2O = 2EtBr + H_2O$; (4) $C_{10}H_7 \cdot OAc + H_2O = C_{10}H_7 \cdot OH + AcOH$; (5) $2AcOH + Et_2O = 2AcOEt + H_2O$, which are in the main consecutive, and are given in order of their velocities, (1) being the most rapid. The foregoing equations, and the evidence on which they are based, are discussed *seriatim*, and it is shown that no equilibrium is ever reached, but that the reactions gradually become immeasurably slow. The final distribution of the acetyl radical and bromine, obtained in experiments with 1 mol. each of the three reactants, is tabulated, and small differences arising from the use of α - or β -naphthol are accounted for. The experimental procedure and numerical results are described in detail, for which the original should be consulted.

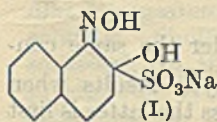
C. W. SHOPPEE.

Mechanism of hydrogen sulphite reaction with naphthol derivatives. N. N. VOROSHOV [with A. G. KASATEIN] (J. Russ. Phys. Chem. Soc., 1929, 61, 483—496).—Sulphur dioxide is passed through a 25% solution of the disodium salt of β -naphthol-1-sulphonic acid; on saturation, crystals of disodium 2-hydroxy-1:2-dihydronaphthalene-1:2-disulphonate separate. The latter substance undergoes hydrolytic dissociation in dilute solutions, sulphurous acid and the monosulphonic acid being formed. This hydrolysis amounts to 0.89% in 0.1*N*- and to 50.17% in 0.0005*N*-solutions. Hydroxyl ions augment this hydrolysis, which attains 78.8% in 0.01*N*-solutions of

the disulphonate and of sodium hydrogen carbonate. The disulphonate is stabilised by hydrogen ions, dissociation amounting to only 4.64% in the presence of 0.001*N*-hydrochloric acid.

R. TRUSZKOWSKI.

Action of sodium hydrogen sulphite on nitroso-naphthols. N. N. VOROSHOV and S. V. BOGDANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 497—514).—Sodium 2-hydroxy-1-nitroso-1:2-dihydronaphthalene-2-sulphonate (I) is prepared by the addition of saturated sodium hydrogen sulphite solution to sodium 1-nitroso- β -naphthoxide solution, and similar compounds are



obtained using the methyl ether of the latter substance and 2-hydroxy-1-nitrosonephthalene-6-sulphonic acid. β -Nitroso- α -naphthol isomeride by the formation of a soluble compound of the latter with sodium hydrogen sulphite, the α -nitroso-form being then regenerated by the action of alkalis.

R. TRUSZKOWSKI.

β -Naphthyl sulphide as a by-product in preparation of β -naphthonitrile. N. A. LANGE and H. S. HAUPT (J. Amer. Chem. Soc., 1929, 51, 2277—2278).—Crude sodium naphthalene-2-sulphonate contains di- β -naphthylsulphone, which is reduced by fusion with sodium cyanide to β -naphthyl sulphide. This is the by-product obtained by Colver and Noyes (A., 1921, i, 409) in the alkaline hydrolysis of β -naphthonitrile prepared by this method.

H. E. F. NOTTON.

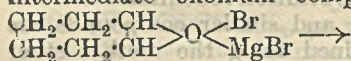
[Preparation of] phenyl- β -hydroxy- α -naphthylmethylamine. M. BETTI (Organic Syntheses, 1929, 9, 60—63).

Derivatives of 2-hydroxyfluorene. C. RUIZ (Anal. Asoc. Quim. Argentina, 1928, 16, 170—186).—The course of nitration and coupling of diazo-compounds with 2-hydroxyfluorene is analogous to that with 4-hydroxydiphenyl under the same conditions. 2-Hydroxyfluorene is prepared in 80% yield by adding fluorene-2-diazonium chloride solution slowly to boiling dilute sulphuric acid. Nitration in acetic acid (cf. Raiford and Colbert, A., 1925, i, 808) yields 1(or 3)-nitro-2-hydroxyfluorene, m. p. 145.6°, which is reduced by sodium hyposulphite to 1(or 3)-amino-2-hydroxyfluorene, m. p. 246° (acetyl derivative, m. p. 215°). The aminophenol cannot be diazotised. It yields phthalic acid on oxidation. Nitration of 2-hydroxyfluorene under vigorous conditions (cf. García Banús and Guiteras, A., 1923, i, 770) yields 1:3-dinitro-2-hydroxyfluorene, m. p. 174°, and the 1:3:7-trinitro-compound, m. p. 233°. Nitration of 2-*p*-toluenesulphonyloxyfluorene, m. p. 174°, in acetic acid and hydrolysis of the product (cf. Bell and Kenyon, A., 1927, 145) yields 7-nitro-2-hydroxyfluorene, m. p. 219—220° (Novelli, Revista Farm., 1927, 68, 244). This is reduced by aluminium amalgam to 7-amino-2-hydroxyfluorene, m. p. 291—292° (decomp., darkening at 190°), which is oxidised by dichromate and sulphuric acid to (?): 7-fluorenoquinone. The action of nitrous acid on 2-hydroxyfluorene yields only traces of the 1(or 3)-nitro-compound. 1(or 3)-Benzeneazo-2-hydroxyfluorene is obtained by coupling diazotised aniline with 2-hydroxy-

fluorene and is reduced to 1(or 3)-amino-2-hydroxy-fluorene.

R. K. CALLOW.

Conversion of a six-ring into a five-ring with magnesium bromide etherate. P. BEDOS (Compt. rend., 1929, 189, 255—257).—By the action of magnesium bromide etherate (2 mols.) in dry ether, benzene, or toluene on *cyclohexene oxide* and decomposition of the product with water a 34% yield of *cyclopentanaldehyde* is obtained, the formation of an intermediate oxonium compound being assumed:



$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CHBr} \cdot \text{OMgBr}$. Under the same conditions only a trace of the aldehyde results when 1-chloro*cyclohexan-2-ol* is used unless the latter is first treated with magnesium ethyl bromide to convert it into the magnesium alcoholate. In this case a 40% yield of *cyclopentanaldehyde* is obtained. The reaction also proceeds at the ordinary temperature and it is concluded that the transition from a six- to a five-ring is always effected through the intermediate formation of *cyclopentanaldehyde* (cf. Bedos and Ruyer, this vol., 558).

J. W. BAKER.

Esters of cyclohexane-1:4- and -1:3-diols (quinitol and resorcitol). L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1929, 189, 188—189).—The following esters of quinitol have been prepared by the action of the acid chlorides in pyridine and chloroform: *trans-dipropionate*, m. p. 75.5—76.5°; *cis-dipropionate*, m. p. 39.5—40°; *diisovalerate* (mixture of isomerides), d_4^{25} 0.9867, n_D^{25} 1.4477; *trans-cinnamate*, m. p. 189°; *cis-cinnamate*, m. p. 122°. The following esters of *cyclohexane-1:3-diol* are also described: *diacetate*, b. p. 130.5—131.5°/15 mm., d_4^{25} 1.0790, n_D^{25} 1.4494; *dipropionate*, b. p. 154°/15 mm., d_4^{25} 1.0355, n_D^{25} 1.4478; *diisovalerate*, b. p. 159—160°/6 mm., d_4^{25} 0.9806, n_D^{25} 1.4458; *di(phenylacetate)*, b. p. 215—217°/1 mm., d_4^{25} 1.1235, n_D^{25} 1.5390; *di(ethyl-oxalate)*, b. p. 187°/2 mm., d_4^{25} 1.1988, n_D^{25} 1.4604; *trans-dibenzoate*, m. p. 122.5°; *cis-dibenzoate*, m. p. 65.5°; *trans-di-p-nitrobenzoate*, m. p. 176.5°; *cis-di-p-nitrobenzoate*, m. p. 154—154.5°. By the reaction of 1:3-di(chloromethoxy)*cyclohexane* with Grignard reagents the following resorcitol ethers are obtained: *dipropyl*, b. p. 113°/15 mm., d_4^{25} 0.9006, n_D^{25} 1.4430; *diisobutyl*, b. p. 160—162°/16 mm., d_4^{25} 0.9006, n_D^{25} 1.4489; *dibenzyl*, b. p. 205—207°/1 mm., d_4^{25} 1.0739, n_D^{25} 1.5440.

R. K. CALLOW.

Reaction of resorcinol and a new coloured indicator. L. BEY and M. FALLEBIN (Compt. rend., 1929, 188, 1679—1681).—The blue colour produced by the action of dilute ammonia on resorcinol in the presence of various cations (Cd⁺⁺, Zn⁺⁺, Cu⁺⁺, Pb⁺⁺, Sn⁺⁺⁺⁺) results from oxidation, catalysed by the foregoing cations, which all afford the same colour. The coloured substance appears to be a loose compound of a colouring matter with one or more of the substances present in solution. The coloured substance, isolated by acidification and extraction with an organic solvent (amyl alcohol), acts as an indicator, being red in acid solution and turning green at p_H 9.8°; it is transformed irreversibly by concentrated ammonia solution into a second substance, which also functions

as an indicator, blue in alkaline and rose-red in acid media, the colour change occurring in the interval p_H 5.9—4.3; the substance is neither a lacmoid nor a lacmosol.

C. W. SHOPPEE.

Hoesch syntheses with thiocyanobenzene. W. BORSCHÉ and J. NIEMANN (Ber., 1929, 62, [B], 1743—1745).—Thiocyanobenzene and resorcinol are converted by hydrogen chloride and zinc chloride in presence of ether into 2:4-*dihydroxybenziminiothiophenyl ether hydrochloride*, m. p. (hydrated) 80—82° (anhydrous) decomp. 222°. The free base, m. p. 150—152°, and its *triacetyl* derivative, m. p. 115°, are described. Orcinol similarly gives the compound (OH)₂C₆H₂Me(SPh):NH₂HCl, m. p. 220° after softening. 2:4:6-*Trihydroxybenziminiothiophenyl ether hydrochloride*, m. p. 232—233° (decomp.), the free base, and the *tetra-acetyl* compound, m. p. 96—98°, are described. The hydrochloride is hydrolysed by *N*-hydrochloric acid to thiophenol and 2:4:6-*trihydroxybenzamide* (+H₂O), decomp. 255° after softening.

H. WREN.

New sulphonephthaleins. W. C. HARDEN and N. L. DRAKE (J. Amer. Chem. Soc., 1929, 51, 2278—2279).—Tetrabromo-phenoltetrabromo-sulphonephthalein (this vol., 441), for which the name "tetrabromophenol-blue" is proposed, is a better indicator than bromophenol-blue, since it shows a colour change from yellow to blue, which is not obscured by dichromatism.

H. E. F. NOTTON.

[Preparation of] phloroglucinol. H. T. CLARKE and W. W. HARTMAN (Organic Syntheses, 1929, 9, 74—76).

Constitution of "olivil" from olive resin. B. L. VANZETTI (Monatsh., 1929, 52, 163—168).—Olivil is obtained in above 50% yield by extraction of olive resin with boiling ethyl or methyl alcohol and crystallises with 1 mol. of alcohol. By heating the crystals in carbon dioxide or hydrogen, olivil is obtained as a glassy, amorphous solid, m. p. 66—70°, crystallising anhydrous, m. p. 142.5°, from acetone, trimethylcarbinol, and benzyl alcohol. The following derivatives of olivil are described: *hydrate*, m. p. about 105°; *methyl alcoholate*, m. p. about 97°; *ethyl alcoholate*, m. p. about 120°; *n-propyl alcoholate*, m. p. about 104°; *isopropyl alcoholate*, m. p. about 101.5°; and *allyl alcoholate*, m. p. 100—105°. In saturated aqueous solution, olivil has $[\alpha]_D^{25}$ —127°. It dissolves readily in strong alkalis, from which it is precipitated by carbon dioxide. Olivil contains two phenolic hydroxyl and two methoxy-groups. Dry distillation yields cresol, whilst concentrated aqueous alkali hydroxide gives vanillin; it dissolves in sulphuric acid with an intense reddish-brown colour and is precipitated on addition of water. Warming with dilute organic acids, especially acetic and formic acids, causes complete conversion into the isomeric *isoolivil*, m. p. 167°, whilst warming with dilute mineral acids (2:1000) results in complete resinification. Potassium permanganate in boiling acetic acid solution gives an almost quantitative yield of acetylvanillic acid. The following alkylated derivatives of olivil are readily prepared, exhibit greater stability than the parent substance, and are not convertible into the isomeric *isoolivil* derivatives: *dimethyl-*, m. p. 156°; *diethyl-*,

m. p. 182°; *dipropyl*-, m. p. 133.5°; *dibenzyl*-, m. p. below 150°; *ethyl*-, m. p. 145°, and *methyl-olivil*-, m. p. 238°. Isomeric monoalkylated olivils could not be prepared, the products, m. p. 169°, obtained by the ethylation of methyl- and methylation of ethyl-olivil being identical; hence the molecule possesses a symmetrical structure. Oxidation of dimethylolivil with potassium permanganate (11—12 atoms of oxygen) in alkaline solution at 100° gave about equal quantities of veratric and veratroylformic acids and also some oxalic acid; ozone had no action. Dimethylolivil and bromine gave two substitution products, a *monobromo*-, m. p. 128°, and a *dibromo-dimethyl-olivil*-, m. p. 132°; the latter is oxidised by potassium permanganate to 3-bromoveratric and 3-bromoveratroylformic acids. It is concluded that in olivil two vanillin residues are connected by means of a six-carbon chain thus: $O < \begin{matrix} C_3H_4(OH) \cdot C_6H_3(OH) \cdot OMe \\ C_3H_4(OH) \cdot C_6H_3(OH) \cdot OMe \end{matrix}$

*iso*Olivil in saturated aqueous solution has $[\alpha]_D^{25} + 352^\circ$, and gives the following alkylated derivatives: *dimethyl*-, m. p. 184.5°; *diethyl*-, m. p. 179.5°; *methyl*-, $2H_2O$, m. p. about 150°, and *ethyl-isoolivil*-, m. p. about 150°. In contradistinction to olivil, it yields two isomeric *methylethyl* derivatives, m. p. 168° and 192°, respectively. No conversion of *isoolivil* into olivil or its derivatives has yet been observed.

A. I. VOGEL.

Condensation products from *p*-halogenated phenols and aldehydes. [*di-o*-hydroxydi- and *tri-phenylmethane* derivatives]. M. WEILER, B. WENK, and H. STÖTTER, Assrs. to I. G. FARBENIND. A.-G.—See B., 1929, 636.

Salts of β -naphtholsulphonic acids, their manufacture and separation. M. L. CROSSLEY and G. S. SIMPSON, Assrs. to CALCO CHEM. Co.—See B., 1929, 637.

Manufacture of arylaminonaphthalene derivatives. I. G. FARBENIND. A.-G.—See B., 1929, 590.

Photochemical oxidising power of cholesterol and ergosterol after irradiation with mercury arc light. E. ROUSSEAU (Compt. rend. Soc. Biol., 1928, 99, 1844—1847; Chem. Zentr., 1929, i, 849).—The sterols and their aqueous and alcoholic solutions differ in their oxidising power towards iodide, but the reaction admits of determination whether or not the sterol has been irradiated. Mercury radiation of short wave-length is most effective in producing oxidation.

A. A. ELDRIDGE.

Transformations of ergosterol. A. WINDAUS and E. AUHAGEN (Annalen, 1929, 472, 185—194; cf. A., 1927, 557).—When ergosterol is heated with finely-divided nickel at 225° in an atmosphere of carbon dioxide a mixture of *ergostadienone* (I), $C_{27}H_{42}O$, m. p. 182—183°, $[\alpha]_D^{25} + 2^\circ$ (all rotatory powers are in chloroform) (*oxime*, decomp. 240—250°), and an impure isomeric *ketone* (II) (termed *u-ergostadienone*), results. Reduction of I with sodium and alcohol gives dihydroergosterol, whilst II yields *u-ergostadienol*, $C_{27}H_{44}O$, m. p. 170°, $[\alpha]_D^{25} + 42^\circ$, purified through its *acetate* (III), m. p. 128°, $[\alpha]_D^{25} + 58^\circ$. Reduction of III with hydrogen in presence of platinum and acetic acid at 60° affords the *acetate* (IV), m. p. 96°, $[\alpha]_D^{25} + 39^\circ$, of *u-ergostanol*, $C_{27}H_{48}O$,

m. p. 184°, $[\alpha]_D^{25} + 34^\circ$. These *u*-alcohols are not precipitated by digitonin. Similar treatment of dihydroergosterol (A., 1928, 1372) with nickel gives a mixture of *ergostatrienone-D* (V), $C_{27}H_{40}O$, m. p. 199—200°, $[\alpha]_D^{25} + 56^\circ$ (*oxime*, decomp. about 245°), and the isomeric *u-ergostatrienone* (VI), m. p. 130—131°, $[\alpha]_D^{25} + 53^\circ$. Etheral solutions of V and VI show absorption maxima at about 240° and 250 μ , respectively. Reduction of V with sodium and alcohol yields *ergostatrienol-D*, m. p. 165—166°, $[\alpha]_D^{25} + 22^\circ$ (*acetate*, m. p. 171°, $[\alpha]_D^{25} + 17.5^\circ$), precipitable by digitonin and formed also by the dehydrogenation of dihydroergosterol with mercuric acetate in alcoholic solution. Similar reduction of VI affords *u-ergostatrienol*, $C_{27}H_{42}O_2$, m. p. 154°, $[\alpha]_D^{25} + 88^\circ$, not precipitable by digitonin. Catalytic reduction of the *acetate*, m. p. 151°, $[\alpha]_D^{25} + 103^\circ$, of the last-named substance yields IV. The *isoergosterol* of Reindel, Walter, and Rauch (A., 1927, 241) is termed *ergosterol-B*, and the isomeride described by Windaus and Rygh (Nachr. Ges. Wiss. Göttingen, 1928, 212) is named *ergosterol-C*.

H. BURTON.

Transformations of ergosterol peroxide. A. WINDAUS, W. BERGMANN, and A. LÜTTRINGHAUS (Annalen, 1929, 472, 195—201).—When ergosterol peroxide (I), $C_{27}H_{42}O_3$ (Windaus and Brunken, A., 1928, 424), is distilled at 180—215°/0.0007 mm. an isomeric *substance* (II), m. p. 159—160°, $[\alpha]_D^{25} + 55.5^\circ$ (all rotatory powers in chloroform), is obtained. This does not give any peroxide reactions, contains one hydroxyl group (Zerevitinov determination), a keto-group, and one double linking (perbenzoic acid titration, whereby the *oxide*, $C_{27}H_{42}O_4$, m. p. 218°, $[\alpha]_D^{25} + 94.6^\circ$, results). The *monoacetate*, m. p. 168—169°, $[\alpha]_D^{25} + 41^\circ$, and the *oxime*, m. p. 260° (decomp.), are described. Magnesium methyl iodide converts II into the tertiary *alcohol*, $C_{25}H_{36}O_3$, m. p. 190°, whilst reduction with hydrogen in presence of palladium-black and alcohol gives the saturated *compound*, $C_{27}H_{44}O_3$, m. p. 152—153°, $[\alpha]_D^{25} + 94.6^\circ$ (*monoacetate*, m. p. 161°, $[\alpha]_D^{25} + 74.6^\circ$). Reduction of I with zinc dust and alkali furnishes the trihydric alcohol (III), $C_{27}H_{44}O_3$, $[\alpha]_D^{25} - 13.7^\circ$ in pyridine (cf. Windaus and Linsert, A., 1928, 1372). Energetic reduction of III with sodium and alcohol gives dihydroergosterol, whilst reduction with hydrogen in presence of palladium-black and alcohol yields *ergostendiol* (IV), $C_{27}H_{46}O_2$, m. p. 234°, $[\alpha]_D^{25} + 14.7^\circ$ [the *monoacetate* (V), m. p. 227°, $[\alpha]_D^{25} + 14.7^\circ$, contains one double linking (perbenzoic acid titration)]. This furnishes an additive compound with digitonin, and distils unchanged in a high vacuum. Reduction of V with hydrogen in presence of platinum-black and acetic acid gives *allo- α -ergostanyl acetate*. Similar reduction of I and III affords *allo- α -ergostanol*, whilst with a palladium catalyst I yields IV.

H. BURTON.

Reaction between magnesium phenyl bromide and phenylglycide. D. R. BOYD and G. J. C. VINEALL (J.C.S., 1929, 1622).—The reaction mixture from phenylglycide and etheral magnesium phenyl bromide is freed from solvent, heated at 100° until frothing occurs, and then decomposed with water. Removal of volatile products by steam distillation and subsequent acidification of the residue affords

75% of the theoretical amount of γ -phenoxy- α -phenylisopropyl alcohol (I), m. p. 92.5°. When the heating at 100° is not carried out the yield of I is negligible and an oil (probably α -bromo- γ -phenoxyisopropyl alcohol), b. p. 165°/15 mm., is isolated from the steam distillate. Phosphorus trichloride converts I into a product which with ice gives an ester of phosphorous acid, soluble in ammonia and less stable than the corresponding derivative of $\alpha\gamma$ -diphenoxyisopropyl alcohol (Boyd, J.C.S., 1901, 79, 1221).

H. BURTON.

Amino-alcohols. I. Phenyl- and *p*-tolyl-propylamine. W. H. HARTUNG and J. C. MUNCH (J. Amer. Chem. Soc., 1929, 51, 2262—2266).—Phenyl α -oximinoethyl ketone is hydrogenated almost quantitatively in presence of hydrogen chloride (3 mols.) and palladised charcoal (cf. this vol., 184) to α -hydroxy- α -phenyl- β -propylamine hydrochloride. *p*-Tolyl α -oximinoethyl ketone, m. p. 125°, is similarly reduced to the hydrochloride, m. p. 205°, of α -hydroxy- α -*p*-tolyl- β -propylamine, m. p. 112°, which is converted by nitrous acid into a product which after, but not before, distillation, gives with semicarbazide the semicarbazone of *p*-tolyl ethyl ketone. The pharmacological properties of the amino-alcohols are compared with those of ephedrine.

H. E. F. NOTTON.

Synthesis of ephedrine and related amino-alcohols. A. SKITA and F. KEIL (Z. angew. Chem., 1929, 42, 501—503).—See this vol., 808.

Preparation of β -methylamino- α -phenyl-*n*-propyl alcohol. W., K., L., W., and F. MERCK.—See B., 1929, 622.

Elimination of the amino-group from tertiary amino-alcohols. VII. Wandering of hydrocarbon radicals in derivatives of the optically active desylamines. A. MCKENZIE and A. K. MILLS (Ber., 1929, 62, [B], 1784—1794; cf. this vol., 317).—The exclusive wandering of the phenyl group during the de-amination of *l*- β -amino- $\alpha\beta$ -diphenyl- α -methyl ethanol is established by the optical inactivity of the product of the change. The product derived from *l*- β -amino- $\alpha\beta$ -diphenyl- α -1-naphthylethanol contains a small amount of *l*-1-naphthyldeoxybenzoin, but the migratory tendency of the phenyl group is much greater than that of the 1-naphthyl residue. Similarly, the action of nitrous acid on *d*- β -amino- $\alpha\beta$ -diphenyl- α -anisylethanol affords anisyl diphenylmethyl ketone containing a very small proportion of *d*-anisyldeoxybenzoin. Steric factors appear to affect the migratory tendencies of the aryl groups.

l- β -Amino- $\alpha\beta$ -diphenyl- α -methyl ethanol, m. p. 73—74°, feebly levorotatory in ethyl alcohol, is obtained by the addition of *l*-desylamine hydrochloride to magnesium methyl iodide; the hydrochloride has m. p. 266—267°, $[\alpha]_{D}^{20} +68^\circ$ in methyl alcohol, $[\alpha]_{D}^{20} +56^\circ$ in methyl alcohol (amongst other values). The *l*-alcohol is also obtained by resolution of the *r*-alcohol by *d*-camphorsulphonic acid in aqueous solution. *d*-Desylamine hydrochloride and magnesium 1-naphthyl bromide yield *l*- β -amino- $\alpha\beta$ -diphenyl- α -1-naphthylethanol, m. p. 177—178°, $[\alpha]_{D}^{17} -381^\circ$ in acetone [hydrochloride, m. p. 219—220° (decomp.), $[\alpha]_{D}^{15} -236^\circ$ in ethyl alcohol]. *r*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethanol, m. p. 161—162° (hydrochloride, m. p. 211—

212°), from *r*-desylamine hydrochloride and magnesium anisyl bromide, is converted by nitrous acid into anisyl diphenylmethyl ketone, m. p. 130—131°, and by boiling dilute hydrochloric acid into anisyldeoxybenzoin, m. p. 87.5—88° (oxime, m. p. 139—140°). *l*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethanol, m. p. 146—147°, $[\alpha]_{D}^{15} -259^\circ$ in methyl alcohol (hydrochloride, m. p. 204—206°, $[\alpha]_{D}^{15} -142^\circ$ in methyl alcohol), is prepared from *d*-desylamine hydrochloride. Resolution of the *r*-alcohol by *d*-camphorsulphonic acid in 96% alcohol affords *d*- β -amino- $\alpha\beta$ -diphenyl- α -anisylethyl *d*-camphorsulphonate, m. p. 220—221° (decomp.), $[\alpha]_{D}^{15} +97^\circ$ in methyl alcohol, from which the homogeneous *d*-alcohol, m. p. 146—147°, $[\alpha]_{D}^{15} +259^\circ$ in methyl alcohol, is derived. *l*- β -Amino- $\alpha\beta$ -diphenyl- α -anisylethyl *d*-camphorsulphonate, m. p. 211—213° (decomp.), $[\alpha]_{D}^{17} -66^\circ$ in methyl alcohol, is isolated from the mother-liquors of the resolution and yields the homogeneous *l*-alcohol. H. WREN.

Reaction between carboxylic halides and organomagnesium halides. H. GILMAN, R. E. FOTHERGILL, and H. H. PARKER (Rec. trav. chim., 1929, 48, 748—751).—Good yields of tertiary alcohols (or their ethylenic dehydration products) are obtained by the action of the Grignard reagent on carboxylic halides in appropriate proportions. Thus by the action of benzoyl chloride (0.2 mol.) on magnesium phenyl bromide (0.5 mol.) at the ordinary temperature and without refluxing the reaction mixture a 91.5% yield of pure triphenylcarbinol is obtained. From the appropriate reagents under similar conditions the following were also prepared: diphenylmethylcarbinol (39% yield), diphenylethylcarbinol (57%) $\alpha\alpha'$ -diphenyl- Δ^a -butene (84%), phenyldiethylcarbinol (93%), phenyldi-*n*-propylcarbinol (81%). An attempt to prepare secondary alcohols by the action of magnesium phenyl bromide on a suspension of cuprous chloride in dry ether saturated with dry hydrogen chloride and carbon monoxide was unsuccessful, the only products being diphenyl (31%), copper (39%), and some phenol. By the interaction of 0.3 mol. of magnesium phenyl bromide and 0.5 mol. of benzoyl chloride, a 45% yield of benzophenone is obtained, with 32.6% of triphenylcarbinol and 10.8% of diphenyl. J. W. BAKER.

Triarylmethyl carbonates: catalytic decomposition in presence of copper. J. O. HALFORD (J. Amer. Chem. Soc., 1929, 51, 2157—2162).—The formation of triphenylmethyl ether and carbon dioxide from triphenylmethyl carbonate (Gomberg, A., 1913, i, 257) in boiling xylene in presence of copper powder is practically quantitative. Diphenyl- α -naphthylmethyl carbonate, m. p. 228—230° (decomp.), is also completely decomposed, but secondary reactions prevent the isolation of the resulting ether. Diphenyl-*p*-tolylmethyl carbonate, m. p. 193—195° (decomp.), yields a trace of the impure ether. 9-Phenyl-9-fluorenyl carbonate, m. p. 218—220° (decomp.), is not decomposed under these conditions, but with copper in boiling mesitylene it gives carbon dioxide, but no phenylfluorenyl ether. The decomposition of triphenylmethyl carbonate is unimolecular at 139°, and the rate of reaction is increased only to a small extent by increasing the amount of catalyst. The effect

cannot, therefore, be explained by adsorption on a small fraction of the catalyst surface. It is suggested that the catalyst acts by increasing the concentration of some reactive intermediate product, the concentration approaching a limiting value as the amount of catalyst is increased. H. E. F. NOTTON.

Heteropolar compounds of carbon. VII. Formulation of dye salts. W. DILTHEY and R. DINKLAGE (Ber., 1929, 62, [B], 1834—1839).—Since in all the groups of dyes salts free from water can readily be obtained, the introduction of solvent into the formulæ of these compounds is arbitrary. The relationship between colourless and coloured salts is expressed: (I) $R_3C \cdot Cl$ (colourless) \rightarrow (II) $[R_3\overset{+}{C}]Cl$ (coloured, dipolar) $\xrightarrow{+O, H, N} [R_3C, C_5H_5N]Cl$ (colourless, dipolar) $\xrightarrow{H_2O} R_3C \cdot OH$ (colourless). The coloured (II) and colourless (III) carbonium salts are distinguished by the presence or absence of an unsaturated state of the central carbon atom. It is proposed to term III and II carbonium and carbenium salts, respectively. The following salts are free from water: *malachite-green perchlorate*, $C_{23}H_{25}O_4N_2Cl$; the *perchlorates* of brilliant-green, rhodamine, decomp. about 150°, crystal-violet, decomp. 190—200°, Victoria-blue, decomp. about 260—265°, pararosaniline, methylene-blue, *p*-aminotriphenylcarbinol, m. p. 209—210°; *picrate* of *p*-dimethylaminotriphenylcarbinol, m. p. 169—170°. H. WREN.

Trisubstituted stereoisomeric glycols. A. MCKENZIE, E. M. LUIS, M. TIFFENEAU, and P. WEILL (Bull. Soc. chim., 1929, [iv], 45, 414—422).—In continuation of earlier work (J.C.S., 1910, 97, 473; A., 1924, i, 825; this vol., 317) stereoisomeric glycols, $Ar \cdot CH(OH) \cdot CRR' \cdot OH$, containing the anisyl radical have been obtained by varying the order of introduction of the radicals. *p*-Anisylpropionylcarbinol (*p*-methoxyphenylhydroxymethyl ethyl ketone), b. p. 175°/15 mm., $d_{1.11}$, $n_D^{1.531}$ (*semicarbazone*, m. p. 220—222°; *oximes*, m. p. 128° and 88—89°), obtained in 48% yield from *p*-methoxyphenylglycollamide and magnesium ethyl bromide, affords with magnesium phenyl bromide 30% of α -*p*-anisyl- β -phenylbutane- $\alpha\beta$ -diol, m. p. 90° (α -isomeride). The β -isomeride, m. p. 112—113°, is similarly prepared (yield 25%) from magnesium ethyl bromide and benzoyl-*p*-anisylcarbinol (*p*-methoxybenzoin), m. p. 100—101° (*semicarbazone*, m. p. 206°; *oxime*, m. p. 132°), obtained in 25% yield from *p*-methoxyphenylglycollamide (cf. Asahina and Terasaka, A., 1923, i, 1023). Similarly, the α -*p*-anisyl- β -ethylhexane- $\alpha\beta$ -diol obtained from magnesium butyl bromide and *p*-anisylpropionylcarbinol has m. p. 74°, whilst magnesium ethyl bromide and *p*-anisylvalerylcarbinol, b. p. 204—208°/24 mm. (from *p*-anisylglycollamide) gives an isomeride, m. p. 65.5—66.5°. *p*-Anisylhydrobenzoin ($\alpha\beta$ -diphenyl- β -*p*-anisylethane- $\alpha\beta$ -diol), m. p. 203—204°, obtained by Tiffeneau and Orékhov (A., 1921, i, 565) from magnesium *p*-anisyl bromide and *r*-benzoin, is isomeric with the compound, m. p. 155—156°, obtained by the action of magnesium phenyl bromide on *p*-methoxybenzoin, m. p. 105.5—106.5° (*semicarbazone*, m. p. 185—186°; *phenylhydrazone*, m. p. 149.5—150.5°; *oxime*, m. p. 136—138°). The

last-named was obtained by adding a mixture of benzaldehyde and *p*-anisaldehyde to an aqueous-alcoholic solution of potassium cyanide (cf. Ekecrantz and Ahlqvist, A., 1908, i, 991); with copper sulphate in aqueous pyridine it affords *p*-methoxybenzil, m. p. 62—63°. Both *p*-anisylhydrobenzoin yield *p*-anisyldeoxybenzoin, m. p. 85—86°, on dehydration with sulphuric acid at 50°. R. BRIGHTMAN.

Halogen-substituted aromatic pinacols: formation of ketyl radicals, $CR_2(OMgI)$. M. GOMBERG and J. C. BAILLAR, jun. (J. Amer. Chem. Soc., 1929, 51, 2229—2238).—Quantitative experiments show that *m*- and *p*-halogenated benzophenones are reduced by magnesium and magnesium iodide to the corresponding pinacols (cf. A., 1927, 1190). *o*-Substituted derivatives undergo, in addition, dehalogenation. Reduction proceeds much more slowly than with the ketones previously examined and magnesium bromide cannot be substituted for the iodide. The following benzophenones were prepared: *p*-chloro-*p*'-bromo-, m. p. 150°; *o*-bromo-*p*'-phenyl-, m. p. 88.5°; *m*-bromo-*p*'-phenyl-, m. p. 119°, and *p*-bromo-*p*'-phenyl-, m. p. 188°, also the following derivatives of ethylene glycol: $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*p*-bromophenyl- (I), $\alpha\beta$ -diphenyl- $\alpha\beta$ -di-*m*-bromophenyl-, tetra-*p*-bromophenyl-, tetra-*m*-bromophenyl-, m. p. 152—156°; $\alpha\beta$ -di-*m*-bromophenyl- $\alpha\beta$ -di-*p*-bromophenyl-, m. p. 160—163°; $\alpha\beta$ -di-*p*-chlorophenyl- $\alpha\beta$ -di-*p*-bromophenyl- (II), m. p. 169°; $\alpha\beta$ -di-*p*-bromophenyl- $\alpha\beta$ -di-*p*-diphenyl- (III), m. p. 158—159°; and $\alpha\beta$ -di-*m*-bromophenyl- $\alpha\beta$ -di-*p*-diphenyl- (IV), m. p. 175°. 1:4-*Di*-*m*-bromobenzoylbenzene has m. p. 217—220°, and 1:3-*di*-*m*-bromobenzoylbenzene, m. p. 172°. The iodomagnesium pinacoloxides [$CR^1R^2(OMgI)$]₂, derived from I, II, and III, are colourless in the solid state, but give coloured solutions which do not obey Beer's law (in complete absence of oxygen). This indicates that they are in equilibrium with highly coloured ketyl radicals. The comparative migratory tendencies of the *p*-diphenyl-, *p*-bromophenyl, and *m*-bromophenyl groups in the pinacol-pinacol rearrangement, calculated indirectly, are 16.5:1.0:0 (cf. Montagne, A., 1910, i, 323, 324; Koopal, A., 1915, i, 693). The ratio given by the following experiments is 21.5:1.0:0. The pinacol, III, is converted to the extent of 96.5% by acetyl chloride in benzene and acetic acid into *p*-bromophenyl *p*-bromophenylbis-*p*-diphenylmethyl ketone, m. p. 227°, and to the extent of 4.5% into the isomeric ketone (not isolated). IV is converted almost completely into *m*-bromophenyl *m*-bromophenylbis-*p*-diphenylmethyl ketone, m. p. 202—203°. The pinacols are hydrolysed by alcoholic potassium hydroxide to *p*-bromo-, m. p. 186°, and *m*-bromo-, m. p. 143°, -phenylbis-*p*-diphenylmethanes, respectively, which were synthesised for comparison from *p*-bromo-, m. p. 248—250°, and *m*-bromo-, m. p. 304°, -phenylbis-*p*-diphenylcarbinols. H. E. F. NOTTON.

Geometrical isomerides of tetraphenylbutenediol. J. SALKIND and V. TETERIN (Ber., 1929, 62, [B], 1746—1750).—The individuality of the β -form of tetraphenylbutenediol is established by the determination of the solubilities of it, tetraphenylbutenediol, and tetraphenylbutinenediol in benzene and ethyl alcohol and the possibility that it is a mixture of the

saturated glycol with the acetylenic or α -ethylenic glycol is excluded, since such mixtures are readily separated into their components; this is not the case with a mixture of the β -compound and the saturated glycol. Catalytic hydrogenation of tetraphenylbutenediol in presence of colloidal palladium gives the highest yields of the β -tetraphenylbutenediol, m. p. 195—196°, when the reaction occurs slowly. Treatment of tetraphenylbutenediol with bromine in chloroform yields 3 : 4-dibromo-2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran, m. p. 198° (cf. Kruglov, unpublished work). Under similar conditions, tetraphenylbutenediol affords tetraphenyltetrahydrofuran, m. p. 182°, and $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m. p. 192—193°. α -Tetraphenylbutenediol gives 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran and a dibromide, $C_{23}H_{20}Br_2$ or $C_{23}H_{22}Br_2$, m. p. 192°, also obtainable from the furan; when very cautiously treated a (?) pentabromide, m. p. 110°, can be isolated which passes when warmed into the dibromide. β -Tetraphenylbutenediol reacts rather more readily than the α -compound with bromine, giving the dibromide, m. p. 192°. Oxidation of the β -isomeride with permanganate yields benzophenone and benzoic acid. Hydrogenation of either butenediol affords tetraphenylbutane-diol, m. p. 202°.

H. WREN.

[Preparation of] *o*-chlorobenzoyl chloride. H. T. CLARKE and E. R. TAYLOR (Organic Syntheses, 1929, 9, 34—35).—*o*-Chlorobenzaldehyde is treated with chlorine.

A. A. ELDRIDGE.

[Preparation of] ammonium hydrogen sulphobenzoate. H. T. CLARKE and E. E. DREGER (Organic Syntheses, 1929, 9, 1—2).

[Preparation of] *o*-sulphobenzoic anhydride. H. T. CLARKE and E. E. DREGER (Organic Syntheses, 1929, 9, 80—82).

[Preparation of] ethyl cinnamate. C. S. MARVEL and W. B. KING (Organic Syntheses, 1929, 9, 38—40).

[Preparation of] hydrocinnamic acid. A. W. INGERSOLL (Organic Syntheses, 1929, 9, 42—45).

Preparation of β -naphthoic acid from magnesium β -naphthyl bromide. H. GILMAN and N. B. ST. JOHN (Rec. trav. chim., 1929, 48, 743—744).—Contrary to the statement of Loevenich and Loeser (A., 1927, 348) magnesium β -naphthyl bromide (prepared in 80% yield) is converted by the action of carbon dioxide in ether-benzene solution into β -naphthoic acid in 62.7% yield.

J. W. BAKER.

Mixed glycerides of salicylic acid. I. II. W. HUMNICKI (Rocz. Chem., 1929, 9, 390—395, 396—401).—See this vol., 811.

Mixed glycerides of salicylic acid. III. W. HUMNICKI and (MLL.) J. LUNKIEWICZ (Rocz. Chem., 1929, 9, 402—409, and Bull. Soc. chim., 1929, [iv], 45, 422—428).—The following mixed aromatic-aliphatic glycerides are prepared by the reaction between the appropriate dichlorohydrin ester and the sodium or silver salt of the acid used: $\alpha\alpha'$ -diisovaleryl β -salicyl, b. p. 237—238°; $\alpha\alpha'$ -dihexoyl β -salicyl, b. p. 256—257°/12 mm.; $\alpha\alpha'$ -dilauryl β -salicyl, m. p. 52—53°; $\alpha\alpha'$ -dimyristyl β -salicyl, m. p. 55—57°;

$\alpha\alpha'$ -disalicyl β -acetyl, m. p. 96—97°, $\alpha\alpha'$ -disalicyl β -isovaleryl, m. p. 52—53°, $\alpha\alpha'$ -disalicyl β -hexoyl, b. p. 268—270°/12 mm., $\alpha\alpha'$ -disalicyl β -lauryl, d^{20} 1.118, $\alpha\alpha'$ -disalicyl β -myristyl, m. p. 34—35°, and $\alpha\alpha'$ -disalicyl β -stearyl, m. p. 42—44°. $\alpha\beta$ -Disalicyl α -monochlorohydrin, m. p. 82—83°, is prepared by the addition of salicyl chloride to excess of α -monochlorohydrin.

R. TRUSZKOWSKI.

Reduction of semicarbazones of α -ketonic acids. Semicarbazides substituted in α -position by acid residues. J. BOUGAULT and L. POPOVICI (Compt. rend., 1929, 189, 186—188).—Reduction of the semicarbazones of phenylglyoxylic and phenylpyruvic acids by sodium amalgam yields, respectively, the semicarbazide acids, $CHPh(CO_2H) \cdot NH \cdot NH \cdot CO \cdot NH_2$, m. p. 208°, and $CH_2Ph \cdot CH(CO_2H) \cdot NH \cdot NH \cdot CO \cdot NH_2$, m. p. 164°. The same compounds are obtained by reduction of the diketotriazines formed from the semicarbazones (A., 1914, i, 1004, 1205). The semicarbazide acids reduce Nessler's reagent quantitatively, and are oxidised by iodine and sodium carbonate to the semicarbazones of the decarboxylated aldehydes.

R. K. CALLOW.

Synthesis of tropic acid. M. CHAMBON (Bull. Soc. chim., 1929, [iv], 45, 524—528).—See A., 1928, 884.

Isomeric monohydroxyphenylalanines. I. New synthesis of the *o*- and *m*-isomerides and a comparison of their properties with those of tyrosine. W. P. DICKINSON and P. G. MARSHALL (J.C.S., 1929, 1495—1498).—Glycine anhydride, prepared by a modification of Fischer's method (A., 1906, i, 808), condenses with salicylaldehyde in the presence of anhydrous sodium acetate and acetic anhydride at 125—135° to give 2 : 5-diketo-3 : 6-di-*o*-acetoxylbenzylidenepiperazine (I), m. p. 272° (yield 15%). A better yield (46%) of piperazine derivative is obtained by replacement of salicylaldehyde by salicylaldehyde methyl ether, obtained by using methyl sulphate and 2*N*-sodium hydroxide at 100° (cf. lit.); 2 : 5-diketo-3 : 6-di-*o*-methoxybenzylidenepiperazine (II) has m. p. 268°, and 2 : 5-diketo-3 : 6-di-*o*-ethoxybenzylidenepiperazine (III), similarly prepared from salicylaldehyde ethyl ether, has m. p. 205—206°. By reduction of I, II, or III with hydriodic acid (d 1.7) and red phosphorus for 7 hrs., *o*-hydroxyphenylalanine, m. p. 249—250° (cf. Blum, A., 1908, ii, 1052), is obtained. Glycine anhydride also condenses with *m*-hydroxybenzaldehyde in the presence of sodium acetate and acetic anhydride at 135—140° to afford 2 : 5-diketo-3 : 6-di-*m*-acetoxylbenzylidenepiperazine, m. p. 272° (yield 90%), which by reduction with hydriodic acid (d 1.7) and red phosphorus for 12 hrs. yields *m*-hydroxyphenylalanine, m. p. 275° (cf. Blum, loc. cit.) (yield 62%).

With Folin and Ciocalteu's modified form of Millon's reaction (A., 1927, 892), *o*-hydroxyphenylalanine gives a much less orange shade, intensity roughly 35%, of that produced by tyrosine. *m*-Hydroxyphenylalanine gives a shade (intensity 60%) identical with that given by tyrosine. With Folin's phenol reagent (loc. cit.) by comparison in the colorimeter, and using tyrosine as standard, the following results are obtained: tyrosine, 100%; *o*-hydroxyphenylalanine,

126.5%; *m*-hydroxyphenylalanine, 123.5%; tryptophan, 84.7% (Folin and Ciocalteu give 84.3%).

