BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1929.

General, Physical, and Inorganic Chemistry.

Method for obtaining simplified spectra. B. DE LA ROCHE (Bull. Soc. chim., 1929, [iv], 45, 706-707).-Electrodes of purified carbon with a gap of about 25 mm. are placed horizontally in the flame of a Méker burner so that the whole gap is in the flame. A condenser of 0.01-0.02 mf. capacity with a self-induction of 0.02-0.05 Henry in the circuit is discharged across the electrodes, a solution of the salt to be examined being simultaneously atomised and passed into the flame. The spectrum shows only the principal lines and "raies ultimes"; the spectrum of the surrounding gas disappears entirely.

Absorption of the H_{α} line. C. A. SILBERRAD. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 193—197).—The intensity distribution in the reversed H_a line has been investigated by a method similar to that of Ladenburg and Loria (Verh. Deut. physikal. Ges., 1908, 10, 858). The "black" and "white" stages described by Wood (A., 1926, 1069) were observed also when a strongly condensed discharge was passed through hydrogen. Only when the "black" stage was obtained in the absorption tube was the core of the Ha line quite black.

J. W. SMITH.

Spectrum of H₂ bands analogous to the orthohelium line spectrum. II. O. W. RICHARDSON and K. DAS (Proc. Roy. Soc., 1929, A, 125, 309-330; cf. this vol., 375) .- The bands recently discovered by Sandeman (Proc. Roy. Soc. Edin., 1929, 49, 245) make it necessary to reconsider the structure of the band system formerly called $3^{3}S \rightarrow 2^{3}S$. Evidence is adduced in support of the view that the upper electronic level is a 2 state and the symbol $2^{3}S'$ is provisionally assigned to it. A detailed description is given of this system and also of the system $3^3S' \longrightarrow$ Is given of this system and also of the system $3^{\circ}S \longrightarrow 2^{3}S$ (*R* strong, *P* weak). The following values are calculated : for $2^{3}S'$: $v_{e}=17733$, $\omega_{0}=2130$, $z\omega_{0}=67$, $B_{0}=26.54$ wave numbers, $r_{0}=1.119 \times 10^{-8}$ cm., *D* (heat of dissociation)= 1.42_{5} volts; for $3^{3}S'$, $v_{e}=8810$, $\omega_{0}=2184$ (?), $z\omega_{0}=43$ (?), $B_{0}=28.52$ wave numbers, $r_{0}=1.114 \times 10^{-8}$ cm., $D=2.20_{5}$ volts. Two new progressions ending on $2^{3}S$ are also described. An investigation of minimum of minimum of the system of the ation of vibrational and rotational structures of the initial levels of the bands indicates that these probably constitute the n'=5 and n'=6 progressions of $2^{3}S' \longrightarrow$ 2³S. A new band in the yellow, of which the final state appears to be the vibrational state n''=1 of 23S, is described. L. L. BIRCUMSHAW.

New regularities in the band spectrum of helium. III. G. H. DIEKE, S. IMANISHI, and T. 1205

TAKAMINE (Z. Physik, 1929, 57, 305-325; cf. A., 1928, 677, 1295; this vol., 732).—Bands which correspond with the combinations of 4s, 5s, 6s, 4d, 5d, and 6*d* terms with a new end term are investigated. The end term 2s' is expressed as $2\pi^{3}\Sigma$ and is analogous to the *B*-state of the hydrogen molecule. A number of bands have the 2p-state as end term. A. J. MEE.

Probability of the forbidden s,d switch in the alkali metals. V. PROKOFIEV (Z. Physik, 1929, 57, 387-393).-By investigating the anomalous dispersion of the forbidden lines, 1s-3d, of the alkali metals the probability of switch was found. It is approximately equal for all the alkali metals and is of the order 10^{-5} to 10^{-6} . For easim, the probability for the 1s-4d lines is approximately equal to that for the 1s-3d lines. The 1s-3d doublet of easim was investigated and the intensity ratio of its components found to be 1.4 within an accuracy of 10%. A. J. MEE.