C. W. SHOPPEE.

Isomerisation of phenylglycidic and phenylhydroxyglycidic esters. M. TIFFENEAU and J. LEVY (Anal. Assoc. Quim. Argentina, 1928, 16, 144—157).—An attempt has been made to study the relative migratory tendencies of groups in the isomerisation of esters of phenylglycidic acids. When the vapour of ethyl phenylglycidate is passed over infusorial earth at 310° it yields a mixture, b. p. 150—151°/18 mm., n_D^{21} 1.532, of ethyl formylphenylacetate, CHO·CHPh·CO₂Et, and ethyl phenylhydroxymethyleneacetate, CH(OH)·CPh·CO₂Et, which are tautomeric. The mixture yields a semicarbazone of the first compound, m. p. 162—165°. Treatment of the product with perbenzoic acid in chloroform yields ethyl β -hydroxy- α -phenylglycidate, b. p. 165—170°/26 mm., n_D^{15} 1.527. When distilled with zinc chloride this yields ethyl hydrogen phenylmalonate. Similarly, from methyl phenylglycidate may be prepared a mixture of methyl formylphenylacetate and phenylhydroxymethyleneacetate, b. p. 153—155°/18 mm., n_D^{20} 1.52425, and methyl β -hydroxy- α -phenylglycidate, b. p. 160—162°/25 mm. Ethyl α -phenyl- α -methylglycidate yields, when the vapour is passed over heated infusorial earth, ethyl phenylmethylpyruvate, b. p. 256—258°/760 mm., n_D^{20} 1.5115 (semicarbazone, m. p. 162—163°), which is hydrolysed by alcoholic potassium hydroxide to give hydratropic acid, or by dilute sulphuric acid to give the aldehyde. The mechanism of these two isomerisations is discussed, and it is concluded that the first occurs by migration of the phenyl group from the β - to the α -position.

R. K. CALLOW.

Hydrogenation of unsaturated compounds.

IV. Hydrogenation of conjugated systems: piperic acid. S. V. LEBEDEV and A. O. YAKUBCHIK (J. Russ. Phys. Chem. Soc., 1929, 61, 551—560).—See this vol., 442.

Alkoxy-esters of polybasic organic acids [phthalic acid]. R. H. VAN SCHAAK, jun., and R. CALVERT, Assrs. to Van Schaack Bros. Chem. Works, Inc.—See B., 1929, 636.

Methylated gallic acids. R. L. SHRINER and P. McCUTCHAN (J. Amer. Chem. Soc., 1929, 51, 2193—2195).—5-Bromovanillin is converted through 5-bromoveratraldehyde into 5-bromoveratric acid, hydrolysed by 8% sodium hydroxide and copper powder at 200° to 5-hydroxyveratric acid, m. p. 184—185° (cf. Herzig and Pollak, A., 1902, i, 482) (acetyl derivative, m. p. 137—138°). 5-Bromovanillin is simultaneously hydrolysed and oxidised by 8% sodium hydroxide and copper powder at 200—210° to 5-methoxyprotocatechuic acid, m. p. 102—103° (Vogl, A., 1899, i, 697, gives 199—200°), which gives a light green colour with ferric chloride.

H. E. F. NOTTON.

Synthesis of substantive dyes of the dicinnamoylmethane group. W. LAMPE (Rocz. Chem., 1929, 9, 144—463).—[With R. NELKEN.]—The copper salt of ethyl α -(4-isopropylcinnamoyl)acetate, m. p. 210°, yields on treatment with sulphuric acid 4-isopropylcinnamoylacetone, m. p. 45—47°

(copper salt, m. p. 236—238°), which on further condensation yields di-(4-isopropylcinnamoyl)methane, m. p. 136—138°.

[With M. TOKARSKA-KOZŁOWSKA.] *m*-Carbomethoxycinnamic acid, m. p. 151—152°, is converted into the chloride, m. p. 68—70°, which is condensed with ethyl sodioacetoacetate to yield ethyl α -*m*-carbomethoxycinnamoylacetate, m. p. 81—83°, which, on treatment with sodium hydroxide, gives ethyl α -*m*-hydroxycinnamoylacetate, m. p. 115—117°, and when heated with water in an autoclave gives *m*-carbomethoxycinnamoylacetone, m. p. 77—79°; this, on hydrolysis with sodium hydroxide, yields *m*-hydroxycinnamoylacetone, m. p. 132—134°. Sodio-*m*-carbomethoxycinnamoylacetone gives on condensation with *m*-carbomethoxycinnamoyl chloride and subsequent hydrolysis di-*m*-carbomethoxycinnamoylmethane, m. p. 120—122°, which on hydrolysis with sodium hydroxide yields di-*m*-hydroxycinnamoylmethane, m. p. 193—195°.

[With C. SIERADZKA.] 2:4-Dicarbomethoxycinnamic acid, m. p. 184—186°, is converted into the chloride, m. p. 87—89°, which is condensed with ethyl sodioacetoacetate to yield ethyl α :2:4-dicarbomethoxycinnamoylacetate, m. p. 95—97°, which decomposes when heated to produce 2:4-dicarbomethoxycinnamoylacetone, m. p. 110—112° (copper salt, m. p. 205—207°). Sodiocinnamoylacetone condenses with 2:4-dicarbomethoxycinnamoyl chloride to yield cinnamoyl-2:4-dicarbomethoxycinnamoylmethane, m. p. 132—134°; it was not possible to accomplish this condensation using dihydroxycinnamoylacetone. The above product yields on hydrolysis cinnamoyl-2:4-dihydroxycinnamoylmethane, m. p. 158—161°.

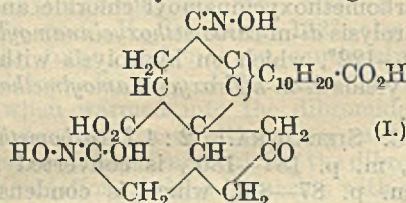
[With E. GLIKSMAN-KORNGOLD.] 2:5-Dicarbomethoxycinnamic acid, m. p. 184—186°, is converted into the chloride, m. p. 104—106°, which is condensed with ethyl sodioacetoacetate to yield ethyl α :2:5-dicarbomethoxycinnamoylacetate, m. p. 95—97°, whence is prepared 2:5-dicarbomethoxycinnamoylacetone, m. p. 108—110°. The sodium salt of the latter substance yields on condensation with 2:5-dicarbomethoxycinnamoyl chloride di-2:5-dicarbomethoxycinnamoylmethane, m. p. 194—196° (corresponding dihydroxy-derivative, m. p. 174—176°).

[With Z. BUCZKOWSKA.] Ethyl 3:4-piperonylacrylacetate, m. p. 98—100°, is converted into 3:4-piperonylacrylacetone, m. p. 123—125°, the sodium salt of which is condensed with the appropriate chloride to yield di-(3:4-piperonylacryl)methane, m. p. 198—200°.

[With J. FRENKIEL.] 4-Carbomethoxy-1-naphthaldehyde, m. p. 124—126°, condenses with malonic acid to yield 4-carbomethoxy-1-naphthylidenemalonic acid, m. p. 195°, which on fusion loses carbon dioxide, giving rise to 4-carbomethoxy-1-naphthylacrylic acid, m. p. 230—235°, the chloride of which (m. p. 152—154°) is condensed with ethyl sodioacetoacetate to yield ethyl α -(4-carbomethoxy-1-naphthylacryl)acetate, m. p. 110—112°; this substance is converted on heating into 4-carbomethoxy-1-naphthylacrylacetone, m. p. 104—106°, which is as before converted into di-(4-carbomethoxynaphthylacryl)methane, m. p. 120—124°. The end-products of the above syntheses

are substantive dyes for cotton, the intensity of coloration depending on the number and position of auxochrome (hydroxyl) groups. R. TRUSZKOWSKI.

Bile acids. XXIV. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1929, 183, 88—97).—Treatment of α -diketocholanic acid dioxime (this vol., 187) with nitric acid (d 1.4) at the ordinary temperature affords deoxybilanic acid in small yield. Reduction of the nitrohydroxamic acid, $C_{24}H_{31}O_9N_2$ (this vol., 558), with zinc dust and 9% ammonia affords the compound (I), $C_{24}H_{36}O_8N_2$, decomp. 224—226° after previous sintering, oxidised by nitric acid (d 1.4) to the nitroso-compound, $C_{24}H_{33}O_8N$ (A., 1928, 1007), previously obtained from bilanic acid dioxime. Partial hydrolysis of I with hydrochloric acid gives hydroxyl-



amine and the acid, $C_{24}H_{35}O_8N$ (I, where upper N:OH=O), decomp. 225° after previous sintering. This is hydrolysed further, with difficulty, to bilanic acid. H. BURTON.

[Preparation of] ammonium aurintricarboxylate. G. B. HEISIG and W. M. LAUER (Organic Syntheses, 1929, 9, 8—10).

Influence of ultra-violet light on aldehydes. Hexahydrophenylacetaldehyde, hexahydro- β -phenylpropaldehyde, and *n*-dodecaldehyde. F. SIGMUND (Monatsh., 1929, 52, 185—191).—The aldehydes were exposed in quartz vessels to the light from a quartz-mercury vapour lamp. Hexahydrophenylacetaldehyde (from its dimethylacetal) yielded, after 6 hrs.' exposure, a gas containing 88% of carbon monoxide, hexahydrotoluene, b. p. 100—110°, and small quantities of polymerised products. Hexahydro- β -phenylpropaldehyde (semicarbazone, m. p. 133°; lit. 128°), which rapidly forms a trimeride, m. p. 100°, on keeping, prepared from the diethylacetal, b. p. 205° or 93—95°/15 mm., similarly yielded, after 10 hrs.' exposure, carbon monoxide, but more slowly and in smaller quantity, and highly polymerised products from which only the above trimeride, m. p. 100°, and no hexahydroethylbenzene could be isolated in the pure state. *n*-Dodecaldehyde, b. p. 227—235°; from the semicarbazone, m. p. 101—102°, after 8 hrs.' exposure, afforded a gas (80% CO) and undecane, b. p. 190—200°. A. I. VOGEL.

Isomerism of dicyclohexylacetaldehyde into the ketone. E. D. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1929, 61, 53—70).—The isomerisation of dicyclohexylacetaldehyde into cyclohexyl cyclohexylmethyl ketone, in the presence of sulphuric acid or an alcoholic solution of mercurous chloride, is investigated.

The aldehyde was obtained from ethyl ethoxyacetate and magnesium cyclohexyl bromide, the resulting dicyclohexylethoxymethylcarbinol, m. p. 53°, b. p. 170—171°/9 mm., being oxidised by heating with

oxalic acid. In the preparation of the carbinol, both ethyl cyclohexylacetate, m. p. 31°, b. p. 211—211.5°, and cyclohexylethoxymethylcarbinol, b. p. 108°/13 mm., were obtained as by-products. The aldehyde has b. p. 153—153.5°/10 mm., d_4^{20} 0.9808, d_4^{25} 0.9676, d_4^{30} 0.9621, and gives a semicarbazone, m. p. 184—184.5°, and oxime, m. p. 108—109°. It oxidises on keeping in air, with the formation of dicyclohexylacetic acid, m. p. 134—135° (amide, m. p. 188—189°; anilide, m. p. 202—202.5°). When the semicarbazone of the aldehyde is heated with moderately concentrated sulphuric acid, cyclohexyl cyclohexylmethyl ketone is obtained, b. p. 172—173°/26 mm. (oxime, m. p. 112—113°; semicarbazone, m. p. 190—191°). The structure of the ketone was determined by synthesising $\alpha\beta$ -dicyclohexylethanol, m. p. 64—65°, b. p. 162—164°/17 mm., from magnesium cyclohexylmethyl iodide and hexahydrobenzaldehyde, and oxidising it to the ketone by chromic acid. The identity of the ketone was also confirmed by its decomposition products, since it gave cyclohexane and cyclohexylacetic acid on treatment with alcoholic potassium hydroxide.

M. ZVEGINTZOV.

2:4-Dinitrobenzaldehyde as a reagent. G. M. BENNETT and W. L. C. PRATT (J.C.S., 1929, 1465—1468).—2:4-Dinitrobenzaldehyde is a valuable reagent for the characterisation of amines (cf. A., 1920, i, 440; 1921, i, 337; 1923, i, 578) and for revealing the reactive methyl or methylene group in heterocyclic bases. Condensation with amines occurs readily in hot alcoholic solution containing a few drops of acetic acid to yield the following dinitrobenzylidene compounds: dinitrobenzylidene-*m*-chloroaniline, m. p. 137°; -*o*-chloroaniline, m. p. 164.5°; -*p*-chloroaniline, m. p. 158°; -3:5-dibromoaniline, m. p. 181°; -*p*-iodoaniline, m. p. 163°; -*p*-aminophenol, m. p. 158°; -*p*-aminoacetanilide, m. p. 199°; bisdinitrobenzylidene-*o*-phenylenediamine, m. p. 158°; -3:4-tolylenediamine, m. p. 153.5°; -4:4'-diaminodiphenylamine, m. p. 263° (decomp.); 6-aminoquinoline, m. p. 206°.

Condensation of 2:4-dinitrobenzaldehyde with substances possessing a reactive methyl or methylene group proceeds rapidly in boiling acetic anhydride, the products crystallising from the reaction mixture. 2-Methylpyridine gives 2-dinitrostyrylpyridine, m. p. 159°, and 2:6-dimethylquinoline yields 2-dinitrostyryl-6-methylquinoline, m. p. 213°. After 0.5—1 hr. 2:4-dimethylquinoline affords 2-dinitrostyryl-4-methylquinoline, m. p. 163.5°, but with excess of the reagent for 6—8 hrs. this compound or the original base furnishes tetranitro-2:4-distyrylquinoline, m. p. 270° (decomp.). 5:8-Dichloro-2-dinitrostyryl-4-methylquinoline has m. p. 198.5°, and 5:6:8-trichloro-2-dinitrostyryl-4-methylquinoline, m. p. 225.5°. 2:4:6-Trimethylquinoline rapidly gives 2-dinitrostyryl-4:6-dimethylquinoline, m. p. 195°, and 2-methylbenzimidazole affords 2-dinitrostyrylbenzimidazole, m. p. 215°. Condensation also occurs with *p*-nitrophenylacetonitrile giving 2:4:4'-trinitro- α -cyanostilbene, m. p. 149°, but no reaction could be detected with dibenzylsulphoxide or dibenzylsulphone.

An improved method of preparation of the reagent is described (cf. Sachs and Kempf, A., 1902, i, 682).

C. W. SHOPPEE.

Substitution in resorcinol derivatives. II. Bromo-derivatives of β -resorcyaldehyde and their orientation. M. G. S. RAO, C. SRIKANTIA, and M. S. IYENGAR (J.C.S., 1929, 1578—1581; cf. A., 1925, i, 675).—When a solution of 2-hydroxy-4-methoxybenzaldehyde in formic acid (d 1.20) is treated with bromine in the presence of anhydrous potassium acetate, 5-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 120—121° (*oxime*, m. p. 148—149°; *phenylhydrazone*, m. p. 177—178°), is obtained; the same substance is produced when 5-nitro-2-hydroxy-4-methoxybenzaldehyde is reduced with sodium hyposulphite, and the reduction product diazotised in the presence of cuprous bromide. The bromoaldehyde may be obtained on a larger scale by working in glacial acetic acid, and passing bromine vapour diluted with carbon dioxide through the solution. Using 2 mols. of bromine in glacial acetic acid, 3:5-dibromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 97—98° (*oxime*, m. p. 215°; *phenylhydrazone*, m. p. 131—132°), is obtained; if the period of bromination is unduly prolonged and an excess of bromine employed, a large quantity of a white *solid*, m. p. above 250°, is formed (cf. Davies, J.C.S., 1923, 123, 1575). All attempts to prepare a tribromo-derivative failed, although small quantities of tribromoresorcinol monomethyl ether were produced. By nitration at 100° in glacial acetic-sulphuric acid with nitric acid (d 1.52), the dibromoaldehyde affords 2:6-dibromo-4-nitroresorcinol 1-monomethyl ether, m. p. 127—128°, also obtained by partial methylation by the Purdie method of 2:6-dibromo-4-nitroresorcinol, m. p. 148°, and previously prepared by Kohn and Löff (A., 1925, i, 1264). Both specimens, by further methylation with methyl iodide, yielded the same dimethyl ether, m. p. 81°, the constitution of which is known definitely (Jackson and Fiske, A., 1903, i, 688).

By bromination in acetic acid in the presence of sodium acetate, 2:4-dimethoxybenzaldehyde, 2-ethoxy-4-methoxybenzaldehyde, and methyl *p*-methoxysalicylate gave respectively: 5-bromo-2:4-dimethoxybenzaldehyde, m. p. 136—137° (*oxime*, m. p. 175—176°), identical with the product obtained by methylating 5-bromo-2-hydroxy-4-methoxybenzaldehyde, and oxidised by hot potassium permanganate in the presence of magnesium sulphate to 5-bromo-2:4-dimethoxybenzoic acid, m. p. 195—196°; 5-bromo-2-ethoxy-4-methoxybenzaldehyde, m. p. 126—127° (*oxime*, m. p. 169—170°), identical with the ethylated product of 5-bromo-2-hydroxy-4-methoxybenzaldehyde, and oxidised by permanganate to 5-bromo-2-ethoxy-4-methoxybenzoic acid; methyl 5-bromo-4-methoxysalicylate, hydrolysed by alcoholic potassium hydroxide to 5-bromo-4-methoxysalicylic acid, identical with that obtained by bromination of 4-methoxysalicylic acid (cf. Fries and Saftien, A., 1926, 849).

C. W. SHOPPEE.

Chemistry of the three-carbon system. XXI. Some cycloheptane compounds. W. E. HUGH, G. A. R. KON, and T. MITCHELL (J.C.S., 1929, 1435—1440).—The point of equilibrium between cycloheptylideneacetic acid (*anilide*, m. p. 90—91°) and Δ^1 -cycloheptenylacetic acid found by Kon and May (A., 1927, 853) has been confirmed; under the standard conditions used by Linstead (A., 1927, 1167) and by

Goldberg and Linstead (A., 1928, 1214), the equilibrium mixture contains 26% of the $\alpha\beta$ -acid, but this value may be 2—3% low; the mobility $(k_1+k_2) \times 10$ is 0.66. The preparation of pure Δ^1 -cycloheptenylacetic acid (cf. Wallach, A., 1901, i, 155) is described; the acid has b. p. 153°/17 mm., 107°/2.5 mm., d_4^{25} 1.01155, n_D^{25} 1.48820 (*anilide*, m. p. 79—80°; ethyl ester, b. p. 104—107°/12 mm., d_4^{25} 0.97172, n_D^{25} 1.44689).

cycloHeptylideneacetone, b. p. 96°/10 mm., d_4^{25} 0.94852, n_D^{25} 1.49518, was obtained from cycloheptylideneacetyl chloride, b. p. 120—121°/13 mm., by the Blaise-Maire reaction, and was regenerated from the *semicarbazone*, m. p. 172—173°, which was identical with the compound previously described by Kon (J.C.S., 1921, 119, 810) as cyclohexenylacetonesemicarbazone. The ketone afforded suberone by oxidation. cycloHeptenylacetone, b. p. 95°/13 mm., d_4^{25} 0.93558, n_D^{25} 1.47595, after regeneration from the *semicarbazone*, m. p. 128—129°, was obtained similarly from cycloheptenylacetyl chloride, b. p. 100—104°/13 mm.; the equilibrium mixture obtained under standard conditions contains 65% of the $\alpha\beta$ -ketone. In contrast with the acids described above, the mobility of the ketones is extremely high, being greater than 3500, whilst the period of half-change is less than 2 min.

C. W. SHOPPEE.

[Preparation of] *p*-bromophenacyl bromide. W. D. LANGLEY (Organic Syntheses, 1929, 9, 20—21).

Dicymyl. E. BOEDTKER and R. KERLOV (Compt. rend., 1929, 188, 1681—1683).—*p*-Tolyl methyl ketone reacts with magnesium methyl iodide to give *p*-tolyl dimethylcarbinol, which cannot be distilled in a high vacuum without dehydration; by treatment with a saturated solution of hydriodic acid in glacial acetic acid at 15° for some hours, it is converted into α -*p*-tolylisopropyl iodide, which with zinc dust yields *s*-pp'-ditolyltetramethylethane, m. p. 157°, identical with the dicymyl obtained by Ciamician and Silber (A., 1910, i, 489) from benzophenone and *p*-cymene in sunlight.

C. W. SHOPPEE.

Additive reactions of phenyl vinyl ketone. I. Phenylnitromethane. C. F. H. ALLEN and M. P. BRIDGESS (J. Amer. Chem. Soc., 1929, 51, 2151—2157).—Phenyl vinyl ketone, isolated as described by Mannich (A., 1922, i, 351), or formed in solution, as required, from phenyl β -chloroethyl ketone and potassium carbonate, gives with phenylnitromethane and sodium methoxide phenyl γ -nitro- γ -phenylpropyl ketone, m. p. 72°. The *sodio*-derivative of this is hydrolysed by dilute hydrochloric acid to $\alpha\beta$ -dibenzoyl ethane (I), and brominated in methyl alcohol to phenyl γ -bromo- γ -nitro- γ -phenylpropyl ketone, m. p. 146°, decomposing at a higher temperature, mainly into 3-bromo-2:5-diphenylfuran. The bromonitroketone is converted by alcoholic sodium hydroxide into I; by boiling glacial acetic acid into 3-bromo- and a little 3:4-dibromo-2:5-diphenylfuran, and by prolonged refluxing with potassium acetate in methyl alcohol into 1-nitro-2-benzoyl-1-phenylcyclopropane, m. p. 131°, together with a mixture, m. p. 80°, probably containing a stereoisomeride. These are both stable towards bromine, hydrogen bromide, and acetyl chloride, but are converted by sodium methoxide

into I. The mechanism of this new type of reaction is discussed (cf. Kohler, A., 1919, i, 330, 582; 1920, i, 59, 61; 1928, 523).

H. E. F. NOTTON.

Stereochemistry of the phenyl styryl ketones. The stereoisomerism of phenyl α -bromo- β -ethoxystyryl ketone. C. DUFRAISSE and R. NETTER (Compt. rend., 1929, 189, 299—301).—A substance, m. p. 85°, noted by Dufraisse and Gillet (this vol., 700), is shown to be a stereoisomeride of phenyl α -bromo- β -ethoxystyryl ketone and not a fourth polymorphic variety of the original compound. The isomerides are interconvertible, the change being accelerated by light, heat, and acids. Their properties are very similar and their separation is difficult.

A. A. GOLDBERG.

Polymorphism of organic substances. C. WEYGAND (Annalen, 1929, 472, 143—179).—Inoculation of the supercooled fused mass from stable (m. p. 74.5°) *p*-tolyl styryl ketone (A) with *p*-ethylphenyl styryl ketone (I), m. p. 61.5°, causes instantaneous crystallisation of modification III of A (=AIII; for notation see this vol., 815), and of the seven principal modifications of A (*loc. cit.*) only AIII causes spontaneous crystallisation of a supercooled fused mass of I. AIII and I are, therefore, corresponding forms. A new, metastable modification, m. p. 64° (II), of the enol form of benzoyl-*p*-toluylmethane (III), m. p. 84° (A., 1928, 291), is described: the velocity of the transformation II \rightarrow III is more rapid than AII \rightarrow AIV, and inoculation experiments show that II and AIII and III and AII are corresponding pairs. Inoculation of the fused mass from II or III with metastable phenyl *p*-methylstyryl ketone, m. p. 91° (A., 1928, 180), affords a further metastable modification, m. p. 42°, of III; occasionally a fourth form, m. p. 38°, is obtained. The less fusible forms are polymorphic modifications of the enol, C₆H₄Me·CO·CH:CPh·OH, whilst the more fusible forms are similarly related to the enol, CPh·CH:C(OH)·C₆H₄·Me. The following, not hitherto described modifications of a series of chalkones have been obtained: phenyl styryl ketone, m. p. 58—49°, 56—57°, 28°, 18° (β -ethoxy-derivative, m. p. 43°; α -bromo-derivative, m. p. 45°); phenyl *p*-methylstyryl ketone, m. p. 96.5°, 91°, 86° (β -ethoxy-derivative, m. p. 91°; α -bromo-derivative, m. p. 66—67°); *p*-tolyl *p*-methylstyryl ketone, m. p. 128—129° (β -hydroxy-derivative, m. p. 127—129°; β -ethoxy-derivative, m. p. 80—81°); *p*-tolyl β -ethoxystyryl ketone, m. p. 73°, 56—58°; *p*-tolyl α -bromostyryl ketone, m. p. 66—67°, 58°. The crystallisation velocities of the various forms have been determined and the various transformations studied.

H. BURTON.

Condensation of piperonaldehyde with certain pinacolins. E. PACE (Atti R. Accad. Lincei, 1929, [vi], 9, 778—782).—3:4-Methylenedioxystyryl tert.-butyl ketone, CH₂ $\left\langle \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right\rangle$ C₆H₃·CH:CH·CO·CMe₃, m. p. 98°, d_4^{20} 1.0765, n_D^{20} 1.34825, is obtained by the condensation of piperonaldehyde with methyl tert.-butyl ketone (this vol., 538) in presence of sodium hydroxide. Piperonylidene-ethyl tert.-amyl ketone, m. p. 106°, d_4^{20} 1.0883, n_D^{20} 1.36132, and piperonylidenepropyl tert.-hexyl ketone, m. p. 117°, d_4^{20} 1.0928, n_D^{20} 1.38576, are

obtained from piperonaldehyde with ethyl tert.-amyl ketone and propyl tert.-hexyl ketone, respectively.

T. H. POPE.

Bivalency of carbon. II. Displacement of chlorine from desyl chloride. Benzoin diethylacetal. A. M. WARD (J.C.S., 1929, 1541—1553; cf. A., 1927, 1061).—Desyl chloride, m. p. 67°, obtained by an improvement of the method of Darzens (A., 1911, i, 513), is completely stable in lime-dried alcoholic or aqueous-alcoholic solution at 25°, but the halogen is very rapidly displaced in the presence of sodium hydroxide or ethoxide at 15°. Quantitative experiments, carried out in an atmosphere of hydrogen to minimise side and subsequent reactions, show that the velocity coefficients of the displacements are those of a bimolecular reaction; their values are dependent, however, on the concentrations of the reactants. These results are in marked contrast with those previously obtained (*loc. cit.*) for diphenylchloromethane, and are not in accordance with the hypothesis of Schroeter (A., 1909, i, 617, 773), that the elimination of chlorine from desyl chloride proceeds through a phase involving bivalent carbon. This conclusion is supported by the products formed in the foregoing reaction. When the final reaction mixture was added to cold dilute hydrochloric acid, benzoin only was obtained; no trace of benzoin ethyl ether, which is stable to dilute hydrochloric acid at 15°, could be detected. The exclusive production of benzoin is found to be due to the prior formation of benzoin diethylacetal, m. p. 68° (crystallographic data), which is rapidly decomposed by dilute hydrochloric acid at 15° giving benzoin. A mechanism is put forward based on the above results, in which the primary reaction in the displacement consists in the addition of an ethoxide ion to the carbonyl group in desyl chloride.

C. W. SHOPPEE.

Dioximes. LIII. M. MILONE (Gazzetta, 1929, 59, 266—272).—A survey of previous work on the arylglyoxime peroxides (cf. Ponzio and others, A., 1927, 470, etc.), and a further application of the cryoscopic method (this vol., 334) to the study of their structure. Oximinophenyl- and oximino-*p*-tolyl-acetonitrile oxides, and phenyl- and *p*-tolyl-glyoxime peroxides (m. p. 112°, 117°, 108—109°, and 100—101°, respectively) all give normal mol. wt. values in 3-phenyl- and 3-*p*-tolyl-1:2:5-oxadiazoles as solvents, and are thus not to be regarded as themselves having an oxadiazole structure (cf. Ponzio, *loc. cit.*).

E. W. WIGNALL.

Dioximes. G. PONZIO (Ber., 1929, 62, [B], 1750).— β -*p*-Methoxybenzildioxime has m. p. 185° (Meisenheimer and others record m. p. 176°). It is dehydrogenated by sodium hypochlorite to a substance, m. p. 106—107°, identical in m. p. with the " α -phenylanisilfuroxan" of Meisenheimer (A., 1925, i, 1075).

H. WREN.

Catalytic reduction of $\alpha\beta$ -diketones and their derivatives. J. S. BUCK and S. S. JENKINS (J. Amer. Chem. Soc., 1929, 51, 2163—2167).—Modifications of the method and apparatus of Adams (A., 1922, ii, 558) suitable for the hydrogenation of about 0.01 g.-mol. of material are described. The following reductions have been effected with almost quantit-

ative yields: benzil, anisil, and piperil to the corresponding benzoin and hydrobenzoin derivatives; furil to furolin; phenyl benzyl ketone to phenylbenzylcarbinol; anisyl *p*-methoxybenzyl ketone to α -di-*p*-anisylethyl alcohol, m. p. 110.4° (Wiechell, A., 1894, i, 507, gives m. p. 170°), and *piperonyl mp-methylene-dioxybenzyl ketone*, m. p. 114.5°, to α -di-*piperonylethyl alcohol*, m. p. 154—155°. The phenylbenzylcarbinols are dehydrated by acetic and hydrochloric acids to stilbenes, which are readily hydrogenated to the corresponding α -diarylethanes. Attempts to hydrogenate veratril were unsuccessful. H. E. F. NOTTON.

Synthesis of ephedrine and structurally similar compounds. III. New synthesis of α -diketones. H. W. COLES, R. H. F. MANSKE, and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 2269—2272).—Propiophenone is oxidised by nitrogen peroxide at 60° in alcoholic hydrogen chloride in presence of calcium chloride to α -phenylpropane- α - β -dione. The method, described in detail, is also applicable to the preparation of α -phenylbutane- α - β -dione, b. p. 130—132°/20 mm., α -*p*-ethylphenylpropane- α - β -dione, b. p. 138—140°/20 mm., and α -2:5-dimethylphenylpropane- α - β -dione, b. p. 140—144°/20 mm., but α -hydrindone gives 2-oximino-1-hydrindone and, on further treatment, resinous products, and α -ketotetrahydronaphthalene gives no crystalline product. H. E. F. NOTTON.

Reactions of oximes with metallic salts. III. Complex-chemical behaviour of stereoisomeric oximes. W. HIEBER and F. LEUTERT (Ber., 1929, 62, [B], 1839—1846).—The occurrence of a reaction between metallic salts and oximes is conditioned by the presence of an oximino-nitrogen atom capable of subsidiary valency action. Transformation or conversion into an internally complex salt usually follows as a consequence of greatly enhanced stability, but this is not universal. Copper acetate and α -benzildioxime in aqueous-alcoholic suspension in the presence of ammonia give the compound

$[\text{CPh}(\text{:N}\cdot\text{OH})\cdot\text{CPh}(\text{NO})]_2\text{Cu}$, converted by hydrogen chloride into the additive product of cupric chloride and α -benzildioxime and the free dioxime. The additive compound is also obtained from γ -benzildioxime and cupric chloride in chloroform. The β -oxime of benzoylformic acid gives adducts with cupric and cobalt chloride, also obtained from the α -oxime (in consequence of isomerisation). The copper, nickel, and cobalt salts,

$\text{Cu}(\text{Co}, \text{Ni})[\text{CPh}(\text{:N}\cdot\text{OH})\cdot\text{CO}_2]_2\cdot 2\text{H}_2\text{O}$, and the potassium copper salt, $\text{K}_2\text{Cu}[\text{CPh}(\text{NO})\cdot\text{CO}_2]_3$, are described. *anti*-Chloroglyoxime shows much less tendency than aromatic *anti*-dioximes towards the formation of complex compounds. Potassium nickel *amphi-chloroglyoxime*, $\text{K}_2\text{Ni}[\text{CCl}(\text{NO})\cdot\text{CH}(\text{NO})]_2$, is described in which potassium may be replaced by barium, lead, or silver. H. WREN.

Reduction of aromatic α -diketones by the binary system, magnesium-magnesium iodide (or bromide). M. GOMBERG and F. J. VAN NATTA (J. Amer. Chem. Soc., 1929, 51, 2238—2245).—Equilibrium in the reversible reaction, $(\text{CR}\cdot\text{O})_2 + 2\text{MgI}_2 \rightleftharpoons (\text{CR}\cdot\text{OMgI})_2 + \text{I}_2$ (cf. A., 1927, 1190), has been approached from both sides in the case of several

benzil derivatives. In presence of magnesium, the reduction proceeds quantitatively and the products give high yields of benzoin when hydrolysed in absence of air. Many of the resulting glycoloxides are deeply coloured in solution, probably owing to the production of free valencies by the partial opening of the double linking. *p*-Tolil is reduced to toluoin in 90% yield using magnesium iodide, and in 82% yield using the bromide. The intermediate *magnesium glycoloxide* is oxidised by dry air to the polymeric *anhydride* (28% of the theoretical yield), m. p. above 360°, of di-*p*-tolylglycollic acid, and to *p*-tolil (45%). *p*-Anisil is quantitatively reduced to a *glycoloxide* which is oxidised by air to the polymeric *anhydride* (31% yield), m. p. above 360°, of di-*p*-anisylglycollic acid. *pp'*-Dichlorobenzil yields a *glycoloxide* which is oxidised by air to the polymeric *anhydride*, decomp. 320—340°, of *pp'*-dichlorobenzilic acid. The last two benzils cannot be reduced by means of magnesium bromide, since they form insoluble compounds with it. α -Naphthil (2:3-di- α -naphthylquinoxaline, m. p. 203—204°), conveniently prepared from α -naphthoin, copper sulphate, and pyridine, is reduced to a *glycoloxide*, which gives di- α -naphthylglycollic acid, m. p. 137—138° (40% yield), but no anhydride, when oxidised by air. *p*-Phenylbenzaldehyde and potassium cyanide in boiling aqueous alcohol give *pp'*-diphenylbenzoin, m. p. 168—170°, oxidised to *pp'*-diphenylbenzil, m. p. 141—142° (2:3-bisdiphenylquinoxaline, m. p. 209—210°). This is quantitatively reduced to a *glycoloxide*, oxidised by air to the polymeric *anhydride*, decomp. 250°, of *pp'*-diphenylbenzilic acid. Benzil *p*-diphenyl ketone is oxidised by potassium permanganate in pyridine to *p*-phenylbenzil, m. p. 105°, which is reduced by magnesium and magnesium iodide, or, better, bromide, to a *p*-phenylbenzoin, m. p. 148—151°. The glycoloxides are converted by benzoyl chloride into the following derivatives of α - β -dibenzoyloxystilbene: *pp'*-dimethyl-, m. p. 135°; *pp'*-dichloro-, m. p. 200—202°, and *pp'*-diphenyl-, m. p. 180°, resolidifying with conversion into an *isomeride*, m. p. 200—203°. H. E. F. NOTTON.

Oximino-derivatives of *p*-bromobenzoyl-acetone and the corresponding dioxime. J. HANUŠ, A. JÍLEK, and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 392—396).—*p*-Bromoacetophenone, treated with sodium and ethereal ethyl acetate, gives *p*-bromobenzoylacetone, m. p. 94—96° (corr.). With aqueous sodium nitrite and acetic anhydride it affords oximino-*p*-bromobenzoylacetone, m. p. 169—170°, which yields with hydroxylamine an *oxime*, m. p. 189—190°. Attempts to prepare the corresponding trioxime gave an isomeric dioxime (?), m. p. 147—148°. Characteristic reactions of the first and second oxime derivatives with metallic cations are recorded. R. J. W. LE FÈVRE.

Conjugated systems. Factors disturbing valency fields. V. Action of compounds with a reactive methylene group on carbindogenides. V. IONESCU and A. GEORGESCU (Bull. Soc. chim., 1929, [iv], 45, 423—435).—In continuation of previous work (A., 1928, 422, 1026) the three isomeric chlorobenzylideneindandiones have been shown to react with ethyl malonate, dimethyldihydroresorcinol, and

1-phenyl-3-methyl-5-pyrazolone analogously with the tolylideneindandiones, the additive product,

$C_6H_4 \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} CH \cdot CH(C_6H_4Cl) \cdot R$, being first formed by addition of one mol. of the reagent, from which further complex products are formed in the case of dimethyldihydroresorcinol and phenylmethylpyrazolone, either by displacement of the indandione group or by reaction of the di-indone formed with unchanged chlorobenzylideneindandione to give mono- or di-substituted derivatives. Small quantities of truxenequinone formed by auto-condensation of the di-indone were present in all cases.

With *o*-, *m*-, and *p*-chlorobenzylideneindandiones in alcohol, ethyl malonate affords the corresponding ethyl chlorobenzylindandionylmalonates, which were not obtained pure and when heated are decomposed into the original indogenide. Dimethyldihydroresorcinol in presence of piperidine yields *o*-chlorobenzylidenebisdimethyldihydroresorcinol, m. p. 203—205°, and -indandionedi-indone, m. p. 288° (decomp.). *m*-Chlorobenzylidene-, m. p. 265—267° (decomp.), and *p*-chlorobenzylideneindandionedi-indones, m. p. 275° (decomp.), are similarly obtained, but the *m*- and *p*-chlorobenzylidenebisdimethyldihydroresorcinols were not obtained pure. *o*-Chlorobenzylidene-, m. p. 229—231°, *m*-chlorobenzylidene-, m. p. 206—207°, and *p*-chlorobenzylidenebis-1-phenyl-3-methyl-5-pyrazolones, m. p. 208°, are accompanied by traces of anhydrobis-1-phenyl-3-methyl-5-pyrazolone (A., 1927, 880).

R. BRIGHTMAN.

Migration of the acyl group in partly acylated phenolic compounds. II. Synthesis of anthragallol 1:2- and 1:3-dimethyl ethers. A. G. PERKIN and C. W. H. STORY (J.C.S., 1929, 1399—1421; cf. A., 1925, i, 1159; 1928, 293).—When anthragallol 2-methyl ether is treated with acetic anhydride and powdered potassium acetate at 15°, 3-acetylanthragallol 2-methyl ether, m. p. 167—169.5°, is obtained; it is converted by diazomethane in ether suspension into a mixture of anthragallol trimethyl ether, m. p. 167—169° (15%), and 3-acetylanthragallol 1:2-dimethyl ether, m. p. 177—179°. Hydrolysis of the latter yields anthragallol 1:2-dimethyl ether, m. p. 230—232°, identical with that present in Chay root (Perkin and Hummel, J.C.S., 1893, 63, 1160; Perkin, *ibid.*, 1907, 91, 2066). Benzoylation of 2:3-diacetylanthragallol in pyridine suspension at 0° affords a mixture of 2-benzoyl-3-acetylanthragallol (I), m. p. 203—206°, and 1- or 3-benzoyl-2-acetylanthragallol (II), m. p. 189—190°, which both yield 2-benzoylanthragallol (III), m. p. 241—243°, by hydrolysis with acetic and hydrochloric acids at 100°, migration of the benzoyl group occurring in the case of II. By acetylation with boiling acetic anhydride and pyridine, III affords triacetylanthragallol, but at 0° both I and III yield 2-benzoyl-1:3-diacetylanthragallol, m. p. 211—213°, whilst II furnishes an isomeric benzoyldiacetylanthragallol, m. p. 203—205°, partial acetylation of III with acetic anhydride in the presence of potassium acetate at 15° yields I. When methylated with ethereal diazomethane, 2-benzoylanthragallol gives 1-benzoylanthragallol 2:3-dimethyl ether (IV), m. p. 216—218° (60%), hydrolysed by boiling 1% methyl-alcoholic potassium hydroxide to

anthragallol 2:3-dimethyl ether, m. p. 160—162°, together with 3-benzoylanthragallol 1:2-dimethyl ether (15.5%) and 2-benzoylanthragallol 1:3-dimethyl ether (V) (13%); the two last-named compounds were not isolated, but their presence was indicated by hydrolysis to anthragallol 1:2-dimethyl ether and anthragallol 1:3-dimethyl ether (acetyl derivative, m. p. 218—220°; cf. Perkin and Hummel, *loc. cit.*). These results involve migration of the benzoyl group from the 2 to the 1, and from the 2 to the 3 position. Anthragallol 2:3-dimethyl ether by hydrolysis with sulphuric acid at 100° yields anthragallol 3-methyl ether (VI), m. p. 242—245° (acetyl derivative, m. p. 204—206°) (cf. *lit.*), identical with the anthragallol methyl ether obtained by Kubota and Perkin (A., 1925, i, 1159), whose preparation from 2:3-diacetylanthragallol, which involves migration of both acetyl groups, is confirmed. By treatment of a mixture of VI and benzoyl chloride with a solution of pyridine in chloroform at 0° 2-benzoylanthragallol 3-methyl ether (VII), m. p. 221—223°, is obtained; it is converted by boiling with acetic anhydride and pyridine into two isomeric benzoylacetylanthragallol 3-methyl ethers, m. p. 195—196° and 214—217°, which are considered to arise by migration of the benzoyl group. When methylated with ethereal diazomethane, VII affords a mixture of IV (76%) and V (15%).

By digestion of 2:3-thionylanthragallol (cf. Green, A., 1926, 1041) with boiling acetic acid 2-acetylanthragallol, m. p. 219—220°, is obtained [described by Green (*loc. cit.*) as the 3-acetyl compound]; when methylated with ethereal diazomethane it affords 1-acetylanthragallol 2:3-dimethyl ether (69%), 2-acetylanthragallol 1:3-dimethyl ether (15%), and 3-acetylanthragallol 1:2-dimethyl ether (15%), with migration of the acetyl group from the 2 to the 1, and from the 2 to the 3 position. A boiling acetone solution of 1:3-diacetylanthragallol 2-methyl ether on treatment with excess of aqueous ammonia yields 1-acetylanthragallol 2-methyl ether, m. p. 205—208°, hydrolysed to anthragallol 2-methyl ether, m. p. 218—220°, and affording by methylation with ethereal diazomethane 1-acetylanthragallol 2:3-dimethyl ether, m. p. 168—170°; no substance other than anthragallol 2:3-dimethyl ether could be obtained by hydrolysis of the methylation product. Hydrolysis of triacetylpurpuroxanthin with ammonia in boiling acetone solution yields 1-acetylpurpuroxanthin, m. p. 231—235°, hydrolysed by hydrochloric acid to purpuroxanthin, m. p. 268—270° (cf. *lit.*), which by reacetylation affords 3-acetylpurpuroxanthin, m. p. 144° (cf. *lit.*). Similar treatment of triacetylpurpurin and triacetylanthragallol yields respectively 1:3-diacetylpurpurin, m. p. 203—205°, and 2:3-diacetylanthragallol, m. p. 223—224°.

3-Nitroalizarin dimethyl ether, m. p. 168—171°, obtained by methylating the potassium salt of 3-nitroalizarin with methyl sulphate at 140°, by reduction with sodium sulphide affords 3-aminoalizarin dimethyl ether, m. p. 203—205° (acetyl derivative, m. p. 237—240°). By diazotisation in sulphuric acid solution, dilution, and boiling, anthragallol 2-methyl ether is obtained [1:3-diacetyl derivative, m. p. 146—150° (cf. *lit.*)], partial demethylation occurring in the latter process.

2 : 3-Ditoluene-*p*-sulphonylanthragallol (VIII), m. p. 196—198° (acetyl derivative, m. p. 212—215°), obtained by treatment of anthragallol with toluene-*p*-sulphonyl chloride in pyridine at 0—15°, furnishes with diazomethane in acetone solution 2 : 3-ditoluene-*p*-sulphonylanthragallol 1-methyl ether, m. p. 210—213°, hydrolysed by 10% alcoholic potassium hydroxide to anthragallol 1-methyl ether, m. p. 248—250° (compound +1MeOH; diacetyl derivative, m. p. 165—166°; barium and lead salts). By treatment with 1% methyl-alcoholic potassium hydroxide in acetone solution, VIII yields monotoluene-*p*-sulphonylanthragallol 1-methyl ether, m. p. 289—291°, which is converted by diazomethane in acetone into 2-toluene-*p*-sulphonylanthragallol 1 : 3-dimethyl ether, m. p. 175—177°, and 3-toluene-*p*-sulphonylanthragallol 1 : 2-dimethyl ether, giving by hydrolysis anthragallol 1 : 3- and 1 : 2-dimethyl ether, respectively, migration of the toluene-*p*-sulphonyl group having occurred.

When 2-ethylcarbonatoalizarin (IX) is acetylated with acetic anhydride and pyridine in the usual manner, diacetylalizarin, m. p. 188—189°, is obtained, but if the pyridine solution of IX is cooled prior to the addition of acetic anhydride 2-ethylcarbonato-1-acetylalizarin, m. p. 177—179°, separates. Reduction of IX with stannous chloride and acetic and hydrochloric acids gives 2-ethylcarbonato-1-hydroxyanthrone (X), m. p. 130—133° after sintering at 120°, affording by acetylation with acetic anhydride and pyridine in the cold 2-ethylcarbonato-1 : 9-diacetylanthranol, m. p. 177—180°, and yielding 1 : 2-dihydroxyanthrone, m. p. 149—151°, by treatment with alcoholic potassium hydroxide in boiling methyl alcohol in an atmosphere of hydrogen. With diazomethane in benzene solution in an atmosphere of hydrogen X affords a mixture of 2-ethylcarbonato-1-methoxyanthrone and 1-ethylcarbonato-2-methoxyanthrone (not isolated, but identified by their respective hydrolysis to alizarin 1- and 2-methyl ethers); in acetone solution, 2 : 2'-diethylcarbonatodianthrone, m. p. above 290°, oxidised by chromic acid to alizarin 1-methyl ether, accompanies the foregoing compounds. Similarly, 3 : 4-dihydroxyanthranol (deoxyalizarin) with diazomethane in tetrachloroethane affords 4 : 4'-dihydroxy-3 : 3'-dimethoxydianthrone, m. p. 290—292°, giving alizarin 2-methyl ether by chromic acid oxidation; replacement of the tetrachloroethane by ether increases the yield of the dianthrone, but by using benzene in an atmosphere of hydrogen its presence could not be detected; in the foregoing methylation experiments 4-hydroxy-3'-methoxyanthranol and 3 : 4-dimethoxyanthranol are produced but were not isolated.

5 : 6-Dihydroxy-1-benzylidenecoumaran-2-one (XI) (diacetyl derivative, m. p. 202—203°), obtained in almost theoretical yield by condensing 5 : 6-dihydroxycoumaranone with benzaldehyde, is converted by treatment with excess of toluene-*p*-sulphonyl chloride and pyridine in chloroform into 5 : 6-ditoluene-*p*-sulphonyloxy-1-benzylidenecoumaran-2-one, m. p. 178—180°, but under special conditions into two isomeric monotoluene-*p*-sulphonyloxy-1-benzylidenecoumaran-2-ones, m. p. 217—219° (fluorescent in alkaline solution; acetyl derivative, m. p. 177—180°), and m. p. 237—240° (acetyl derivative, m. p. 145—146°); the latter compound, together with XI, is obtained when the

ditoluene-*p*-sulphonyl derivative is treated with 2 mols. of alcoholic potassium hydroxide in the cold. By treatment with ethyl chloroformate and pyridine in chloroform solution, XI affords a monoethylcarbonato-derivative, m. p. 177—180°, giving by acetylation 5 : 6-diacetoxy-1-benzylidenecoumaran-2-one, m. p. 200—202°, and in the presence of excess of ethyl chloroformate, 5 : 6-diethylcarbonato-1-benzylidenecoumaran-2-one, m. p. 104—107°.

The theory of acyl migration in phenolic compounds (cf. Perkin and Storey, A., 1928, 293), under the influence of diazomethane, is further discussed.

C. W. SHOPPEE.

[Di- and tri-quinones of the anthracene series.] R. E. SCHMIDT, B. STEIN, and C. BAMBERGER (Ber., 1929, 62, [B], 1884—1889).—Contrary to Heller and others (this vol., 701), ψ -nitropurpurin is not a "quinonenitronic acid," but a nitrohydroxyanthradiquinone, converted by reducing agents which do not affect the nitro-group, into 3-nitro-1 : 2 : 4-trihydroxyanthraquinone. Similarly, Heller's "1 : 2 : 5 : 6-tetrahydroxyanthraquinone-4 : 3, 8 : 7-diquinone-nitronic acid" is 3 : 7-dinitro-2 : 5 : 6 : 8-tetrahydroxyanthradiquinone, reduced to 3 : 7-dinitro-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone, from which it is obtained by gentle oxidation. The phenylhydrazine salt of the supposed "quinonenitronic acid" is the salt of dinitrohexahydroxyanthraquinone, the production of which is due to the reducing action of phenylhydrazine. Heller's "third yellow variety" is 3 : 7-dinitro-2 : 6-dihydroxyanthraquinone, reduced successively to 3 : 7-dinitro-2 : 5 : 6 : 8-tetrahydroxyanthradiquinone and 3 : 7-dinitro-1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone.

H. WREN.

Condensation products of the pyrenequinone series. I. G. FARBENIND. A.-G.—See B., 1929, 590.

Santenol. G. KOMPPA (Ber., 1929, 62, [B], 1751—1752).—Santenol is converted by diphenic anhydride at 140—150° or in presence of pyridine at 100° into santenyl hydrogen diphenate, m. p. 119—120°, from which homogeneous santenol, m. p. 86°, is derived.

H. WREN.

Bixin. P. KARRER, A. HELFENSTEIN, R. WIDMER, and T. B. VAN ITALLIE (Helv. Chim. Acta, 1929, 12, 741—756).—A review of analytical results given by previous workers for bixin, together with those of the present authors for bixin, perhydrobixin, bixin methyl ester (obtained from bixin by methylation in chloroform solution with diazomethane), m. p. 163—164°, and perhydrobixin methyl ester (prepared from perhydrobixin either by the action of diazomethane or by treatment with alkali and methyl sulphate), b. p. 203—205°/0.3—0.4 mm., d_4^{20} 0.924, n_D^{20} 1.45597, supports the bixin formula $C_{24}H_{27}O_3 \cdot OMe$.

Hydrolysis of bixin by methyl-alcoholic potassium hydroxide at 65° affords a norbixin, m. p. 255° after sintering at 250°; this, by reduction with titanium trichloride, sodium hydroxide, and ammonia, gives successively dihydronorbixin, sintering at 197°, and tetra- or hexa-hydronorbixin, an oil. Bixin is similarly reduced to dihydrobixin, m. p. 207—208° after sintering at 190°.

Hydrolysis of bixin by boiling alcoholic potassium hydroxide leads to isonorbixin, m. p. above 300°

(sodium and pyridine salts), methylation of which yields the same *isobixin* methyl ester as is obtained from *bixin* methyl ester by heating with iodine in acetic acid solution. *isoBixin*, m. p. 216—217° (methyl ester, m. p. 200—201°), is obtained from *bixin* by treatment with iodine in chloroform solution. *Perhydronorbixin diamide* (prepared from *perhydronorbixin* through the *dichloride*) has m. p. 111°.

R. J. W. LE FÈVRE.

Isomerisation and catalytic hydrogenation of Sandaraco-pimarinic acid. F. BALÁŠ and J. BRZÁK (Coll. Czech. Chem. Comm., 1929, 1, 352—359; cf. this vol., 811).—Isomerisation of the *pimarinic acid* (I) is not effected by boiling with acetic acid, alcoholic sulphuric acid, or 50% potassium hydroxide solution. Distillation at 0.3 mm. gives mainly unchanged material together with a small amount of an acid, m. p. 182°, $[\alpha]_D^{20}$ —34.9° in alcohol. When heated at 240° in carbon dioxide, I furnishes an *isomeride*, m. p. 156°, $[\alpha]_D^{20}$ +64.5° in alcohol (crystalline *ammonium salt*); at 310° considerable decomposition occurs and there are formed an amorphous acid, m. p. 125—130°, $[\alpha]_D^{20}$ +32.5°, and a *hydrocarbon*, $C_{19}H_{28}$, b. p. 195°/12 mm., d_4^{20} 0.9784, n_D^{20} 1.5465. Reduction of I with hydrogen in presence of colloidal platinum and acetic acid at 60° yields a *dihydropimarinic acid*, $C_{20}H_{32}O_2$, m. p. 180°, $[\alpha]_D^{20}$ +23.9° in alcohol (crystallographic data by NOVÁČEK). Dehydrogenation of I with sulphur gives indefinite products. The *i-pimarinic acids* of Henry and Tschirch are probably impure specimens of I, and it is probable that I differs constitutionally from *abietic* and *d-* and *l-pimarinic acids*.

H. BURTON.

[Preparation of] *l*-menthone. L. T. SANDBORN (Organic Synthesis, 1929, 9, 52—53).

α -Pinene oxide in Grignard's reaction. N. PRILESCHAEV and V. VERSCHUK (J. Russ. Phys. Chem. Soc., 1929, 61, 473—482).— Δ^1 . *Menthenol*, b. p. 109—110°/13 mm., is prepared by the action of magnesium methyl iodide on *l*- α -pinene oxide. The above alcohol yields the corresponding oxy-alcohol on oxidation with perbenzoic acid, whilst reduction by the Sabatier method gives a saturated *alcohol*, b. p. 223—224°/756 mm.; hydrogenation does not take place when other methods are used. The product of interaction of *l*- α -pinene oxide with magnesium ethyl iodide is *ethylisopropylhexen- α -ol*, b. p. 142—143.5°/50 mm. With magnesium *isopropyl chloride* an *alcohol*, $C_{12}H_{22}O$, b. p. 133°/17 mm., is obtained, whilst with the corresponding bromide a mixture of products results, from which an *alcohol*, $OH \cdot C_{10}H_{16} \cdot C_4H_9$, b. p. 140—143°/17 mm., was isolated. With magnesium phenyl bromide an *alcohol*, $C_{10}H_{16} \cdot Ph \cdot OH$, b. p. 189—190°/17 mm., was obtained.

R. TRUSZKOWSKI.

Fenchene series. II. Homologue of *iso*-fenchene. G. KOMPPA (Annalen, 1929, 472, 179—184).—Magnesium methyl iodide and *isofenchone* give *methylisofenchol*, b. p. 82°/10 mm., m. p. 47°, dehydrated by sodium hydrogen sulphate at 155—160° in carbon dioxide to a mixture of hydrocarbons, $C_{11}H_{18}$, b. p. 157—162°, separable into a small fraction, b. p. 157—160°, d_4^{20} 0.84848, n_D^{20} 1.46082, and a main fraction, b. p. 160—162°, d_4^{20} 0.85205, n_D^{20} 1.46261. Treatment of the mixture with ozone in acetic acid

solution with subsequent decomposition by warming gives, after removal of the solvent, *4-acetyl-2:2:4-trimethylcyclopentanal*, together with the corresponding *acid*. Oxidation of this last substance with sodium hypobromite affords *dl-cis-fenchocamphoric acid*. The hydrocarbon mixture is, therefore, essentially *methylisofenchene* (I).

No Wagner rearrangement occurs during the dehydration.

H. BURTON.

Auto-oxidation of cedrene. A. BLUMANN, W. HELLRIEGEL, and L. SCHULZ (Ber., 1929, 62, [B], 1697—1700).—Cedrene, d^{20} 0.938, α_D^{20} —52° 30', is converted by protracted treatment with moist oxygen at 30—35° in presence of a cobalt drier into the *alcohol*, $C_{15}H_{24}O$, m. p. 103.5—104°, b. p. 160°/12 mm., d^{20} 0.821, $[\alpha]_D^{20}$ —217.5° in alcohol, converted by acetic anhydride and sodium acetate mainly into a doubly unsaturated *sesquiterpene*, $C_{15}H_{22}$. Oxidation of the alcohol with chromic acid affords cedrene, b. p. 157—159°/12 mm., m. p. 32—33°, d^{20} 1.014, n_D^{20} 1.51293, $[\alpha]_D^{20}$ —91.67° in alcohol (semicarbazone, m. p. 239—241°).

H. WREN.

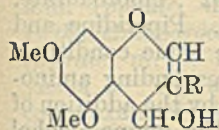
***iso*Flavone group. V. General method applicable to synthesis of derivatives of 7-hydroxyisoflavone.** W. BAKER, A. POLLARD, and R. ROBINSON (J.C.S., 1929, 1468—1473).—*m*-Methoxyphenol reacts with phenacyl bromide in presence of acetone and aqueous sodium hydroxide, forming *ω -m-methoxyphenoxyacetophenone* (I), m. p. 85—86°, converted by sulphuric acid at —5° into *6-methoxy-3-phenylcoumarone*, m. p. 43°. Treatment of an ethereal solution of I with aqueous potassium cyanide and 30% sulphuric acid affords *α -m-methoxyphenoxy-methylmandelonitrile* (II), m. p. 84—85.5°, converted by treatment with ethereal methyl-alcoholic hydrogen chloride and subsequent hydrolysis with aqueous-alcoholic potassium hydroxide into a mixture of *α -m-methoxyphenoxy-methylmandelic acid*, $+H_2O$, m. p. 74—76°, m. p. (anhydrous) 96—97° [*methyl ester* (III)], m. p. 48—49°, by the action of diazomethane on the acid], and its *amide*, m. p. 122—123°. Treatment of III with 80% sulphuric acid at 60° affords 7-methoxy-3-phenylcoumarin in poor yield. When II is treated with hydrogen chloride in presence of ether and anhydrous zinc chloride and the reaction product hydrolysed with water, *3-hydroxy-7-methoxyisoflavanone*, m. p. 133—135°, results. This is reduced by sodium amalgam and methyl alcohol to *3:4-dihydroxy-7-methoxyisoflavane*, m. p. 153°, whilst treatment with sulphuric acid gives 7-methoxyisoflavone (IV), m. p. 156°.

Oxidation of 7-methoxy-2-styrylisoflavone in pyridine solution with aqueous potassium permanganate below 40° (cf. A., 1925, i, 1299) gives *7-methoxyisoflavone-2-carboxylic acid*, m. p. 241° with loss of carbon dioxide. Thermal decomposition of this acid also yields IV (cf. *loc. cit.*).

H. BURTON.

Substances derived from anhydrocatechin tetramethyl ethers. W. BAKER (J.C.S., 1929, 1593—1604).—Anhydrocatechin tetramethyl ether (I) (cf. Drumm, A., 1923, i, 1221) is oxidised by potassium permanganate in slightly diluted acetone

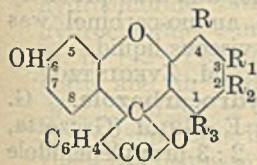
at 12—22°, yielding about 12% of 5:7:3':4'-*tetra-methoxy-3-phenylcoumarin* (II), m. p. 177°, and a substance which when boiled with hydrochloric acid gives 5:7:3':4'-*tetramethoxyisoflavylum chloride* (III) (about 8%). Demethylation of II with hydriodic acid (*d* 1.7) at 140° produces 5:7:3':4'-*tetrahydroxy-3-phenylcoumarin*, m. p. 337° (decomp.). Phloroglucinaldehyde reacts with sodium homoveratrate in presence of acetic anhydride, forming the *diacetyl* derivative, m. p. 151°, of 5:7-*dihydroxy-3':4'-dimethoxy-3-phenylcoumarin*, m. p. about 327° (decomp.). Methylation of the last-named substance with methyl sulphate yields II. Oxidation of I with potassium permanganate in slightly diluted pyridine affords about 25% of II and a trace of III. 5:7:3':4'-*Tetramethoxyisoflavylum bromide* is identical with the bromide described by Drumm (*loc. cit.*) and formulated as a pyrylium salt. Oxidation of the ψ -base from III with potassium permanganate in slightly diluted acetone or pyridine gives a trace of II and 2-hydroxy-4:6-dimethoxybenzoic acid; the major part of the material is unchanged. The annexed constitution [R=C₆H₃(OMe)₂] is assigned to the ψ -base. It is improbable that isoflavones are derived from catechin-like substances.



stances:

The "hydrochloride" of anhydrocatechin tetramethyl ether (Freudenberg, Carrara, and Cohn, A., 1926, 73) is identical with III and is conveniently prepared by saturating a solution of I in acetic acid and anhydride with hydrogen chloride. When this is carried out in an atmosphere of hydrogen, III is formed only slowly and in small amount, indicating that aerial oxidation takes place during the change I→III. The "hydrochloride" of anhydroepicatechin tetramethyl ether (Freudenberg, Fikentscher, and Wenner, A., 1925, i, 692) is identical with tetramethyl-luteolinidin chloride (Pratt, Robinson, and Williams, A., 1924, i, 306), now shown to be 5:7:3':4'-*tetramethoxyflavylum chloride hydrochloride dihydrate*, C₁₉H₁₉O₅Cl·HCl·2H₂O, m. p. 161—162° (decomp.). H. BURTON.

Fluoresceins and rhodamines of mixed type. N. N. GHATAK and S. DUTT (J. Indian Chem. Soc., 1929, 6, 465—471).—A number of unsymmetrically substituted phthaleins have been prepared by condensing *o*-2':4'-*dihydroxybenzoylbenzoic acid* with phenols or aminophenols, generally by heating with concentrated sulphuric acid or stannic chloride. Condensation always occurs in the *o*-position of the phenol to give the fluoran (annexed formula). The colours of the products deepen when the substituent hydroxy- or amino-groups are nearer to the bridge oxygen atom (cf. Dutt, A., 1927, 1006). The following fluorans



are described, and their absorption maxima, shades on silk and wool, and colour and fluorescence in solution tabulated: 6-*hydroxy*-, m. p. 181°; 4:6-*dihydroxy*-, m. p. 179°; 1:6-*dihydroxy*-, m. p. above

280°; 2:6-*dihydroxy*-, m. p. 177°; 3:4:6-*trihydroxy*-, m. p. 189°; 1:3:6-*trihydroxy*-, m. p. above 285°; 6-*hydroxy-4-methyl*-, m. p. 135°; 6-*hydroxy-3-methyl*-, m. p. 143°; 6-*hydroxy-2-methyl*-, m. p. 152°; 6-*hydroxy-1-methyl-4-isopropyl*-, m. p. 166°; 6-*hydroxy-4-methyl-1-isopropyl*-, m. p. 134°; 6-*hydroxy-3:4-benzo*-, m. p. 117°; 6-*hydroxy-2:3-benzo*-, m. p. 113°; 6-*hydroxy-2:3-(4'-hydroxy)benzo*-, m. p. 183°; 3-*dimethylamino-6-hydroxy*-, m. p. 169°; 3-*diethylamino-6-hydroxy*-, m. p. 163°.

R. K. CALLOW.

Plant colouring matters. Carotinoid pigment from maize: zeaxanthin. P. KARRER, H. SALOMON, and H. WEHRLI (Helv. Chim. Acta, 1929, 12, 790—792).—Extraction of maize with ethyl alcohol and light petroleum gives *zeaxanthin*, C₄₀H₅₆O₂, m. p. 201—202°, and a yellow pigment (flavone derivative?). With sulphuric acid *zeaxanthin* gives a stable deep blue coloration. R. J. W. LE FEVRE.

Mononitro- and dinitro-thiophens. II. Vapour pressures. V. S. BABASINTAN and J. G. JACKSON (J. Amer. Chem. Soc., 1929, 51, 2147—2151).—The vapour pressures of pure (a) nitro- and (b) dinitro-thiophens (cf. A., 1928, 1378) have been measured by an improved dynamic method at (a) 105—170°, (b) 115—250°. The calculated b. p., molecular latent heats of vaporisation, and entropies of vaporisation (cf. Hildebrand, A., 1915, ii, 416), respectively, are (a) 218.2°, 12,300 g.-cal., 14.7, and (b) 293.3°, 14,300 g.-cal., and 14.8. Nitrothiophen is stable at 170°; dinitrothiophen decomposes at 250° and reacts with mercury at 195°. H. E. F. NOTTON.

Thionaphthen derivatives. G. KOMPPA (J. pr. Chem., 1929, [ii], 122, 319—331).—In the nitration of thionaphthen with nitric and acetic acids an intermediate *substance*, m. p. 154.5°, is obtained if a deficiency of nitric acid is used for a short period. Reduction of nitrothionaphthen with stannous chloride yields the *double tin* salt, m. p. 204°, of aminothionaphthen. The free base is obtained by steam distillation of the basified reduction product and is isolated from the aqueous distillate as its acetyl, m. p. 166—167°, or *benzoyl* derivative, m. p. 132°, since the free base is unstable and, moreover, cannot be converted into hydroxythionaphthen (cf. Friedländer, A., 1907, i, 335). Sulphonation of pure thionaphthen obtained by reduction of 2-hydroxythionaphthen yields a monosulphonic acid isolated as its *sodium* salt, but with commercial thionaphthen only a mixture of mono- and di-sulphonic acids could be obtained, whence a pure disulphonic acid was isolated as its *sodium* salt. Thionaphthen and bromine in carbon tetrachloride give 2-*bromothionaphthen*, b. p. 136—137°/13 mm., *d*₄²⁰ 1.6294, the bromine atom of which is not replaced by hydroxyl either by boiling 30% aqueous sodium hydroxide or methyl-alcoholic potassium hydroxide at 200—210°, although in the latter case an acidic *substance*, C₉H₁₀O₂S, m. p. 125°, is obtained. Dibromothionaphthen, m. p. 57.5° (Komppa, A., 1894, i, 130), is also stable to 30% alkali, nitric and hydrochloric acids. Chlorination of thionaphthen in carbon tetrachloride yields 1:2(?)*-dichlorothionaphthen*, b. p. 125—127°/10 mm., m. p. 54°. 2-Thionaphthenyl methyl ketone, m. p. 64° (*semicarbazone*, m. p. 244—

245°), is obtained in 30% yield by the action of anhydrous aluminium chloride on acetyl chloride and thionaphthen in carbon disulphide solution, and is oxidised by sodium hypobromite to *thionaphthen-2-carboxylic acid*, m. p. 174—175°. J. W. BAKER.

Thiophen analogues of di-, tri-, and tetraphenylmethane compounds. W. MINNIS (J. Amer. Chem. Soc., 1929, 51, 2143—2147).—The thiophen derivatives are obtained by the methods applicable to their benzene analogues, but usually in smaller yield. Phenyl 2-thienyl ketone (Comcy, A., 1884, 1168) and phosphorus pentachloride at 60—80° give *dichlorophenylthienylmethane*, which cannot be distilled at 20 mm., whilst aluminium amalgam and ammonia give *phenyl-2-thienylcarbinol*, m. p. 57—58°. Diphenylthienylcarbinol (cf. Gomberg, A., 1913, i, 641), from phenyl thienyl ketone and magnesium phenyl bromide, is reduced by formic acid to diphenylthienylmethane and a bimolecular substance, m. p. 174°, and converted by hydrogen bromide in benzene into *diphenylthienylmethyl bromide*, m. p. 110—111° (decomp. when kept), and by hydrogen chloride into *diphenylthienylmethyl chloride*, m. p. 80—81°. *Diphenylthienylmethylamine* has m. p. 118—119°. The chloride or bromide reacts quantitatively with molecular silver in benzene, giving red solutions of *diphenylthienylmethyl*, from which a pink solid, m. p. 157—162°, was obtained. This radical resembles phenylthioxanthyl in its reactions (cf. A., 1921, i, 163). An attempt to prepare triphenylthienylmethane from triphenylmethyl chloride and magnesium thienyl iodide gave instead 5:5'-*bistriphenylmethyl-2:2'-dithienyl*, m. p. 277° (*dibromo-derivative*, m. p. 287°), also formed from triphenyl-2-iodothiophenylmethane and copper powder at 200—250°. Magnesium thienyl iodide gives with fluorenone 9-*thienylfluoren-9-ol*, m. p. 81—82°, with phenyl α -naphthyl ketone, *phenyl- α -naphthylthienylcarbinol*, m. p. 131°, and with xanthone, 9-*thienylxanthen-9-ol*, m. p. 168—169°. This gives with hydrogen chloride in ethyl acetate 9-*chloro-9-thienylxanthen*, from which a *ferrichloride*, m. p. 198°, *mercurichloride*, m. p. 182—198° (decomp.), and *zincichloride*, m. p. 225—227°, are obtained.

H. E. F. NOTTON.

Synthesis of hexahydro- β -collidine. M. DE MONTMOLLIN and M. MARTENET (Helv. Chim. Acta, 12, 1929, 604—609).—*n*-Propyl alcohol is oxidised catalytically (Sabatier-Seeders) to *n*-propaldehyde, converted by saturated potassium carbonate solution into the corresponding aldol. Reduction of the crude aldol is carried out *in situ* by aluminium turnings. From the resulting β -methylpentane- α -diol α - *dibromo- β -methylpentane*, b. p. 80—82°/12 mm., and a *bromohydroxy- β -methylpentane*, b. p. 86—94°/12 mm., are obtained by the action of phosphorus tribromide in benzene solution.

The related β -methylpentane- α -dicarboxylonitrile, b. p. 189—193°/12 mm., is reduced by sodium and boiling alcohol to γ -methyl- β -ethylpentamethylene-diamine, b. p. 100—103°/12 mm., which gives hexahydro- β -collidine hydrochloride when its ethereal solution is treated with dry hydrogen chloride. Catalytic hydrogenation (pyrophoric nickel) of β -methylpentane- α -dicarboxylonitrile results in the

direct production of about 30% of the disubstituted piperidine owing to simultaneous hydrogenation and cyclisation. R. J. W. LE FÈVRE.

[Preparation of] benzoylpiperidine. C. S. MARVEL and W. A. LAZIER (Organic Synthesis, 1929, 9, 16—19).

Action of piperidine and piperazine on the α -oxides of ethylene, isobutylene, and trimethylethylene. K. A. KRASUSKI and K. G. KOSENKO (Ukraine Chem. J., 1929, 4, 38—59).—The action of piperidine and piperazine on ethylene, isobutylene, and trimethylethylene α -oxides with the formation of α -amino-alcohols was investigated. The reaction was much more vigorous with piperidine than with piperazine, in accordance with the rule, suggested by the author, that the rate depends on the electrolytic dissociation constant of the amine. Piperidine and isobutylene oxide reacted in a sealed tube at 100° to give piperidinotrimethylcarbinol, b. p. 202—202.5°, d_4^{20} 0.9114 (hydrochloride, m. p. 191—192°; chloroaurate, m. p. 118—119°; picrate, 111.5°). Piperidine and trimethylethylene oxide under the same conditions gave only a 12% yield of the corresponding amino-alcohol, but this was raised to 70% by the addition of water to the reaction mixture. The amino-alcohol was dimethylpiperidinoethylcarbinol, b. p. 219.5—220.5° (hydrochloride, m. p. 187—179°; chloroaurate, m. p. 73—74.5°; picrate, m. p. 83—84°).

Piperazine reacted with 2 mols. of the oxides in every case, to give dihydroxy-carbinols; the monohydroxy-compounds could not be obtained. Piperazine and isobutylene oxide gave 1:4-*di- β -hydroxyisobutylpiperazine*, m. p. (+2H₂O) 78—79°, m. p. (anhydrous), 102—102.5° [*hydrochloride*, m. p. 224° (decomp.); *chloroaurate*, m. p. 198° (decomp.); *picrate*, decomposes above 200°]. With trimethylethylene, piperazine reacted less readily to give a 40% yield of 1:4-*di- β -hydroxy- α - β -dimethylpropylpiperazine*, (OH·OMe₂·CHMe)₂·C₄H₉N₂, b. p. 124—124.5° [*hydrochloride*, does not melt at 300°; *chloroaurate*, m. p. 180—182° (decomp.); *picrate*, decomposes above 220°]. Considerable quantities of trimethylethylene glycol, b. p. 176—178°, which yielded a *hexahydrate*, m. p. 23.5—24° were also obtained. If the reaction was carried out at 160—180° the yield of the carbinol was not increased, but methyl isopropyl ketone was obtained, owing apparently to the decomposition of the amino-carbinol, as the olefine oxide does not isomerise to the ketone in alkaline solution. From the higher fraction of the reaction mixture, a compound which did not form a hydrochloride, chloroaurate, or picrate, and was probably a dehydration product of the amino-carbinol was isolated in an impure state as a viscous liquid.

M. ZVEGINTZOV.

Homologues of tetrahydrocarbazole. G. PLANCHER, B. CECCHETTI, and E. GHIGI (Gazzetta, 1929, 59, 334—347).—When 2:3-propyleneindole (dihydropentindole; Perkin and Plant, J.C.S., 1923, 123, 3243) in alcoholic sodium ethoxide solution is treated with chloroform a vigorous reaction takes place in which it is assumed that the dichloromethyl group enters the 11 position and the pyrrole ring is

enlarged with the formation of 3-chloro-2:4-cyclopropylenequinoline (annexed formula), m. p. 208°. 2:3-Pentamethyleneindole, m. p. 143° (picrate, m. p. 140°), is obtained by heating cycloheptanonephenylhydrazone with 10% sulphuric acid. Only a

trace of basic product is obtained by treatment of this with chloroform and sodium ethoxide. cyclo-Heptanone-p-nitrophenylhydrazone has m. p. 137°. cycloHeptanone condenses with *as*-methylphenylhydrazine, and the product, treated with 10% sulphuric acid, yields *N*-methyl-2:3-pentamethyleneindole, m. p. 50° (picrate, m. p. 78°), which on long heating with methyl iodide yields the *hydriodide*, m. p. 249° (decomp.), of a base, C₁₅H₁₉N, m. p. 55° (picrate, m. p. 138°). When tetrahydrocarbazole is heated in a sealed tube with excess of ethyl iodide, 9:11-diethyl-Δ^{10,1}-carbazolenine *hydriodide* (I), m. p. 190—200° (decomp.), is obtained. The phenylhydrazone of 2-ethylcyclohexanone yields with sulphuric acid a mixture of 11-ethyl-Δ^N-carbazolenine, b. p. 190—195°/12 mm. (picrate, m. p. 138°) (II), and acid-soluble 1-ethyltetrahydrocarbazole, b. p. 160—175°/17 mm. (picrate, m. p. 145°) (III). With ethyl iodide, II yields I. The *as*-ethylphenylhydrazone of 2-ethylcyclohexanone yields with sulphuric acid a mixture of 1:9-diethyltetrahydrocarbazole, b. p. 200—210°/15 mm. (picrate, m. p. about 65°), and I (picrate, m. p. 131°). The postulated course of these reactions is supported by a similar series with methyl derivatives. The phenylhydrazone of 2-methylcyclohexanone, b. p. 220°/35—40 mm., yields 1-methyltetrahydrocarbazole, b. p. 208°/25 mm., m. p. 65° (picrate, m. p. 145°) (IV), and 11-methyl-Δ^N-carbazolenine, b. p. 176—177°/25 mm., m. p. 65° (picrate, m. p. 169°) (V). Reduction of IV by tin and hydrochloric acid yields 1-methylcarbazoline hydrochloride, m. p. 268°. Reduction of V yields 11-methylcarbazoline hydrochloride, m. p. 220°. With methyl iodide IV yields 1:9:11-trimethylcarbazole (picrate, m. p. 157°), whilst V yields 9:11-dimethyl-Δ^{10,1}-carbazolenine *hydriodide*, m. p. 211°. The phenylosazone of 2-hydroxycyclohexanone yields with sulphuric acid 1-ketotetrahydrocarbazole, m. p. 167° [picrate, m. p. 162°; semicarbazone, m. p. 227° (decomp.); semicarbazone picrate, m. p. 182°].

R. K. CALLOW.

Natural rotation of polarised light by optically active bases. III. Rotation, refraction, and volume of organic bases in solution. W. LEITHE (Monatsh., 1929, 52, 151—162; cf. A., 1928, 1022; this vol., 647).—The rotatory powers, refractive indices, and densities of α-pipecoline and its hydrochloride, α-phenylethylamine, γ-phenylethylamine hydrochloride, tetrahydro-2-methylquinoline and its hydrochloride, α-methylindoline and its hydrochloride, m. p. 142—143°, have been determined in the pure state and in various solvents and the values of $M_{\text{solution}} - M_{\text{substance}}$ and $V_{\text{solution}} - V_{\text{substance}}$ calculated. With α-pipecoline in water, alcohol, and methyl alcohol there is a decrease in the value of M , in carbon tetrachloride, ether, heptane, and acetone there is an increase, whilst benzene, chloroform, ethyl acetate, and pyridine have little or no influence. For com-

parison the effect of solvent on cyclohexane is examined: here the values increase throughout the series, indicating that the differences with α-pipecoline are due to solvent action on the imino-group. With phenylethylamine all the solvents used except benzene, pyridine, and water, cause generally an increase; similar differences are shown by ethylbenzene except in heptane and halides. The phenyl group has also a considerable influence on the rotatory power. Tetrahydro-2-methylquinoline and α-methylindoline give increased values, again due to the phenyl group. Ether exerts an abnormal effect on the molecular volume of the bases examined, but apart from this the variation in the rotatory powers and V is more in agreement than with the rotatory power and M . The rotatory power of α-pipecoline hydrochloride is much lower in chloroform than in water or alcohols.

H. BURTON.

Two *ms*-tetrahydro-9:9'-diacridyls (?). K. LEHMSTEDT and H. HUNDERTMARK (Ber., 1929, 62, [B], 1742—1743).—The constitution of 9:9'-diacridyl (Lehmstedt and Wirth, A., 1928, 1259) is confirmed by its conversion by zinc dust and acetic acid into tetrahydrodiacridyl, m. p. 214° with decomposition into acridine and acridan. This latter compound is not identical with the tetrahydrodiacridyl, m. p. 279°, of Schlenk and Bergmann (A., 1928, 1031 *seq.*). The "insoluble hydroacridine" of Graebe and Caro has the composition C₂₆H₂₂ON₂ and hence differs from Schlenk's compound; under certain conditions it loses water with formation of 9:10:9':10'-tetrahydro-10:10'-diacridyl, m. p. 220°. H. WREN.

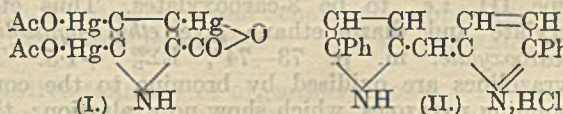
[Preparation of] pyrrole. S. M. McELVAIN and K. M. BOLLIGER (Organic Syntheses, 1929, 9, 78—79).

Inner complex salts of 2-pyridyl methyl ketoxime. B. EMMERT and K. DIEHL (Ber., 1929, 62, [B], 1738—1742).—Cobaltic hydroxide is transformed by a boiling aqueous solution of 2-pyridyl methyl ketoxime into the compound,

Co($\left\langle \begin{array}{c} \text{NO} \\ \text{NC}_5\text{H}_4 \end{array} \right\rangle \text{CMe}$)₃,⁻ decomp. 275—280°. The nickel compound is isolated as the substances 2C₁₄H₁₄O₂N₄Ni, PhOMe, C₁₄H₁₄O₂N₄Ni, 4C₅H₅N, and C₁₄H₁₄O₂N₄Ni, 2C₅H₅N, 4H₂O. The substances C₁₄H₁₄O₂N₄Zn, H₂O, 2C₁₄H₁₄O₂N₄Zn, ZnO, and C₂₈H₃₀O₄N₈Cd, decomp. above 250°, are described.

H. WREN.

Pyrrole derivatives. G. PLANCHER, G. ROSSI, and E. GHIGI (Gazzetta, 1929, 59, 347—355).—Interaction of pyrrole-2-carboxylic acid with mercuric acetate in aqueous-alcoholic solution in presence of a little acetic acid yields a compound to which the constitution I is assigned.



5-Phenylpyrrole-2-aldehyde, m. p. 138° (semicarbazone, m. p. 190°; p-nitrophenylhydrazone, m. p. 222°; azine, m. p. 240°; azlactone, m. p. 180°; compound with 1 mol. (?)5-dimethylcyclohexane-1:3-

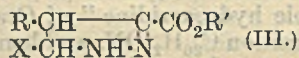
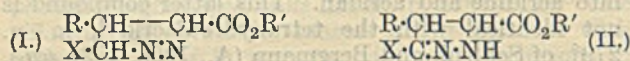
dione, m. p. 129°), is obtained in poor yield by the action of chloroform on 2-phenylpyrrole in aqueous-alcoholic potassium hydroxide solution, but in good yield by the Adams-Levine modification of the Gattermann synthesis (A., 1924, i, 860) from 2-phenylpyrrole. In the latter reaction (5-phenyl-2-pyrrolyl-(5-phenyl-2-pyrrolyl)methane hydrochloride, blue (II) (perchlorate), is formed as a by-product.

R. K. CALLOW.

Action of piperazine on isosafrole oxide. T. S. KUSNER (Ukraine Chem. J., 1929, 4, 85—88; cf. A., 1928, 999).—An equimolecular mixture of piperazine and isosafrole oxide was kept in ethyl-alcoholic solution at the ordinary temperature. Slow combination occurred, giving a compound (2 oxide + 1 base), a white powder, m. p. 238—240° (decomp.), insoluble in most organic solvents.

M. ZVEGINTZOV.

Δ^1 - and Δ^2 -Pyrazolines. K. VON AUWERS and E. CAUER (Annalen, 1929, 470, 284—312).—When a pyrazoline is formed by the addition of an aliphatic diazo-compound to an unsaturated ester, a nitrogen atom becomes attached to the α -carbon atom, and an intermediate compound of the type I is formed; this then changes, by migration of hydrogen, to give a



compound of type II or of type III (cf. Buchner, A., 1893, i, *passim*; von Pechmann, A., 1898—1901, i, *passim*). Buchner considered that compounds of type I (Δ^1 -pyrazolines) underwent immediate isomeric change; since in the cases investigated by him the groups X· and ·CO₂R' were identical, being the carbethoxyl group, types II and III (Δ^2 -pyrazolines) became identical. Compounds of each of the three types are now described.

There being no suitable chemical method, compounds of types II and III are distinguished by optical means. It has been shown (A., 1927, 1203) that 3-phenylpyrazolines, unlike the 5-phenyl isomerides, give a strong exaltation of the refractivity and dispersivity; since compounds of type III contain a conjugated system of double linkings, whilst those of type II do not, it can be assumed that compounds having exaltations comparable with that of 3-phenylpyrazoline are of type III. The author, as usual, employs the specific exaltation, EΣ, as the characteristic spectrochemical property.

Pyrazolines are prepared by the addition of diazomethane or diazoethane to a number of esters in ether at -5°, and the products are all found to be of type III, *i.e.*, to be 3-carboxylates. Thus ethyl acrylate and diazomethane give ethyl pyrazoline-3-carboxylate, m. p. 73—74°, EΣ_D²⁰ +1.5. The pyrazolines are oxidised by bromine to the corresponding pyrazoles, which show no exaltation; thus the above compound yields ethyl pyrazole-3(5)-carboxylate, m. p. 157—158°, which hydrolyses to the known acid. The addition of diazomethane takes place readily, but that of diazoethane (obtained by the

gradual addition of methyl-alcoholic potassium hydroxide to a boiling ethereal solution of nitrosoethylurethane) is slower; with methyl acrylate, methyl 5-methylpyrazoline-3-carboxylate, m. p. 42.5—44°, b. p. 138°/12 mm., EΣ_D²⁰ +1.65°, is formed, which gives a 1-acetyl derivative, b. p. 140°/12 mm., a 1-carbethoxy derivative, m. p. 84—85.5°, and, with sodium methoxide and methyl iodide, a 1-methyl derivative, b. p. about 105°/12 mm.

The preparation of conjugation-free compounds, of type II, is more difficult, but is effected by the condensation of unsaturated esters with hydrazine. With hydrazine itself, methyl β-acetylacrylate gives mainly the hydrazide of the acid, but when the hydrochloride is used, methyl 3-methylpyrazoline-5-carboxylate, b. p. 117°/12 mm., *d*₄²⁰ 1.139, *n*_D²⁰ 1.476, EΣ_D²⁰ +0.05, is obtained. This ester gives, with phenylcarbamide, a 1-phenylcarbamyl derivative, m. p. 117.5—118.5°; the acetyl derivative has m. p. 52.5—55°; the 1-carbethoxy-derivative, m. p. 53—54.5°, would be expected to be formed by ring-closure from methyl β-acetylacrylate carbethoxyhydrazone, m. p. 127—127.5°, but actually the hydrazone is regenerated. The action of methylhydrazine on methyl β-acetylacrylate gives rise to a largely resinified product, identified as methyl 1:3-dimethylpyrazoline-5-carboxylate, b. p. 104°/11 mm., *d*₄²⁰ 1.152, *n*_D²⁰ 1.501, EΣ_D²⁰ -0.05.

Similarly, methyl crotonate with diazomethane (cf. von Pechmann and Burkard, A., 1901, i, 167) yields methyl 4-methylpyrazoline-3-carboxylate, m. p. 33—35°, b. p. 139°/13 mm., EΣ_D²⁰ +1.5 (benzoyl derivative, m. p. 89—90°), which is oxidised to methyl 4-methylpyrazole-3(5)-carboxylate, m. p. 170—171°, hydrolysed to the acid. With diazoethane, methyl 4:5-dimethylpyrazoline-3-carboxylate, b. p. 139—140°/14 mm., *d*₄²⁰ 1.101, *n*_D²⁰ 1.506, EΣ_D²⁰ +1.55, is formed, which gives a 1-phenylcarbamyl derivative, m. p. 111—113°; methyl 4:5-dimethylpyrazole-3-carboxylate and its parent acid will be described later. Methyl crotonate reacts very slowly with phenyldiazomethane, to give an impure pyrazoline, oxidised and hydrolysed to 3(5)-phenyl-4-methylpyrazole-5(3)-carboxylic acid, m. p. 234—236° (decomp.).

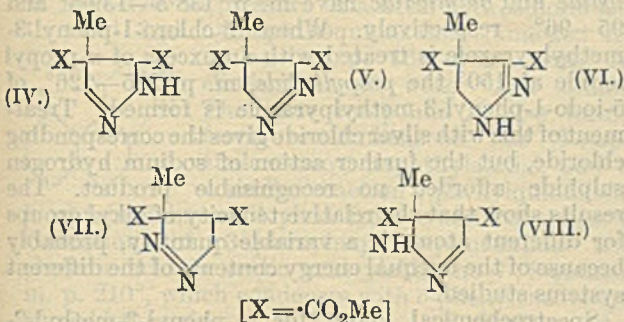
Ethyl cinnamate and diazomethane give ethyl 4-phenyl pyrazoline-3-carboxylate, m. p. 100—100.5°, oxidised to ethyl 4-phenylpyrazole-3(5)-carboxylate, m. p. 162—162.5°. From amyl cinnamate, amyl 4-phenylpyrazoline-3-carboxylate, m. p. 109—111°, *d*₄²⁰ 1.095, *n*_D²⁰ 1.617, EΣ_D²⁰ +1.05 (in quinoline, which may be responsible for the small relative deficiency of the exaltation).