Spectrum of beryllium. W. H. SANDERS and V. M. ALBERS (Physical Rev., 1928, [ii], **31**, 151).----No lines of wave-length greater than 5271 Å. have been photographed with the vacuum spark, but some appear between 5000 and 8500 Å. when an air spark is used as a source. The band spectrum of the oxide is strong when the arc in air is used as source and weaker with the spark in air. L. S. THEOBALD.

Spectra of boron. W. D. LANSING and W. F. TYLER (Trans. Illinois Acad. Sci., 1928, 21, 210-211). -The preparation of the material for a study of the spectral regions 2050-5200 and 4500-6680 Å. is described. CHEMICAL ABSTRACTS.

Pressure shift in the spectrum of ionised nitrogen. W. E. PRETTY (Proc. Physical Soc., 1929, 41, 442-455).-The shifting of certain lines in the spectrum N II caused by a change in the pressure of gas in the discharge tube is investigated. More than S0 lines in the region λ 6800–1850 were found to shift, and the amount in most cases was measured. The shift is in the direction of increasing wave-length in all cases. The shifts are considered in relation to the terms giving rise to the lines concerned and three new singlet terms identified. It is concluded that the phenomenon is in the main a Stark effect.

C. J. SMITHELLS.

Cathode phenomena in Geissler discharges through oxygen and nitrogen. (MISS) N. M. CARMICHAEL (Phil. Mag., 1929, [vii], 8, 362-368).-A search was made in the Geissler discharges through

oxygen and nitrogen for a primary dark space, the absence of which, in these gases, was not explained by a recent theory (cf. A., 1928, 677). The results were negative. A new dark space was discovered in the discharge through oxygen between the negative glow and the cathode dark space, and was investigated by the method of exploring electrodes; it appears to be a positive ion sheath between these two regions of the discharge. N. M. BLIGH.

Spectrum of the negative glow in oxygen. K. G. EMELÉUS and (MRS.) F. M. EMELEUS (Phil. Mag., 1928, [vii], 8, 383-392; cf. Seeliger and Lindow, A., 1925, ii, 739).—A detailed investigation of the negative glow in oxygen was made, using a discharge tube with electrodes of degassed nickel. In addition to the visible and ultra-violet negative bands of oxygen, the ozone bands, and the nickel lines, there were present lines of OI, OII, and OIII; O IV lines were not detected. The spectroscopic data and discharge conditions are correlated; the ionisation is treated with the help of the Langmuir analysis. Three groups of electrons are present and the number in each group able to effect ionisation at dissociation voltages is calculated irrespective of probability N. M. BLIGH. considerations.

Higher spark spectra of neon and argon in the extreme ultra-violet. J. C. BOYCE and K. T. COMPTON (Proc. Nat. Acad. Sci., 1929, **15**, 656—658; cf. A., 1928, 338, 565, 1067).—By using an electrodeless ring discharge, the lines due to Ne III, Ne IV, A III, and A IV were investigated and their measurements and classification are tabulated. The lowest ionisation limit of Ne III was 63.2 volts and of A III 40.7 volts. N. M. BLIGH.

Afterglow of lamps containing neon, argon, and a mixture of neon with a little argon. M. J. DRUYVESTEYN (Z. Physik, 1929, 57, 292-304).-The afterglow of lamps filled with neon, argon, and neon with 0.5-3% of argon was investigated by visual and photographic methods. By comparing the spectrum of the afterglow with that of the principal discharge it is possible to find out whether the principal discharge is an excitation or a recombination glow. In pure neon the glow contains the lines due to atoms and positive ions. The strongest lines were the red arc lines, 1s-2p. The argon spectrum is similar. With 0.5-3% of argon, the neon lines were confined to the discharge glow, whilst the argon lines appeared only in the aurora. The following statements appear to be justified. In the first place, the glow in argon is chiefly an excitation glow. Secondly, the argon glow in the neon+argon tube is chiefly a recombination glow. Thirdly, the afterglow is a recombination glow for both the argon and neon+argon tubes. The use of the afterglow affords a simple means of separating lines due to atoms and positive A. J. MEE. ions.