The product described by Gabriel and Colman (A., 1899, i, 390) as the hydrazone of benzoylacrylic acid, from which it is obtained by the action of hydrazine, is actually 3-phenylpyrazoline-5-carboxylic acid, m. p. 186°; with acetic acid this gives a 1-acetyl derivative, m. p. 216—217.5°, and with nitrous acid a 1-nitroso-compound, m. p. 133.5° (decomp.). Attempted esterification by methyl alcohol and sulphuric acid or hydrochloric acid gave resinous products, but by the action of diazomethane the methyl ester, b. p. 178°/12 mm., *d*₄²⁰ 1.179, *n*_D²⁰ 1.578, EΣ_D²⁰ +1.35, is obtained; although this is a 5-carboxylate, it gives an exaltation, since there is a phenyl group in the 3-posi-

tion. The ester reacts with phenylcarbimide to give a 1-phenylcarbonyl derivative, m. p. 136.5—137.5°; the acid, with bromine to give 4-bromo-3(5)-phenylpyrazole-5(3)-carboxylic acid, m. p. 256—257°, identical with a specimen prepared by bromination of the parent acid.

Dimethyl malate and diazoethane yield methyl 5-methylpyrazoline-3:4-dicarboxylate, b. p. 145—153°/2 mm., $E\Sigma_D^{20} +1.4$, which is oxidised and hydrolysed to 5-methylpyrazole-3:4-dicarboxylic acid, m. p. 229—230°.

In the investigation of the possibility of the existence of compounds of type I (Δ^1 -pyrazolines), it was considered that such compounds would be most likely to have independent existence when the product to which they would invert would be non-conjugated. In the reaction between methyl citraconate and diazomethane, the conceivable products are as formulated below:



but of these IV and V can be excluded, since IV could be obtained only by inversion of V, and since V would itself invert in the opposite direction to give the conjugated compound VI. Von Pechmann and Burkard investigated the reaction (A., 1901, i, 167), and oxidised their product to the pyrazole; they considered the first product to be VII or VIII. The reaction is actually more complex, and the product from 18 g. of the original ester yields three fractions, A (3 g.), B (12 g.), and C (2 g.). A consists of methyl 1-methylcyclopropane-1:2-dicarboxylate, b. p. 104°/14 mm., $d_4^{20} 1.112$, $n_{D,20}^{20} 1.4466$, which shows exaltation of refractivity and of dispersivity, and is hydrolysed to the acid (mixed isomerides, m. p. 100—120°); the last is converted into the anhydride (cf. Ingold, A., 1925, i, 357), which takes up water from the atmosphere to form the *cis*-acid. The high-boiling fraction C is identified from its exaltation as the co-ordinated methyl 4-methylpyrazoline-3:4-dicarboxylate, m. p. 58—60°, b. p. 178°/12 mm., $E\Sigma_D^{20} +0.95$ (the somewhat low value of the exaltation is attributed to the effect of the *gem*-grouping); with phenylcarbimide, the 1-phenylcarbonyl derivative, m. p. 148—149°, is formed. Oxidation and hydrolysis gives a methylpyrazoledicarboxylic acid, m. p. 313°; such an acid could be formed by the migration of either the 4-methyl or the 4-carbomethoxyl group to the 5-position, and could thus be either 4-methylpyrazole-3:5-dicarboxylic acid, or 5-methylpyrazole-3:4-dicarboxylic acid. The latter of these is formed (m. p. 229—230°) from methyl malate (see above), and

the present substance has thus the former structure (cf. Klages, A., 1903, i, 528). The migration of the carbomethoxyl group in this oxidation is noteworthy; its elimination would have been expected.

The main fraction B, which is optically normal, must have one of the structures VII or VIII, and these can be distinguished chemically. All the Δ^2 -pyrazolines described above react vigorously with ethyl chloroformate or with phenylcarbimide; the present substance is indifferent to the former, and reacts only slowly with the latter, giving ill-defined products, and thus does not possess a secondary nitrogen atom. It must therefore be a Δ^1 -pyrazoline, namely, methyl 3-methyl- Δ^1 -pyrazoline-3:4-dicarboxylate, b. p. 148°/12 mm., $d_4^{20} 1.200$, $n_{D,20}^{20} 1.464$, $E\Sigma_D^{20} 0.0$. This is confirmed by the fact that the action of hydrogen chloride converts it into the hydrochloride, m. p. about 120°, of methyl 5-methylpyrazoline-4:5-dicarboxylate (the structure VIII above), b. p. 172°/20 mm., $d_4^{20} 1.230$, $n_{D,20}^{20} 1.479$, $E\Sigma_D^{20} +0.05$, which reacts with phenylcarbimide, giving unidentified products. Oxidation of either the Δ^1 - or of this Δ^2 -pyrazoline gives 3(5)-methylpyrazole-4-carboxylic acid (cf. von Pechmann and Burkard, *loc. cit.*); carbomethoxyl has been eliminated from the *gem*-grouping.

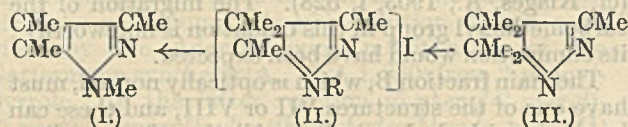
Methyl dimethylmalate, b. p. 106°/17 mm., obtained from the anhydride (Ott, A., 1928, 1351), reacts with diazomethane to form a product which is optically normal, and is identified as methyl 3:4-dimethyl- Δ^1 -pyrazoline-3:4-dicarboxylate, m. p. 49—51°, b. p. 149°/11 mm., $d_4^{20} 1.172$, $n_{D,20}^{20} 1.446$, $E\Sigma_D^{20} 0.0$, since it reacts only very slowly with phenylcarbimide, and since it is converted by hydrogen chloride into the hydrochloride, m. p. about 160°, of methyl 4:5-dimethyl- Δ^2 -pyrazoline-4:5-dicarboxylate, m. p. 71—73°, $E\Sigma_D^{20} -0.05$, which reacts more rapidly with phenylcarbimide, forming the same product as the Δ^1 -compound, a 1-phenylcarbonyl derivative, m. p. 136—137°. An attempt to oxidise the Δ^1 -compound by bromine yielded the hydrobromide of the isomeride.

It was hoped that methyl 4-phenyl-3-methyl- Δ^1 -pyrazoline-3-carboxylate might be obtained by the interaction of methyl α -methylcinnamate and diazomethane, but the product was unstable and lost nitrogen to give a substance which from spectrochemical evidence could not be a cyclopropane derivative, and was considered to be a methyl $\alpha\beta$ -dimethylcinnamate (probably the *cis*-form, since hydrolysis gave an oil), b. p. 134°/17 mm., $d_4^{20} 1.051$, $n_{D,20}^{20} 1.5347$, of exaltation comparable with that of ethyl *trans*- $\alpha\beta$ -dimethylcinnamate (von Auwers, A., 1917, i, 267).

A tabular conspectus is given of various spectrochemical properties of the Δ^1 - and Δ^2 -pyrazolines described above; an investigation of the stereochemistry, stability, and chemical properties of Δ^1 -pyrazolines is promised. E. W. WIGNALL.

Relative tenacity of organic radicals. K. VON AUWERS and F. BERGMANN (Annalen, 1929, 472, 287—314).—Knorr and Oettinger's observation (A., 1894, i, 546; Diss., Jena, 1894) that 1:3:4:5-tetramethylpyrazole (I) is formed by thermal decomposition of the methiodide (II, R=Me) of 3:4:4:5-

tetramethylpyrazole (III) is confirmed. Similar de-

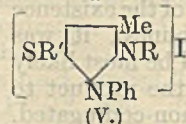


composition of a series of *iodides* corresponding with II, namely, *ethyl* (II, R=Et), m. p. 167°; *n-propyl*, m. p. 142—142.5°; *isopropyl*, m. p. 157—158.5°; *allyl*, m. p. 165°, and *benzyl*, m. p. 132—133°, shows that with the exception of the *isopropyl* derivative elimination of both R and 4-methyl groups occurs. The percentages of 4-methyl group eliminated in the above series are 74, 89, 100, 35, and 33.5, respectively. The strength of attachment of the Pr^β group to nitrogen is greater than that of the Pr^α group (cf. A., 1928, 306). 1-*Ethyl*-, b. p. 192—193° (*picrate*, m. p. 156—157°); 1-*n-propyl*-, b. p. 94—95°/15 mm. (*picrate*, m. p. 107—107.5°); 1-*isopropyl*-, b. p. 89—91°/15 mm. (*picrate*, m. p. 137—138.5°); 1-*allyl*-, b. p. 94—96°/13 mm. (*picrate*, m. p. 119—120°), and 1-*benzyl*-3:4:5-*trimethylpyrazoles*, b. p. 163°/16 mm. (*picrate*, m. p. 148—148.5°), are prepared by the action of the requisite alkyl iodide and benzyl chloride on 3:4:5-trimethylpyrazole. In order to determine the difference in the attachment of methyl and ethyl groups to carbon, decompositions of the following quaternary *iodides* of 3:5-dimethyl-4:4-diethylpyrazole, b. p. 130—133°/17 mm., m. p. 52—53° and 72—73.5° (when kept in a desiccator) (*picrate*, m. p. 193° after previous softening) (obtained from diethylacetylacetone and hydrazine), were carried out: *methyl*, m. p. 186°; *n-propyl*, m. p. 106—112°; *isopropyl*, m. p. 161.5—162°; *allyl*, m. p. 123.5—125°, and *benzyl*, m. p. 148.5—149°. The percentages of 4-ethyl group eliminated are 79, 100, 100, 90, and 75.5, respectively, indicating a stronger attachment of methyl than of ethyl to carbon. In both these series of decompositions the temperature has an effect on the ratio C-alkyl:N-alkyl obtained; the amount of C-alkyl fission is usually lowered with rise of temperature. Hydrazine hydrate and ethylacetylacetone yield 3:5-dimethyl-4-ethylpyrazole (IV), b. p. 133—135°/15 mm., m. p. 53.5—54.5° (*picrate*, m. p. 211—212°); with methylhydrazine, 1:3:5-trimethyl-4-ethylpyrazole, b. p. 84—86°/12 mm. (*hydrochloride*, m. p. 114.5—115°; *picrate*, m. p. 134.5—135.5°), results. 1-*Ethyl*-, b. p. 86—89°/13 mm. (*picrate*, m. p. 108—109°); 1-*n-propyl*-, b. p. 98—100°/12 mm. (*picrate*, m. p. 116.5—117°); 1-*isopropyl*-, b. p. 90—92°/13 mm. (*picrate*, m. p. 112.5—113.5°); 1-*allyl*-, b. p. 100—103°/14 mm. (*picrate*, m. p. 75—76°), and 1-*benzyl*-3:5-dimethyl-4-ethylpyrazoles, b. p. 162—164°/12-mm. (*picrate*, m. p. 126—127.5°), are prepared by the action of the requisite alkyl iodide and benzyl chloride on IV. γ -Dibenzoyl-*n*-pentane reacts with hydrazine, yielding 3:5-diphenyl-4:4-diethylpyrazole, m. p. 155.5° (*picrate*, m. p. 160—161°). Thermal decomposition of the *methiodide*, m. p. 196.5°, of this gives 3:5-diphenyl-1-methyl-4-ethylpyrazole, m. p. 80—82° (*picrate*, m. p. 138—139°), also obtained by methylation of 3:5-diphenyl-4-ethylpyrazole, m. p. 167°. 3:5-Diphenyl-1:4-diethyl-, m. p. 63—64°

(*picrate*, m. p. 122.5—123.5°), and 3:5-diphenyl-1-benzyl-4-ethylpyrazole, m. p. 83—83.5° (*picrate*, m. p. 111.5—112.5°), are also described. 3:5-Diphenylpyrazole *picrate* has m. p. 161—163°.

Knorr's observation (A., 1897, i, 108) that thermal decomposition of antipyrine ψ -ethiodide yields ethyl iodide and antipyrine, is also confirmed. From this and various observations recorded in the literature it is concluded that the strength of attachment of alkyl groups to oxygen is much less than that to nitrogen.

Decomposition of a series of thiopyrine ψ -alkyl iodides (V) (cf. Michaelis, A., 1904, i, 780), shows that elimination of both R and R' occurs. Thus when R=Me and R'=Et, Pr, Bu, and C₃H₅, the percentages of R eliminated are 13—28,



45—46, 55, and 10.5, respectively. When R'=Me and R=Et and C₃H₅, the corresponding elimination is 89—94 and 87%, respectively. Thiopyrine ψ -propyl iodide and butyl iodide have m. p. 138.5—139.5° and 95—96°, respectively. When 5-chloro-1-phenyl-3-methylpyrazole is treated with an excess of *n*-propyl iodide at 150° the propyl iodide, m. p. 225—226°, of 5-iodo-1-phenyl-3-methylpyrazole is formed. Treatment of this with silver chloride gives the corresponding chloride, but the further action of sodium hydrogen sulphide afforded no recognisable product. The results show that the relative tenacity of alkyl groups for different atoms is a variable quantity, probably because of the unequal energy contents of the different systems studied.

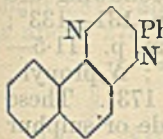
Spectrochemical data for 1-phenyl-3-methyl-2-ethyl-, 1-phenyl-2:3:4-trimethyl-, and 1-phenyl-3:4:4-trimethyl-5-pyrazolones, and 5-methoxy- and 5-methylthiol-1-phenyl-3-methylpyrazoles, are given. These support Knorr's structure for antipyrine but do not afford a certain proof. 1-Phenyl-4-ethyl-5-pyrazolone has m. p. 114—115.5° (lit. 78°).

H. BURTON.

Isomerism of diphenylmethylpyrazoles. K. VON AUWERS and K. SCHAUM (Ber., 1929, 62, [B], 1671—1677).—In the cases of the isomeric 1:5-diphenyl-3-methylpyrazoles, m. p. 63° and 72°, respectively, and 1:3-diphenyl-5-methylpyrazoles, m. p. 47° and 77°, respectively, it is found that the stable modification causes transformation of the isomeric as well as its own labile form. The existence of isomeric forms of 3-phenylindazole, 5-chloro-, 5-bromo-, and 7-acetamido-5-methyl-indazoles, can be explained by assuming structures analogous to C₆H₄< $\begin{array}{c} \text{CPh} \\ \text{NH} \end{array}$ >N and C₆H₄< $\begin{array}{c} \text{CPh} \\ \text{N} \end{array}$ >NH, but the validity of the hypothesis is rendered doubtful by its non-applicability to the diphenylmethylpyrazoles in which a free imino-hydrogen atom is not present. The capacity of transformation of the diphenylmethylpyrazoles in the crystalline state appears to consign this case of isomerism to the large group of polymorphism. The main types of the latter phenomenon are considered at length under the headings: physical polymorphism, chemical polymorphism, cryptochemical polymorphism, cryptochemical-metamerism, and cryptochemical-polymeric polymorphism. H. WREN.

Inner complex salts of pyrrole derivatives. B. EMMERT, K. DIEHL, and F. GOLLWITZER (Ber., 1929, 62, [B], 1733—1738; cf. A., 1927, 1204).—*Nickel pyridylpyrrole*, $\text{Ni} \left(\begin{array}{c} \text{NC}_5\text{H}_3 \\ \text{NC}_5\text{H}_3 \end{array} \right)$, m. p. 165°, is prepared by the action of nickel oxide on 2-2'-pyridylpyrrole in boiling naphthalene. The corresponding *aluminium salt*, m. p. about 310°, and *cadmium compound* are described. Pyrrole-2-aldehyde affords a *copper compound*, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{Cu}$. The aldehyde is converted by aqueous methylamine into the corresponding *methylimide*, $\text{C}_4\text{H}_4\text{N}\cdot\text{CH}\cdot\text{NMe}$, m. p. 57°, which yields a *copper salt*, $\text{C}_{12}\text{H}_{14}\text{N}_4\text{Cu}$, m. p. 163—165°, and a *cobalt compound*, $\text{C}_{18}\text{H}_{21}\text{N}_6\text{Co}$, m. p. 250—252° (additive compound, $\text{C}_{25}\text{H}_{29}\text{ON}_6\text{Co}$, with anisole). H. WREN.

Formation of the quinoxaline nucleus. G. B. CRIPPA (Gazzetta, 1929, 59, 330—334).—Benzene-azo- β -naphthylamine condenses with acetophenone at 165—170° in presence of a little hydrochloric acid to yield 3-phenyl-naphthoquinoxaline (annexed formula), m. p. 161—162°, with the elimination of water and aniline. The same compound is also formed from *m*-nitrobenzene- or 1-naphthalene-azo- β -naphthylamine, and by a similar reaction 2-phenylquinoxaline is obtained in small yield from *o*-aminoazobenzene. Oxidation of 3-phenyl-naphthoquinoxaline with chromic acid in acetic acid yields the 7:8-quinone, m. p. 210°, which condenses with *o*-phenylenediamine to yield the *azine*, m. p. 272°. R. K. CALLOW.



Complexes derived from triazinetricarboxylic acid. P. PASCAL and R. LECUIR (Compt. rend., 1929, 189, 49—51; cf. A., 1925, i, 984).—The following complex derivatives of triazinetricarboxylic acid were prepared by adding the appropriate heavy metal salt to a solution of the potassium salt of the acid until the precipitate formed just ceases to redissolve in the excess of the alkali salt [$\text{X} = \text{C}_3\text{N}_3(\text{CO}_2)_3$]: $\text{K}_6\text{Fe}(\text{FeX}_2)_2 \cdot 24\text{H}_2\text{O}$, greyish-violet; $\text{K}_2\text{Mn}(\text{MnX}_6) \cdot 6\text{H}_2\text{O}$, yellow; $\text{K}_3\text{Cr}(\text{CrX}_2)_2 \cdot 40\text{H}_2\text{O}$, greyish-violet; $\text{K}_3\text{Co}(\text{CoX}_2)_2 \cdot 24\text{H}_2\text{O}$, pale violet; $\text{K}_3\text{Fe}(\text{FeX}_2) \cdot 3\text{K}_3(\text{FeX}_2) \cdot 40\text{H}_2\text{O}$, orange-yellow; $\text{K}_2\text{Ni}(\text{NiX}_2) \cdot \text{H}_2\text{O}$, green; $\text{K}_6\text{Co}(\text{CoX}_2)_2 \cdot 8\text{H}_2\text{O}$, yellow. By adding the potassium salt to that of the heavy metal with the latter always in excess, there were formed the complexes $\text{Fe}(\text{FeX}_2)_2 \cdot 24\text{H}_2\text{O}$, yellow; $\text{Co}_2(\text{CoX}_2)_2 \cdot 9\text{H}_2\text{O}$, yellow; and $\text{Ni}_2(\text{NiX}_2)_2 \cdot 4\text{H}_2\text{O}$, green; but not the corresponding derivatives of manganese or chromium. Using concentrated solutions containing a large excess of the potassium salt, the following derivatives were separated by the addition of alcohol: $\text{K}_4(\text{FeX}_2)$, wine-red, and $\text{K}_3(\text{FeX}_2) \cdot 20\text{H}_2\text{O}$, orange-yellow. The yellow compound, $\text{Co}_2(\text{CoX}_2)_2 \cdot 9\text{H}_2\text{O}$, already mentioned, undergoes internal hydrolysis of the triazinetricarboxylic chain, in presence of a slightly acid solution, to form the pink isomeric double salt, $\text{Co}_2(\text{CoX}_2)_2 \cdot 9(\text{NH}_4)_2(\text{Co}[\text{C}_2\text{O}_4]_2)$. B. W. ANDERSON.

Poly-membered ring system. B. EMMERT and F. MEIKNER (Ber., 1929, 62, [B], 1731—1733).—

4:4'-Dipiperidyl is converted by benzaldehyde in the presence of alcohol into *dibenzylidenedipiperidyl*, $\text{CHPh} \left\langle \begin{array}{c} \text{NC}_5\text{H}_9 \cdot \text{C}_5\text{H}_9\text{N} \\ \text{NC}_5\text{H}_9 \cdot \text{C}_5\text{H}_9\text{N} \end{array} \right\rangle \text{CHPh}$, m. p. 189°, readily hydrolysed to its components by dilute hydrochloric acid. Formaldehyde and dipiperidyl afford the compound $(\text{C}_{11}\text{H}_{20}\text{N}_2)_2$, m. p. about 285° after darkening, whilst with *p*-hydroxybenzaldehyde the substance $[\text{C}_5\text{H}_9\text{N}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2$, m. p. 153°, is produced. H. WREN.

Alkylxanthines. D. W. MACCORQUODALE (J. Amer. Chem. Soc., 1925, 51, 2245—2251).—8-Chloroxanthine, prepared by Fischer's method (A., 1898, i, 48), is converted by ethyl iodide and *N*-potassium hydroxide at 90—95° into 8-chloro-3:7-diethylxanthine (I), m. p. 207° (all m. p. corr.) (cf. Biltz and Peukert, A., 1925, i, 1462). This with 10% potassium hydroxide in absolute alcohol gives 8-ethoxy-3:7-diethylxanthine, m. p. 212°, hydrolysed by hydrochloric acid to 3:7-diethyluric acid, m. p. 371—376°. Methylation of I gives 8-chloro-1-methyl-3:7-diethylxanthine, m. p. 114.5°, from which 8-ethoxy-1-methyl-3:7-diethylxanthine, m. p. 112°, and 1-methyl-3:7-diethyluric acid are prepared, and ethylation of I gives 8-chloro-1:3:7-triethylxanthine, m. p. 79—80°, reduced by hydriodic acid at 100° to 1:3:7-triethylxanthine. 8-Chloroxanthine, *n*-butyl iodide, and potassium hydroxide at 130° give 8-chloro-3:7-dibutylxanthine, m. p. 145°, from which 3:7-dibutylxanthine, m. p. 127°, 8-chloro-1:3:7-tributylxanthine, b. p. 232—240°/10 mm. (uncorr.), and 1:3:7-tributylxanthine, m. p. 41—42° (hydrochloride, m. p. 131—134°), are prepared. H. E. F. NOTTON.

Hæmin synthesis. H. FISCHER (Naturwiss., 1929, 17, 611—617).—See this vol., 333.

Amino-derivatives of 1-thio- and furo-3:4-diazoles. R. STOLLÉ and K. FEHRENBACH (J. pr. Chem., 1929, [ii], 122, 289—318).—Treatment of 2-amino-1:3:4-thiodiazole (Freund and Meinecke, A., 1897, i, 122) with nitrous acid yields a diazonium salt which couples with phenol to yield 2-*p*-hydroxybenzeneazo-1:3:4-thiodiazole, decomp. 270°. Similarly, from the corresponding 5-methyl compound (*loc. cit.*) is obtained 2-*p*-hydroxybenzeneazo-5-methyl-1:3:4-thiodiazole, decomp. 270°. The action of nitrous acid on 2:5-diamino-1:3:4-thiodiazole (I) (Fromm, A., 1923, i, 1239) in 12% acetic acid converts it into the 2-nitrosoamino-derivative, identical with the compound erroneously described as di-iminotetrahydrothiodiazole by Busch and Lotz (A., 1915, i, 317). This is reduced by stannous chloride to 2-hydrazino-5-amino-1:3:4-thiodiazole dihydrochloride, decomp. 207° [benzylidene derivative of the free base, m. p. 232° (decomp.)]; hydrochloride of benzylidene derivative, m. p. 250° (decomp.), converted by nitrous acid into the 2-azido-compound. Diazotisation of I in concentrated hydrochloric acid yields the 2-diazonium chloride, which couples with phenol to yield 2-*p*-hydroxybenzeneazo-5-amino-1:3:4-thiodiazole hydrochloride, decomp. 260° [ON-diacetyl derivative of the free base, m. p. 315° (decomp.)], and by heating

in hydrochloric acid solution is converted into the hydrochloride, m. p. 110°, of 2-chloro-5-amino-1:3:4-thiodiazole, m. p. 192° (decomp.), which is oxidised with bleaching powder to 2:2'-dichloro-5:5'-azo-1:3:4-thiodiazole, m. p. 274° (decomp.). Diazotisation of I with sodium nitrite and concentrated hydrochloric acid at -10° yields the bisdiazonium salt, since on warming the solution 2:5-dichloro-1:3:4-thiodiazole, m. p. 74°, is obtained. If, however, nitrogen trioxide is passed into the boiling diazonium solution the product is 2-chloro-5-hydroxy-1:3:4-thiodiazole, m. p. 107°. Similar diazotisation of I in 40% hydrobromic acid at -10° yields the corresponding 2:5-dibromo-derivative, m. p. 111°. The action of nitrous acid on 2-thiol-5-amino-1:3:4-thiodiazole (Freund and Imgart, A., 1895, i, 400; cf. Busch and Lotz, *loc. cit.*) in dilute hydrochloric acid yields bis-(5:5'-nitrosoamino-1:3:4-thiodiazole) 2:2'-disulphide, decomp. 120°, reduced by stannous chloride to 2-thiol-5-hydrazino-1:3:4-thiodiazole hydrochloride, decomp. 212° (benzylidene derivative of the free base, decomp. 255°). Corresponding aminofurodiazoles are prepared by the action of lead oxide on the appropriate acylthiosemicarbazide, hydrogen sulphide being eliminated. Thus acetylthiosemicarbazide, +H₂O, m. p. 105°, and anhydrous, m. p. 165° (cf. Freund and Meinecke, *loc. cit.*), yields 2-amino-5-methyl-1:3:4-furodiazole, m. p. 183° [acetyl derivative, m. p. 180°, identical with that obtained by the action of acetic anhydride on 5-amino-1:2:3:4-tetrazole (Stollé, this vol., 828)]. Benzoylthiosemicarbazide yields 2-amino-5-phenyl-1:3:4-furodiazole (II), decomp. 245° (hydrochloride, decomp. 177°; acetyl derivative, m. p. 223°; benzoyl derivative, m. p. 203°); the same compound is prepared from 1:4-dibenzoylthiosemicarbazide, m. p. 176°, obtained by the action of benzoylhydrazine on benzoylthiocarbimide, one benzoyl group being eliminated. By the action of nitrous acid in dilute hydrochloric acid II yields the 2-nitrosoamino-derivative, decomp. 101°, reduced by zinc dust and water to the 2-hydrazino-compound, which is isolated as its benzylidene derivative, m. p. 242° (decomp.) (decomposed by boiling dilute hydrochloric acid to benzoic acid, benzaldehyde, and carbonylhydrazide), or is converted by the further action of nitrous acid (in acetic acid) into 2-azido-5-phenyl-1:3:4-furodiazole, m. p. 89°. Oxidation of II with bleaching powder yields 5:5'-diphenyl-2:2'-azo-1:3:4-furodiazole, m. p. 330° (decomp.), reduced by alcoholic ammonium sulphide to the corresponding hydrazo-derivative, m. p. 233° (decomp.). An attempt to prepare 2:5-diamino-1:3:4-furodiazole by the action of lead oxide on hydrazothiodicarbonyl amide yielded only hydrazodicarbonyl amide. J. W. BAKER.

Formation and stability of 2-thio-1:2-dihydrobenzothiazoles. E. W. McCLELLAND, L. A. WARREN, and (MISS) J. H. JACKSON (J.C.S., 1929, 1582—1588).—2-Dithiobenzoyl (improved method of preparation given) reacts with phosphorus pentasulphide in boiling xylene yielding 2:3-dithiosulphindene, m. p. 94—95° (lit. 98°), which when treated with primary amines, usually in alcoholic

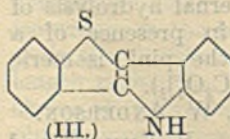
solution, gives 1-substituted 2-thio-1:2-dihydrobenzothiazoles, C₆H₄<S>NR (I). The following are described: 1-methyl- (I, R=Me), m. p. 138—139°; 1-ethyl-, m. p. 63—64°; 1-benzyl-, m. p. 122—123°, and 1-phenyl-, m. p. 77°. These compounds are converted by treatment with hydrogen sulphide into 2:3-dithiosulphindene, but are unaffected by sulphur dioxide. 2-Keto-1-methyl-1:2-dihydrobenzothiazole (I, CS=CO, R=Me) and 2-keto-1-phenyl-1:2-dihydrobenzothiazole are reduced by sulphur dioxide to 2:2'-dithiobenzomethylamide and 2:2'-dithiobenzanilide, respectively (cf. McClelland and Longwell, J.C.S., 1923, 123, 3310). Replacement of oxygen by sulphur in these benzothiazoles thus causes an increase in the stability of the N-S linking. Oxidation of the above thiodihydrobenzothiazoles with hydrogen peroxide in acetic acid solution at 100° gives N-substituted o-benzoic sulphinides, C₆H₄<SO₂>NR (II), also formed by similar oxidation of 2:2'-dithiobenzamides. The following are described: N-methyl- (II, R=Me), m. p. 131—133°; N-ethyl-, m. p. 94—94.5°; N-benzyl-, m. p. 111.5—113.5° (lit. 118°); N-phenyl-, m. p. 191°; N-propyl-, m. p. 75—76°, and N-o-tolyl-, m. p. 173°. These are also unaffected by hydrogen sulphide or sulphur dioxide. 2:2'-Dithiobenzonitrile (from the corresponding amide by dehydration with phosphoric oxide in boiling xylene) is converted by treatment with hydrogen sulphide in presence of alcohol and a small amount of sodium ethoxide into 2:3-dithiosulphindene. 2-Thio-1:2-dihydrobenzothiazole could not be prepared.

The increased stability of the S-N linking in I and II is probably due to an increase in the positive character of the o-sulphur atom; if this effect is due to an electronic displacement the CS group must exert a greater influence than the CO group in series I. H. BURTON.

Determination of methylene-blue. M. FRANÇOIS and L. SEGUIN (J. Pharm. Chim., 1929, [viii], 10, 5—9).—Methylene-blue can be determined by precipitation with picric acid as methylene-blue picrate trihydrate. R. J. W. LE FÈVRE.

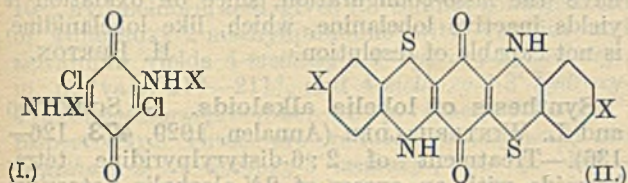
Thionaphthindole. E. W. McCLELLAND (J.C.S., 1929, 1588—1593).—When 2-keto-1:2-dihydrobenzothiazole is treated with acetic anhydride and anhydrous potassium acetate at 120°, 1-acetyl-2-methylene-1:2-dihydrobenzothiazole (I),

C₆H₄<S>C(CH₂)NAc, m. p. 168—170°, is obtained together with o-thiolacetophenone (II) [semicarbazone, m. p. 235° (decomp.)], and 2-acetyl-3-oxy-1-thionaphthen. Formation of I occurs presumably by loss of carbon dioxide from the intermediate unsaturated carboxylic acid. Hydrolysis of I with 2N-hydrochloric acid affords 3-oxy-1-thionaphthen, whilst treatment with bromine in chloroform solution gives a bromo-derivative, m. p. 201—202°. Treatment of II with phenyl-



hydrazine in warm, glacial acetic acid solution yields *thionaphthindole* (III), m. p. 252—253° (*N*-acetyl derivative, m. p. 160—161°), also obtained from 2-thioacetophenone synthesised from *o*-aminoacetophenone by Leuckart's method (G.P. 198,509). Treatment of *o*-thiolbenzoic acid with *o*-nitrobenzyl chloride in presence of alcoholic potassium ethoxide, subsequent treatment of the product formed with alcoholic potassium ethoxide, and further reduction of the intermediate thionaphthen so formed with zinc dust and acetic acid also yields III. The ready formation of III from II indicates that a sulphur atom *ortho* to carbonyl promotes enolisation, thus rendering the indole transformation facile. H. BURTON.

Derivatives of dibenzodithiazinequinone—vat dyes. II. R. SHIBATA, S. TESHIMA, and Y. ASAGI (Tech. Rep. Tôhoku, 1929, 8, 279—295).—Condensation of chloranil in boiling alcoholic solution with *p*-chloroaniline or *p*-bromoaniline gives *dichloro-* or *dibromo-*condensation products (I; X=C₆H₄hal.), m. p. 305—307° (after decomp. and sublimation at about 287°) and m. p. 285—289° (with sublimation at about 275°), respectively. Both substances give



amorphous *mercaptans* by treatment with aqueous sodium sulphide solution; those, by oxidation with boiling nitrobenzene, yield *dichloro-* and *dibromo-dibenzodithiazinequinone* (II; X=Cl or Br), both decomp. above 360°.

Condensation of chloroanil with *p*-aminophenol similarly gives a *product* (I; X=C₆H₄·OH), m. p. 264° (decomp.), from which is derived, through the corresponding *mercaptan*, *dihydroxydibenzodithiazinequinone* (II; X=OH) (also obtained by treatment of the analogous *ethoxy-*derivative [*sulphoxide* described] from *p*-phenetidine with aqueous hydrobromic acid under pressure; the *ethoxy-*intermediate compound [I; X=C₆H₄·OEt], decomp. 263°). *p*-Aminophenyl acetate condenses with chloroanil in boiling alcoholic solution giving a *compound* (I; X=C₆H₄·OAc), decomp. 280°; treatment of this with aqueous sodium sulphide solution gives the *mercaptan* derived from the substance, m. p. 264° (decomp.), above.

From the condensation of chloroanil with β -naphthylamine *dinaphthodithiazinequinone* (corresponding *sulphoxide* and its sodium *salt*) is obtained, a *compound* (I; X=C₁₀H₇), decomp. 273°, being obtained immediately. R. J. W. LE FÈVRE.

Ketosulphonic acids. I. **Synthesis of 1:2:3-thiodiazole derivatives.** P. MAZÁK and J. SUSZKO (Rocz. Chem., 1929, 9, 431—443).—Phenylmethyl-dihydrothiodiazole dioxide (see this vol., 829) is extremely resistant to the action of acids, and the nitrogen atoms possess no tendency towards salt-formation with acids. Alkali hydroxides, on the other hand,

hydrolyse it to acetonesulphonic acid phenylhydrazone. The m. p. of the dioxide is 84—85°, and of the 5-bromo-derivative, 123°. R. TRUSZKOWSKI.

Alkaloids of chinese *Corydalis ambigua*, Cham. et Sch. (Yen-Hu-So). III. **Corydalis-I and monomethyl ethers of corydalis-F and -G.** T. Q. CHOU (Chinese J. Physiol., 1929, 3, 301—305).—In addition to the eight alkaloids previously obtained from the tubers of this plant (cf. A., 1928, 927; this vol., 477), another has now been isolated, *corydalis-I*, m. p. 104°, [α]_D²⁵ in alcohol +112.5° (*hydrogen oxalate*, m. p. 185°; *hydrochloride*, m. p. 236°; *hydrobromide*, m. p. 241°), which appears to act as a depressor towards the central nervous system. The monomethyl ether, C₂₁H₂₅O₄N, m. p. 140°, [α]_D²⁵ -275° (in alcohol), of corydalis-F, prepared by the action of nitrosomethylurethane in presence of sodium hydroxide on corydalis-F, appears to be *l*-tetrahydropalmitate (Späth, Mosettig, and Tröthandl, A., 1923, i, 593). The monomethyl ether, m. p. 135°, [α]_D²⁵ +300°, of corydalis-G, prepared similarly, is identical with corydaline (corydalis-A), whence corydalis-G is the corybulbine of Freund and Josephi (A., 1894, i, 100).

C. C. N. VASS.

Lobelia alkaloids. III. **Constitution of lobelia alkaloids.** H. WIELAND and O. DRAGENDORFF (Annalen, 1929, 473, 83—101).—Oxidation of lobelanidine and lobeline with chromic oxide in acetic acid solution gives lobelanine (I), which when treated with phenylhydrazine in presence of 50% acetic acid affords an additive *compound*,

C₂₂H₂₅O₂N₂NH₂·NHPh, m. p. 187° (decomp.). Oxidation of I with hydrogen peroxide in acetic acid solution yields *lobelanine N-oxide*, m. p. 84—86° (not sharp; *hydrochloride*, m. p. 169°), reduced by sulphurous acid to I and unaffected by heating with 20% sulphuric acid. Distillation of lobelanine hydrochloride (II), m. p. 196°, with zinc dust gives rather more than 1 mol. of acetophenone, indicating the presence of two phenacyl groups in I. *Lobelaninedioxime*, m. p. 209° (decomp.; prepared in not very good yield from II, hydroxylamine hydrochloride, and potassium acetate in aqueous solution), probably exists in stereoisomeric forms, and is converted by treatment with cold thionyl chloride in chloroform into the *dianilide*, m. p. 218—219°, of *lobelinic acid* [1-methylpiperidine-2:6-diacetic acid], m. p. 225—228° (decomp.; *chloroaurate*, decomp. 215—217°). Oxidation of I with chromic oxide and 33% sulphuric acid affords benzoic and scopolinic [1-methylpiperidine-2:6-dicarboxylic] acids. Treatment of I with methyl iodide and dissolution of the product in methyl alcohol affords a small amount of the hydriodide of I, together with a soluble quaternary iodide, which on treatment with silver oxide eliminates trimethylamine. Extraction of the residue with hydrochloric acid affords 50% of unchanged material together with a *hydrochloride*, C₂₃H₂₉O₃N·HCl, m. p. 236° (decomp.) [the free *base*, m. p. 164°, is probably CH₂Bz·CHNMe₂·[CH₂]₃·CH(OH)·CH₂Bz], and a neutral fraction (A). Hydrogenation of A in presence of palladium-black and alcohol affords $\alpha\eta$ -dibenzoyl-*n*-heptane (III), m. p. 56—57° (lit. 44°),

oxidised by chromic oxide in acetic acid solution to ζ -benzoyl-*n*-heptoic acid, m. p. 84—85°, benzoic and impure pimelic acids. Catalytic reduction of *A* in presence of acetic acid gives α -diphenyl-*n*-nonane- α -diol, oxidised by chromic oxide and acetic acid to III.

Lobelanine is, therefore, 2 : 6-diphenacyl-1-methylpiperidine, whilst lobeline and lobelanidine are respectively the mono- and di-alcohols derived by successive reduction of the keto-groups in I (cf. A., 1925, i, 1087). Since I is a β -aminoketone, hydrolysis (with ring fission) occurs readily and the formation of diphenylcarbinol and fluorene during alkaline and acid hydrolysis of I (*loc. cit.*) is readily explained by assuming successive elimination of acetophenone and methylamine, and subsequent ring closure to partly hydrogenated benzophenone derivatives. Ring fission occurs also during the action of methyl iodide on I.

H. BURTON.

Lobelia alkaloids. IV. Synthesis of lobelia alkaloids. H. WIELAND and I. DRISHAUS (Annalen, 1929, 473, 102—118).—Reduction of 2 : 6-distyrylpyridine with sodium and alcohol gives a mixture of stereoisomeric 2 : 6-di- β -phenylethylpiperidines, separable through the hydrochlorides into *meso*-norlobelan, $C_{21}H_{27}N$ [hydrochloride, m. p. 195°; the methiodide, $C_{22}H_{29}N, MeI$, m. p. 234°, obtained by the action of methyl iodide is identical with lobelan methiodide (A., 1925, i, 1087)], and *trans*-norlobelan (hydrochloride, m. p. 162—165°; hydriodide, m. p. 187—189°; methiodide, $C_{22}H_{29}N, MeI$, m. p. 217—219°, also obtained by the action of methyl iodide on the base). Condensation of ethyl glutarate and acetophenone in presence of ether and sodamide gives $\alpha\gamma$ -dibenzoyl-*n*-heptane- $\beta\zeta$ -dione (I), m. p. 72°, and δ -keto- ϵ -benzoyl-*n*-hexoic acid, m. p. 130° [methyl ester (II), m. p. 43°], together with a base, $C_{19}H_{15}N$, m. p. 64.5° (picrate, m. p. 185°), and a substance, $C_{27}H_{20}O$, m. p. 135°. Similar condensation of II and acetophenone affords I. When I is treated at 100° with dry ammonia 2 : 6-di(benzoylmethylene)piperidine (III), m. p. 237° with coloration (tetrabromide, m. p. 183°), results. Reduction of III with hydrogen in presence of platinum oxide and pyridine at 40—50° yields the isomeric unsaturated glycols, α (racemic)- and β (*meso*)-norlobelanidienes, $C_{21}H_{23}O_2N$, m. p. 148° and 173°, respectively, together with a substance, $C_{21}H_{21}O_2N$, m. p. 125°. Further reduction of the β -form with aluminium amalgam and moist ether affords norlobelanidine, m. p. 120° (hydrochloride, m. p. 244°), but the main product is an oil, oxidised by chromic oxide in acetic acid to norlobelanine (IV), m. p. 120° [hydrochloride, m. p. 195° (cf. *loc. cit.*)]. Similar reduction of the α -form gives a mixture of bases oxidised by chromic acid to IV. The stereochemistry of the above bases is discussed.

H. BURTON.

Lobelia alkaloids. V. Bases accompanying lobeline and the mutual relationships of the lobelia alkaloids. H. WIELAND, W. KOSCHARA, and E. DANE (Annalen, 1929, 473, 118—126).—The substance previously described (A., 1921, i, 802) as lobelidine is now shown to be dl-lobeline (I), $C_{22}H_{27}O_2N$, m. p. 110° (hydrochloride, m. p. 170° with

coloration; nitrate, decomp. 159—160°), oxidised by chromic oxide in acetic acid solution to lobelanine [nitrate, m. p. 160° (cf. A., 1925, i, 1087)]. isoLobelanine (A., 1925, i, 1087) is now formulated as norlobelanine (II) [2 : 6-diphenacylpiperidine] (*N*-benzoyl derivative, m. p. 125—126°). Reduction of II with 1% sodium amalgam and dilute acetic acid affords norlobelanidine (III), m. p. 120° (hydrochloride, m. p. 244° with slight coloration and decomp.; nitrate, m. p. 179—180°; hydriodide, m. p. 211°), methylated by methyl *p*-toluenesulphonate to lobelanidine (IV). Oxidation of III with chromic oxide in acetic acid solution gives II, whilst oxidation of IV with potassium permanganate and *N*-sulphuric acid yields I. Treatment of the hydrochloride of I with sodium *d*-tartrate affords the not very soluble *l*-lobeline *d*-tartrate, from which *l*-lobeline, m. p. 130—131°, [α]_D -38.6° in alcohol, is obtained. Separation of III from the minor alkaloids of lobelia is effected through its hydrochloride.

Of the five chief alkaloids of the lobelia group only lobeline occurs in an optically active form. The asymmetric ring carbon atoms in this compound have the *meso*-configuration, since on oxidation it yields inactive lobelanine, which, like lobelanidine, is not capable of resolution.

H. BURTON.

Synthesis of lobelia alkaloids. G. SCHEUING and L. WINTERHALDER (Annalen, 1929, 473, 126—136).—Treatment of 2 : 6-distyrylpyridine tetrabromide with an excess of 2*N*-alcoholic potassium hydroxide solution affords 2 : 6-di- β -phenylethynylpyridine (I), m. p. 137—138°, reduced by hydrogen in presence of palladised barium sulphate and methyl alcohol to 2 : 6-distyrylpyridine. Treatment of I with 50% sulphuric acid gives 2 : 6-diphenacylpyridine (II), m. p. 92° [sulphate, m. p. 197°; hydrochloride, m. p. 223° (decomp.)], reduced by hydrogen in presence of platinum oxide, barium sulphate, and methyl alcohol to 2 : 6-di- β -hydroxy- β -phenylethylpyridine. Similar catalytic reduction of the hydrochloride, m. p. 219° (decomp.), of the last-named compound gives norlobelanidine [2 : 6-di- β -hydroxy- β -phenylethylpiperidine], m. p. 120°, methylated to lobelanidine. Catalytic reduction of norlobelanine with 1 mol. of hydrogen gives dl-norlobeline, m. p. 104°, reduced further to norlobelanidine. Treatment of I with methyl *p*-toluenesulphonate in benzene solution affords the corresponding meth-*p*-toluenesulphonate, m. p. 168°, converted by treatment with slightly diluted sulphuric acid at 125° into the meth-*p*-toluenesulphonate, m. p. 224°, of II. Reduction of this with hydrogen (5 mols.) in presence of platinum oxide, barium sulphate, and methyl alcohol affords lobelanidine (III). With 3 mols. of hydrogen lobelanine results; this is reduced further to III. 2- β -Phenylethynylpyridine, b. p. 148—150°/1 mm., is converted by treatment with 50% sulphuric acid into 2-phenacylpyridine (IV), b. p. 159°/1 mm., m. p. 59°, also obtained by oxidation of 2- β -hydroxy- β -phenylethylpyridine (V) with chromic oxide in acetic acid solution. Reduction of IV with hydrogen in presence of platinum oxide, barium sulphate, and methyl alcohol affords V; in acetic acid as solvent

the product is 2- β -hydroxy- β -phenylethylpiperidine, b. p. 165°/4 mm., m. p. 85°. H. BURTON.

Phenol bases from *Angostura* bark. Synthesis of galipoline. E. SPÄTH and G. PAPAIOANOU (Monatsh., 1929, 52, 129—140).—Galipoline (I), C₁₉H₁₉O₃N, m. p. (vac.) 193°, has been isolated in a yield of 3 g. from the phenolic bases of the alcoholic extract of 16 kg. of *Angostura* bark. The presence of two methoxyl groups in I and the formation of galipine (Späth and Eberstaller, A., 1924, i, 1335) by methylation with diazomethane indicates that I is a hydroxy-dimethoxy-2- β -phenylethylquinoline. It is shown to be 4-hydroxy-2- β -3':4'-dimethoxyphenylethylquinoline by the following synthesis. 4-Chloro-2-methylquinoline condenses with veratraldehyde in presence of zinc chloride at 120° yielding 4-chloro-2-3':4'-dimethoxystyrylquinoline, m. p. 144—145°, which with sodium benzyloxide affords 4-benzyloxy-2-3':4'-dimethoxystyrylquinoline, m. p. 138—139°. Reduction of the last-named substance with hydrogen in presence of palladised charcoal, alcohol, and acetic acid, and subsequent hydrolysis of the product formed with 10% hydrochloric acid, gives I. Similar condensation of 4-methoxy-2-methylquinoline with vanillin and isovanillin yields 4-methoxy-2-4'-hydroxy-3'-methoxy-, m. p. (vac.) 210—211°, and 4-methoxy-2-3'-hydroxy-4'-methoxy-styrylquinoline, m. p. (vac.) 267—268°, respectively. These are reduced catalytically to 4-methoxy-2- β -4'-hydroxy-3'-methoxy-, m. p. 186—187°, and 4-methoxy-2- β -3'-hydroxy-4'-methoxy-phenylethylquinoline, m. p. 147—148°, respectively. 4-Hydroxy-2-methylquinoline, m. p. (vac.) 241—242° (lit. 230—231°), is converted by phosphoryl chloride into 4-chloro-2-methylquinoline, m. p. 25—26° (lit. 42—43°), which when treated with methyl-alcoholic sodium methoxide at not too high a temperature yields 4-methoxy-2-methylquinoline, b. p. 79—81°/1 mm., m. p. 84—85° (lit. 63—65° and 82°). Treatment of the last-named substance with methyl-alcoholic sodium methoxide at 150—155° gives 4-hydroxy-2-methylquinoline. 4-Methoxy-2:6-, -2:7-, and -2:8-dimethylquinolines are similarly converted into the corresponding 4-hydroxy-derivatives.

H. BURTON.

Quaternary bases from *Berberis vulgaris*. E. SPÄTH and N. POLGAR (Monatsh., 1929, 52, 117—128).—The dry root is extracted with methyl alcohol, the extract freed from solvent, re-extracted with water, and separated by acid into (a) basic and (b) non-basic constituents. An amorphous substance was isolated from b; it does not contain any appreciable quantity of oxyberberine. Treatment of a with an excess of sodium carbonate solution and subsequent extraction with ether removes tertiary bases (3.9% of dry material; separation not carried out), and the remaining quaternary bases were converted, by treatment with acetic acid and potassium iodide, into the corresponding iodides. The mixture is separated further by washing with a mixture of potassium iodide and hydroxide into (c) phenolic (2.03% of dry material) and (d) non-phenolic (9.4%) fractions. Fraction d consists mainly of berberine iodide together with a small amount of palmatine iodide, since reduction

of the residue from the crystallisation liquor with zinc dust and acetic acid affords tetrahydroberberine (I) and tetrahydropalmatine. Similar reduction of the berberine chloride obtained from the above iodide and silver chloride, yields small amounts of an amorphous substance and tetrahydrojatrorrhizine, in addition to I, indicating incomplete removal of phenolic bases by the potassium iodide-hydroxide washing. Treatment of c with hydrochloric and sulphurous acids gives a crystalline product, which when reduced affords tetrahydrojatrorrhizine, tetrahydrocolumbamine, m. p. (vac.) 221—223°, and a small amount of tetrahydroberberine.

H. BURTON.

Synthetical experiments on aporphine alkaloids. VI. isoThebaine. Attempted syntheses of 3:4:5-trimethoxyaporphine. R. K. CALLOW, J. M. GULLAND, and R. D. HAWORTH (J.C.S., 1929, 1444—1456).—Various unsuccessful attempts to synthesise 3:4:5-trimethoxyaporphine [Klee's isothebaine methyl ether (A., 1914, i, 1086)] are described. β -4-Methoxyphenylethylamine (I) (improved method of preparation given) reacts with 2-nitro-3:4-dimethoxyphenylacetyl chloride in presence of benzene and aqueous sodium hydroxide, forming 2'-nitro-3':4'-dimethoxyphenylaceto- β -4-methoxyphenylethylamide (II), m. p. 97.5—98°. Conversion of II into an isoquinoline by the action of various dehydrating agents is not possible, but when a solution of II in benzene or toluene is heated with a mixture of phosphoric oxide and chloride dehydration to 2'-nitro-3':4'-dimethoxyphenyl-(β -4-methoxyphenylethylamino)-acetylene, m. p. 143.5—144°, occurs. Nitration of the sulphate of I with nitric (d 1.4) and sulphuric acids affords β -3-nitro-4-methoxyphenylethylamine-5-sulphonic acid, +H₂O, dimorphous, m. p. 297° with effervescence after blackening at 293°; elimination of the sulpho-group with superheated steam was not practicable. Nitration of I with cold nitric acid (d 1.5) gives β -3:5-dinitro-4-methoxyphenylethylamine nitrate (III), m. p. 161° (decomp.), together with a small amount of impure β -3:5-dinitro-4-hydroxyphenylethylamine (picrate, m. p. 209—209.5°). It was not possible to obtain the free base from III, and hydrolytic dissociation and demethylation occurs when III is boiled with water. Nitration of β -4-methoxyphenylpropionic acid (improved method of preparation given) with nitric acid (d 1.42) at 10—25° yields β -3-nitro-4-methoxyphenylpropionic acid, m. p. 128—130.5°, together with a small amount of β -3:5-dinitro-4-hydroxyphenylpropionic acid, m. p. 136—139°. β -3-Nitro-4-methoxyphenylpropionamide, m. p. 123—127°, is converted by alkaline sodium hypochlorite into β -3-nitro-4-methoxyphenylethylamine (IV) (hydrochloride, m. p. 231—232°; benzoyl derivative, m. p. 129—130°); when a deficiency of alkali is used a substance, C₂₀H₂₂O₇N₄, m. p. 197—198°, results. Reduction of IV with stannous chloride and hydrochloric acid in acetic acid solution gives β -3-amino-4-methoxyphenylethylamine [dihydrochloride, m. p. 253—254° (decomp.)], which reacts with 2-nitro-3:4-dimethoxyphenylacetyl chloride, forming 2'-nitro-3':4'-dimethoxyphenylaceto- β -3-(2''-nitro-3'':4''-dimethoxyphenylacetamido)-4-methoxyphenylethylamide,

m. p. 158—159°. Dehydration of this with phosphoric chloride in cold chloroform solution or with phosphoric oxide in boiling toluene affords a product which when hydrolysed with concentrated hydrochloric acid at 100° yields 2'-nitro-3':4'-dimethoxyphenyl-(β -3-amino-4-methoxyphenylethylamino)acetylene, m. p. 169.5—170° [picrate, m. p. 194—195° (decomp.)]; benzoyl derivative, m. p. 206—208°, together with a small amount of a substance, m. p. 168.5—170.5°. H. BURTON.

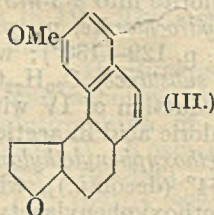
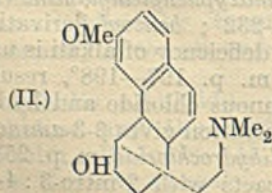
Constitution of sinomenine. H. KONDO and E. OCHIAI (Annalen, 1929, 470, 224—254).—A review of the properties of sinomenine (VII) (cf. Kondo and others, A., 1923, i, 1222; Goto, A., 1926, 1160; A., 1927, 146; this vol., 944), followed by new work. The oxime has (new) m. p. 254°; the semicarbazone, decomp. 264°, and methylsinomenine semicarbazone, decomp. 250—252°, were prepared. The dihydro-derivative, new m. p. 199°, $[\alpha]_D^{25} +170.5^\circ$ (in alcohol—all values of $[\alpha]$ are in alcohol unless otherwise stated), forms a semicarbazone, m. p. 207°; the ketonic character thus persists. For the two bromosinomenines the new m. p. 138° and 205° are found. The iodine value of sinomenine appears to show the presence of two double linkings, but this is due to a substitution reaction, since benzoylsinomenine shows one only. Sinomenine reacts with ethyl chloroformate in chloroform to give a substance $C_{25}H_{32}O_8NCl$, m. p. 166—183° (decomp.), $[\alpha]_D^{25} -108.4^\circ$ (in chloroform); this behaviour is characteristic of tetrahydroisoquinoline derivatives, as is that with benzoic anhydride, with which sinomenine gives dibenzoylsinomenol (cf. Goto, *loc. cit.*). These and earlier results show that sinomenine belongs to the morphine group.

Reduction of sinomenine by amalgamated zinc and hydrochloric acid yields deoxytetrahydrosinomenine, $C_{18}H_{25}O_2N, 0.5H_2O$, (I), m. p. 150—151°, $[\alpha]_D^{25} +48.2^\circ$, which has no phenolic properties, and reacts with phenylcarbimide. In general behaviour the substance closely resembles dihydrothebaine (Ia), $[\alpha]_D^{25} -47.22^\circ$, obtained by Speyer and Siebert (A., 1921, i, 685) by the electrolytic reduction of dihydrothebaine, and now by the Clemmensen method. It is actually found that the two bases are optical antipodes; the racemic compound has m. p. 132° (decomp. after sintering at 125°), and $[\alpha]_D^{25} 0^\circ$. The hydriodides of the two bases have the same m. p., 250—251° (cf. Speyer and Siebert, *loc. cit.*). The methiodide of I, m. p. 265°, when treated with potassium hydroxide gives de-N-methyldeoxytetrahydrosinomenine, $C_{19}H_{27}O_2N$, (II), m. p. 140°, $[\alpha]_D^{25} -41.59^\circ$ (in methyl alcohol); the methiodide of this compound

elimination of trimethylamine, the substance $C_{17}H_{20}O_2$, m. p. 93°, $[\alpha]_D^{25} -181.6^\circ$, is obtained. This last substance contains no hydroxyl or vinyl group, and is stable towards potassium permanganate in the cold (giving, on heating, a product, m. p. 115°); it probably is III. Wieland and Kotake (A., 1925, i, 1093) have observed a similar reaction with dihydrode-N-methyl-dihydrothebaine. The elimination of the phenolic hydroxyl group during the Clemmensen reduction of sinomenine or dihydrothebaine is remarkable: it may be assumed that the group occupies the 4-position. This is confirmed by the reduction of dihydro-sinomenine by sodium amalgam, when demethoxydihydrosinomenol, $C_{18}H_{25}O_3N$, m. p. 95—105° (decomp.), $[\alpha]_D^{25} +32.02^\circ$ [unaffected by hydroxylamine; methiodide, m. p. 268—272°, $[\alpha]_D^{25} +23.9^\circ$ (in methyl alcohol)], is formed, which is identified as an optical isomeride of dihydrothebaine (Speyer and Siebert, *loc. cit.*). This last, now prepared from dihydrothebaine by sodium amalgam reduction, has m. p. 144°, $[\alpha]_D^{25} -46.2^\circ$, and forms a methiodide, m. p. 278° (decomp.), $[\alpha]_D^{25} -24.25^\circ$ (in methyl alcohol); the racemic compound of the two methiodides has m. p. 270—272° and $[\alpha]_D^{25} 0^\circ$. Sinomenine reduced by sodium amalgam gives a substance, $C_{18}H_{25}O_3N$, m. p. 180°, $[\alpha]_D^{25} -11.24^\circ$ (methiodide decomp. 250°), which does not form a semicarbazone.

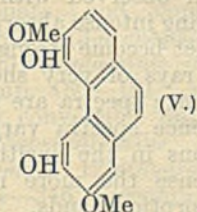
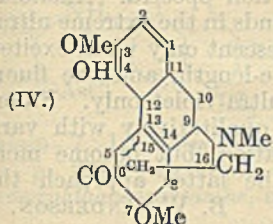
The phenolic hydroxyl group in sinomenine occupies the 4-position, and the keto-group the 6-position, in a phenanthrene skeleton. A methoxyl group probably occupies the 5- or the 7-position, and its actual situation is determined as follows. Sinomenol, obtained by the alkali fusion of sinomenine (Goto, *loc. cit.*), is a dihydroxydimethoxyphenanthrene; assuming this to have been formed by the enolisation of the keto-group of sinomenine, and by the loss of methyl-ethylamine, sinomenol dimethyl ether must be either 3:4:5:6- or 2:3:5:6-tetramethoxyphenanthrene. This is confirmed by the synthesis of these two compounds. When sodium homoveratrate is treated in acetic anhydride with o-nitroveratraldehyde, the product is 2-nitro-3:4-dimethoxy- α -3':4'-dimethoxyphenylcinnamic acid, m. p. 191—192°, which when reduced to the amino-compound, m. p. 146°, and treated in sulphuric acid and methyl alcohol with sodium nitrite, gives rise to the isomeric 3:4:5:6- and 3:4:6:7-tetramethoxyphenanthrene-9-carboxylic acids, m. p. 232—234° and 210°, respectively. The last heated at 250—260° in acetic acid gives 2:3:5:6-tetramethoxyphenanthrene, m. p. 124—125° (picrate, m. p. 123—125°), identical with dimethoxysinomenol. The actual differentiation between the above two isomerides was effected by synthesising the compound of m. p. 232—234° from 2-nitro-3:4-dimethoxy- α -6-bromo-3':4'-dimethoxyphenylcinnamic acid, m. p. 216°; this was obtained by the interaction of sodium 6-bromohomoveratrate and o-nitroveratraldehyde in acetic anhydride at 100—110°, and was reduced to the amino-compound, m. p. 187°, and converted as before into 8-bromo-3:4:5:6-tetramethoxyphenanthrene-9-carboxylic acid, m. p. 187—188° (decomp.); this last was reduced by zinc in alcoholic sodium hydroxide to the bromine-free compound, identical with the compound of m. p. 232—234°.

This shows that sinomenine has a 7-methoxyl group,

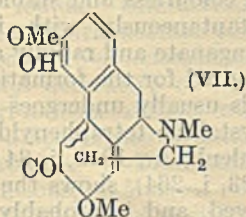
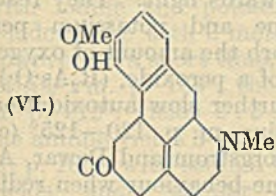


is prepared, converted into the methochloride, and treated with potassium hydroxide, when, with the

and leads to the formulæ IV and V for dihydro-sinomenine and sinomenol, respectively. Sinomenine



is thus an optical isomeride of 7-methoxythebainone, and its structure is bound up with that of codeine. The formula for thebainone put forward by Gulland and Robinson (J.C.S., 1923, 123, 999) is now criticised, on the ground that when thebainone is neutralised and catalytically reduced in presence of palladium chloride, a new β -dihydrothebainone, m. p. 76° (after sintering at 62–64°), $[\alpha]_D^{25}$ –83.94°, is obtained [*picrate*, m. p. 245°; *semicarbazone*, m. p. 199–201° (decomp.)], and not thebainol. In order to explain this, Robinson's formula for thebainone is abandoned, and the formula VI is substituted; addition of hydrogen to the $\Delta^{8:14}$ double linking in different directions is considered to give either dextrorotatory thebainol or levorotatory β -dihydrothebainone.



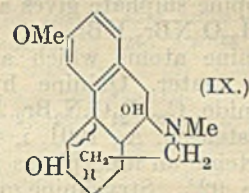
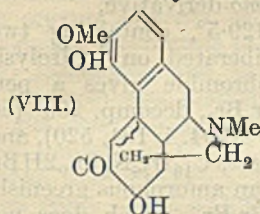
Sinomenine has a double linking; since it has none of the properties of an enol methyl ether, this linking must lie not between the atoms 7 and 8, but between 8 and 14. The formula VII is therefore proposed for sinomenine.

When sinomenine is reduced by sodium amalgam, *isodemethoxydihydrosinomeninol*, m. p. 180°, is formed; this is isomeric with *demethoxydihydrosinomenol*, and it is suggested that this is a case of *cis-trans*-isomerism.

Sinomenine is of particular interest as being the first alkaloid of the thebainone group to be found in nature.

A comparison of sinomenine with substances of the thebainone type leads to some further results. From the analogy between dihydrosinomenine and hydroxydihydrothebainone, which Speyer (A., 1923, i, 128) obtained by the sodium amalgam reduction of hydroxydihydrocodeinone, and to which he ascribed the formula VIII, the 7-hydroxyl group in the second substance would be expected to be very labile; it is not, however, removed in the above reduction process. When now hydroxydihydrocodeinone is reduced by Clemmensen's method, the product is not dihydrothebaine, as would be expected if the hydroxyl group were in the 7-position, but *hydroxydihydrothebaine*, m. p. 138–139°, $[\alpha]_D^{25}$ –58.15° (in acetone), which contains two free hydroxyl groups. It is

therefore concluded that Speyer's formula VIII is incorrect, and by analogy with Gulland and Robin-

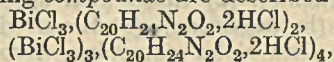


son's formula for hydroxycodeinone, the formula IX is proposed for hydroxydihydrothebaine.

Silver nitrate acts on sinomenine to form *dehydrosinomenine nitrate*, not decomp. at 280°, from which *dehydrosinomenine*, $(C_{19}H_{23}O_4N)_2$ (cf. Goto, J. Chem. Soc. Japan, 1925, 44, 821), m. p. 218–220°, $[\alpha]_D^{25} +97.38^\circ$ (in methyl alcohol), is obtained. The changed sign of the rotation, due to the action of silver nitrate, is to be noted. Catalytic reduction of dehydrosinomenine in presence of palladium gives rise to an isomeride of dihydrosinomenine, *isodihydrosinomenine*, which sinters at 220° (decomp. 271°), has $[\alpha]_D^{25} +171.16^\circ$, and forms a *methiodide*, and an *oxime*, m. p. 245–250° (decomp.). Dihydrosinomenine is oxidised by silver nitrate to *isodihydrosinomenine*, together with a bimolecular product, $(C_{19}H_{25}O_4N)_2$, m. p. 270°, $[\alpha]_D^{25} +113.8^\circ$ (in methyl alcohol). Thebainone is converted by silver nitrate into ψ -thebainone, $C_{18}H_{21}O_3N$, decomp. 227°, $[\alpha]_D^{25} -339.5^\circ$ (in acetone) (*semicarbazone*, decomp. 290°), which is reduced by hydrogen in presence of palladium to *dihydro- ψ -thebainone*, m. p. 270° (decomp.), $[\alpha]_D^{25} -71.77^\circ$ (in acetone). E. W. WIGNALL.

Reduction of disinomenine and ψ -disinomenine. K. Goro (Bull. Chem. Soc. Japan, 1929, 4, 129–132).—Reduction of disinomenine by hydrogen in presence of colloidal palladium gave *tetrahydrosinomenine*, $(C_{19}H_{24}O_4N)_2$, m. p. 247–252° (decomp.), $[\alpha]_D^{25} +264.41^\circ$ [*oxime*, m. p. 227°; *methiodide*, m. p. 275° (decomp.); *semicarbazone*, m. p. above 290°]. Similarly, ψ -disinomenine yielded ψ -*tetrahydrosinomenine*, m. p. 271° (decomp.), $[\alpha]_D^{25} +167^\circ$ [*oxime*, m. p. 242°, *methiodide*, m. p. 285° (both decomp.); *semicarbazone*, m. p. above 290°]. These bases were also obtained by mild oxidation of dihydrosinomenine. B. W. ANDERSON.

Preparation and properties of some double chlorides of bismuth and quinine. H. LENORMAND (J. Pharm. Chim., 1929, [viii], 10, 69–74).—The following compounds are described:



$BiCl_3 \cdot C_{20}H_{24}N_2O_2 \cdot 2HCl$; all of them are decomposed by water and are sparingly soluble in most organic solvents. E. H. SHARPLES.

Bromination of natural alkaloids by acidified hydrogen peroxide. A. MOREL, A. LEULIER, and P. DENOYEL (Bull. Soc. chim., 1929, [iv], 45, 435–456).—In the action of a mixture of 2% hydrogen peroxide and hydrobromic acid on natural alkaloids, bromine derivatives of the alkaloids are obtained, unaccompanied by amine oxides. Cocaine hydrochloride yields a dibromo-derivative,

$C_{17}H_{21}O_4NBr_2 \cdot 2HBr$, m. p. 130° , probably identical with the product obtained by Jong (A., 1906, i, 301). Atropine sulphate gives a bromo-derivative, $C_{17}H_{23}O_3NBr_3 \cdot HBr$, m. p. 129.5° , containing two bromine atoms which are liberated on hydrolysis with water. Quinine hydrobromide gives a perbromide, $C_{20}H_{24}O_3N_2Br_2 \cdot 2HBr \cdot Br_2$, decomp. 200° (cf. Christensen, A., 1901, i, 481; 1904, i, 184, 520), and sparteine an amorphous product, $C_{15}H_{26}N_2Br_3 \cdot 2HBr$, m. p. 92° . Strychnine gives an amorphous greenish-yellow product, $C_{21}H_{21}O_2N_2Br \cdot Br_2$, which does not give the characteristic strychnine colorations with ammonium sulphovanadate or Denigès' reagent. Morphine hydrochloride affords the monobromo-derivative, $C_{17}H_{18}O_3NBr \cdot HBr \cdot 3H_2O$, m. p. 221° (decomp.), $[\alpha] -1.25^\circ$, which gives the intense violet coloration with Marquis' reagent, characteristic of morphine, and is free from hydroxydimorphine, and with excess of both reagents, the β -tetrabromo-derivative, $C_{17}H_{15}O_3NBr_4 \cdot HBr$, decomp. 200° . Heroine yields the hydrobromide of bromodiacetylmorphine. The toxicity towards white mice of bromomorphine hydrobromide is about twice and of bromoheroine about eight times as great as that of morphine hydrochloride. R. BRIGHTMAN.

Bromination of novocaine by acidified hydrogen peroxide. A. MOREL, A. LEULIER, and P. DENOYEL (Bull. Soc. chim., 1929, [iv], 45, 457—463).—Bromination of novocaine by the hydrogen peroxide-hydrobromic acid method (cf. preceding abstract) yields a dibromo-derivative, $C_{13}H_{16}O_2N_2Br_2 \cdot HBr$, m. p. 217° , probably 3:5-dibromo-4-aminobenzoyldiethylaminoethyl alcohol, which with cold sulphuric acid in presence of sodium nitrite gives on warming an intense yellow coloration. Dibromonovocaine hydrobromide has an anæsthetic power on rabbits about ten to thirteen times as great as novocaine and about equal to that of cocaine hydrochloride. Addition of adrenaline slightly increases the anæsthetic power. Towards white mice dibromonovocaine hydrobromide is ten times as toxic as novocaine and three times as toxic as cocaine.

R. BRIGHTMAN.

Relations between the chemical constitution, absorption [spectra], and fluorescence of alkaloids. A. ANDANT (Compt. rend., 1929, 189, 98—100; cf. A., 1927, 538, 1124).—Alkaloids may be divided into four groups in accordance with their fluorescence spectra: (1) alkaloids with weak or non-present fluorescence spectra (morphine, cocaine, strychnine, brucine), (2) those with spectra in the visible region (hydrastinine), (3) those with spectra only in the ultra-violet (atropine, hyoscyamine), (4) those with spectra in the visible and ultra-violet regions (caffeine, quinine, hydrastine, etc.). Isomeric alkaloids have identical or very similar fluorescence; substitution of a methyl or methoxyl group for a hydrogen atom intensifies the fluorescence and causes displacement towards the red, as is the case with benzene derivatives. Etherification of a phenol group in the nucleus also intensifies the fluorescence, but causes displacement towards the violet. The salts of alkaloids have a slightly more intense fluorescence than the corresponding free bases; the spectra are

more spaced out towards the red and the maxima displaced in the same sense. Similar variations have been observed with absorption spectra. Alkaloids having intense absorption bands in the extreme ultra-violet become strongly fluorescent only when excited by rays of very short wave-length, and the fluorescence spectra are in the ultra-violet only. Fluorescence spectra vary little qualitatively with variations in the exciting radiation, but become more intense the more nearly the latter approach the absorption bands. B. W. ANDERSON.

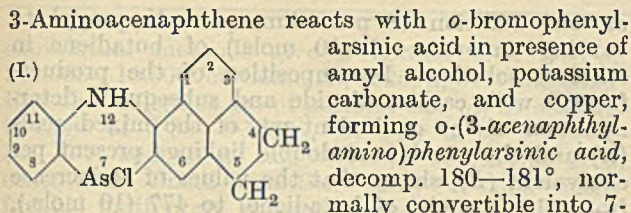
Action of ammonia on halogenated arsines. V. IPATIEV, G. RAZUBAIEV, and V. STROMSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 3—12).—See this vol., 584.

Action of arsenic acid and its derivatives on nitrophenols. O. R. PEPE (Rev. Fac. Cien. quim. La Plata, 1928, 5, I, 105—179; Chem. Zentr., 1929, i, 643).—Attempts to prepare nitrohydroxyphenylarsinic acids failed. A. A. ELDRIDGE.

Tetra-aryldiarsines. I. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 2272—2276).—Iododiarylsarsines (cf. this vol., 833) in ether or benzene react readily with mercury and more slowly with finely-divided silver or zinc, giving quantitatively tetra-aryldiarsines. In solution these are colourless and stable towards light. They react instantaneously with iodine and potassium permanganate and rapidly absorb the amount of oxygen required for the formation of a peroxide, $(R_2As \cdot O)_2$. This usually undergoes a further slow autoxidation. Crystalline tetraphenyldiarsine, m. p. $120—125^\circ$ (cf. Schlenk, A., 1913, i, 34; Borgstrom and Dewar, A., 1923, i, 264), shows the same behaviour when redissolved, and is probably partly dissociated into free radicals. Iododiphenylarsine and triphenylmethyl bromide in bromobenzene give bromodiphenylarsine and the strongly dissociated triphenylmethyl iodide, but the solution absorbs more oxygen than is accounted for by the amount of triphenylmethyl produced. H. E. F. NOTTON.

10-Chloro-5:10-dihydrophenarsazine and its derivatives. X. 1- and/or 3-Methyl derivatives. Condensation of arsenious chloride and phenyl-*m*-tolylamine. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 1473—1476).—Phenol reacts with *N-m*-tolylbenzimidochloride in presence of sodium ethoxide solution yielding *N-m*-tolylbenzimidophenyl ether, m. p. 60° , which at $280—300^\circ$ gives the benzoyl derivative, m. p. $104—106^\circ$, of phenyl-*m*-tolylamine (I), b. p. $183—184^\circ/17$ mm., m. p. 27.5° . This benzoyl derivative is obtained similarly from *N-phenylbenzimidino-m-tolyl ether*, m. p. 65° . Arsenious chloride and I in boiling *o*-dichlorobenzene give 10-chloro-1- and/or 3-methyl-5:10-dihydrophenarsazine (II), m. p. $215—216^\circ$ (this vol., 710). Razubaiev's "10-chloro-2(4)-methyl-9:10-dihydrophenarsazine," m. p. $195—196^\circ$ (this vol., 834), is an impure specimen of II. H. BURTON.

Substances of phenarsazine type containing the acenaphthene nucleus. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 1621—1622).—



(I), m. p. 241° (decomp.), or 7-bromo-7:12-dihydroisoacenaphthabenzarsazine, m. p. 244—246° (decomp.).

H. BURTON.

[Preparation of] mercury diphenyl. H. O. CALVERY (Organic Syntheses, 1929, 9, 54—55).

Position occupied by acetatomercuri (Hg·OAc)-groups in anilines containing in the nucleus a halogen group or a hydrocarbon residue. IV. L. VECCHIOTTI and G. SPERANZINI (Gazzetta, 1929, 59, 363—372; cf. A., 1928, 655, 783).—Substitution by the acetatomercuri-group in *m*-halogeno-anilines generally yields, according to the proportion of mercuric acetate used, 4-mono-, 4:6-, or occasionally 2:5-, di-, and 2:4:6-tri-acetatomercuri-derivatives. As a by-product in the preparation of 3-iodo-4-acetatomercurianiline (A., 1927, 1098) 3-iodo-4:6-diacetatomercurianiline, m. p. 190°, separates very slowly from the mother-liquors. The acetyl derivative, m. p. 202°, yields 2:4:5-tri-iodoacetanilide with iodine and potassium iodide. Interaction of 3-iodoaniline with 2 mols. of mercuric acetate yields, however, in a short time, 3-iodo-2:5-diacetatomercurianiline, m. p. 163°, the acetyl derivative of which, m. p. 212°, yields 2:3:5-tri-iodoacetanilide, whilst the aniline yields 3-iodo-2:5-dihydroxymercurianiline, m. p. 186°, with sodium hydroxide. *m*-Bromoaniline yields, under similar conditions, 3-bromo-4:6-diacetatomercurianiline, m. p. 172° (acetyl derivative, m. p. 198°, yielding 3:4:6-tribromoacetanilide). The 2:5-derivative could not be obtained.

R. K. CALLOW.

Mercuration in alkaline solution. A. L. FOX and F. C. WHITMORE (J. Amer. Chem. Soc., 1929, 51, 2196—2197).—3-Hydroxy-2-naphthoic acid is mercurated by mercuric acetate more rapidly in alkaline than in acid solution to anhydro-3-hydroxy-4-hydroxymercuri-2-naphthoic acid. Salicylic acid in alkaline solution yields hydroxymercurisalicylic acid and phenol yields anhydrohydroxymercuriphenol, but α -naphthol, *o*-nitrophenol, and anthranilic, sulphanilic, benzenesulphonic, α -naphthoic, and phthalic acids are not mercurated.

H. E. F. NOTTON.

Organo-alkali compounds. I. Reaction between unsaturated hydrocarbons and alkali metal alkyls. K. ZIEGLER, F. CRÖSSMANN, H. KLEINER, and O. SCHÄFER. II. Schlenk's addition of alkali metals to unsaturated hydrocarbons. K. ZIEGLER, H. COLONIUS, and O. SCHÄFER. III. Polymerisation of unsaturated hydrocarbons under the influence of alkali metals and alkali metal alkyls. K. ZIEGLER and H. KLEINER (Annalen, 1929, 473, 1—35, 36—56, 57—82).—I. Alkali metal alkyls are of three types. (1) Colourless and insoluble in organic media (e.g., simple sodium and potassium alkyls and aryls). In

combination with zinc alkyls they are electrolytes and even in the solid state are probably heteropolar. (2) More or less intensively coloured, usually soluble in organic solvents, especially ether, and such solutions are conductors (e.g., NaCH₂Ph and KCM₂Ph). (3) Colourless and mostly soluble. They usually distil or sublime unchanged, are non-electrolytes, and slight conductors only in presence of zinc alkyls. Compounds of type 1 are readily decomposed by ether, those of type 2 are usually stable towards ether and react instantaneously with alkyl halides, whilst those of type 3 are very slowly decomposed by ether and react only slowly with alkyl halides. Potassium phenylisopropyl, K·CM₂Ph, prepared by the action of potassium-sodium alloy (5:1) on phenylisopropyl methyl ether (cf. Ziegler and Bähr, A., 1928, 404), does not react with ethylene or triphenylethylene. When addition of the metal does occur reaction is almost instantaneous. Decomposition of the additive product first with dry carbon dioxide and then with dilute alkali gives an acid, formed by replacement of the potassium atom with carboxyl. Thus, benzylidenefluorene yields an acid, C₃₀H₂₆O₂, m. p. 205—206° with elimination of carbon dioxide; propenylbenzene gives an acid, C₁₉H₂₂O₂, m. p. 146—147° (silver salt); isopropenylbenzene affords an isomeric acid, an oil (silver salt), and ethylidenefluorene furnishes an acid, C₂₅H₂₄O₂, m. p. 113° (silver salt). In the remainder of the cases studied substitution takes place (usually in a methyl group) and reaction occurs only slowly. Thus, $\omega\omega$ -dimethylstyrene yields an unsaturated acid, C₁₁H₁₂O₂ (β -benzylidene-*n*-butyric acid), m. p. 80—81° (silver salt), reduced by hydrogen in presence of palladised barium sulphate and alcohol to β -benzyl-*n*-butyric acid; $\alpha\alpha$ -diphenyl- Δ^{α} -propylene gives the acid, C₁₆H₁₄O₂ ($\gamma\gamma$ -diphenyl- Δ^{β} -butenoic acid), m. p. 112—113°, reduced to $\gamma\gamma$ -diphenylbutyric acid; $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylethylene affords a mixture of impure β -diphenylmethylene-glutaric acid, m. p. 153—154° (silver salt), and an acid, m. p. 108°, reduced to β -benzhydryl-*n*-butyric acid, m. p. 113°; $\alpha\alpha$ -diphenyl- Δ^{α} -butylene furnishes an acid, C₁₇H₁₆O₂ (silver salt); $\alpha\alpha\gamma$ -triphenyl- Δ^{α} -propylene yields $\alpha\gamma\gamma$ -triphenyl- Δ^{β} -butenoic acid, m. p. 166—167° (silver salt), also obtained by the action of potassium on $\alpha\alpha\gamma$ -triphenyl- γ -methoxy- Δ^{α} -propylene with subsequent decomposition by carbon dioxide. $\alpha\gamma\gamma$ -Triphenylbutyric acid has m. p. 111—112°, whilst $\alpha\alpha\gamma$ -triphenylbutyric acid has m. p. 181°. α -Methylstilbene gives β -phenyl- β -benzylidene-propionic acid, m. p. 168° (silver salt). With $\alpha\delta$ -diphenyl- Δ^{α} -butylene addition of potassium phenylisopropyl occurs, the acid C₂₆H₂₈O₂ (silver salt) being finally isolated. With $\alpha\delta$ -diphenyl- Δ^{β} -butylene substitution of potassium occurs in one or both methylene groups, and the decomposition products are $\alpha\delta$ -diphenyl- Δ^{β} -pentenoic acid (silver salt) and $\alpha\delta$ -diphenyl-dihydromuconic acid, m. p. 233—234° (silver salt). This last acid is probably stereoisomeric with the acid described by Schlenk and Bergmann (A., 1928, 1031). Addition also takes place with $\alpha\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butadiene yielding the acid C₂₆H₂₆O₂ (silver salt), but with $\alpha\delta$ -dibenzyl- $\Delta^{\alpha\gamma}$ -butadiene substitution of potassium occurs in both methylene groups, affording $\alpha\zeta$ -diphenyl- $\Delta^{\beta\delta}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid, m. p. 240—

242° (*silver salt*). Standardisation of solutions of potassium phenylisopropyl is readily effected by treatment with butyl bromide and subsequent determination of bromide ions by the Volhard method. The rates of addition of lithium ethyl, propyl, and butyl to *as*-diphenylethylene in benzene solution have been determined at 50°; the velocity coefficients are 1.5, 3.4, and 2.8, respectively. The additive compound from lithium butyl is decomposed by carbon dioxide to $\alpha\alpha$ -diphenyl-*n*-heptioic acid, m. p. 104—105°, obtained also by the action of potassium-sodium alloy on $\alpha\alpha$ -diphenyl-*n*-hexyl methyl ether, m. p. 58°, and subsequent decomposition with carbon dioxide. $\alpha\alpha$ -Diphenyl-*n*-hexyl alcohol, m. p. 46.5—47.5°, is obtained from ethyl hexoate and excess of magnesium phenyl bromide. Addition of lithium butyl to stilbene occurs in ethereal solution and decomposition of the product with carbon dioxide affords $\alpha\beta$ -diphenyl-*n*-heptioic acid, m. p. 102°. Benzene solutions of lithium butyl containing ether do not alter appreciably after 3—4 hrs. The determination of simple lithium alkyls in solution is carried out by addition of butyl bromide and then, in small portions, mercury dibenzyl. The lithium benzyl formed reacts immediately with the butyl bromide.

II. Treatment of *as*-diphenyldimethylethylene with potassium-sodium alloy (5 : 1) in concentrated ethereal solution and decomposition of the product with carbon dioxide affords $\alpha\alpha$ -diphenylisovaleric acid (I), m. p. 168—169°, obtained also by the successive action of potassium and carbon dioxide on the methyl ether, b. p. 124—126°/0.5 mm., of diphenylisopropylcarbinol. In dilute ethereal solution both I and β -diphenylmethylene-*n*-butyric acid (II), m. p. 108° (cf. Part I), are formed. The reactions taking place are: $\text{CPh}_2\cdot\text{CMe}_2 \rightarrow \text{CKPh}_2\cdot\text{CKMe}_2$ ($\text{CPh}_2:\text{CMe}_2$), $\text{CKPh}_2\cdot\text{CHMe}_2 + \text{CPh}_2\cdot\text{CMe}_2\cdot\text{CH}_2\text{K}$ (cf. Schlenk and Bergmann, A., 1928, 1031). The *thioanilides* of I and II, m. p. 144—145° and 161°, respectively, are obtained by the action of phenylthiocarbimide on the potassium derivatives. Treatment of a solution of *as*-diphenylethylene in toluene with a solution of sodium in liquid ammonia at a low temperature, and decomposition of the red sodium derivative formed with ammonium chloride affords $\alpha\alpha$ -diphenylethane. No trace of $\alpha\alpha\delta\delta$ -tetraphenylbutane is formed (cf. Schlenk and Bergmann, *loc. cit.*). Decomposition of the above sodium derivative with benzyl chloride gives $\alpha\beta\beta$ -triphenylpropane. The reactions taking place are, therefore, $\text{CPh}_2\cdot\text{CH}_2 \xrightarrow{\text{NH}} \text{CNaPh}_2\cdot\text{CH}_2\text{Na} \xrightarrow{\text{NH}} \text{CNaPh}_2\cdot\text{CH}_3 + \text{NaNH}_2$. When sodium is added in small portions, with good stirring, to a mixture of *as*-diphenylethylene, toluene, and liquid ammonia, a small amount of $\alpha\alpha\delta\delta$ -tetraphenylbutane is probably formed. $\alpha\alpha$ -Diphenyl- β -benzylethylene affords $\alpha\alpha\gamma$ -triphenylpropane, whilst cyclohexene is unaffected by potassium in liquid ammonia. Aryl-substituted ethylenes add primarily two atoms of alkali metal across the double linking. This additive product can either remain unchanged (*e.g.*, stilbene, tetraphenylethylene) or undergo secondary reactions, which can occur under the influence of excess of the hydrocarbon used. These consist of addition or substitution processes.

III. A series of experiments has been carried out

on the addition of potassium phenylisopropyl to varying amounts (1—10 mols.) of butadiene in ethereal solution. Decomposition of the products formed with carbon dioxide and subsequent determination of the equivalent wt. of the mixed acids (*A*) and the number of double linkings present per equivalent (*B*), shows that the values of *A* increase from 218 (2 mols. of butadiene) to 477 (10 mols.), whilst the values of *B* increase correspondingly from 1.32 to 5.55. Maximum values are given with 8 mols. of butadiene, namely, 493 and 6.04. The following primary reactions are presumed to occur (1:4-addition is assumed arbitrarily): (1) $\text{CKPhMe}_2 + \text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2 \rightarrow \text{CPhMe}_2\cdot\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{K}$; (2) $2\text{CKPhMe}_2 + \text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{CH}_2 \rightarrow \text{CH}_2\text{K}\cdot\text{CH}=\text{CH}\cdot\text{CH}_2\text{K} + 2\text{CPhMe}_2$. H. BURTON.

Lead aryl-alkyl compounds. H. GILMAN, O. R. SWEENEY, and J. E. KIRBY (Iowa State Coll. J. Sci., 1928, 3, 1—4).—By interaction of lead triphenyl bromide with the appropriate Grignard reagent, lead triphenyl butyl, m. p. 47°, isobutyl, m. p. 68—68.5°, *sec.*-butyl, m. p. 84°, and *tert.*-butyl, m. p. 150—150.5°, have been obtained.

CHEMICAL ABSTRACTS.

Metallic derivatives of thiophen. II. Thallium, silicon, bismuth, tellurium, and mixed tin and lead thienyls. E. KRAUSE and G. RENWANZ (Ber., 1929, 62, [B], 1710—1716; cf. A., 1927, 891).—Thiophen is converted by bromine in glacial acetic acid into 2-bromothiophen, b. p. 42—46°/13 mm. Addition of ethereal magnesium 2-thienyl bromide to ethereal thallium chloride affords thallium di-2-thienyl bromide, $\text{Tl}(\text{C}_4\text{H}_3\text{S})_2\text{Br}$, decomp. 270° after darkening at 250°. Silicon tetrachloride and magnesium 2-thienyl iodide yield silicon tetra-2-thienyl, m. p. 135.5° (corr.). Bismuth tri-2-thienyl, m. p. 137.5° (corr.), is more advantageously prepared from magnesium 2-thienyl bromide than from the corresponding iodide. Tellurium di-2-thienyl dibromide, m. p. 195° (corr.), decomp. about 220°, is reduced by stannous chloride and hydrochloric acid to tellurium di-2-thienyl, from which tellurium di-2-thienyl dichloride, m. p. 189.5°, decomp. about 250° after darkening at 210°, and the corresponding di-iodide, m. p. 126.5° (corr.), decomp. about 190°, are prepared. Magnesium 2-thienyl bromide and tellurium di-2-thienyl dibromide afford tellurium tri-2-thienyl bromide, m. p. 253° (corr. decomp.) [corresponding iodide]. Tin triphenyl 2-thienyl, m. p. 206° (corr.), is prepared from magnesium 2-thienyl iodide and tin triphenyl bromide; it is converted by bromine in pyridine at -48° into tin triphenyl bromide. Lead triphenyl 2-thienyl, m. p. 208° (corr.), decomp. 305° is converted by bromine into lead triphenyl bromide. H. WREN.