Influence of foreign gases on the intensities of the magnesium resonance lines 4571 and 2852. J. G. FRAYNE (Physical Rev., 1929, [ii], 34, 590– 596).—The 4571 line, which is weak in the arc, was obtained fairly prominently when magnesium vapour at 500° was excited in an evacuated tube by an

electrodeless short-wave discharge. The inert gases enhanced the line, the intensity relative to the triplet 3838 increasing up to about 20 mm. in argon and 10 mm. in neon and helium. At these pressures argon increased the line 100, neon 70, and helium 40 times; nitrogen and carbon monoxide increased it up to about 2 mm.; hydrogen caused a slight increase at about 2 mm. Intensity-pressure curves are given and analysed mathematically. Collisions of excited metastable atoms with the walls are shown to be of the second kind, and the enhancing action of the inert gases is shown to be one of reducing diffusion to the walls. All gases reduced the line 2852 in intensity, and also all singlets terminating on the 31P level. Increasing pressure of hydrogen reduced the line intensity faster than that of the singlets. Dissociation of the hydrogen molecule by magnesium atoms in the 31P state reduced radiation from that N. M. BLIGH. state.

New terms in the spectra of Al I, Ga I, and In I. W. D. LANSING (Physical Rev., 1929, [ii], 34, 597-598).—The spectra were investigated, using a tungsten vacuum furnace. Lines arising from the term sp^2 ²D were discovered in Al I. No emission lines of gallium were observed. A ²P-⁴P combination was found in In I from previous data.

N. M. BLIGH.

Vacuum spark spectrum of aluminium. R.F. PATON and G. M. RASSWEILER (Physical Rev., 1928, [ii], **31**, 151).—Forty lines between 2200 and 5000 Å. have been obtained with high vacua.

L. S. THEOBALD.

Spectrum of phosphorus in the extreme ultraviolet. P. QUENEY (J. Phys. Radium, 1929, [vi], 10, 299—302).—The spectrum of phosphorus was investigated by the electrodeless discharge for the range 1200—2700 Å. Complete wave-lengths and intensities are tabulated. In addition to known lines about 250 new lines were found. N. M. BLIGH.

Band systems of titanium oxide. F. LOWATER (Proc. Physical Soc., 1929, 41, 557—568).—The bands of TiO have been extended towards the infra-red some 800 Å. further than the range previously known. Bands in the orange, red, and infra-red regions have been analysed into two systems, distinct from the blue-green system. One of these is due to the transition $^{1}\Pi \longrightarrow ^{1}\Sigma$, the other to $^{3}\Sigma \longrightarrow ^{3}\Pi$, the latter having the same final energy level as the blue-green system $^{3}\Pi \longrightarrow ^{3}\Pi$. C. J. SMITHELLS.

Spectrum of gallium II and the $(4s4p^2)$ configuration in gallium I and indium I. R. A. SAWYER and R. J. LANG (Physical Rev., 1929, [ii], 34, 712—719; cf. Lang, A., 1928, 99; Rao, A., 1927, 390).—The spectrum of gallium excited in a hollow cathode discharge in helium was photographed in the region λ 10000—200, and about 90 lines excited were classified in singlet and triplet series of Ga II. Absolute term values are calculated and the lowest term is $(4s^2)^{1}S=165458$ corresponding with an ionisation potential for Ga II of 20.43 volts. Classified lines and term values are tabulated. The lines arising from combinations of $(4p^2)^{4}P$ and $(4p^2)^{2}S$ with $(4s4p)^{2}P$ of Ga I were identified and term values are given. For the indium spectrum in helium $(4p^2)^{4}P$ of In I was located, and its term values and combinations with $(4s4p)^2P$ are given. N. M. BLIGH.

Spark spectra of germanium. R. J. LANG (Physical Rev., 1929, [ii], 34, 697-711; cf. A., 1928, 99; Rao and Narayan, *ibid.*, 929).—The first three spark spectra of germanium were extended by the discovery of new terms and combinations: Ge II $s4p^2 {}^2S$ and $p^3 {}^2P$. Ge III $s4s {}^1S_0, s5s {}^1S_0, s4p {}^1P_1, s5s {}^1P_1, s4d {}^1D_2, s4f {}^1F_3, p4p {}^1D_2, p4d {}^1P_1 {}^1F_3 {}^1D_2, d4d {}^1D_2, and$ $possibly <math>s5g {}^3G {}^1G$. Ge IV $d^{10}6p {}^2P$, $d^{10}5g {}^2G$, $d^9s {}^2D$. A full classification of the lines of Ge II, Ge III, and Ge IV is given. N. M. BLIGH.