Mol. wt. of edestin. T. SVEDBERG and A. J. STAMM (J. Amer. Chem. Soc., 1929, 51, 2170—2185).—The solubility of edestin in aqueous sodium chloride and in phosphate buffer solutions, with and without sodium chloride, has been determined. Three independent methods give p_{H} 5.5 as its isoelectric point (cf. Michaelis and Mendelssohn, A., 1914, i, 1007). Its partial specific vol. is 0.744 at 19.8°, and its ultraviolet absorption spectrum shows a maximum at 276 μ and a minimum at 254 μ . Determinations by the sedimentation velocity and sedimentation

equilibrium methods give a normal mol. wt. of $212,000 \pm 10,000$ (cf. Cohn, A., 1925, ii, 641) and show that the molecules are of uniform size (*a*) at concentrations of 1.38—0.155%, (*b*) over a p_H range of 5.5—9.7, and (*c*) in salt solutions of varying concentration. Small quantities only of non-centrifugable matter are present. These results indicate that the methods are applicable to proteins in salt solutions of considerable concentration. At p_H 3.1 and p_H 11.3, and in neutral solutions at concentrations below 0.1%, edestin dissociates, or decomposes into smaller molecules.

[With O. LAMM.]—A modification (to be described later; cf. this vol., 129) of the sedimentation velocity method, involving the measurement of changes in the refractive index of the sedimenting solution, shows that a 0.487% solution at p_H 11.3 contains edestin (15%) and dissociation products of one half (30%) and one third (55%) its mol. wt., approximately in the proportions stated. It is significant that both edestin and its dissociation products have, like most of the proteins hitherto examined, mol. wts. which are integral multiples (6, 3, and 2 times, respectively) of that of egg-albumin (cf. this vol., 26, 203, 458). The edestin molecules are practically spherical.

H. E. F. NOTTON.

Combination between basic dyes and proteins. L. M. C. RAWLINS and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 82, 709—716).—Titration of gelatin, caseinogen, and edestin with three basic dyes shows that, at pa_H 11, gelatin combines with 70×10^{-5} , caseinogen with 210×10^{-5} , and edestin with 70×10^{-5} equivalents of dye. The results can be correlated with the base-binding capacity of the proteins, and support the previous conclusion that combination of acid dyes with proteins takes place in stoichiometric proportions (cf. A., 1927, 686). C. R. HARRINGTON.

Fractionation of casein. K. LINDERSTRÖM-LANG (Compt. rend. Lab. Carlsberg, 1929, 17, 1—116).—Casein previously purified by the usual methods has been separated into several fractions by mild treatment, e.g., by warming with 60% alcoholic hydrochloric acid (0.002*N*), when one part is obtained as an alcohol-soluble and the other as an alcohol-insoluble fraction. The fractions, which are not claimed to be chemically pure, have been subjected to thorough examination by chemical and physical methods, including the determination of phosphorus, nitrogen, arginine, tyrosine, tryptophan, specific rotation, and solubility, and titration of acid and basic groups. Probably no irreversible processes are involved in the fractionations, as mixing the fractions in their proper proportions produces a substance physically and chemically identical with the original casein. It is concluded that casein consists of at least three fractions, one of which is alcohol-soluble and contains no phosphorus. The bearing of these results on the rennin reaction is discussed.

W. O. KERMACK.

Determination of tyrosine and tryptophan in 0.1 g. of protein. Colorimetric determination of cystine in protein. Preparation of uric acid reagent free from phenol reagent. O. FOLIN and A. D. MARENZI (J. Biol. Chem., 1929, 83, 89—102,

103—108, 109—113).—The precipitation of tyrosine from protein hydrolysates with mercuric acetate and sodium chloride recommended by Hanke (A., 1928, 1389) is incomplete and variable, and the results of this author are criticised on this and other grounds. A modification of the method of Folin and Ciocalteu (A., 1927, 892) in which the error in the tyrosine determinations due to the presence of cystine is eliminated is described; it is applicable to 0.1 g. of protein (except caseinogen) after hydrolysis with 20% sodium hydroxide at 100°. Figures are given for the tyrosine and tryptophan content of a number of proteins. The method of Folin and Looney (A., 1922, ii, 539) for the determination of cystine has been modified by reducing the cystine in acid solution, which enables the amount of sodium sulphite, and hence the blank, to be diminished, and by using an improved uric acid reagent (cf. A., 1924, ii, 634), in the course of preparation of which traces of molybdate are removed by treatment with hydrogen sulphide and extraction with alcohol. C. R. HARRINGTON.

Determination of nitrogen by Dumas' method. I. MAREK [with KRAJČNOVIČ and G. ZALJESOV] (Bull. Soc. chim., 1929, [iv], 45, 555—560).—See A., 1928, 1346.

Determination of iodine in organic substances which lose iodine with ease. E. I. VAN ITALLIE (Pharm. Weekblad, 1929, 66, 629—632).—The substance (10—200 mg.) is heated with 8—10 c.c. of sulphuric acid in a small retort and the iodine evolved is absorbed in 30—50 c.c. of 5% sodium hydroxide solution. The iodine may be determined either by titration or by reduction to iodide by hydrogen peroxide and precipitation as silver iodide.

H. F. GILLBE.

Determination of sulphur in organic liquids. S. LANDA (Coll. Czech. Chem. Comm., 1929, 1, 397—400).—The liquid is burnt in a lamp (substantially the procedure of petroleum testing is followed), the combustion products are passed into hydrogen peroxide, and the sulphuric acid is titrated with alkali hydroxide.

R. J. W. LE FÈVRE.

Analysis of organic mixtures. E. BENESCH (Chem.-Ztg., 1929, 53, 566—567).—A semi-mathematical paper in which it is indicated how the composition of appropriate mixtures of organic substances may be determined from a combination of analytical determinations.

J. S. CARTER.

Colorimetric determination of butyric acid. R. J. ALGHEIER, W. H. PETERSON, and E. B. FRED (J. Bact., 1929, 17, 79—87).—The solution is treated with a solution containing cupric chloride dihydrate (85.26 g.) in *N*-hydrochloric acid (1000 c.c.), shaken with chloroform, and the solution compared with controls. Acetic or formic acid does not interfere.

CHEMICAL ABSTRACTS.

Colour reaction of adrenaline. A. ORRÙ (Annali Chim. Appl., 1929, 19, 239—240).—When a trace of either natural or synthetic adrenaline, suspended in 1 c.c. of water, is heated to boiling with 2 drops of a solution of 0.1 g. of triketohydrindene hydrate in 300 c.c. of water, a blue colour is obtained. The reaction is given only by the free base. T. H. POPE.

Biochemistry.

Determination of carbon monoxide in blood. W. M. M. PILAAR (J. Biol. Chem., 1929, 83, 43—50).—See A., 1928, 1149.

Physico-chemical system of blood in relation to respiration and circulation. I. M. HOCHREIN, D. B. DILL, and L. J. HENDERSON. **II. Determination of blood circulation during rest and work.** M. HOCHREIN, J. H. TALBOTT, D. B. DILL, and L. J. HENDERSON. **III. Ionic distribution during rest and work.** H. T. EDWARDS, M. HOCHREIN, D. B. DILL, and L. J. HENDERSON. **IV. Carbonic acid respiration and hyperpnœa.** M. HOCHREIN, D. B. DILL, and L. J. HENDERSON (Arch. exp. Path. Pharm., 1929, 143, 129—146, 147—160, 161—169, 170—183).—I. A number of tables and curves summarise the changes of the physico-chemical properties of arterial and venous blood and respiratory changes of normal individuals at rest and during work.

II. The Haldane-Bock method is applied to determine the blood circulation in normal individuals at rest and during work, and it is shown how the position of the arterial and venous lines in the Hender-son nomogram can be fixed by this method.

III. In experiments with twelve normal individuals it is shown that during slight fatigue the difference between the value of r_{Cl} (ratio of chlorine in cell to that in serum) at rest and during work is smaller than for r_{HCO_2} . During exhaustion the value of r_{Cl} is twice and of r_{HCO_2} , four times as great as in the condition of slight fatigue. If lactic acid is added to the blood *in vitro*, both r_{Cl} and r_{HCO_2} increase and $r_{lactate}$ decreases, the degree of change depending on the concentration of lactic acid added. From these experiments *in vitro*, approximate values of $r_{lactate}$ during work can be calculated.

IV. The physico-chemical composition of blood during inspiration of a gas mixture of 6% of carbon dioxide, 20% of oxygen, and 74% of nitrogen and during hyperpnœa is indicated by a series of tables and nomograms. P. W. CLUTTERBUCK.

Cataphoretic velocity of mammalian red blood-corpuscles. H. A. ABRAMSON (J. Gen. Physiol., 1929, 12, 711—725; cf. this vol., 478).—The suspensions of blood cells were made up in *M*/15-phosphate, p_H 7.35±0.03, which had a specific resistance of 126±1 ohms at 25°. The temperatures used varied from 22° to 27° and results were corrected to 25°. The mean velocity for ten normal white adults was found to be 1.31±0.02μ/sec./volt/cm., and that for negroes 1.30±0.05μ. Results found on the same day were constant to within about 5%, but varied considerably over several weeks in the same individual. The cataphoretic velocity of mammalian red cells was found to be constant for all ages in the same species, and no variation in the average value was detected in various types of anæmia. No direct relationship appeared to hold between mobility and sedimentation velocity.

The relative mobilities of some different species were as follows: (in μ/sec./volt/cm.) rabbit 0.55, pig 0.98, guinea-pig 1.11, man 1.31, monkey 1.33, mouse 1.40, dog 1.65. No appreciable change in mobility occurred

in 24 hrs. in the phosphate buffer used. Unlike cholesterol, red cells did not adsorb gelatin even in 24 hrs. and retained their original velocity.

P. G. MARSHALL.

Structure of the hæmoglobin molecule. I, II. A. POLJAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 173—182, 183—191).—See this vol., 338.

New inorganic factor as supplement to iron in hæmoglobin building. E. B. HART (Wisconsin Med. J., 1929, 28, 60).—Experiments with anæmic rats indicate that copper plays a definite and specific part as a supplement to iron in the production of hæmoglobin. No evidence of the existence in liver of an indispensable organic factor for hæmoglobin production in anæmia was found.

CHEMICAL ABSTRACTS.

Influence of hæmocyanin on distribution of chloride between sea-water and blood of *Limulus polyphemus*. G. W. THOMAS (J. Biol. Chem. 1929, 83, 71—77).—The ratio Cl in *Limulus* blood-serum : Cl in sea-water is 0.981, concentrations being expressed as g. per kg. of water; the difference in concentration in the two fluids can be largely accounted for by the Donnan equilibrium due to the hæmocyanin of the blood. C. R. HARRINGTON.

Hæmochromogen and related compounds. H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1929, 6, 79—89).—The relative dissociation of a number of hæmochromogens and the quantitative relationships between reduced hæmatin and certain proteins are determined. The effect of treatment with nitrous acid on the ability of proteins to form hæmochromogens and parahæmatins is described. Some hæmochromogens are dissociated by formaldehyde. Native proteins do not form hæmochromogens.

P. W. CLUTTERBUCK.

Reduced hæmatin and hæmochromogen. R. HILL (Proc. Roy. Soc., 1929, B, 105, 112—130).—Hæmochromogens are formed by the union of 1 mol. of reduced hæmatin with 2 mols. of a nitrogenous compound. This conclusion is supported by spectroscopic observations on solutions containing reduced hæmatin in presence of pyridine, nicotine, or cyanide. Reduced hæmatin also forms a compound with 1 mol. of cyanide, but this compound combines with a second molecule of cyanide to form the true cyan-hæmochromogen or with 1 mol. of nicotine to form a mixed nicotine-cyan-hæmochromogen. It is therefore proposed to call the equimolecular compound of reduced hæmatin and cyanide cyan-reduced hæmatin and to reserve the name cyan-hæmochromogen for the compound containing 2 mols. of cyanide (cf. Anson and Mirsky, this vol., 87). The dissociation constants of the pyridine-, cyan-, and nicotine-hæmochromogens are, respectively, 8.9×10^{-6} , 4.8×10^{-8} , and 1.1×10^{-7} . The mixed nicotine-cyan-hæmochromogen has a dissociation constant of 0.38×10^{-8} and the cyan-reduced hæmatin of 1.3×10^{-8} .

W. O. KERMAK.

Inhibition by hydrogen sulphide of catalysis by hæmatin. H. A. KREBS (Biochem. Z., 1929, 209, 32—33).—The rapid oxidation which occurs when

hæmin is added to linoleic acid is almost completely checked when sodium sulphide is added also.

W. McCARTNEY.

Blood-catalase. E. SCHILLING (Klin. Woch., 1928, 7, 2202; Chem. Zentr., 1929, i, 760).—Catalase, by protecting tissue from the oxidising action of peroxide, is considered a protective enzyme.

A. A. ELDRIDGE.

Is fibrinogen in natural plasma present in the free state or as a complex? E. HEKMA (Biochem. Z., 1929, 209, 90—102).—A discussion of theories of the coagulation of the blood, the author's views being contrasted particularly with those of Pickering (cf. Pickering, "The Blood Plasma in Health and Disease," London, 1928).

W. McCARTNEY.

Existence, in plasmatic liquids, of fibrinogen-containing complexes together with free fibrinogen. E. HEKMA (Biochem. Z., 1929, 209, 128—133; cf. preceding abstract).—Examination of the appearance of the precipitates produced when plasmatic fluids are treated with suitable precipitants leads to the conclusion that both free fibrinogen and a complex containing it may be present together in the fluids.

W. McCARTNEY.

Chemical characterisation of serum-proteins. H. K. BARRENSCHEEN and L. MESSNER (Biochem. Z., 1929, 209, 251—262).—When serum-protein is phosphorylated by Rimington's method (A., 1927, 581) more phosphoric acid is taken up by the globulin than by the albumin. When serum-protein is methylated by methyl sulphate in alkaline solution the methoxyl values of the fractions are analogous to but rather higher than the phosphorylation values, and the methylated protein can be further phosphorylated. The methylimide and the *N*-methyl values show with globulin (except pseudoglobulin) lower values than with albumin.

P. W. CLUTTERBUCK.

Influence of hydrogen-ion concentration on the precipitation of serum-proteins by salts. II. D. VON KLOBUSITZKY (Biochem. Z., 1929, 209, 304—311).—Electrodialysed serum-albumin and -globulin are precipitated by saturated sodium chloride only below their isoelectric points, p_H 4.8 and 5.4, respectively (distinction from the albumin and globulin of whole serum), when the precipitating power and the concentration of hydrogen ions run parallel. Pseudo-globulin-euglobulin mixtures are stable at the isoelectric point.

P. W. CLUTTERBUCK.

Concentration of protein in serum and the reactions of coagulation. L. BLAS and M. MAGALLÓN (Anal. Fís. Quím. [Techn.], 1929, 27, 129—134).—The concentration of protein in blood-serum exerts a definite influence on coagulation reactions. Irregularities occasionally observed in the Wassermann and Meinecke reactions are ascribed to this influence.

H. F. GILLBE.

Determination of hydrogen-ion concentration in circulating blood. K. GOLLWITZER-MEIER and W. STEINHAUSEN (Klin. Woch., 1928, 7, 2426—2428; Chem. Zentr., 1929, i, 1030).—The effect on the results of the velocity of flow is pointed out.

A. A. ELDRIDGE.

Determination of the alkaline reserve of blood-plasma and determination of acetoacetic acid in blood. P. CRISTOL (Bull. Soc. Chim. biol., 1929, 11, 731—744).—The methods at present in use for the determination of the alkaline reserve of the blood-plasma are subject to an error due to decarboxylation of acetoacetic acid when applied to the blood of acetonuric subjects. If sodium fluoride is substituted for hydrochloric acid in the method of Lesœur and Manjean (A., 1928, 724) no decarboxylation occurs and a true measure of the carbon dioxide is obtained. By using the original and the modified method the acetoacetic acid of the blood may be determined.

J. H. BIRKINSHAW.

Bile-acid content of blood under various physiological conditions. M. CHARLET (Biochem. Z., 1929, 210, 42—69).—The method of Aldrich and Bledsoe (A., 1928, 788) with slight modification (principally the use of "norit" for decolorisation) was used to determine bile acids. These were shown to be present in the blood of normal men, rats, and cats. In rats the bile-acid content of the blood is a function of the activity of the liver. It is increased after protein and thyroid feeding. Thus the view that the liver supplies to the blood a hormone regulating the heart's activity receives new support.

J. H. BIRKINSHAW.

[Serum]-nitrogen coefficient in the normal state. M. LABBE, F. NEPVEUX, and A. HIERNAUX (Compt. rend. Soc. Biol., 1928, 99, 1492—1493; Chem. Zentr., 1929, i, 667).—The ratio urea-nitrogen : total nitrogen in the serum is normally 40—48 (average 44.2) mg.-%.

A. A. ELDRIDGE.

Colorimetric micro-determination of residual nitrogen in blood and serum. B. GROÁK (Biochem. Z., 1929, 209, 148—153).—If gum arabic is added to the solution obtained after the trichloroacetic acid filtrate from blood or serum has been digested with sulphuric acid and hydrogen peroxide, residual nitrogen can be determined accurately by the Nessler method.

W. McCARTNEY.

Determination of iron in blood. P. FLEURY (J. Pharm. Chim., 1929, [viii], 9, 561—568).—The blood is ashed in the presence of magnesium nitrate, the product dissolved in hydrochloric acid, and after dilution with water a little orthophosphoric acid is added. The ferric salt is reduced with zinc, the solution filtered, and titrated against potassium permanganate in the presence of phosphomolybdic acid and manganese sulphate.

F. C. HAPPOLD.

Determination of iron in blood. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 9, 568—570).—The ferric salt is reduced with mercury (see preceding abstract).

F. C. HAPPOLD.

Determination of phosphorus in blood. A. IONESCO-MATIU and M. VITNER (Bull. Soc. Chim. biol., 1929, 11, 776—781).—The colorimetric method of Bordeiano (B., 1927, 422) is applied to the micro-determination of inorganic and total phosphorus in blood. The inorganic phosphorus is determined directly in the filtrate after precipitation of the blood with trichloroacetic acid. The total phosphorus is determined after oxidation with nitric acid and permanganate.

J. H. BIRKINSHAW.

Inorganic phosphoric acid content of arterial and venous blood. A. HOFF (Biochem. Z., 1929, 209, 195—199).—In dogs the inorganic phosphoric acid content of the venous blood is higher than that of the arterial blood. W. McCARTNEY.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipid phosphorus in the blood of rabbits. II. A. R. HARNES (J. Exp. Med., 1929, 49, 287—301).—Values for animals kept in the laboratory or in the open air are recorded. Mean values are: calcium 15.7 ± 0.05 , inorganic phosphorus 4.65 ± 0.05 mg. per 100 c.c. of serum; cholesterol 58.2 ± 0.39 , lecithin 118.4 ± 1.13 mg. per 100 c.c. of whole blood. CHEMICAL ABSTRACTS.

Distribution of copper in blood. C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART (J. Biol. Chem., 1929, 83, 21—25).—Horse blood contains about 0.05 mg. of copper per 100 c.c., the larger proportion being in the red blood-corpuscles. Hæmoglobin contains amounts of copper which, on the basis of the accepted mol. wt. of this protein, are so small as to indicate that the metal does not form a part of the hæmoglobin molecule. C. R. HARRINGTON.

Combined sugar and its ratio to total nitrogen in the normal Japanese [blood?] K. KITAMURA (Kyoto Ikwad. Zasshi, 1928, 2, 241—246).—The following values [? for the blood] are recorded: combined sugar 0.067—0.107, average 0.091%; total nitrogen: combined sugar 9.15—10.70 (average 10.10), free: combined sugar 0.83—1.37 (1.15), combined: total sugar 0.420—0.545 (0.485), free: total sugar 0.455—0.578 (0.518). CHEMICAL ABSTRACTS.

Fixation of dextrose by blood-corpuscles. F. HÖGLER, A. THOMANN, and K. ÜBERRACK (Biochem. Z., 1929, 209, 1—31).—The analysis of a large number of experimental results shows that, in Loewi's phenomenon, the influence of swelling must be taken into account and that even so the method is not sufficiently accurate to enable definite conclusions to be reached. There is evidence that the uptake of sugar by erythrocytes is chiefly or entirely the result of a process of diffusion. W. McCARTNEY.

Salts and blood-sugar. H. MASAMUNE (Fukuoka Ikwad. Zasshi, 1927, 20, 1437—1522).—Potassium phosphate, magnesium salts, and to some extent calcium salts produce hyperglycæmia; sodium salts, or potassium acetate, chloride, or sulphate, have no effect. Ammonium chloride produces acidosis and magnesium salts alkalosis. CHEMICAL ABSTRACTS.

Dependence of the blood-sugar curve on the sugar preparation used. P. NIEDERHOFF (Biochem. Z., 1929, 210, 226—230).—Oral administration to fasting dogs or men of a paste of dextrose freshly crystallised from water with mother-liquor adhering gives a less marked initial hyperglycæmia than ordinary dextrose moistened with water. A secondary hyperglycæmia is observed with the freshly crystallised sugar. J. H. BIRKINSHAW.

Gasometric determination of fermentable sugar in blood and urine. D. D. VAN SLYKE and J. A. HAWKINS (J. Biol. Chem., 1929, 83, 51—70).—Fermentable sugar is determined in protein-free blood-filtrates or in urine cleared with Lloyd's reagent,

by application of the authors' ferricyanide method (A., 1928, 1358) before and after removal of dextrose with yeast. Normal urine contains 0.05—0.25% of total reducing substances, of which about one tenth is fermentable. This fermentable fraction is not affected, in normal individuals, by ingestion of 1 g. of dextrose per kg. The extra carbon dioxide produced by the action of yeast carboxylase on amino- and keto-acids introduces an error into the determination of fermentable sugar by direct measurement of carbon dioxide production in normal urines; in urines from glycosuric patients this error is insignificant. C. R. HARRINGTON.

Folin's micro-method for determination of blood-sugar. Blood-sugar and fermentable blood-sugar determined by different methods. O. FOLIN and H. MALMROS (J. Biol. Chem., 1929, 83, 115—120, 121—127).—Filtration of the light through filter-paper stained with picric acid eliminates the disturbing effect of the unchanged ferricyanide, and enables the colour comparisons in the method of Folin (A., 1928, 786) to be made over wider ranges of concentration.

Comparative determinations of total and fermentable sugar have been made in a large number of samples of blood by different methods. C. R. HARRINGTON.

Nature of blood-sugar. II. M. SOMOGYI (J. Biol. Chem., 1929, 83, 157—164).—The previous conclusions of Somogyi and Kramer (this vol., 207) as to the identity of the true blood-sugar determined by different methods are confirmed by experiments with four different methods on protein-free blood-filtrates prepared by the author's zinc technique (Proc. Soc. Exp. Biol. Med., 1929, 26, 353) which removes non-fermentable reducing substances. Folin's criticism (this vol., 462) of the author's work fails to take into account that in the application of Folin's recent method (A., 1928, 786) the oxidation of non-fermentable reducing substances in the tungstic acid blood-filtrate is, under the conditions prescribed by him, inhibited by the competing effect of the dextrose. The assumption of a second fermentable sugar in blood is unnecessary. C. R. HARRINGTON.

Determination of sugar in blood. S. R. BENEDICT (J. Biol. Chem., 1929, 83, 165—168).—Experimental results are given in disproof of the validity of Everett's criticism (this vol., 837) of the author's method (A., 1928, 438). C. R. HARRINGTON.

Hyperglycæmia associated with anaphylactic shock in the dog. I. T. ZECKWER and J. E. NADLER (J. Exp. Med., 1929, 49, 481—495).—The factors responsible for the condition are discussed. CHEMICAL ABSTRACTS.

Blood-nitrogen in sensitised animals. Z. M. DIENERSTEIN and S. GUENES (Zhur. exp. Biol. Med., 1929, 10, 520—529).—Anaphylactic shock, or any disturbance of the nitrogen of the tissues, does not disturb the nitrogen balance of the blood. CHEMICAL ABSTRACTS.

Hæmolytic action of some hydrolysis products of lecithin, lecithides, and phosphatides. I. Products of intermediary hydrolysis. H. MAGIS-

TRIS (Biochem. Z., 1929, 210, 85—119).—The hydrolytic action of cobra or bee-sting poison on egg-lecithin and kephalin liberates a fatty acid giving a lysolecithin and a lysokephalin. The former has a strong hæmolytic power (active at 1 in 26,000), the latter very little. The pure lysokephalin is probably inactive. Similar products were prepared from various animal and vegetable lecithides. A lysokephalin and a lysosphingomyelin from brain showed little hæmolytic power; a lysolecithin from the same source showed marked activity. Lysolecithins from horse pancreas, horse brain, or ox testes all showed fair hæmolysis, although much less than the product from egg-yolk. Active lysolecithins were also obtained from peas, oats, and soya beans. From the last-named, two products (α - and β -lysolecithin) differing widely in activity were obtained.

Irradiation of lecithin with ultra-violet light eliminates choline, and the lysolecithin derived from it is much less active. A slight diminution in activity is also observed on irradiation of lysolecithin. It seems that the hæmolytic activity depends on the presence of the choline radical, and it is suggested that in the hydrolysis of lecithin to lysolecithin the nitrogen atom of the choline radical becomes linked through oxygen to the free glycerol-hydroxyl group.

J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on hæmolysis by solanine. R. FISCHER (Biochem. Z., 1929, 209, 319—325).—The hæmolytic action of solanine at p_H 5.5 is very slight and rapidly lost on diluting, but at p_H 10 is retained down to dilutions of 1 in 266,000.

P. W. CLUTTERBUCK.

Mechanism of hæmolysis by complement.

I. Complement fixation as an essential preliminary to hæmolysis. H. EAGLE and G. BREWER (J. Gen. Physiol., 1929, 12, 845—862).—The influence of electrolytes on the hæmolysis of sensitised cells by complement is studied. For sodium chloride the two zones of inhibition are (1) below a concentration of 0.025—0.03*N*, (2) above 0.4*N*, a partial destruction of complement also occurring in the lower zone. The observation of Muir and Browning that hypertonic saline allows complement to pass through a Berkefeld filter is explained on a physical basis, viz., that adsorption of complement by the minute particles of the filter is inhibited by the saline. Increase in the valency of the cation has a marked effect in increasing the degree of inhibition of complement; barium chloride exhibits an effect twenty times as powerful as that of sodium chloride in a concentration of 0.07*N*. Electrolytes are shown (within the limits of experimental error) to produce an inhibition of complement fixation exactly similar to that of hæmolysis (same optimum p_H etc.), and the authors therefore regard it as proved that adsorption is an essential preliminary to hæmolysis.

Variations of p_H are also shown to produce zones of inhibition of hæmolysis and complement fixation, the optimal range being p_H 6.5—8.0, but in addition to these zones an irreversible inactivation takes place below p_H 4.8 or above p_H 8.8. It is assumed that the adsorption demonstrated is of the "midpiece" fraction of complement.

P. G. MARSHALL.

Titration of complement. H. EAGLE (J. Gen. Physiol., 1929, 12, 821—823).—A convenient and rapid method for the determination of complement, based on the fact that the time required for hæmolysis is a function of the amount of complement, under standard conditions of temperature and volume, is described. A time-complement reference curve is given and the complement content of an unknown solution is determined by interpolation. P. G. MARSHALL.

Mechanism of complement fixation. H. EAGLE (J. Gen. Physiol., 1929, 12, 825—844).—A fixation of complement by sensitised red cells is shown to occur, just as has previously been demonstrated with agglutinated bacteria and an immune precipitate. Complement fixation precedes hæmolysis. The degree of complement fixation by a globulin suspension can be altered by variation of the amounts of either globulin or complement. The rapid initial rise and the change in slope of the fixation curves on approach to the equilibrium point are difficult to explain, although widely differing adsorption processes show a similar phenomenon on increasing either constituent. Evidence of the effect of temperature on complement fixation by globulin suspensions, agglutinated bacteria, and sensitised red cells shows that the process is essentially the same in all three cases. The temperature coefficient, however expressed, averages only about 1.3 between 0° and 40°, and this is taken as evidence that the process is a physical rather than a chemical one.

In a quantitative study of the complement fixation reactions the same type of deviation from Freundlich's empirical rule is encountered as is the case with adsorption from dilute solutions. Experiments are described which indicate that complement fixation is determined entirely by some change in the cell surface, both in the case of bacteria and with red cells, such change being proportional to the degree of sensitisation. It is considered that during sensitisation an aggregation of immune-serum globulin occurs on the surface of the cells, and that this aggregation is responsible for complement fixation by adsorption. In support of this, the optimum p_H for agglutination of sensitised bacteria is the same (p_H 5.0) for *Pneumococcus*, *B. typhosus*, and *B. pertussis*, and differs from that of the normal bacteria. Nevertheless the possibility of the existence of a thermo-labile substance with a chemical affinity for complement is admitted, although positive evidence is at present lacking. P. G. MARSHALL.

Occurrence and behaviour of methæmoglobin in cadavers. W. LAYES (Deut. Z. ges. gerichtl. Med., 1928, 12, 549—575; Chem. Zentr., 1929, i, 932).—Bacterial methæmoglobinæmia is relatively seldom observed. Poisoning with nitrite is characterised by a gradual post-mortal conversion of the methæmoglobin into nitric oxide-hæmoglobin; presence of the spectra of both substances affords a trustworthy diagnosis. Differentiation from spontaneously formed nitric oxide-hæmoglobin by nitrite-forming bacteria is based on the uniform distribution of the substance in cases of poisoning.

A. A. ELDRIDGE.

Biochemistry of the sense organs. F. BERENSTEIN (Russ. Fisiol. Zhur., 1926, 9, 205—216).—The

eyes of rabbits (1), sheep (2), cows (3), and dogs (4) contain the following enzymes: amylase, 1, 2, 4; invertase, 1, 2, 3; glucosidase, 4; erepsin, 2, 3, 4; trypsin, 1; catalase, 1, 2, 3, 4; reductase, 2, 3, 4; oxidase, 1, 2, 3, 4; peroxidase, 1, 2, 3, 4; lactolase, 3; chymosin, 2, 4. Lactase, maltase, urease, pepsin, lipase, lecithinase, alcoholase, and zymase were not found.

CHEMICAL ABSTRACTS.

Distribution of the enzymes in the organs and tissues of the animal body. F. BERENSTEIN (Russ. Fisiol. Zhur., 1926, 9, 383—394).—The testicles or ovaries of the dog (1), ram (2), bull (3), sow (4), ewe (5), and cow (6) contain the following enzymes: amylase, peroxidase, catalase, lipase, trypsin, and autolytic enzyme in all; invertase, 2, 6; glucosidase, 3; oxidase, 2, 3, 4, 5, 6; reductase, 2, 3, 4, 6; lecithinase, 2, 3, 4; erepsin, 2, 3, 4, 5, 6; pepsin, 1, 4; lactolase, 2, 3, 4, 6; alcoholase, 2. Lactase, maltase, urease, and zymase were not found.

CHEMICAL ABSTRACTS.

Composition of body and organs of homeotherms and poikilotherms. E. VOLT (Z. Biol., 1929, 89, 114—138).—Analyses have been made for water, ash, fat, and nitrogen of the organs and whole bodies of various warm- and cold-blooded animals under varying physiological conditions. The results are discussed in relation to the fundamental nature of the metabolic processes concerned.

E. A. LUNT.

Presence of aluminium in plant and animal matter. L. KAHLBERG and J. O. CLOSS (J. Biol. Chem., 1929, 83, 261—264).—Spectroscopic examination indicates the presence of aluminium in a number of samples of plant and animal material. The contrary conclusions of McCollum and others (A., 1928, 793) are therefore erroneous. C. R. HARRINGTON.

Iron content of the albino rat at different stages of the life cycle. C. V. SMYTHE and R. C. MILLER (J. Nutrition, 1929, 1, 209—216).—At birth, during suckling, and at 20—40 days (and after), rats contain 0.0055, 0.0026, and 0.0045% Fe, respectively. The iron content of females is depleted during pregnancy, but returns to the normal value during lactation.

CHEMICAL ABSTRACTS.

Iodine content of human organs. B. BUCHHOLZ (Z. ges. exp. Med., 1928, 63, 188—197; Chem. Zentr., 1929, i, 915).—Iodine was detected in all the organs examined; individuals exhibit differences. The thyroid gland contains most iodine; the adrenals, ovaries, thymus, and sometimes the spleen contain fairly large amounts. Chronic pathological conditions affect the values. The total iodine content of the human body varies considerably around 11 mg.

A. A. ELDRIDGE.

Nucleic phosphorus of tissues and its determination. M. JAVILLIER (Bull. Soc. Chim. biol., 1929, 11, 644—678).—A lecture.

Titanium in animals. G. BERTRAND and (MME.) VORONCA-SPIRT (Compt. rend., 1929, 189, 221—223).—The titanium has been determined in various organs of a large number of animals and fish by the method previously used for its detection in plants (this vol., 855). In the horse, cow, sheep, and pig the liver is richest in this element (0.5—

0.6 mg./kg.), the heart, lungs, and kidneys containing about one half of this amount, whilst the element is absent from the muscles, brain, and spinal cord. Titanium could not be detected, however, in the corresponding organs of a rabbit, but the fur contains 2.2 mg./kg. Small quantities (0.3—0.9 mg.) are found in most fish, whilst *Crustacea* and molluscs are relatively rich in this element, the combined head and thorax organs of the edible crab containing 32.5 mg./kg.

J. W. BAKER.

Sulphur content of melanotic pigments. F. SCHAAP (Biochem. Z., 1929, 209, 79—82).—A method by which melanotic pigments rich in sulphur can be freed almost completely from this element is described. The last traces of sulphur are almost as difficult to remove as are those of iron. The view that sulphur is not an integral part of the pigment is confirmed.

W. MCCARTNEY.

Determination of the mineral constituents of rabbit's and dog's muscle. BOUTRON and GENAUD (Compt. rend. Soc. Biol., 1928, 99, 1730—1731; Chem. Zentr., 1929, i, 765).—Determinations of water, chlorine, potassium, sodium, and phosphorus are recorded.

A. A. ELDRIDGE.

Pyrophosphate fraction in muscle. K. LOHMANN (Naturwiss., 1929, 17, 624—625).—The pyrophosphate fraction of muscle can be isolated through the barium salt. Neutral hydrolysis of the complex salt results in the formation of pyrophosphoric acid and adenosinephosphoric acid (adenylic acid). Adenylpyrophosphoric acid, after brief treatment with hot dilute acid, yields 2 mols. of orthophosphoric acid and 1 mol. of adenine and pentose (ribose)-phosphoric acid. The results are discussed in relation to other work on muscle.

R. A. MORTON.

Enzymic action of the muscle of a mummy 3000 years old (precipitin reaction, glycolysis, and respiratory enzyme). E. SEHR (Arch. exp. Path. Pharm., 1929, 143, 35—45).—The glycolytic activity of a powder prepared from ox pancreas after extraction with acetone is distinct although weak, but a mixture of an acetone powder of mummy muscle, which itself has no appreciable glycolytic activity, with the acetone powder from ox pancreas possesses very considerable glycolytic activity, approximately equal to that of a similar mixture from fresh ox tissues. Powder from mummy muscle gives the indophenol oxidase reaction.

W. O. KERMAK.

Influence of hæmolysis on the secretion of bile. K. SUGIU and O. HISASI (Okayama Ig. Zasshi, 1927, 39, 1902—1913).—In dogs with gall bladder fistulas, splenectomy caused for 20—30 days a diminution in the iron and bilirubin contents of the bile. Injection of water or hæmolysin caused an increase in the biliary iron and bilirubin either before or after splenectomy. The effects of phenylhydrazine, nitrobenzene, and tolylenediamine were examined.

CHEMICAL ABSTRACTS.

Excretion of iodine by the gastric glands. L. HELMEYER and A. STURM (Klin. Woch., 1928, 7, 2381—2383; Chem. Zentr., 1929, i, 555).—A few minutes after intravenous administration of iodine the gastric juice contains considerable amounts of

iodine and an increased quantity of free hydrochloric acid. Iodine appears in the stomach soon after inhalation of ethyl iodide vapour.

A. A. ELDRIDGE.

Phosphorus, calcium, and potassium contents of artificially induced peritoneal exudates. X. CHAHOVITCH and M. VICHNJITCH (Compt. rend. Soc. Biol., 1928, 99, 1267—1270; Chem. Zentr., 1929, i, 552).—The values do not correspond with those of the blood.

A. A. ELDRIDGE.

Normal day-to-day variability of yield of milk and fat of individual cows. S. BARTLETT (J. Agric. Sci., 1929, 19, 438—451).—A statistical study of the variability of milk and fat yield of cows as affected by such factors as stage of lactation and season of the year is presented.

E. HOLMES.

Variations in the composition of the milk of an abnormal cow. H. T. CRANFIELD and E. R. LING (J. Agric. Sci., 1929, 19, 491—499).—Details are recorded of a cow which, during three lactation periods, gave milk of which the fat percentages were very variable; the solids-not-fat were consistently low, the value exceeding 8.5% in only 2% of the total number of samples analysed. Protein, lactose, phosphoric acid, and lime percentages were much below normal, whilst the soluble portion of the ash was high and the insoluble low. Porcher's contention that there is a definite lactose-chlorine ratio in milk is supported. Feeding first with "non-mineralised" and later with "mineralised" cake had no apparent effect, but these abnormalities may have been incipient signs of disease affecting the milk-secreting organs, for the cow was eventually found to be suffering from tuberculosis.

E. HOLMES.

Buffer intensities of milk and milk constituents. I. Buffer action of caseinogen. E. O. WHITTIER (J. Biol. Chem., 1929, 83, 79—88).—Titration curves were obtained for skimmed milk and for whey, and the curve for the caseinogen was constructed by difference. Milk showed maximum buffering at p_H 5.5 and the caseinogen at p_H 5.2, whence it appears that caseinogen is one of the predominant buffers of milk. Curves obtained for different samples of purified caseinogen showed different characteristics. The curve for milk lost its characteristic form on addition of rennet, owing to the conversion of the caseinogen into casein.

C. R. HARINGTON.

Effect of diet on copper content of milk. C. A. ELVEHJEM, H. STEENBOCK, and E. B. HART (J. Biol. Chem., 1929, 83, 27—34).—Cow's milk contains about 0.15 mg. of copper per litre with no significant geographical variation. The copper content of cow's and goat's milk was not increased by 5-fold increase in the dietary intake of copper (in the form of copper sulphate).

C. R. HARINGTON.

Is the iron content of milk increased by the ingestion or injection of iron salts? V. HENRIQUES and A. ROCHE (Bull. Soc. Chim. biol., 1929, 11, 679—692; cf. this vol., 93).—Daily ingestion of 0.5 g. of ferrous sulphate by women and of 5 g. of ferrous lactate by goats does not cause any change in the iron content of the blood, which is normally 1 mg.

per litre in each case. Intravenous injection of lactate in the goat likewise produces no increase.

J. H. BIRKINSHAW.

Aroma of butter. C. B. VAN NIEL, A. J. KLUYVER, and H. G. DERX (Biochem. Z., 1929, 210, 234—251).—The aroma of butter is parallel with its content of acetylmethylcarbinol, and *Streptococcus cremoris*, *S. citrovorus*, and *S. paracitrovorus*, which produce the aroma, all produce the carbinol. Pure acetylmethylcarbinol has no odour, whereas diacetyl in dilute solution possesses the characteristic butter aroma. The aroma of butter is due to the presence of chemically undetectable amounts (0.0002—0.0004%) of diacetyl formed by the oxidation of acetylmethylcarbinol.

J. H. BIRKINSHAW.

Volumetric determination of potassium in urine. A. BOLLIGER and E. M. DAY (Austral. J. Exp. Biol., 1929, 6, 91—95).—A method for determination of urinary potassium depending on its precipitation as perchlorate from the unashed urine and titration with methylene-blue is described.

P. W. CLUTTERBUCK.

Colorimetric determination of small amounts of sugar in urine. C. STICH (Pharm. Zentr., 1929, 70, 437).—Urine is heated with Fehling's solution and the precipitated copper oxide separated by centrifuging, dissolved in pure nitric acid, and suitably diluted. The colour produced by the addition of ferrocyanide and ammonia is then compared with that produced from a standard solution of dextrose treated in a similar way.

W. O. KERMAK.

Determination of dextrose in urine. F. JÜSTEN (Apoth.-Ztg., 1928, 43, 1436; Chem. Zentr., 1929, i, 565).—Addition of excess of Fehling's solution and titration of the excess with iodine and thiosulphate is preferred to Meyer's direct method.

A. A. ELDRIDGE.

Test for protein in urine. C. BOSE (Indian Med. Gaz., 1929, 64, 17—19).—A supersaturated aqueous solution of saccharin is employed, the test being performed in the same manner as Heller's nitric acid test. The reagent has the advantage of failing to precipitate mucin, urica, or urates.

CHEMICAL ABSTRACTS.

Iron in nutrition. VIII. Ineffectiveness of large doses of iron in curing anæmia in the rat. J. WADDELL, H. STEENBOCK, and E. B. HART [with E. VAN DONK]. **IX. Deficiency of copper as cause of anæmia.** J. WADDELL, H. STEENBOCK, C. A. ELVEHJEM, and E. B. HART [with E. VAN DONK] (J. Biol. Chem., 1929, 83, 243—250, 251—260).—VIII. Relief of nutritional anæmia in young rats was obtained by heavy dosage with iron salts only when the latter contained traces of copper.

IX. Anæmia in young rats on a diet of milk and pure iron salts could be cured by addition of liver extracts, the acid-insoluble sulphides of the ash of such extracts, and copper sulphate, all additions containing equivalent amounts of copper.

C. R. HARINGTON.

Xanthine calculi in sheep. T. H. EASTERFIELD, T. RIGG, H. O. ASKEW, and J. A. BRUCE (J. Agric. Sci., 1929, 19, 573—585).—Xanthine calculi in the kidneys of sheep, reported on certain poor pastures on the Moutere Hills in the Nelson district, N.Z.,

occur where the soils and pasture are notably deficient in lime and phosphate. Samples of pasture show a great deficiency of iron and an abnormally high content of manganese. "Bush" sickness, definitely associated with iron deficiency, is unknown in the district. Calculus formation does not occur on the small areas where good pastures have been established by lime and phosphate treatment. E. HOLMES.

Vitamin-B in cancer. H. JACKSON, jun., and C. I. KRANTZ (J. Clin. Invest., 1929, 6, 609—612).—Malignant tissue contains less vitamin-B than normal liver. CHEMICAL ABSTRACTS.

Action of various proteins on blood-sugar [in diabetes]. H. GLATZEL (Arch. exp. Path. Pharm., 1929, 143, 234—245).—In diabetics after oral administration of protein, a strong tendency to hyperglycæmia is obtained. The hyperglycæmia after a single administration of 20 g. of dextrose by mouth to a diabetic after an egg-protein diet is less and lasts for a shorter time than after a pure fat-vegetable diet. If the egg-protein be replaced by a corresponding amount of flesh-protein, the hyperglycæmia is greater and lasts longer. P. W. CLUTTERBUCK.

Effect of oral administration of bile acids on the sugar metabolism of the diabetic. H. HORSTERS and H. ROTHMANN (Arch. exp. Path. Pharm., 1929, 142, 261—270).—Oral and intravenous administration of bile acids or salts lowers the blood-sugar of normal and diabetic individuals; the action is comparable with that of insulin. In the fasting diabetic the lowering is greater than that produced by lack of food alone; when food is taken the usual rise in blood-sugar is suppressed. In mild cases of diabetes an improvement in the carbohydrate tolerance is observed, in severe diabetes mellitus there is frequently no improvement. The bile acids probably act by stimulating the portion of pancreas tissue which is still active. J. H. BIRKINSHAW.

Blood-sugar in insulin-treated diabetes. N. A. NIELSEN (Z. klin. Med., 1929, 109, 636—646; Chem. Zentr., 1929, i, 1229).—Determination of blood-sugar before, and 5 hrs. after, the injection is recommended. A. A. ELDRIDGE.

Effect of insulin on the properties of the blood in diabetes mellitus. E. ZUCKERSTEIN and A. STREICHER (Deut. Arch. klin. Med., 1928, 161, 323—337; Chem. Zentr., 1929, i, 1229).

Hyperinsulinism. F. N. ALLAN (Arch. Int. Med., 1929, 44, 65—70).—It has been definitely established that spontaneous hypoglycæmia, due to over-production of insulin by the pancreas or perhaps, in some cases, to failure of the liver, sometimes occurs in man. Distinction between the two causes may be difficult. W. MCCARTNEY.

"Oxantin" (dihydroxyacetone); relation between metabolism and blood-sugar changes. A. Löw and A. KRÖMA (Klin. Woch., 1928, 7, 2432—2435; Chem. Zentr., 1929, i, 1019).—Dihydroxyacetone, orally administered, passes into the blood of diabetics, but not of normal individuals. A. A. ELDRIDGE.

Phloridzin diabetes. III. Effect of phloridzin on glycogen storage in dogs with ligated ureters. T. P. NASH, jun. (J. Biol. Chem., 1929, 83, 139—155).—Procedures such as fasting, exposure to cold, and administration of adrenaline do not invariably reduce the glycogen stores of the dog to a significant extent. Phloridzin was without effect on the sugar, non-protein nitrogen, and acetone of the blood, and on the glycogen of the liver and muscles of dogs with ligated ureters. The results, however, fail to provide conclusive evidence that the site of action of phloridzin is exclusively renal. C. R. HARRINGTON.

Fructosuria. P. A. HEERES and H. Vos (Arch. Int. Med., 1929, 44, 47—64).—Experiments on a subject suffering from essential fructosuria gave the following results. Fructosuria at once disappears if only food free from lævulose is consumed. The quantity of lævulose excreted in the urine is constant (about 14%), and independent of the amount administered, whether in one large or several small doses, and whether orally or intravenously. Administration of lævulose causes a rise in the blood-sugar content due to fructosæmia. Inulin does not cause or influence fructosuria. Lævulose when given together with other sugars causes a fructosuria more severe than that produced when it is given alone. The metabolism of dextrose, galactose, maltose, and mannose is not disturbed, but when sorbose is administered it is largely excreted in the urine. There is no rise in the respiratory quotient following administration of lævulose. Freshly-dissolved lævulose produces a greater degree of fructosuria than lævulose which has been in solution for some time before administration. Crystalline lævulose, administered *per rectum*, produces a more severe fructosuria than lævulose given by the mouth. W. MCCARTNEY.

Decomposition of protein in fever. I. MA (Monatsschr. Kinderheilk., 1928, 36, 363—376; Chem. Zentr., 1929, i, 1031—1032).—In infection and fever (in children) the action of the serum-peptidase was increased. Comparison of the urinary nitrogen and peptidase did not suggest that the increase was due to cellular breakdown. A. A. ELDRIDGE.

Iodine and exophthalmic goitre. A. SPRINGBORN and A. GOTTSCHALK (Deut. Arch. klin. Med., 1928, 161, 338—352; Chem. Zentr., 1929, i, 1234).—The effect of administration of iodine in simple and in exophthalmic goitre is described. A. A. ELDRIDGE.

Calcium content of blood of normal and thyroidectomised sheep. P. V. BOTCHKAREFF and M. P. DANILOVA (Compt. rend., 1929, 189, 304—305).—The difference between the calcium content of the blood of normal sheep (10 mg. per 100 c.c.) and that of thyroid-parathyroidectomised sheep is negligible. A. A. GOLDBERG.

Changes in the alkali reserve and chloride content of the blood in experimental intestinal closure. F. D. ALSINA and J. R. PIJOAN (Compt. rend. Soc. Biol., 1928, 99, 1278; Chem. Zentr., 1929, i, 549).—Closure of the upper intestine increases the alkali reserve and reduces the blood-chlorine; closure of the lower intestine reduces the blood-chlorine without affecting the alkali reserve. A. A. ELDRIDGE.

Cholesterol content of Indian blood in health and leprosy. T. C. BOYD and A. C. ROY (Indian J. Med. Res., 1928, 15, 643—651).—Normal values range from 0.082 to 0.184 g. per 100 c.c.; values for early and advanced leprosy, respectively, are 0.070—0.109 and 0.080—0.130. CHEMICAL ABSTRACTS.

Blood-calcium in leprosy. M. C. CRUZ, C. B. LARA, and E. M. PARAS (J. Philippine Is. Med. Assoc., 1928, 8, 216—221).—Serum-calcium values are unchanged. CHEMICAL ABSTRACTS.

Effect of [intravenous injection of] calcium or ergotamine on the blood-sugar curve after administration of dextrose as a test of liver function. T. REDNIK (Z. klin. Med., 1929, 109, 720—724; Chem. Zentr., 1929, i, 1228—1229).—Injection of calcium or ergotamine diminishes the rise of the blood-sugar curve caused by administration of dextrose. A. A. ELDRIDGE.

Physico-chemical changes in the blood and histological changes in the kidneys in experimental nephritis. N. ISHIYAMA (Z. ges. exp. Med., 1928, 63, 699—716, 717—719; Chem. Zentr., 1929, i, 1119).—Excessive feeding of rabbits with vegetable protein leads to albuminuria and increase of the blood-residual nitrogen and plasma-protein, changes differing from those in man. Injection of mercuric chloride, cantharidin, or habu-poison, but not uranium, caused a diminution of the serum-albumin and an increase of the serum-globulin; these changes correspond with those observed in man. A. A. ELDRIDGE.

Chlorine ions in the blood in chloride retention of nephritis. H. THIERS (Bull. Soc. Chim. biol., 1929, 11, 693—709).—The chloride of plasma shows very variable values in nephritis. The acidity drives the chlorine ions from the plasma to the erythrocytes, lowering the ratio plasma-chloride/erythrocyte-chloride. Consequently when the total chlorine ions are insufficient in nephritis these are increased in the erythrocytes and tissues but reduced in the plasma, which then gives subnormal values. With strong acidosis the blood may show a reduced chloride content, the chloride being found in the tissues. J. H. BIRKINSHAW.

Blood-chlorides in conditions associated with pneumonia. C. A. L. BINGER, R. V. CHRISTIE, J. S. DAVIS, jun., and A. HILLER (J. Exp. Med., 1929, 49, 603—614).—Ingestion of much water, and experimental pneumococcal infection but not starvation, anoxemia, tissue destruction, anaphylactic shock, leucocytosis, or fever diminished the serum-chloride of dogs. CHEMICAL ABSTRACTS.

Determination of respiratory exchange of small animals. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 307—313).—A simple closed-circuit method involving determinations of carbon dioxide and oxygen is described. C. C. N. VASS.

Basal metabolism of omnivorous and vegetarian rats. H. WU and T. T. CHEN (Chinese J. Physiol., 1929, 3, 315—323).—The basal metabolism of 95 vegetarian rats determined by means of the respiratory exchange method (preceding abstract)

was slightly lower than that of the 96 omnivorous rats examined. C. C. N. VASS.

Respiratory metabolism in eviscerated dogs. A. BORNSTEIN (Biochem. Z., 1929, 209, 172—180).—When fasting dogs are eviscerated but not decapitated the gaseous exchange always falls on the average about 45% and the respiratory quotient always rises but remains below 1.0 (average 0.8—0.9). The increase in the respiratory quotient is largely due, however, to over-ventilation of the lungs. It follows that, after evisceration, considerable amounts of fat can be burnt. If dextrose is injected into eviscerated dogs in amounts greater than that necessary for their calorie requirements the respiratory quotient rises to a value considerably higher than that found when no dextrose is injected. It is concluded that the fat and carbohydrate metabolism of eviscerated dogs depends mainly on the quantities of these substances present in the food supplied. W. MCCARTNEY.

Inorganic salt metabolism. I. Methods. W. BAUER and J. C. AUB (J. Amer. Dietet. Assoc., 1927, 3, 106—115).—Clinical routine for the study of calcium and phosphorus metabolism is described. New determinations of these elements in various foods are recorded. CHEMICAL ABSTRACTS.

Calcium metabolism in the human female. R. F. MATTERS (Austral. J. Exp. Biol., 1929, 6, 119—125).—The blood-calcium shows a pre-menstrual rise followed by a fall just prior to the onset of menstrual flow, the variation being 5—8% of the normal calcium level. P. W. CLUTTERBUCK.

Effect of intragastric administration of calcium on the urinary C:N quotient in rabbits. A. BICKEL and D. MARSCHALKOWITZ (Z. ges. exp. Med., 1928, 62, 747—755; Chem. Zentr., 1929, i, 552).—Administration of 0.011—0.013 g. of calcium per kg., but not of greater doses, caused a transitory fall in the urinary C:N quotient. A. A. ELDRIDGE.

Cholesterol metabolism. M. WICHERT, S. POSPELOV, and A. JAKOVLEVA (Z. klin. Med., 1929, 109, 678—697; Chem. Zentr., 1929, i, 1233).—Increased ingestion of cholesterol increases the blood-cholesterol only when the lipid metabolism is seriously disturbed. There appears to be a relationship between the urinary bile acids and the excretion of cholesterol. A. A. ELDRIDGE.

Ageing of tissue. M. BÜRGER and G. SCHLOMKA (Z. ges. exp. Med., 1928, 63, 105—116; Chem. Zentr., 1929, i, 920).—The cholesterol content of the skin decreases with increasing age. Values for the dry matter and nitrogen content (g-%), respectively, are: 5 weeks 24.6—35.5, 3.68—4.86; 5 years 29.7—42.1, 4.74—6.36; 60 years 35.4—44.1, 5.91—7.25. A. A. ELDRIDGE.

Ammonia metabolism of the kidneys and its relation to the acid-base balance. H. WASSERMAYER (Arch. exp. Path. Pharm., 1929, 143, 117—128).—Determinations of ammonia in blood from the carotid artery, vena cava, and kidney vein confirm the view that ammonia is produced by the kidneys. The probable source of this ammonia is adenosinephos-

phoric acid, from which it is formed during enzymic deamination.

W. O. KERMACK.

Protein metabolism of organs of animals kept in air under reduced pressure. H. ANGELESCU (Biochem. Z., 1929, 209, 236—239).—Lack of oxygen produces the following changes in the nitrogen content of the spleen, heart, liver, and muscles of guinea-pigs: a 2—7% decrease in the total nitrogen, with the greatest lack of oxygen investigated (barometric pressure, 230 mm.), an increase of total residual nitrogen amounting to about 9% for heart and muscle and to 100% for spleen and liver, and an increase of from 20% (muscle and heart) to almost 100% (spleen and liver) in the amino-acid fraction of the residual nitrogen. These changes appear first in the spleen, then in the liver, and finally, as rarefaction is increased to its greatest extent, in heart and muscle.

W. MCCARTNEY.

Embryonic metabolism. III. Nitrogen distribution in the developing hen's egg. H. O. CALVERY (J. Biol. Chem., 1929, 83, 231—241).—Figures are given for the analysis by the Van Slyke method of the alcohol-insoluble contents of the hen's egg at varying stages of development. The most conspicuous change is a decrease in the amino-nitrogen and a corresponding increase in the non-amino-nitrogen of the filtrate. Arginine shows a preliminary decrease, followed by an increase above the initial level; histidine shows considerable fluctuations.

C. R. HARINGTON.

Production of choline from the suprarenal capsule. S. ONO (Fukuoka Ikwad. Zasshi, 1927, 20, 1187—1212).—Venous blood of the suprarenal capsule contains more choline than blood from any other abdominal organ. The formation of choline is regulated by the nervous system. Extirpation of the suprarenal capsule decreases the choline content of the serum.

CHEMICAL ABSTRACTS.

Urea content of frog muscle. J. HELLER (Biochem. Z., 1929, 209, 74—78).—The urea content of frog muscle varies widely from animal to animal and from species to species, being much higher in *Rana temporaria* than in *R. esculenta*. Changes in the urea content run parallel with changes in glycogen content. In frogs kept for several days with insufficient water or at temperatures above normal the urea content of the muscle rises. The urea in the muscle does not take part in the traumatic production of ammonia.

W. MCCARTNEY.

Purine metabolism. II. Effect of ingestion of glycine on excretion of endogenous uric acid. A. A. CHRISTMAN and E. C. MOSIER (J. Biol. Chem., 1929, 83, 11—19).—The previous conclusion of Lewis and others (A., 1918, i, 559) that ingestion of glycine is followed by increased excretion of uric acid is confirmed, the contrary results of Zwarenstein (A., 1928, 547) being explained by his employment of the method of Benedict and Franke (A., 1922, ii, 669), which gives low results for uric acid in presence of large amounts of amino-acids.

C. R. HARINGTON.

Variation of acetone substances in the living organism. K. WATANABE (Aichi J. Med., 1928, 35, 381—534).—Administration of butyric, valeric,

or, particularly, isovaleric acid to rabbits increases the blood-acetone substances and causes the appearance of acetone substances in the urine; poisoning by yellow phosphorus has a similar effect, but causes no marked change in the blood-sugar. Injection of adrenaline, followed by that of butyric acid, has a specially marked effect. Adrenaline decreases the acetone concentration which has been increased by fatty acid. The combined use of fatty acid and insulin causes an increase in acetone concentration which is comparable with that produced by fatty acid alone, the urinary excretion being small. Insulin does not inhibit the formation of acetone substances. On injection of sodium butyrate and dextrose recovery is more rapid than with sodium butyrate alone. In phosphorus-poisoned rabbits the velocity of increase in the blood-acetone is retarded, its excretion in the urine being small.

CHEMICAL ABSTRACTS.

Behaviour of carbohydrates during muscle perfusions. A. BORNSTEIN and H. VÖLKER (Biochem. Z., 1929, 209, 103—118).—In the isolated hind limbs of a dog perfused with dog's blood the amount of blood-sugar tends to fall, and addition of 0.225 g. of dextrose per kg. per hr. is necessary to maintain it at physiological level. The amount of lævulose necessary for the same purpose is 0.25 g. per kg. per hr., whilst additions of lactic acid or of alcohol have a slight sugar-saving effect. If insulin is added to the blood-stream along with sufficient sugar to produce an increase in blood-sugar, the amount of this falls considerably, the quantity of insulin required for the purpose being of the same order as is necessary in the whole animal. There is no constant relationship between the glycogen and the total carbohydrate content of the muscle and the amount of sugar administered, although the glycogen content usually increases during 1½—2 hrs. when sufficient sugar for maintaining a constant level of blood-sugar is given, and usually decreases without appearance of convulsions when insulin is given simultaneously. The amount of sugar necessary to maintain constancy of the blood-sugar level corresponds with about 50% more than the oxygen requirement of the limbs. Part of the sugar which disappears from the blood is stored as reserve carbohydrate or reserve fat.

W. MCCARTNEY.

Critical temperature of freezing. Living muscle. T. MORAN (Proc. Roy. Soc., 1929, B, 105, 177—197).—Experiments carried out on living sartorius and gastrocnemius muscles in the frog indicate that the effects of freezing are similar to those produced by desiccation. A 78% removal of water produces instant death and corresponds with freezing to equilibrium at -2° . Muscles frozen below -2° exhibit on thawing loss of osmotic properties and express an acid liquid. Super-cooling below -2° produces no changes. A freezing or desiccation resulting in a loss of water of not more than 40% of the original weight of muscle is shown to be completely reversible.

E. A. LUNT.

Formation of lactic acid in the muscles in the frozen state. E. C. SMITH (Proc. Roy. Soc., 1929, B, 105, 198—207).—The rates of accumulation of lactic acid have been determined in the case of the gastrocnemius of the frog exposed to temperatures between 0° and -10° . With falling temperature

of storage the rate of accumulation increases, reaching a maximum at -25° , and is negligible at -10° . Muscles frozen above -1.6° appear capable on thawing of returning to their normal lactic acid content, whilst in muscles frozen below this temperature the lactic acid on thawing increases to that of the normal rigor maximum.
E. A. LUNT.

Oxidation of lactic acid in muscle. A. HAHN and E. FISCHBACH (*Z. Biol.*, 1929, 89, 149—158).—A review of current investigations on the existence of a thermostable co-enzyme for the oxidation of lactic acid in muscle suggests that admissible evidence for such an enzyme can only be obtained by establishing the identity of the respiration process in unwashed muscle with that occurring in washed muscle, the respiration of which has been restored by the addition of boiled aqueous extract of muscle which was thought by Meyerhof to contain the thermostable co-enzyme. Experiments are described in which finely-divided unwashed muscle and finely-divided washed muscle + boiled aqueous extract are shaken in a vacuum and in oxygen; the oxygen consumption and lactic acid contents are determined for various times of shaking. No sensible difference between the lactic acid content in oxygen and in a vacuum was observed in the experiments with washed muscle + extract; with unwashed muscle the lactic acid content after shaking was markedly higher in vacuum than in oxygen. The degree of restoration of respiration in these experiments ranged from 0.52 to 0.92 as measured by the ratio of the rate of oxygen consumption of washed muscle + extract to the corresponding rate for unwashed muscle. It is concluded that no detectable oxidation of lactic acid results from the restoration of the respiration of washed muscle by extract. Since it is thus shown that the original and the restored respiratory processes are essentially different, Meyerhof's assumption of a co-enzyme is held to be unnecessary.
E. A. LUNT.

Oxidation of succinic acid. II. A. HAHN and W. HAARMANN (*Z. Biol.*, 1929, 89, 159—166).—A method has been developed for the analysis of mixtures containing succinic, malic, and fumaric acids. The fumaric acid is first determined by the authors' method (cf. A., 1928, 323) as mercurous salt; in a second sample the malic acid is converted into fumaric acid, from the amount of which the malic acid may be calculated. In a third sample the succinic acid is determined by means of the silver salt after the other two acids have been preferentially oxidised by neutral aqueous permanganate. Under the conditions described the conversion of malic into fumaric acid takes place to the extent of about 94%, and the mean error in the determination of succinic acid is about 2%.

This method has been used to investigate the oxidation of succinic acid by means of muscle in the presence of (a) methylene-blue, (b) oxygen. In (a) about 9% of fumaric acid and 25% of malic acid are produced, corresponding with about 40% decomposition of the original succinic acid. In (b) succinic acid is completely oxidised to fumaric and malic acids approximately in the ratio 1 : 2.5. If, however, the muscle be first washed with toluene-water, no sensible

oxidation takes place in the presence of oxygen, but the reaction velocity with methylene-blue remains approximately unchanged.
E. A. LUNT.

Physical chemistry in the service of biology. F. G. DONNAN (*J.C.S.*, 1929, 1387—1398).—Liversidge lecture, delivered on Nov. 29, 1928.

Influence of certain water conditions, especially dissolved gases, on trout. J. S. GUTSELL (*Ecology*, 1929, 1, 77—96).—A study of the effect of variations in p_{H} and dissolved oxygen and carbon dioxide. Marked increase in the carbon dioxide and decrease in the oxygen content of spring- and brook-water as the warm season advanced is attributed to increased bacterial activity.
CHEMICAL ABSTRACTS.

Basal and resting metabolism after irradiation with ultra-violet light. I. Resting metabolism of birds. II. Basal metabolism of man. III. Resting metabolism of rabbits. E. CROFTS (*Amer. J. Hyg.*, 1928, 8, 1014—1019, 1020—1023, 1024—1029).—With canaries a 14% fall in oxygen consumption, followed by a delayed rise of 21%, was observed; in the other cases no effect was observed.
CHEMICAL ABSTRACTS.

Absorption by dyes and leuco-compounds as a pre-condition of photobiological sensitisation in the ultra-violet. W. HAUSMANN and O. KRUMPEL (*Biochem. Z.*, 1929, 209, 142—147).—The ultra-violet absorption spectra of a dye containing two pyrrole nuclei and of the corresponding leuco-compound as well as of mesoporphyrinogen have been studied and evidence has been obtained that photobiological sensitisation in the ultra-violet region may be caused by the uncoloured precursor of the dye (or porphyrin).
W. McCARTNEY.

Behaviour and action of undigestible substances (keratin, kaolin) in the organism of mammals. A. GOLDFEDER (*Biochem. Z.*, 1929, 209, 154—171).—Experiments on mice by which food containing up to 60% of keratin or 80% of kaolin was consumed show that these substances have practically no influence of any kind. Keratin has no mechanical influence (increase of length) on the intestine.
W. McCARTNEY.

Action of active iron oxide on blood formation and growth of white rats. W. LINTZEL (*Biochem. Z.*, 1929, 210, 76—84).—Only about 7% of active iron oxide ("siderac") was soluble in hydrochloric acid at the concentration of gastric juice. It had no specific action on the growth of rats. It was much inferior to ferric chloride weight for weight when added to an iron-free ration.
J. H. BIRKINSHAW.

Histochemical investigations on the behaviour of various iron compounds in the organism. V. HENRIQUES and H. OKKELS (*Biochem. Z.*, 1929, 210, 198—225).—By the intravenous injection of various forms of iron into rabbits it is shown that iron exists in the cell in two forms often present together, the diffuse and the granular. When the histochemical (Turnbull) reaction is negative, this is due to the presence of iron in traces only, or in complex form, or as very slightly soluble compounds in colloidal solution. The examination of various organs shows that the question as to whether and how iron is taken up

by an organ depends largely on the physico-chemical structure of the iron compound used.

J. H. BIRKINSHAW.

Elimination of drugs introduced intravenously and subcutaneously. L. STRADA (Arch. Farm. sperim., 1929, 47, 36—55).—As regards elimination from the system, some drugs, such as sodium thio-sulphate, behave similarly whether administered intravenously or subcutaneously in similar doses. Others, such as sodium salicylate, are eliminated in slightly larger amounts in the former than in the latter case, whilst others again, like potassium iodide, show a similar but much more marked difference in this respect.

T. H. POPE.

Analogous action of sodium fluoborate and sodium perchlorate on skeletal muscle. G. BOEHM (Biochem. Z., 1929, 209, 489—491).—The analogous action of sodium fluoborate and sodium perchlorate on the frog's preparation in causing fibrillar contractions and rigidity is attributed to the similarity in constitution of the respective anions.

P. W. CLUTTERBUCK.

Effect of colloidal sulphur on blood-sugar. G. BUCCIARDI (Arch. Farm. sperim., 1928, 46, 90—96; Chem. Zentr., 1929, i, 1229).—Intraperitoneal administration of "sulfosol" (0.5% S) to guinea-pigs in doses less than 0.0005 g. per kg. does not affect the blood-sugar, in doses of 0.0007—0.01 g. per kg. causes a fall, and in doses of more than 0.013 g. per kg. causes a rise, in the blood-sugar.

A. A. ELDRIDGE.

Pathological formation of fat. I. Does fat arise from protein? G. ROSENFELD (Biochem. Z., 1929, 209, 312—318).—In phosphorus poisoning, migration, but not formation, of fat occurs.

P. W. CLUTTERBUCK.

Effect of acids and alkalis on the actual reaction of the tissue and blood. S. KAPLANSKI and N. TOLKATSHEVSKAYA (Z. ges. exp. Med., 1928, 63, 90—101; Chem. Zentr., 1929, i, 918).

Influence of electrolytes on the activity of specific diuretics and on the normal secretion of urine. D. BERGER (Biochem. Z., 1929, 209, 218—235).—Intraperitoneal injection of urea (2.0—1.0% solution) into rabbits greatly reduces the characteristic action of a specific diuretic, but the addition of an electrolyte to the injected solution immediately increases that action to an extent proportional to the concentration of the added electrolyte. The theories of Curtis (*ibid.*, 1925, 163, 109) are confirmed.

W. MCCARTNEY.

Hypnotics and diuresis. Water and salt excretion in sleep with and without pituitrin. M. A. KUGEL (Arch. exp. Path. Pharm., 1929, 142, 166—188).—The effect of various hypnotics and pituitrin on the urine excretion of rabbits was observed. Paraldehyde increases the excretion of water and salt, "sandoptal" (isobutylallylbarbituric acid), urethane, and veronal increase the water and lessen the salt diuresis. "Luminal" decreases the water diuresis; this effect is nullified by veronal. "Chloretone" may increase the water and lessens the salt diuresis. Chloral hydrate and chloralose inhibit the water excretion in light, and increase it in deep, hypnosis. Pituitrin subcutaneously injected inhibits

the water diuresis in urethane, veronal, chloral hydrate, chloralose, chloretone, and sandoptal hypnosis, but not in deep paraldehyde hypnosis, and produces a general increase in the salt excretion. J. H. BIRKINSHAW.

Influence of hypnotics and other drugs on thyroxine diuresis. E. Z. EPSTEIN (Arch. exp. Path. Pharm., 1929, 142, 214—235).—Subcutaneous injection of thyroxine after oral administration of water to rabbits produces an increased water excretion; the percentage salt excretion is only slightly increased. This diuresis is inhibited by subcutaneous injection of pituitrin, ergotamine, and hypertonic dextrose solution.

Paraldehyde, "sandoptal," and deep "chloretone" hypnosis increases the thyroxine water diuresis; luminal and light chloretone hypnosis inhibits it, veronal inhibits only when administered at the same time as the thyroxine. The thyroxine salt excretion is mostly lessened by luminal, veronal, sandoptal, and chloretone, and increased by paraldehyde. These substances probably act not only on the kidneys, but also on the central and sympathetic nervous system.

J. H. BIRKINSHAW.

Diuresis after oral and intravenous administration of liquid and changes produced by hypnotics. E. Z. EPSTEIN (Arch. exp. Path. Pharm., 1929, 142, 236—247).—Intravenous injection of physiological salt solution into rabbits produces only a small water excretion and a pronounced increase in salt elimination. This low water diuresis is increased by paraldehyde, "sandoptal," and "luminal" narcosis; veronal and urethane produce no change. The salt excretion is independent of the water excretion. The sudden hydræmia probably excites central regulatory processes which alter the normal fluid exchange between blood and tissue.

J. H. BIRKINSHAW.

Pharmacology of brominated valeric esters. E. RATH (Arch. exp. Path. Pharm., 1929, 142, 162—165).—Experiments on fishes and mice showed that the introduction of a bromine atom into the acid radical of *tert.*-amyl isovalerate increased its hypnotic action more than when the bromine was introduced into the alkyl radical.

J. H. BIRKINSHAW.

Detoxication of chloroform. P. HOLTZ (Arch. exp. Path. Pharm., 1929, 142, 139—156).—The harmful after-effects of chloroform narcosis on a strain of white mice were lessened when the chloroform contained 10—20% of hexane. In the case of a more sensitive strain the addition of hexane merely delayed death and was not more effective than alcohol or acetone. Keeping the mice at a higher temperature after narcosis did not increase the number of survivors, but the food prior to narcosis had considerable influence. Repeated narcosis had a cumulative effect. 7% of alcohol in the chloroform lessened the blood-pressure lowering of cats and rabbits caused by chloroform alone.

J. H. BIRKINSHAW.

Toxicity of various hydrocarbon vapours. N. W. LAZAREV (Arch. exp. Path. Pharm., 1929, 143, 223—233).—The toxicity of 35 saturated and unsaturated cyclic and straight-chain hydrocarbons to white mice is tabulated. The toxicity decreases in the order aromatic hydrocarbons, cycloparaffins,

olefines, paraffins. The decrease in toxicity runs parallel with the decrease in solubility.

P. W. CLUTTERBUCK.

[Lack of] injurious effects to health of the methyl alcohol formed in alcoholic fermentations. O. WINDHAUSEN (Naturwiss., 1929, 17, 631—634).—The capacity to withstand the effects of consumption of methyl alcohol varies widely amongst individuals, but the small amounts which occur in spirits, beverages, tobacco, and vegetables are decomposed in the body at once or excreted and are harmless.

W. McCARTNEY.

Comparison of lactones with santonin. I. Chemical constitution and pharmacological action. W. F. VON OETTINGEN (J. Pharm. Exp. Ther., 1929, 36, 335—354).—Butyro-, valero-, iso-hexo-, α - and β -angelica-lactones, valerolactone-carboxylic acid, and the dilactone of acetonediacetic acid have vermicial effects on earthworms, the last three having, in 0.04*M*-concentration, *in vitro*, the same efficiency as santonin. At higher dilutions these three are less effective than santonin. The introduction of a double linking or of a carboxyl group into valerolactone (α - and β -angelicalactones, valerolactone-carboxylic acid) considerably increases efficiency. Of the seven compounds β -angelicalactone and the dilactone are the most effective vermicials.

W. McCARTNEY.

Toxicity and vermicial properties of the dilactone of acetonediacetic acid and β -angelicalactone in cats. Dilactone and β -angelicalactone as anthelmintics. W. F. VON OETTINGEN and F. GARCIA (J. Pharm. Exp. Ther., 1929, 36, 355—362; cf. preceding abstract).—The minimum lethal dose of β -angelicalactone is 0.7—1.25 g. per kg. in the cat: that of the dilactone of acetonediacetic acid is much higher and 2.6 g. per kg. produces only slight transient depression. In treating *Ascaris* in cats seven out of ten experiments with the dilactone were completely successful, a single dose of 0.3 g. per kg. being sometimes sufficient.

W. McCARTNEY.

Salicylates. XVIII. [Pharmacological] actions of ammonium salicylate compared with [those of] sodium salicylate. C. C. JOHNSON and P. J. HANZLIK (J. Pharm. Exp. Ther., 1929, 36, 319—333).—The physiological properties of ammonium salicylate are very similar to those of sodium salicylate. The former salt shows no advantage over the latter.

W. McCARTNEY.

Changes in the serum-inorganic phosphorus, calcium, and potassium in rabbits on intracardiac or subcutaneous injection of peptone. X. CHAHOVITCH and M. VICHNJITCH (Compt. rend. Soc. Biol., 1928, 99, 1264—1267; Chem. Zentr., 1929, i, 551).—A temporary fall in the blood-phosphorus, calcium, and potassium occurs, normal values being reached in a few days whether the injections are continued or discontinued.

A. A. ELDRIDGE.

Combination of curare with some proteins and dyes and dependence of this process on p_{H} . V. M. KARASSIK, A. PETRUNKINA, and M. PETRUNKIN (Biochem. Z., 1929, 210, 70—75).—Gelatin and brain proteins at high p_{H} have the power of removing curare

from its solutions, which lose their colour and toxic property, these being transferred to the protein. At low p_{H} there is no such action. The power of Congo-red to detoxicate curare is ascribed to its sulphonic acid groups.

J. H. BIRKINSHAW.

Ouabain (*g*-strophanthin or accantherin) as a physiological standard for digitalis, strophanthus, and squill. E. W. SCHWARTZE, R. M. HANN, and G. L. KEENAN (J. Pharm. Exp. Ther., 1929, 36, 481—491).—Purification of ouabain for use as a physiological standard is facilitated by successive crystallisations from alcohol-ether and water. The substance has no definite m. p. Revised data concerning its crystalline forms, optical and crystallographic properties, degrees of hydration, and its specific rotation are given.

W. McCARTNEY.

Relationship between pharmacological action and chemical constitution and configuration in optical isomerides of ephedrine and related compounds. K. K. CHEN, C. K. WU, and E. HENRIKSEN (J. Pharm. Exp. Ther., 1929, 36, 363—400).—Twenty-seven derivatives of β -phenylethylamine having the general formula $CHPhH \cdot CHR \cdot NR' R''$ ($H = H$ or OH and $R, R', R'' = H$ or alkyl), including six optical isomerides of ephedrine, have been studied pharmacologically. The actions of the compounds related to ephedrine are similar to those of ephedrine itself. When H' is OH toxicity is reduced and mydriatic action is favoured. Most of the compounds studied inhibit the movements of the isolated rabbit's intestine, stimulate the isolated uterus of the virgin guinea-pig, and contract the congested nasal mucous membrane in man. With increase in the number of carbon atoms in $R, R',$ and R'' the cardiac depressant action increases, the pressor action becomes a depressor action, and the toxicity rises. When H' is OH , R'' is H , and R or R' becomes Me or Et , the sympathomimetic action is preserved, but weakened as compared with β -phenylethylamine, the ethyl being weaker than the methyl derivatives. Those compounds have mydriatic action. The primary amines are more active than the corresponding methylated secondary or tertiary amines, especially with reference to pressor action. When $R = Me$ or Et , the compound acquires a prolongation of action and loss of pressor response on repeated intravenous injections in animals. The methyl members are easily absorbed from the gastro-intestinal tract to produce systemic effects in men (ephedrine and nor-*d*- ψ -ephedrine). The ephedrines are qualitatively similar in their actions. The mydriatic action of *l*-ephedrine and *d*- ψ -ephedrine is greater than that of *d*-ephedrine and *l*- ψ -ephedrine, respectively. When indirectly compared for pressor action in pithed cats with adrenaline, *l*-ephedrine is found to be three times as strong as *d*-ephedrine and *d*- ψ -ephedrine seven times as strong as *l*- ψ -ephedrine. *l*-Ephedrine, the strongest isomeride, is thirty-five times as powerful as *l*- ψ -ephedrine, the weakest isomeride of the six. When orally administered to men in the same quantity, *d*-ephedrine and *l*- ψ -ephedrine do not raise the systolic blood pressure: the other isomerides do so. *d*-Ephedrine and *l*- ψ -ephedrine have the least toxicity of the two sets of isomerides.

W. McCARTNEY.

[Physiological effects of] quaternary pyridine bases. O. Y. MAGIDSON and G. P. MENSCHIKOV (Trans. Sci. Chem.-Pharm. Inst. Moscow, 1926, No. 16, 7—22).—Pyridine benzyl chloride, methiodide, and amyl iodide, in order of decreasing effect, induced paralysis in the frog. Less effective were the propyl, isomyl, ethyl, and allyl iodides. The compounds which show a strong paralytic effect have a low conductivity and a low dissociation constant.

CHEMICAL ABSTRACTS.

Effect of ergotamine on alimentary hyperglycæmia. E. COELHO and J. C. DE OLIVEIRA (Compt. rend. Soc. Biol., 1928, 99, 1527—1530; Chem. Zentr., 1929, i, 667).—In normal and diabetic individuals ergotamine reduces hyperglycæmia produced by dextrose or adrenaline. A. A. ELDRIDGE.

Inactivation of enzymes by tannins. A. OPARIN and A. KIRSANOV (Biochem. Z., 1929, 209, 181—194).—The inactivating effect of tannins on enzymes is due to the formation of protein precipitates on which the dissolved enzymes are adsorbed. Enzymes so inactivated can be completely regenerated by the addition of egg-albumin or of peptone. Determination of enzymes in the presence of tannins (*e.g.*, in leaves rich in tannins) can thus be carried out.

W. MCCARTNEY.

Oxidation-reduction potentials of mammalian tissues. E. A. H. FRIEDHEIM (Compt. rend., 1929, 189, 266—268).—The oxidation-reduction potentials of various macerated organs of different mammals (guinea-pig, rabbit, pig, ox, and mouse) have been determined with the rigid exclusion of oxygen with a mercury, platinum, gold, or gold-plated platinum electrode, the same values being obtained with each. All the values of E_h are negative and form series in which the value for the liver is the lowest and that for the spleen the highest. Contrary to the conclusion of Drew (Brit. J. Exp. Path., 1920, 1, 115), no diminution in reducing power is observed with cancerous tissue. All the values of r_H are less than 9.9, and thus, in agreement with other authors, all organs, in the absence of oxygen, reduce Clark's indicators. The values of r_H diminish exponentially with dilution of the suspension of the tissue, thus explaining the positive values obtained by some authors in dilute suspension.

J. W. BAKER.

Oxidation-reduction systems of biological importance. IV. Cysteine complexes with metals of the iron group. L. MICHAELIS and E. S. G. BARRON.—See this vol., 1011.

Catalase. A. MADINAVEITIA (Unters. Enzyme, 1928, 1, 381—399; Chem. Zentr., 1929, i, 1115).—On crystallisation of oxyhæmoglobin most of the catalase remains in the mother-liquor, although the yield is only 7%. Hæmolysed corpuscle mash affords 40% of the "hæmase" originally present. Attempts to purify the enzyme by precipitation or adsorption were unsuccessful. Battelli's method for the preparation of liver-catalase is preferred.

A. A. ELDRIDGE.

Peroxidase. VII. Soluble and insoluble peroxidase. R. WILLSTÄTTER and A. POLLINGER. VIII. Formation of peroxidase. R. WILLSTÄTTER, A. POLLINGER, and H. WEBER. IX.

Peroxidase from grain. R. WILLSTÄTTER and A. POLLINGER (Unters. Enzyme, 1928, 1, 512—515, 516—520, 521—525; Chem. Zentr., 1929, i, 1224—1225; cf. A., 1926, 1275).—Peroxidase occurs in the plant partly dissolved in the cell sap, and partly adsorbed. For complete dissolution of the peroxidase the plant-substance must be thoroughly ground with sand and kept for a long time in water. Preliminary treatment with sodium hydrogen carbonate or barium hydroxide solution is favourable. The fractions of peroxidase which are dissolved readily or with difficulty, when examined by adsorption on alumina, behave similarly. The increase in extractable enzyme occasioned by the use of sodium hydrogen carbonate is also observed with dialysed plant material. The increase observed when running water is used is attributed to the calcium hydrogen carbonate which it contains. The increase depends on the time and on the concentration of the reagent. A still greater increase is observed if the root is ground in a mill and well pressed. The turbid hydrogen carbonate extract or press-juice shows after several days an increase in peroxidase activity, owing to gradual dissolution of the enzyme from the colloidal carrier. Cereal grains, although exhibiting considerable individual variations, contain as much peroxidase as dehydrated horse-radish (800 units per kg.). The quantity varies irregularly when the grain is kept. The enzyme content increases during germination, reaching a maximum in about 4 days. The peroxidase extracted from cereal grains is less pure than that obtained from horse-radish. Purification can be effected by adsorption on kaolin from a solution in very dilute acetic acid, and elution with very dilute ammonia solution.

A. A. ELDRIDGE.

Effect of antiseptics on the action of salivary diastase. E. PRECHTL (Biol. gen., 1928, 4, 181—190; Chem. Zentr., 1929, i, 912).—The lower limits of interference with the action of salivary diastase are: toluene 0.2%, chloroform 2.0%, chloral hydrate 1.5%, sodium fluoride 1.0%. Thymol is without effect.

A. A. ELDRIDGE.

Qualitative test for invertase. Z. I. KERTÉSZ (Biochem. Z., 1929, 209, 492—494).—A small amount of invertase may be detected by allowing it to act on a solution of sucrose and testing for the presence of lævulose in the liquid by covering a small piece of sodium or potassium hydroxide with a few drops of the solution. If lævulose is present a brownish-red colour is produced.

P. W. CLUTTERBUCK.

Mechanism of the action of muscle-phosphatase, -cozymase, and insulin. J. BODNAR and B. TANKÓ (Biochem. Z., 1929, 210, 143—174).—A mixture of disodium hydrogen phosphate, sodium fluoride, glycogen, and muscle powder (from pigeon breast muscle) was used to study the esterification of phosphoric acid. The amount of phosphoric acid esterified increases considerably with the concentration of phosphate; boiled muscle juice scarcely increases the esterification, since the muscle powder already contains sufficient cozymase. When this is washed out with water at the ordinary temperature the esterification is greatly reduced. The washed powder is reactivated by boiled muscle juice or boiled yeast

juice. The enzyme is harmed less by washing the powder at 0°. The muscle powder, unlike fresh muscle, loses only 20% of its activity in 5 weeks. Insulin produces no effect on the activity of fresh muscle or muscle powder (whether washed or not). An apparent increase in the esterification in some cases is due to the inorganic phosphate present in insulin.

J. H. BIRKINSHAW.

Effect of skeletal muscle on blood-sugar *in vitro*. M. SARYUN and C. L. ALSBERG (J. Biol. Chem., 1929, 83, 129—136).—The extent of disappearance of dextrose from blood on incubation was not affected by normal muscle alone, but was increased by normal muscle in presence of insulin; the glycogen-free muscle obtained from animals treated with adrenaline caused increased glycolysis in blood in the absence of insulin, and also caused the disappearance of dextrose from a solution of the latter in dilute sodium chloride.

C. R. HARRINGTON.

Enzymic transformation of uric acid into allantoinic acid. R. FOSSE, A. BRUNEL, and R. DE GRÆVE (Compt. rend., 1929, 189, 213—215).—The pea, soya bean, and numerous other leguminous seeds contain enzymes capable of transforming uric acid into allantoinic acid. The action is accelerated in presence of ammonium carbonate. The existence of two enzymes is postulated, an oxidase which yields allantoin, and a second enzyme which transforms allantoin into allantoinic acid (cf. this vol., 847).

R. K. CALLOW.

Purification of pepsin. J. PLÉ (Rev. gén. Colloid., 1929, 7, 193—201).—The precipitating action of acetone and of alcohol on pepsin has been studied as a function of hydrogen-ion concentration, time, and temperature. The weight of precipitate obtained is always less than the amount taken initially. In strongly acid solution acetone causes an irreversible coagulation; at p_H 1.03, the precipitate is quite inactive. In agreement with the observations of Fenger and Andrew (A., 1927, 793), the most active pepsin is that precipitated at p_H 2.5, using 75% acetone. Alcohol is a less effective precipitating agent, the yield of precipitate being only about one half of that given by acetone. Applying these methods to the purification of pepsin, the following procedure is recommended: 1 g. of the pepsin is dissolved in 6 c.c. of water at 18° with the addition of 1 c.c. of *N*-hydrochloric acid, and water is added to 10 c.c.; 30 c.c. of pure, anhydrous acetone are added, the mixture is centrifuged, the supernatant liquid decanted off, and the purified pepsin dried in a vacuum. The yield is about 55% by weight, but the activity is increased by about 75%.

E. S. HEDGES.

Enzymic proteolysis. V. Structure of animal tissue substances. E. WALDSCHMIDT-LEITZ and G. VON SCHUCKMANN (Ber., 1929, 62, [B], 1891—1896).—The products of the degradation of keratin by hydrogen peroxide or bromine and glacial acetic acid are hydrolysed by trypsin, but not by erepsin, and therefore do not contain dipeptides but only polypeptides which cannot arise by fission of diketopiperazines. Similar treatment of silk fibroin yields only small amounts of soluble products which do not

suffer enzymic fission. Silk peptone, obtained by incomplete hydrolysis of silk fibroin by acids, suffers extensive hydrolysis by trypsin, yielding products which suffer fission with erepsin. Polypeptides with long chains therefore appear to be present in silk peptone.

H. WREN.

Optimum p_H for trypsin and the reaction of the intestinal contents. H. J. VONK and H. P. WOLVEKAMP (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 440—443).—The influence of bile on the digestion of fibrin by trypsin at p_H 6 has been studied. At volume concentrations from 0.25 to 0.025 the activity is doubled, but at lower concentrations the digestion is retarded. The bile thus appears to compensate for the low p_H value and this action may be considered as specific for the p_H of the intestinal contents. A similar influence is produced by multivalent anions, e.g., the ferrocyanide ion.

H. F. GILLBE.

Action of adrenal tissue on lecithin. A. DA CRUZ (Compt. rend. Soc. Biol., 1928, 99, 1530—1532; Chem. Zentr., 1929, i, 666).—Choline is produced in lecithin solutions by addition of adrenal tissue or minced liver. The decomposition is attributed to lecithinase; it is increased by addition of cholesterol.

A. A. ELDRIDGE.

Pyocyanase. S. HOSoya (Compt. rend. Soc. Biol., 1928, 99, 771—773; Chem. Zentr., 1929, i, 1010).—The preparation of pyocyanase, which may be identical with pyocyanolysin, is described.

A. A. ELDRIDGE.

Conditions of activation of washed zymin in relation to co-enzyme. A. A. STHEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 426—434).—Zymin inactivated by washing for a short period is reactivated by addition of acetaldehyde, methylene-blue, hexosediphosphate, or of a co-enzyme, but after washing for a longer period addition of the first two substances no longer has any effect. After more intensive washing neither of these nor hexosediphosphate produces reactivation, which can, however, be produced by addition of hexosediphosphate together with either a protein sol (prepared from zymin) free from co-enzyme or with the original washings, even after boiling. If the zymin be washed for a still longer period addition of the boiled wash-liquor is essential for the production of reactivation. Excessive washing causes irreversible inactivation of the enzyme.