Absorption of light by bromine and iodine. P. Bovis (J. Phys. Radium, 1929, [vi], 10, 267-272). -Films of solid iodine, liquid bromine, and solutions of bromine in organic solvents, a few microns thick, were prepared between quartz plates, and absorption spectra down to wave-length 0.290 µ obtained. All the spectra are characterised by two bands, the larger of which is in the region of shorter wave-length. This also applies to solutions, and the previous distinction between brown and violet solutions of iodine and bromine is attributed to the attenuation of the band in the visible region. The spectral absorption of chlorine, bromine, and iodine in the gaseous state shows a shift in the position of the two bands towards longer wave-length with increasing at. wt. The same bands exist in the liquid state, the weaker one occupying exactly the same position as in the vapour, but the bands partly overlap. As the physical state becomes denser the ultra-violet band extends until it becomes continuous with the violet band.

C. J. SMITHELLS.

Series in the arc spectrum of bromine. T. L. DE BRUIN and C. C. KIESS (Science, 1929, 69, 360— 361).—The arc spectrum of bromine has been photographed beyond 9300 Å. in the infra-red, and with the help of Turner's data (A., 1926, 550) the structure of the arc spectrum of Br I has been worked out. Certain of the terms form a Rydberg series and give a calculated ionisation potential of 12.2 volts for the neutral bromine atom. L. S. THEOBALD.

Resonance radiation of silver vapour. W. KAPUŚOIŃSKI (Bull. Acad. Polonaise, 1929, A, 284-286).—To examine the resonance radiation of silver vapour a silver wire was heated to 900° in a quartz vessel and the vapour illuminated by the light from a condensed spark passed between silver electrodes. The spectrum of the resultant fluorescence was photographed (exposure 10 hrs.). The two resonance lines (3280.66 and 3382.86 Å.) appeared much stronger in the fluorescence than in the control spectrum. The resonance radiation first became perceptible at 780° (pressure of silver vapour 10⁻⁴ mm.), and increased steadily in intensity to 900°. These results are further confirmed by the absence of fluorescence if the source of light is a condensed spark between copper electrodes. C. A. SILBERRAD.

Band spectrum of lanthanum monoxide. W. JEVONS (Proc. Physical Soc., 1929, 41, 520-545).— The spectrum has been observed from λ 8700 to 2850Å., and the band-heads, mostly not hitherto recorded, are arranged into several systems. The analysis differs in some respects from that of Mecke. A note on the general theory of electronic band spectra of diatomic molecules is given. C. J. SMITHELLS.

Hyperfine structure in spectral lines, especially those of singly-ionised praseodymium. R. C. GIBBS, H. E. WHITE, and J. E. RUEDY (Proc. Nat. Acad. Sci., 1929, 15, 642—646; cf. King, Astrophys. J., 1928, 68, 194).—The spectrum of Pr II was investigated with high dispersion over the region 3900—5000 Å., and the component separations of 33 lines exhibiting complex structure were measured. All of the completely resolved fine structures consisted of six components. This is shown to be in agreement with quantum theoretical requirements. Nine or ten weaker components are predicted. N. M. BLIGH.

Band spectra of the oxides of praseodymium, neodymium, and samarium. G. PICCARDI (Nature, 1929, **124**, 618).—The oxides have been volatilised and their emission spectra between 8000 and 2400 Å. have been photographed. The most intense bands are : praseodymium 6475, 6282, 6022, 5765, 5692, 5597, 5352 Å.; neodymium 6580 Å.; samarium 6506 Å. A. ELDRIDGE.