H. F. GILLBE.

Soluble enzymes secreted by fungi. Phenolic constituents of essential oils and the anti-oxygenic function. L. LUTZ (Compt. rend., 1929, 189, 62—63).—Small quantities of various phenols and phenol ethers found in essential oils were added to cultures of *Stereum purpureum*, *S. hirsutum*, and *Coriolus versicolor* with methylene-blue as a reducible indicator. It was found that those phenolic constituents of essential oils which contain one or more free hydroxyl groups behave as antioxidants in regard to the oxido-reducing action provoked by the soluble enzymes secreted by *Hymenomyces*.

B. W. ANDERSON.

Soluble enzymes secreted by fungi. Comparison of the anti-oxygenic power of tannin and

of the phenolic constituents of essential oils. L. LUTZ (Compt. rend., 1929, 189, 134—135).—The development of colour which occurs when certain fungi (*Stereum hirsutum*, *S. purpureum*, and *Coriolus versicolor*) are grown in a medium containing a phenolic substance such as *m*-cresol, *p*-cresol, thymol, carvacrol, guaiacol, eugenol, anethole, creosole, or methyl salicylate is inhibited by the presence of tannin, which itself undergoes oxidation very readily. The antioxygenic property of tannin is probably of biological significance. W. O. KERMAK.

Enzyme action of *Alternaria Solani*. G. VON SZELÉNYI and G. VON BECZE (Zentr. Bakt. Par., 1929, II, 76, 121—124; Chem. Zentr., 1929, i, 760).—Invertase, lactase, and maltase are present; sucrose, lactose, and maltose are quickly attacked, raffinose and starch more slowly. Acid was not formed.

A. A. ELDRIDGE.

Penetration of luminous bacteria by ammonium salts of the lower fatty acids. I. Effects of strong acids and alkalis. S. E. HILL (J. Gen. Physiol., 1929, 12, 863—872).—*B. Fischeri* was grown on a calcium carbonate-buffered medium in Petri dishes and suspended in 0.5*M*-sodium chloride. Sucrose is nearly as efficient as sodium chloride for preserving the luminescence of the bacteria, thus showing that disappearance of light is merely an osmotic pressure phenomenon, due to rupture of the cells. Alcohol and glycerol penetrate the bacteria, although the effect is inhibited by presence of sufficient sodium chloride. Urea does not penetrate so readily. Decrease of oxygen pressure to less than 0.0053 mm. will cause disappearance of light and in these experiments the presence of sufficient oxygen has been assured. None of the ammonium salts used was more acid than p_H 5.0, and injury due to presence of hydrogen ions may be excluded, as may also any effect due to hydroxyl ions. Penetration by strong acids and alkalis takes place suddenly and does not occur until the cell membrane is destroyed, in sharp contrast to the effect of ammonium salts and weak acids. P. G. MARSHALL.

Fluorescent bacteria from water, soil, and plants. C. HÜTTIG (Ber. deut. bot. Ges., 1929, 47, 395—400).—The fluorescent bacteria isolated from the milk of cows fed on turnips feed have no denitrifying properties, whilst the strains isolated from pond-water are strongly denitrifying. The strains isolated from milk contain diastase, hydrolyse fats and proteins, have a low optimum temperature, and exhibit generally the characteristics of *B. fluorescens*, whilst those from pond-water do not. E. A. LUNT.

Bacterial oxidation of crude oils. V. O. TAUSSON (Neft. Choz., 1928, 14, 220—230; cf. A., 1928, 447).—*Bacillus fluorescens liquefaciens*, *B. pyocyaneus*, and *B. Stutzeri* and others utilise paraffins as well as kerosene. *Penicillium* develops on paraffins, *m. p.* 45—56°, utilising 80% of the hydrocarbon; *Aspergillus flavus* and bacteria from Baku can utilise both hard and soft paraffins and white vaseline. The paraffins are oxidised to carbon dioxide and water, there being no evidence of the production of fatty acids. Olefines, and probably terpenes, are also oxidised. The conditions of oxidation are: presence

of an aqueous solution of mineral salts (including nitrate, or ammonium salts and calcium carbonate), neutrality, and free access of oxygen. The oxidation of benzene, toluene, and xylene by *B. benzoli*, of naphthalene by *B. naphthalinicus liquefaciens*, *B. naphthalinicus*, and *B. naphthalinicus non-liquefaciens*, and of phenanthrene by *B. phenanthrenicus* is described. The facts that the soil in the oil-bearing regions is rich in a great variety of micro-organisms utilising hydrocarbons and displaying considerable specificity, and that the conditions are nearly optimal, indicate that they play an important part in effecting alterations of the crude oil *in situ*.

CHEMICAL ABSTRACTS.

Biochemical preparation of fats. V. KULIKOV (Oil Fat Ind. Russia, 1928, No. 4, 21—23).—In molasses-broth a non-virulent strain of *B. tuberculosus* produced 22—36% of fatty substances containing glyceryl palmitate and stearate (*m. p.* 66°) and waxes (*m. p.* 70°).

CHEMICAL ABSTRACTS.

Lipins of tubercle bacilli. III. Phthioic acid. R. J. ANDERSON (J. Biol. Chem., 1929, 83, 169—175).—The phosphatide obtained from tubercle bacilli (A., 1927, 1114) was hydrolysed with dilute sulphuric acid; the fatty acids were converted into lead soaps and the latter extracted with ether; the acids regenerated from the ether-soluble portion were hydrogenated, and again subjected to the lead soap fractionation. The ether-soluble portion, on decomposition, gave crude *phthioic acid*, a saturated acid having mol. wt. 313, $[\alpha]_D^{20} +1.6^\circ$.

C. R. HARRINGTON.

Metabolism of *Bacillus coli* and *paratyphosus*. B. H. BRAUN and R. GOLDSCHMIDT (Zentr. Bakt. Par., 1928, I, 109, 353—361; Chem. Zentr., 1929, i, 763).—The ease of aerobic or anaerobic growth in various media was studied. Sodium aspartate or glutamate or tryptophan with dextrose favours anaerobic growth. A. A. ELDRIDGE.

Proteolysis by *Streptococcus lactis*. L. T. ANDEREGG and B. W. HAMMER (J. Dairy Sci., 1929, 12, 114—128).—Certain cultures (particularly butter cultures) of *Streptococcus lactis* showed proteolytic activity in milk, especially in presence of calcium carbonate. Addition of peptone retarded the decomposition of protein. *S. citrovorus* and *S. paracitrovorus* did not exhibit proteolytic activity in milk.

CHEMICAL ABSTRACTS.

Action of streptococci on caseinogen. G. J. HUCKER (Zentr. Bakt. Par., 1929, II, 76, 321—328; Chem. Zentr., 1929, i, 763—764).—Pure caseinogen is not attacked by streptococci unless a large quantity of unwashed cells are added. Caseinogen can also serve as a source of nitrogen. A. A. ELDRIDGE.

Influence of some metals on acetic acid fermentation. M. ROSENBLATT and M. MORDKOVITSCH (Biochem. Z., 1929, 209, 83—89, and Ukraine Chem. J., 1929, 4 [Tech.], 1—10).—Up to a certain concentration nickel, cobalt, iron, and manganese (as sulphates) stimulate the fermentation of alcohol to acetic acid by *B. Pasteurianum* and by *B. vini aceti*. The optimum concentration of metal in each case is about 0.000033%. At higher concentrations the metals have a paralyzing effect the strength of which

varies very widely from metal to metal in the descending order nickel, cobalt, iron, manganese.

W. McCARTNEY.

Conversion of hexosediphosphate into lactate under the influence of *B. Delbrücki*. A. TYCHOVSKI and M. KOBEL (Biochem. Z., 1929, 209, 134—141).—From aqueous solutions of magnesium hexosediphosphate (but not from those of the sodium salt) by the action of large amounts of fresh cultures of *B. Delbrücki* or of the material prepared from them by dehydration with alcohol and ether *dl*-lactic acid is very rapidly produced in yields of 50—100%.

W. McCARTNEY.

Symbiosis among lactic acid organisms. H. LANDAU (Naturwetensch. Tijds., 1929, 11, 115—117).—*Oidium lactis* has practically no influence on lactic acid bacteria, since milk develops acidity in presence of the latter at the same rate, whether the former is present or not.

S. I. LEVY.

Action of minute doses of sea-water on fermentation. C. RICHTER and M. FAGUET (Compt. rend., 1929, 189, 219—221).—The effect of varying doses of sea-water (Mediterranean) and of artificial sea-water (NaCl 28.90, MgSO₄ 2.80, MgCl₂ 2.35, CaSO₄ 0.90, KCl 0.80 g. per litre) on the fermentation of lactose by a lactic acid organism for 24 hrs. at 40° has been determined by measurements of the acidity produced. With decreasing doses of sea-water a decrease in the activity of the ferment occurs with 50% of sea-water (acidity 89; control experiment 100), then with 10⁻⁴% a slight increase (118) occurs; a second decrease occurs with doses of 10⁻⁶%, and finally a second slight increase (105) with minute doses of 10⁻¹⁰%. The same results are obtained with artificial sea-water and agree with earlier results obtained with various metallic salts.

J. W. BAKER.

Assimilation of nitrogen by pure cultures of *Clostridium Pasteurianum* and related organisms. E. MCCOY, W. M. HIGBY, and E. B. FRED (Zentr. Bakt. Par., 1928, II, 76, 314—320; Chem. Zentr., 1929, i, 762).—In Vinogradsky's nutrient solution for 15—20 days at 28°, the nitrogen assimilated per 100 c.c. was (max.): *C. acetobutylicum*, Weizmann, 1.06 mg., *C. Pasteurianum* 3.98 mg., *B. saccharobutylicus* 2.35 mg., *Plectridia* 2.75 mg. The ratio of sugar used to nitrogen fixed changes as growth proceeds.

A. A. ELDRIDGE.

Use of carbamide solutions as culture media. A. J. J. VANDE VELDE (Naturwetensch. Tijds., 1929, 11, 118—122).—The decomposition of carbamide in solutions sterilised by heating has been examined; the formation of ammonium salts is reflected in the p_H value and results of titrations using various indicators. In media containing dipotassium hydrogen phosphate the effect of heating on the carbamide is not apparent.

S. I. LEVY.

Bacterial toxins. Tetanus toxin. S. HOSOYA and S. MIYATA (Compt. rend. Soc. Biol., 1928, 99, 773—776; Chem. Zentr., 1929, i, 1013).—The procedure described affords a product of antigenic character which no longer gives the biuret reaction. Tetanus toxin is not a protein. Nessler's reagent produces an orange-red precipitate.

A. A. ELDRIDGE.

Purification of *Bacillus botulinus* toxin. S. HOSOYA, G. J. STÉFANOPOULO, and S. MIYATA (Compt. rend. Soc. Biol., 1928, 99, 1465—1467; Chem. Zentr., 1929, i, 763).—The toxin, after precipitation with zinc chloride and liberation with ammonium sulphide, no longer gives a protein reaction, and is not precipitated by picric or picrolonic acid.

A. A. ELDRIDGE.

So-called specific dynamic action of foods. G. MANSFELD and Z. HORN (Biochem. Z., 1929, 209, 34—54).—The oxygen consumption of the bacillus of mouse-typhoid varies directly in proportion to the concentration of the food which the organism receives and there is no increase in the consumption when substances which it cannot consume are provided. The phenomena characteristic, in higher organisms, of the specific dynamic action of foods are observed in the case of the bacillus, the only difference between the higher and unicellular organisms being quantitative.

W. McCARTNEY.

Oligodynamic action of silver. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1928, 16, 158—169; cf. A., 1927, 992).—The bactericidal action of water which has been in contact with finely-divided silver under certain conditions is due to the presence of silver ions in a concentration of the order of 0.00005 g./litre. The silver may be removed and collected by passing the solution slowly over electrodes of special construction, and the bactericidal action is found to decrease proportionally as the silver is removed.

R. K. CALLOW.

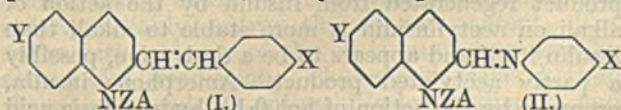
Disinfecting action of metallic salts. J. VIGNATI and P. SCHNABEL (Zentr. Bakt. Par., 1928, I, 109, 464—475, 475—481; Chem. Zentr., 1929, i, 763).—The disinfecting action of copper salts is not an adsorption phenomenon, but a coagulation process depending on interaction between protein or lipin molecules and copper ions. Bacterial action is revived by the action of sodium thiosulphate, which also neutralises the disinfecting action of silver, lead, or zinc salts and alcohol.

A. A. ELDRIDGE.

Disinfectant action of weak acids. H. FUST (Arch. exp. Path. Pharm., 1929, 142, 248—260).—A well-buffered lactic acid-lactate mixture of p_H 3.7 or 3.3 at physiological or lower concentrations has a definitely toxic action on *B. coli* and on the bacteria of the rat's tail; the p_H 3.3 mixture is superior to 65% alcohol if the tail is first washed with soap and water. The action appears to be due both to the hydrogen ions and to the undissociated lactic acid molecules. Lactic acid-lactate buffers are suggested as useful skin disinfectants.

J. H. BIRKINSHAW.

Trypanocidal action of some derivatives of anil- and styryl-quinoline. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1929, B, 105, 99—111; cf. A., 1926, 1153; 1928, 1141).—The action of a large number of quinoline derivatives, mostly of the general formula



where Z is an alkyl group, A an anion, and X and Y are other substituent groups, has been tested in

respect of their curative action on rats infected with *T. brucei*. The anil compounds of formula II are in general without activity, but certain of the styryl derivatives are active, especially where X and Y represent an acylamino- and an amino- or alkylamino-group. The compounds with X=NMe₂ and Y=NHAc and X=NHAc and Y=NH₂ (Z=Me) were active when administered to infected rabbits. The active compounds were not particularly trypanocidal *in vitro*. The following compounds have been prepared: 7-dimethylamino-2-methylquinoline methiodide by the method previously described for the 6-isomeride; propionamidobenzaldehyde, m. p. 170—181°, by the action of propionic anhydride on *p*-aminobenzaldehyde; and 6-dimethylamino-2-styrylquinoline methochloride from the corresponding methiodide prepared by the interaction of benzaldehyde and 6-dimethylamino-2-methylquinoline methiodide.

W. O. KERMAK.

The Gram stain. A. ZEISSIG (Stain Tech., 1929, 4, 91—92).—A modification of the Gram stain in which an alcoholic solution of iodine is substituted for 95% alcohol as decolorising agent is advantageous in staining Gram-positive organisms in tissues and smears.

H. W. DUDLEY.

Differentiation of bacteria by means of a mixture of acid and basic dyes at different p_H values. A. V. TOLSTOUHOV (Stain Tech., 1929, 4, 81—89).—A mixture of methylene-blue and eosin-Y satisfactorily stains bacteria differentially from p_H 3 upwards. From p_H 3 to 0.8 a mixture of methylene-blue and acid-fuchsin is used. This mixture is used to study the chemical composition of different parts of the bacterial cell. Polar bodies in the typhoid group of organisms and in *B. diphtheriae* are stained differentially by it.

H. W. DUDLEY.

Mechanism of staining: physical theories. W. C. HOLMES (Stain Tech., 1929, 4, 75—80).—Adsorption is held to be the principal factor in biological staining.

H. W. DUDLEY.

Stain solubilities. IV. W. C. HOLMES (Stain Tech., 1929, 4, 73—74).—The solubilities, in water and 95% alcohol, of 28 dyes are tabulated.

H. W. DUDLEY.

Active substances of the heart. Heart hormone. D. IONESCO and A. T. BERNARD (Arch. Int. Physiol., 1928, 30, 267—279; Chem. Zentr., 1929, i, 1014).—Alcoholic extracts from various parts of the heart and skeletal muscle of the ox have a regulative effect on the frog's heart.

A. A. ELDRIDGE.

Insulin. K. FREUDENBERG, W. DIRSCHERL, and H. EYER (Naturwiss., 1929, 17, 603—604).—The slow inactivation of insulin by means of formaldehyde is partly reversible under the action of very dilute hydrochloric acid, and the inactivation is not due to the action of formaldehyde on amino-groups. The product regenerated from insulin by the action of alkali on acetylinsulin is more stable to alkali than insulin itself and appears to be a derivative, possibly a partly acetylated product. Amorphous insulin, prepared by the action of hot 0.1*N*-hydrochloric acid containing 1% of sodium chloride on technical insulin, and exhibiting 80% of the activity of crystalline

insulin, is also labile. The sulphur content of insulin increases with increasing purity, but the relationships disclosed between activity and the alkali-stable and alkali-labile sulphur indicate that whilst the protein which contains the effective group may be rich in stable and labile sulphur, the sulphur does not appear to form part of the active group. A relationship exists between optical and physiological activities. The absorption spectrum of crystalline insulin shows a strong band near 2700 Å. By the Debye-Scherrer method the crystals do not behave differently from amorphous insulin, the crystals thus resembling protein crystals. There is no certainty that the molecules comprising the crystal are all identical. With increasing purification the sulphur and the methyl content of insulin increases by equivalent amounts.

R. A. MORTON.

Orally effective compounds of insulin with bile acids. B. STUBER and K. LANG (Naturwiss., 1929, 17, 546).—In a weakly alkaline medium condensation products are formed between insulin and cholic or deoxycholic acids. Chollynsulin and deoxychollynsulin are physiologically active when administered orally or subcutaneously. Whilst the two methods of administration are equally effective, the dose must be large (200—300 units per dose) measured in terms of the initial material.

R. A. MORTON.

Effect of insulin on regeneration. Biological rôle of potassium and calcium. B. SCHAZILLO and M. KSENDZOWSKY (Pflüger's Arch., 1928, 220, 774—781; Chem. Zentr., 1929, i, 665).—Insulin stimulates the regeneration of bone. Calcium ions favour, and potassium ions retard, the formation of callus.

A. A. ELDRIDGE.

Inhibiting action of insulin on dextrose hyperglycaemia. G. SOLARINO (Boll. Soc. Ital. Biol. sper., 1928, 3, 108—111; Chem. Zentr., 1928, ii, 2481—2482).—The hyperglycaemia caused by insulin in variable degree is related to the hydrochloric acid content of the gastric juice and the more or less rapid degradation of the insulin. The effect of insulin in inhibiting hyperglycaemia is comparable with that of lævulose.

A. A. ELDRIDGE.

Antagonistic action of posterior lobe hormone and insulin. K. VELHAGEN, jun. (Arch. exp. Path. Pharm., 1929, 142, 127—138).—The substance of the posterior lobe of the pituitary which increases the blood-sugar and opposes the action of insulin is present both in *pars neuralis* and *pars intermedia*. Large amounts of the extract must be injected into rabbits to prevent insulin hypoglycaemia. Repeated injection does not inhibit the action of the insulin circulating in the body. The secondary hypoglycaemia which is frequently produced by administration of the posterior lobe is probably the result of increased insulin secretion; it does not occur in pancreas-diabetic animals. Insulin does not inhibit the action of the posterior lobe in increasing blood-pressure and stimulating the uterus.

J. H. BIRKINSHAW.

Relations of the pituitary gland to carbohydrate metabolism. A. PICKAT (Med.-biol. Zhur., 1927, 3, 40—62).—Extirpation of the pituitary is followed by long-continued hypoglycaemia. Sub-

cutaneous injection of an extract of the posterior lobe of the pituitary, or puncture of the tuber cinereum, increases the blood-sugar in both normal and hypophysectomised dogs. CHEMICAL ABSTRACTS.

Testing of commercial ovarian preparations. M. KOCHMANN (Arch. exp. Path. Pharm., 1929, 143, 57—64; cf. this vol., 102).—A number of commercial preparations of ovarian hormone have been assayed by administering them to immature mice and observing the effect on the vaginal smear. Less precise determinations have also been made by observing their effects on the metabolism of castrated rats. W. O. KERMAK.

Internal secretion of the placenta. J. PAZOUREK (Rozh. chir. gynaekol., 1928, 7, 115—121).—All the ovarian glands contain a common hormone; the action of the human hormone is identical with that of animals. The hormone is resistant to both low and high (193°) temperatures, and is unchanged by the digestive process. CHEMICAL ABSTRACTS.

Secretin. V. Preparation. L. TAKÁCS (Z. ges. exp. Med., 1928, 63, 553—556; Chem. Zentr., 1929, i, 1016).—A 10% aqueous solution of the substance obtained by the picrate method is filtered through a collodion ultra-filter at 1 atm. pressure, affording a colourless filtrate which gives no reaction with sulphosalicylic acid. The substance contains 9—10% N, but no phosphorus. A. A. ELDRIDGE.

Effect of secretin in the regulation of the alkali reserve of the blood. I. Experimental alkalosis. A. O. WOJNAR (Zhur. Exp. Biol. Med., 1928, 10, 414—442).—There is direct dependence between variations in alkalinity of, and the amount of secretin in, the pancreatic juice and the alkalinity of the blood. CHEMICAL ABSTRACTS.

Cod-liver oil and the antimony trichloride reaction for vitamin-A. P. B. HAWK (Science, 1929, 69, 200).—The antimony chloride reaction is not a trustworthy means of determining the vitamin-A content of a cod-liver oil. Samples of this oil exposed to the atmosphere gave a deeper blue coloration with the reagent than those kept in the dark to preserve the vitamin present. L. S. THEOBALD.

Effect of vitamin-A on hypercholesterolaemia. H. KIMURA (Acta Schol. Med. Univ. Imp. Kyoto, 1928, 11, 319—324).—The reduction of experimental hypercholesterolaemia in rabbits is not accelerated, but rather retarded, by addition of vitamin-A to the diet. Also feeding cod-liver oil did not influence the hypercholesterolaemia. CHEMICAL ABSTRACTS.

Water-soluble vitamins of group B. L. RANDOIN and R. LECOQ (Bull. Soc. Chim. biol., 1929, 11, 745—775).—A review. J. H. BIRKINSHAW.

Changes in blood constituents during avitaminosis. T. MUTO (Fukuoka Ikw.-Zasshi, 1927, 20, 1269—1279).—The blood-sugar, haemoglobin, fatty acids, cholesterol, and residual nitrogen are increased; the blood-phosphate is diminished. Acetone substances and lactic acid tend to increase. In rice-fed chickens the blood-acetaldehyde is increased. CHEMICAL ABSTRACTS.

Vitamin-C content of pasteurised milk. M. MIURA (Bull. Inst. Phys. Chem. Tokyo, 1929, 8, 502—505).—Autoclaved milk still retains a small quantity of vitamin-C, pasteurised milk retains a larger quantity, and raw milk contains still more of this vitamin. B. W. ANDERSON.

Sources of vitamin-C in India. R. C. WATTS (Indian Med. Gaz., 1929, 64, 79—85).—Experiments on feeding guinea-pigs with vegetable marrow, melon, pumpkin, and *Citrus medica* var. *acida* are described. CHEMICAL ABSTRACTS.

Vitamin-C. IV. Carbohydrate and nitrogen metabolism of experimental scurvy in guinea-pigs fed on an exclusive oat diet. K. TOMITA (Sei-I-Kwai Med. J., 1928, 47, No. 9, 6—7).—The blood-sugar and the urinary nitrogen increased. The glycogen content of the liver decreased just before death. Excretion of calcium, uric acid, and creatinine decreased, whilst that of creatine increased, with the development of scurvy. CHEMICAL ABSTRACTS.

Experimental scurvy. II. Carbohydrate metabolism of the animal fed on a vitamin-C diet. T. NAGAYAMA, H. MACHIDA, and Y. TAKEDA. **III. Nitrogen metabolism.** T. NAGAYAMA and N. SATO (J. Biochem. Japan, 1928, 10, 17—26, 27—44).—The carbohydrate metabolism is not appreciably disturbed during scurvy. Urinary creatine and ammonia increase, and the creatinine coefficient rises; uric acid excretion is unchanged. The creatine content of the muscle is normal. CHEMICAL ABSTRACTS.

Antiscorbutic potency of infusions of Japanese green tea. M. MIURA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 506—509).—When two successive infusions of green tea are made with water at 60—65°, decanting after several minutes at the ordinary temperature, two thirds of the vitamin-C contained in the tea is present in the first infusion and practically all the remainder in the second. Heating the tea with water at 70—75° for 5 min. destroys about 74% of its antiscorbutic activity. B. W. ANDERSON.

Evaluation of vitamin-D preparations. I. A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1929, 209, 290—303).—A method for evaluation of vitamin-D preparations depends on the determination of that amount of active substance (=1 antirachitic unit) which is just sufficient to protect young rats from rickets. Of the commercial preparations, 1 c.c. of "vigantol" contains 25,000, of "radiostol" 2000, and of "preformin," 800—1000 units. P. W. CLUTTERBUCK.

Experimental rickets. II. Influence of ultra-violet irradiation on the antirachitic value of soya-bean oil. S. IZUME, Y. YOSHIMARU, and I. KOMATSUBARA (J. Biochem. Japan, 1928, 10, 177—182).—Oil extracted by pressure has the highest, and by alcohol the lowest, antirachitic value; petroleum affords an oil of intermediate value. Refining does not appreciably destroy the vitamin content. The antirachitic potency of the oil is much increased by ultra-violet irradiation. Phytosterol isolated from the oil was rendered antirachitic by irradiation, and exhibited the ergosterol absorption band in the ultra-violet. CHEMICAL ABSTRACTS.

Effect of growth-promoting substances of the character of vitamin-D on the yeast cell. H. LACROIX (Zentr. Bakt. Par., 1929, II, 76, 417—428; Chem. Zentr., 1929, i, 1118).—Large, but not small, inoculations grew in mineral nutrient free from amino-acid. The dead cells evidently liberate growth-promoting substances on autolysis; these substances can be withdrawn by adsorption on charcoal or fuller's earth. A. A. ELDRIDGE.

Action of "vigantol." H. BEHRENDT and J. BERBERICH (Münch. med. Woch., 1928, 75, 2134—2135; Chem. Zentr., 1929, i, 1019).—Administration to man of the usual doses of "vigantol" did not lead to a change in the blood-cholesterol value. In rabbits the value was increased. A. A. ELDRIDGE.

Epiphyses and liver extracts from rats after feeding with carotinoids. B. VON EULER, H. VON EULER, and P. KARRER (Biochem. Z., 1929, 209, 240—245).—Histological examination of the epiphyses of rats obtaining both carotinoid material and sufficient amounts of vitamin-D shows that, under this condition, bone formation is nevertheless deficient, although growth continues. In rats which receive more than the minimum necessary amount of carotin this accumulates in the liver. The results of previous experiments (cf. this vol., 358) are confirmed by the histological examination. W. MCCARTNEY.

Relation between water content and amount of photosynthesis. J. G. WOOD (Austral. J. Exp. Biol., 1929, 6, 127—131).—When a leaf (cherry laurel) is injected with water the rate of assimilation is low and remains low until nearly all the water of injection has disappeared from the intercellular spaces. The rate then rapidly assumes the normal value and remains at that value over a period represented by a change in water content of about 10% of the fresh weight of the leaf. P. W. CLUTTERBUCK.

Immediate effect of change of light on the rate of photosynthesis. T. T. LI (Ann. Bot., 1929, 43, 587—601).—Determinations by the bubble-counting method of photosynthetic activity in plants of the genera *Elodea*, *Myriophyllum*, *Potamogeton*, and *Ceratophyllum* when exposed to light of different colours, intensities, and available energies show that there is an initial inhibitory effect when the plant is changed from exposure to light of high available photosynthetic energy to light of low available photosynthetic energy and an initial accelerating effect when the reverse change takes place. It is concluded that these phenomena support the surface action theory of photosynthesis. W. MCCARTNEY.

Carbohydrate content of detached, partially-shaded leaves. R. GANE (Proc. Leeds Phil. Soc., 1929, 1, 497—505).—The effect of irradiation on detached leaves has been followed by determinations of the starch, sucrose, and reducing substance contents of the distal, median, and proximal portions of the leaves of *Plantago media* and *Scolopendrium vulgare*, the median portions only being shaded. Leaves of the former showed a marked increase in starch content during exposure to light, but leaves from which the main veins were removed formed little starch. *Scolopendrium* leaves continued to lose

starch during illumination, especially in the unshaded portions. Increases in the sucrose content and in the amounts of reducing substances occurred in both cases. The differences in the sucrose content found in the leaves appear to be associated with shading, but are not sufficient to explain the failure of starch to appear in the shaded portion. Carbohydrates can also move from illuminated to shaded regions in spite of a dislocation of the vein system. L. S. THEOBALD.

Nitrogen and carbohydrate distribution in organs of bearing apple spurs. A. E. MURNEER (Mo. Agric. Exp. Sta. Res. Bull., 1928, No. 119, 3—50).—Flowering is characterised by marked increase in all active forms of carbohydrates and nitrogen; a considerable part of the soluble carbohydrate is supplied by hemicellulose. Both carbohydrates and nitrogen appear to be reabsorbed from the dropping blossoms prior to abscission. Throughout the growing season the carbohydrate and nitrogen increasingly accumulate in the fruit, but the percentage of nitrogen does not necessarily increase. CHEMICAL ABSTRACTS.

Chemical relationship between scion and stock in *Citrus*. A. R. C. HAAS and F. F. HALMA (Plant Physiol., 1929, 4, 113—121).—Determinations of ash, and total and water-soluble calcium and magnesium, were made. CHEMICAL ABSTRACTS.

Angiosperm seeds and factors in germination. IV. Permeability to dyes and salts of the skin of fruits and seeds. A. NIETHAMMER (Biochem. Z., 1929, 209, 263—275).—A discussion of the penetration, changes of permeability, and ageing of seeds with reference to the mechanism of stimulation (cf. A, 1928, 1239). P. W. CLUTTERBUCK.

Transformation of acetaldehyde in higher plants. J. BODNAR and C. BERNAUER (Biochem. Z., 1929, 29, 458—470).—Pea meal added to acetaldehyde converted it into acetaldol and aldehyde resins, but neither acetic acid nor alcohol was formed; the meal after inactivation of its enzymes by heat still caused the same reaction. Pea meal is able to convert the nascent aldehyde arising from pyruvic acid into alcohol, but it is not decided whether this is by simple reduction or by a reaction of the Cannizzaro type. P. W. CLUTTERBUCK.

Iodine value of fatty acids from plant phosphatides. J. E. WEBSTER (Ohio J. Sci., 1929, 29, 39—42).—The following values refer, respectively, to acetone-insoluble phosphatides from wheat, maize, soya beans, and oats: N 0.99, 1.14, 0.70, 1.61%; P 1.26, 1.65, 0.495, 0.535%; iodine value (Hanus) 81.49, 65.30, 92.48, 88.80. CHEMICAL ABSTRACTS.

Concentration effect in *Nitella*. W. J. V. OSTERHOUT and E. S. HARRIS (J. Gen. Physiol., 1929, 12, 761—781).—The concentration effect due to the cell-wall tends to increase the values for the protoplasm, and a method for differentiation of the two effects is described, by means of which the chemical effect of the protoplasm is shown to be considerably greater than that of the cell-wall. No change of sign of the concentration effect in *Nitella* is found between p_H 5.0 and 9.5 if the c_H is small compared with that of other cations. P. G. MARSHALL.

Apparent storage of carbamide in mycotrophic plants. J. WEISSFLOG (Planta, Arch. wiss. Bot., 1927, 4, 358—372; Chem. Zentr., 1929, i, 762).—No accumulation of carbamide could be detected (cf. Weyland, Jahrb. wiss. Bot., 1912, 51).

A. A. ELDRIDGE.

Titanium in Cryptogams. G. BERTRAND and C. VORONCA-SPIRT (Compt. rend., 1929, 189, 73—75).—Titanium occurs to the extent of a few mg. per kg. in cryptogamic plants (ferns, algae, and fungi), although baker's yeast contained only 0.1 mg. per kg. and *Aspergillus niger* gave no definitely positive reaction (cf. this vol., 855).

J. GRANT.

Glucosides containing hydrogen cyanide. L. FLORIANI (Rev. Centr. Est. Farm. Bioquim., 1928, 17, 343—357; Chem. Zentr., 1929, i, 761).—A discussion of behaviour on hydrolysis and of significance in plants.

A. A. ELDRIDGE.

Cyanogenetic glucosides in Australian plants. H. FINNEMORE and C. B. COX (J. Proc. Roy. Soc. N.S.W., 1928, 62, 369—378).—The isolation of sambunigrin (cf. Bourquelot and Danjou, A., 1905, i, 912) from *Acacia glaucescens* and *A. Cheelii* is described. The hydrogen cyanide content of the dry phylloides of the former plant is 0.12—0.41%. Cyanogenetic glucosides have also been detected in the leaves of the following plants: *Euphorbia Drummondii*, Boiss. (in 11 of 113 examined), *Goodia lotifolia*, Salisb. (0.57% of hydrogen cyanide in air-dried leaves), *Poranthera microphylla* (0.051% of hydrogen cyanide), *P. corymbosa* (only faint reaction), *Eucalyptus corynocalyx* (0.179% of hydrogen cyanide). E. H. SHARPLES.

Absence of galactans from skeletal incrustation of cell-walls. E. SCHMIDT, M. ATTERER, and H. SCHNEGG (Cellulosechem., 1929, 10, 126—134).—Complex compounds of cellulose and hemicelluloses, known as skeleton substances, have been obtained from the cell walls of archegoniates and phanerogams by means of chlorine dioxide and sodium sulphite. The hemicelluloses were quantitatively separated from the cellulose residues by means of 5% sodium hydroxide and recovered from the latter by treatment with alcohol and acid. The hemicelluloses from the skeleton substances of spruce, flax-straw, and of a number of plants belonging to the gymnosperms, have been examined and found to contain no *d*-galactose; hence it is concluded that skeleton substances are free from this material, and it is presumed that they are formed from *d*-glucose and other carbohydrates. Sodium sulphite has no specific dissolution properties towards galactans and its action does not depend on the p_H of its solution. The hydrolysis of hemicelluloses by means of sulphuric, nitric, oxalic, and other acids, fermentation in the presence of nutritive solutions (buffered sugar solutions), the production and properties of hemicelluloses from the skeleton substances, and the fermentation of the hydrolysates prepared by the action of various acids on the hemicelluloses of various origin are described.

B. P. RIDGE.

Preparation of gentianose from gentian root without fermentation. M. BRIDEL and M. DESMAREST (Bull. Soc. Chim. biol., 1929, 11, 710—723).—

By cold percolation of dried powdered gentian root with 10 parts of 90% alcohol 96% of the gentianose is extracted. The resulting supersaturated solution deposits crystalline gentianose. An unstable complex more soluble than gentianose is probably present in the root.

J. H. BIRKINSHAW.

Grape pigments. II. Anthocyanins of Clinton grapes. R. J. ANDERSON and F. P. NABENHAUER.

III. Anthocyanins of Seibel grapes. R. J. ANDERSON (N.Y. Agric. Exp. Sta. Tech. Bull., 1928, 146, 3—12, 13—21).—The pigment of Clinton grapes consists principally of a monoglucoside (hydrochloride, $C_{23}H_{25}O_{12}Cl$; picrate), affording on hydrolysis the anthocyanidin chloride, $C_{17}H_{15}O_7Cl$, which consists largely of delphinidin monomethyl ether, but contained some delphinidin dimethyl ether. The anthocyanin of Seibel grapes appears to be identical with cénin.

CHEMICAL ABSTRACTS.

Banana. D. W. MAY (Porto Rico Agric. Exp. Sta. Rep., 1927, 7—8).—The dry matter of different varieties contained 1.8—12.2% K_2O . A high potash content is associated with freedom from disease.

CHEMICAL ABSTRACTS.

Pineapple. H. C. HENDRICKSEN (Porto Rico Agric. Exp. Sta. Rep., 1927, 19—24).—Moisture contents of various portions of leaves were determined. The p_H of the sap varied from 6 to 6.3. Young leaves contained 13%, and red, senescent leaves 30—40%, of carbohydrate; the average protein content was 6%. A high protein:carbohydrate ratio accompanied a low chlorophyll content, and a high reducing sugar content accompanied a high anthocyanin content. The normal leaves contain peroxidase, catalase, reductase, and diastase in greater amounts than do red or chlorotic leaves. The results of fertiliser experiments are recorded.

CHEMICAL ABSTRACTS.

Constituent of the bark of the peach. J. SHINODA and S. UYEDA (J. Pharm. Soc. Japan, 1929, 49, 97—98).—From the methyl-alcoholic extract of the bark of the peach, there has been isolated a compound, m. p. 248° (acetyl derivative, m. p. 194—195°; oxime, m. p. 233°), apparently identical with naringenin.

W. O. KERMAK.

Phytosterol of stinging nettle. I. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1929, 183, 74—77).—The sterol is isolated from the dry leaves of the nettle (*Urtica urens*) in 0.04% yield, and is shown to be sitosterol. Stigmasterol is not present.

H. BURTON.

Biological activity of sandy forest soil of the Hungarian lowlands. D. FEHER and R. BOKOR (Biochem. Z., 1929, 209, 471—488).—The bacterial flora of sandy forest soil is less than for heavier forest soils, but the soil respiration is greater, due to greater aëration. The number of nitrifying bacteria is higher in the sandy soil and the p_H approximates closely to 7.

P. W. CLUTTERBUCK.

Carpenter's form of the Haldane gas analysis apparatus. T. M. CARPENTER, E. L. FOX, and A. F. SEREQUE (J. Biol. Chem., 1929, 83, 211—230).—Technical modifications in the construction and use of the authors' apparatus (J. Metabol. Res., 1923, 4, 1) are described.

C. R. HARRINGTON.

Glass electrode apparatus for measuring p_H values of very small volumes of solution. D. A. MACINNES and M. DOLE (J. Gen. Physiol., 1929, 12, 805—811).—A glass electrode by means of which the p_H of about 0.14 c.c. of liquid can be determined is described; the error is shown to be not greater than 0.02 unit. With this apparatus it is shown that the penetration of brilliant-cresyl-blue (which poisons the hydrogen electrode) raises the p_H of the vacuolar sap of living cells of *Nitella*. P. G. MARSHALL.

Validity of the glass electrode in ammonium chloride buffers. S. E. HILL (J. Gen. Physiol., 1929, 12, 813—819).—The saturated potassium chloride in contact with the glass membrane is standardised against 0.05M-potassium hydrogen phthalate (p_H 3.97). The p_H values of a solution obtained by adding varying amounts of 0.5M-ammonium chloride to 0.5M-ammonia plus 0.5M-ammonium chloride could be accurately determined in this apparatus, the values (when plotted against the logarithm of the concentration of ammonia) falling on a straight line. A slight deviation occurs above p_H 8.6 when sodium chloride (0.5M in the original solution) is present and a table of corrections is given for p_H values higher than 8.6. P. G. MARSHALL.

Quinhydrone electrode for measuring hydrogen-ion concentration in very small portions of tissue. N. OKUNEV (Biochem. Z., 1929, 210, 1—6; cf. A., 1928, 916).—An improvement on a previous modification of the Biilmann-Lund-Cullen micro-quinhydrone electrode is described. The platinum wire is replaced by a gilded platinum plate and a potassium chloride-agar mixture in the capillary point serves as bridge. This electrode may be used for buffer solutions or for small pieces of tissue. J. H. BIRKINSHAW.

Effect of amino-acids on methods for the determination of sugar. Y. OKUDA and K. KATAI (Bul. Sci. Fak. Terkultura, 1929, 3, 182—186).—In Bang's method cysteine, cystine, and tryptophan behaved as dextrose; glycine, aspartic acid, tyrosine, alanine, leucine, and cleavage products of gelatin had little or no action. Cystine and cysteine influenced the results obtained by the methods of Folin and Wu, Benedict, Hagedorn, and Schaffer and Hartmann. CHEMICAL ABSTRACTS.

Determination of lactic acid in animal fluids and tissues. S. TANAKA and M. ENDO (Biochem. Z., 1929, 210, 120—142).—An improvement in the von Fürth-Charnass technique for the determination of lactic acid consists in carrying out the oxidation with permanganate in an atmosphere of carbon dioxide. The hydrogen sulphite solution is also kept saturated with carbon dioxide. Further oxidation of the acetaldehyde is thus prevented. The method when applied to the determination of lactic acid in muscle, tissue, blood, urine, etc. is preceded by an ether extraction in the Kumagawa-Suto apparatus (A., 1903, ii, 702). The charcoal used for removing frothing substances must be thoroughly extracted with sodium carbonate solution. The improved method gives results accurate to within 1%. J. H. BIRKINSHAW.

Detection of fats and their constituents. A. NIETHAMMER (Biochem. Z., 1929, 209, 447—457).—Examples are given of the use of Sudan III, of hydrolysis methods, of the setting form, and of the sublimation method for the detection of small amounts of fat. P. W. CLUTTERBUCK.

Volumetric-micro-determination of cholesterol. A. HENRICHS and L. KLEMM (Biochem. Z., 1929, 210, 191—197).—The method of Szent-Györgyi (A., 1923, ii, 344) can be used to determine cholesterol volumetrically with an error not exceeding 7% on 2 c.c. of blood. J. H. BIRKINSHAW.

Colorimetric determination of bile acids. R. GREGORY and T. A. PASCOE (J. Biol. Chem., 1929, 83, 35—42).—When a solution of bile acids in presence of sulphuric acid is heated with furfuraldehyde a blue colour is produced; in combination with a special source of monochromatic light, this is made the basis of a method for the determination of bile acids with an error of $\pm 5\%$. Bile acids are absent from normal human blood. C. R. HARRINGTON.

Manometric measurement of peptide hydrolysis. H. A. KREBS and J. F. DONEGAN (Biochem. Z., 1929, 210, 7—23).—A method of measuring peptide hydrolysis depends on the fact that peptides are stronger acids than their amino-acid constituents. If the hydrolysis mixture contains hydrogen carbonate and is in contact with an atmosphere of carbon dioxide, the change in pressure produced gives a measure of the hydrolysis. The "constant of the vessel" may be measured directly, when all experiments must be carried out under exactly similar conditions, or may be calculated from the acid dissociation constants of the peptide and of the amino-acid and the first dissociation constant of carbonic acid. The method gives results within 1% and agrees well with the older methods. J. H. BIRKINSHAW.

Solubility of lead salts in physiological salt solutions. L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1929, 36, 279—293).—The solubility product law does not apply to the behaviour of lead orthophosphate, $Pb_3(PO_4)_2$, in solutions containing excess of phosphate probably because intermediate ions, solubility data for which are unknown, are formed. In a salt solution of the ionic strength of blood at p_H 7.35 and containing 4 mg. of phosphorus per 100 c.c. the solubility of lead orthophosphate is equivalent to 3.6×10^{-7} mol. of lead per litre. The solubility of lead carbonate in a salt solution of the ionic strength of blood containing hydrogen carbonate and under a carbon dioxide tension comparable with that of blood is equivalent to 1.0×10^{-6} mol. of lead per litre. W. MCCARTNEY.

Micro-determination of phosphate. F. HOLTZ (Biochem. Z., 1929, 210, 252—260).—In a gravimetric micro-method for phosphate the substance is heated with sulphuric and nitric acids to destroy organic matter. After dilution with 25% ammonium nitrate solution containing nitric acid the mixture is precipitated hot with nitric acid ammonium molybdate-sulphate reagent. The precipitate is dried and weighed together with a porcelain filter crucible, dissolved out with alkali, and the tare weight of the crucible obtained. J. H. BIRKINSHAW.