Zeeman effect for the arc spectrum of gold. A. S. M. SYMONS and J. DALEY (Proc. Physical Soc., 1929, 41, 431—441).—The Zeeman effect for about 50 gold lines has been observed, using a field strength of about 23,000 gauss. McLennan and McLay's assignment of terms to the Au I spectrum is verified to some extent, but modifications are suggested. Suggestions are made as to the identity of a few terms not previously identified. C. J. SMITHELLS.

Variations in the spectrum of the light emitted by quartz mercury lamps. T. TAKAHASHI and L. H. CLARK (J. Sci. Instr., 1929, 6, 273-277).--Variations in the intensity of the light emitted by quartz mercury lamps have been studied photometrically and shown usually to lead to the reversal of the intensities at the extreme ends of the spectra. They are due to irregularities in the curvature and thickness of the quartz envelope and may be eliminated by the insertion of a plane quartz (or pyrex) window in the side of the burner. J. GRANT.

Spectrum of the mercury arc in atmospheres of foreign gases. B. VENKATESACHAR and L. SIBATYA (Indian J. Physics, 1929, 4, 179—193).— The behaviour of the mercury arc spectrum in the presence of carbon dioxide and of hydrogen has been observed. W. E. DOWNEY.

Fluorescent and phosphorescent excitation of mercury vapour by the resonance frequency and by lower frequencies. (LORD) RAYLEIGH (Proc. Roy. Soc., 1929, A, 125, 1—23).—Experiments are described in which the green band fluorescence is excited in dense mercury vapour by radiation of wave-length 3450 Å., and the spectrum of the fluorescence, consisting of the structureless bands 3300 and 4850 Å., has been photographed with excitation beginning at 3360 Å. and upwards. The fluorescence in the neighbourhood of the resonance line ha been observed only with less dense vapour. When excitation extends over the resonance line the fluorescence shows a discontinuity of intensity, and is sharply 1208

divided into "core effect," excited by a range of 0.1 Å. at the resonance line and attributed to line absorption, and "wing effect," excited by the region beyond the atomic line and attributed to band absorption. These effects are examined in a moving stream of vapour (Phillips' effect), the velocity of the stream being under control. Square silica tubes are used. The visual and ultra-violet effects can be separated in space, since the visual core and wing effects begin to pass along the vapour stream at lower velocities than the corresponding ultra-violet effects. With increased velocity of the stream the ultra-violet fluorescence eventually shows persistence also. Starting at atmospheric temperature in a vacuum, it is shown that by raising the temperature a continuous transition can be traced between Wood's "resonance radiation" and the phenomenon of the persistent L. L. BIRCUMSHAW. ultra-violet core effect.

Theory of intermittent action and series spectra. K. C. KAR (Z. Physik, 1929, 57, 416-428).—Mathematical. The Bohr principle of switches from one level to another is considered from the point of view of intermittent action, the theory of which has previously been put forward by the author.

A. J. MEE. Secondary diffraction maxima of spectral lines. A. G. SHENSTONE (Physical Rev., 1929, [ii], 34, 726—729).—The secondary diffraction maxima around a spectral line can be easily photographed under suitable conditions. The relative intensities usually show divergence from Rayleigh's theory, indicating peculiar forms of aberration due to modern spectrographic lenses. The practical difficulties introduced by the peculiar intensities are discussed.

N. M. BLIGH.

Anomalous Zeeman effect, Stern and Gerlach's experiment, and the magneton. J. KUNZ (Prob. mod. Physik; Debye-Sommerfeld Festschr., 1928, 25-29; Chem. Zentr., 1929, i, 2619).—A discussion. A. A. ELDRIDGE.

Coarse structure of band spectra. A. KRATZER (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 149—156; Chem. Zentr., 1929, i, 2618).—The formula for the energy of a diatomic molecule is derived from wave-mechanics, and the general disposition of the band edges and the magnitude of the rotation terms are discussed. A. A. ELDRIDGE.

Effect of collisions on the structure of Fraunhofer lines. A. UNSÖLD (Prob. mod. Physik; Debye-Sommerfeld Festschr., 1928, 95—104; Chem. Zentr., 1929, i, 2619).—The fact that the light intensity in the centre of a Fraunhofer line is not zero indicates that the theory takes no account of the effect of collisions. A. A. ELDRIDGE.

Emission lines accompanying absorption lines in the spectra of stars. W. H. McCREA (Z. Physik, 1929, 57, 367—379).—The effect of repeated scattering of light in stellar atmospheres discussed by Franck is further investigated. The cases quoted by Franck of emission lines accompanying the absorption lines are easily explained by gas motion. A. J. MEE.

Absorption lines of the infra-red solar spectrum. C. G. ABBOT and H. B. FREEMAN (Smithsonian Miscell. Coll., 1929, 82, 1—17).—Langley's original bolographic investigations were extended with apparatus of higher resolving power, employing three glass prisms. The infra-red solar energy spectrum was recorded on moving photographic plates, three curves being impressed on a single plate. Greatly increased detail was obtained; the identification of the lines by comparator is described; intensities were assigned and wave-lengths determined. Full results for more than 1200 lines are tabulated. N. M. BLIGH.

Satellites of the X-ray lines $L\alpha$, $L\beta_1$, and $L\beta_2$. F. K. RICHTMYER and R. D. RICHTMYER (Physical Rev., 1929, [ii], **34**, 574—581).—The X-ray satellites, faint lines which do not fit the energy level diagram, were investigated for the elements rubidium to tin, and were found to be of somewhat complex structure, with a continuous spectrum extending beyond them towards shorter wave-lengths. Tables are given of wave-lengths, values of ν/R , and of $\Delta\nu/R$, where $\Delta\nu$ is the difference in frequency between satellite and parent line, for five to seven satellites of $L\alpha$, four of $L\beta_1$, and five of $L\beta_2$. The empirical relation previously reported (cf. A., 1928, 939) was found to hold.

N. M. BLIGH. Scattering power of X-rays and the electron distribution of the H-ion. J. M. BIJVOET and W. A. FREDERIKSE (Rec. trav. chim., 1929, 48, 1041— 1046).—A quantitative investigation of the diffraction intensities of lithium hydride shows that the observed decline in the scattering power with increasing diffraction angle is in good agreement with that calculated from the atomic model of quantum mechanics.

F. G. TRYHORN.

Ratio of intensities of modified to unmodified radiation in scattering of X-rays. E. ALBRECHT (Z. Physik, 1929, 57, 326-340).-The occurrence of the Compton effect is demonstrated by the scattering of hard X-rays from the lighter elements. The method used was that of absorption analysis. Monochromatic rays were used of wave-length 0.210 Å., from the spectrum of a Coolidge tube arranged with a filter. The observations were made with lithium, carbon, silica, aluminium, sulphur, and copper as scattering bodies. With increasing angle of scattering and decreasing atomic number the ratio of modified to unmodified radiation became greater. Lithium shows modified radiation only. The ratio $s_1/(s_1+s_2)$, where s_1 and s_2 represent the intensities of unmodified and modified radiation, respectively, is shown to be proportional to $e^{-(c/N)^*}$, where N is the atomic number of the element. The results are compared with those of other workers using softer rays. A. J. MEE.

Critical determination of the K-, L_1 -, and M_1 levels for the lighter elements. B. C. MUKHERJEE and B. B. RAY (Z. Physik, 1929, 57, 345-353).—It is shown that the true K-absorption limit is calculable from accurate measurement of characteristic X-radiation and optical lines. The values of the L_1 and M_1 levels were also derived by the use of the Sommerfeld regular doublet interval. The curves of $\sqrt{\nu/R}$ against the atomic number were constructed and the discontinuities discussed. The values for the critical potentials of the lighter elements obtained by the electron collision method are compared with those here derived. A. J. MEE.

Diffraction of cathode rays. III. G. P. THOMson (Proc. Roy. Soc., 1929, A, 125, 352-370; cf. A., 1928, 3, 938).-The metal films used in previous work on this subject were prepared from beaten foil thinned in a suitable reagent and were never free from holes. By a method involving cathode sputtering on to a base of cellulose acetate, perfectly continuous films of the order of 10⁻⁶ cm. thick have now been obtained, and cathode-ray diffraction patterns are described and discussed for films of gold, silver, lead, iron, and nickel. An unexpected structure is found for nickel (hexagonal closest packing), but the results for the other metals are in close agreement with those determined by X-ray analysis, with the exception of certain lead and iron films which probably contained compounds. The lowest voltages at which rings could be obtained have been determined for a number of films. A curve giving the variation of wave scattering with angle for the individual atoms is deduced by photometric measurements of the diffraction rings in gold. The curve falls much more steeply than the corresponding F curve for X-rays, indicating that the mean position of the scattering material is further from the centre of the atom. The fact that the present method gives a smooth curve is strong evidence that the crystals are distributed at random in the film. L. L. BIRCUMSHAW.

Calculation of matrices for the hydrogen atom. W. GORDON (Ann. Physik, 1929, [v], 2, 1031-1056).-Mathematical. R. A. MORTON.

Revision of the value of e/m derived from measurements of the Zeeman effect. H. D. BABCOCK (Astrophys. J., 1929, 69, 43–48).—Revision of the former value (*ibid.*, 1923, 58, 149) by elimination of uncertain lines, by the use of more recent analyses of the spectra of chromium and titanium and of the latest value for the velocity of light, gives, as the weighted mean of 48 determinations, $e/m=(1.7606\pm0.0012)\times10^7$ e.m.u./g.

L. S. THEOBALD.

Masses of proton and electron. R. FURTH (Naturwiss., 1929, 17, 728—729; cf. this vol., 1123).— Preliminary. Following Eddington (this vol., 231) in certain respects, it is shown that it is possible to deduce, not only the charge, but also the mass of a proton or an electron from the fundamental magnitudes of the theory of relativity and the quantum theory. R. A. MORTON.

Statistical interpretation of Maxwell's equations. M. S. VALLARTA (J. Math. Phys. Mass. Inst. Tech., 1929, 8, 155-161).—Mathematical.

Active nitrogen. P. K. KICHLU and S. BASU (Indian J. Physics, 1929, 4, 161-174).—Experimental evidence is adduced to support the views of Birge (Nature, 1924, 94, 642) with slight modification.

W. E. DOWNEY.

Detection of dissociation of halogen molecules effected directly by irradiation. H. SENFTLEBEN and E. GERMER (Ann. Physik, 1929, [v], 2, 847-864). —A method is described for detecting the dissociation of halogen molecules by the direct action of light. The effective wave-lengths extend almost as far as the optically determined convergence frequencies, radiations on the short-wave side of 4722 and 5086 Å. being effective for chlorine and bromine, respectively. the convergences being at 4785 and 5107 Å. In the case of iodine, the convergence occurs at 4995 Å., whilst dissociation occurs directly for rays 4600— 5000 Å. and is absent for the region 5000—5300 Å.

R. A. MORTON.

Chemical combination as an electrostatic phenomenon. XI—XIII. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 450—453, 478— 482, 490—492; cf. this vol., 1129).—XI. The molecular configurations of ammonia, ammonium compounds, and some simple carbon compounds are discussed.

XII. The electrostatic forces within and between molecules of the general type XY_n are considered from the aspect of crystal lattice formation, and it is concluded that where *n* is greater than two, lattice formation is possible only if the Y ion is small relative to the central ion, and not easily polarised.

XIII. The forces causing deformation of the ions in crystal lattices are considered. S. I. LEVY.

Structure of trebly-ionised chlorine. S. C. DEB (Nature, 1929, 124, 513).—Certain lines of treblyionised chlorine, due to the transition $M_2(N_1-N_2)$, have been found, and the chief lines of the group have been located by using Bowen's results (A., 1928, 210). A. A. ELDRIDGE.

Equilibrium in a polyatomic gas according to the new statistics. H. LUDLOFF (Z. Physik, 1929, 57, 227-241).—Mathematical. Dissociation equilibria in molecules containing 3 or 4 equal atoms are discussed in a manner analogous with Gibson and Heitler's treatment of simple cases (A., 1928, 941). It is shown that the numerical value of the equilibrium constant depends on whether the molecule in question exists in enantiomorphic forms or not (cf. Hund, A., 1927, 809). J. W. SMITH.

Geometrical treatment of Dirac's theory of the electron. V. FOCK (Z. Physik, 1929, 57, 261-277). --Mathematical. J. W. SMITH.

Energy functions of the H₂ molecules. O. W. RICHARDSON and P. M. DAVIDSON (Proc. Roy. Soc., 1929, A, 125, 23-50).—The results given by the vibrational (cf. Kemble, A., 1926, 224) and rotational (cf. Birge, *ibid.*, 12) determinations of the terms in the expansion of the force function near the equilibrium position are in fair agreement, but the former method permits of far greater accuracy than the latter. The total energy of the H_2 molecules is calculated, and proof is obtained that the molecule in which the electron has total quantum number nbreaks up into an unexcited atom and an atom in which the electron is excited to quantum number n. The estimated values of the dissociation energies of all the known electronic levels of the H₂ molecule are tabulated, together with several other constants of the levels. A formula is derived for the mean kinetic energy of a system of particles in motion under their mutual forces, some being held fixed and the others remaining in their neighbourhood, and this is applied to the case of two nuclei.

L. L. BIRCUMSHAW.

Thomson's experiment. S. C. KAR (Naturwiss., 1929, 17, 727).—Thomson's work (A., 1928, 938) with reference to the de Broglie theory of electron waves is discussed. Thomson's observations are consistent with light waves, although the deflexion by means of magnetic and electric fields remains a difficulty.

R. A. MORTON.

Interaction of radiation and the electron. R. D. KLEEMAN (Science, 1929, 69, 380-381).-It has been shown thermodynamically that the electron may possess internal apart from kinetic energy, and that it can radiate in two entirely different ways : (i) on undergoing acceleration and (ii) on emitting a part of its internal energy as radiation, which is not necessarily connected with its motion. Further, the surrounding radiation gradually slows down its motion, which is attended by an increase in internal energy, and the force acting on it when placed in an electric field depends on its internal energy. The difficulties of the Bohr atom, and its antagonism to the Lewis-Langmuir atom, disappear in the light of L. S. THEOBALD. the above.

Possible relation between Planck's constant hand the radiation pressure of circularly polarised rays. S. POKROVSKY (Z. Physik, 1929, 57, 278— 282).—Mathematical. J. W. SMITH.

Method for determining the temperature of glowing filaments. K. SCHESINGER (Ann. Physik, 1929, [v], 2, 933—975).—A method is described whereby the temperature of a glowing filament can be determined from the temperature variations in its characteristic vibrations when it is used as a stretched string. R. A. MORTON.

Absorption law for the penetrating heightradiation. H. KULENKAMPFF (Physikal. Z., 1929, **30**, 561-567).—The decrease in intensity of ultra- γ -radiation effected in its passage through matter is influenced by the long-wave radiation which results from scattering. A method of calculation analogous to that used in the theory of radioactive disintegration is suggested as giving a good approximate description of the phenomena. The decrease in intensity of a primary monochromatic radiation is shown to depart considerably from the exponential law. The admixture of radiation of longer wave-length must also affect the other properties of the radiation.

R. A. MORTON.

Method for determining whether or not an electron has a magnetic moment comparable with that of a hydrogen atom. V. M. ALBERS and T. E. PHIPPS (Physical Rev., 1928, [ii], **31**, 149).—A modification of the method suggested by Brillouin is proposed. L. S. THEOBALD.

Dielectric cohesion of rare gases. M. CURLE and A. LEPAPE (J. Phys. Radium, 1929, [vi], 10, 294-298).—See this vol., 121.

Dependence of δ -radiation on outgassing of platinum foil. S. MATTHES (Ann. Physik, 1929, [v], 2, 631-645).—The initial intensity of δ -emission depends on the purity of the surface. Repeated heating to redness effects an increase in emission, but further heating to higher temperatures causes the emission to fall below the initial value. The changes can be reproduced by recharging the surface with air or hydrogen. R. A. MORTON.

Wave-mechanical character of the β-ray change. J. KUDAR (Z. Physik, 1929, 57, 257-260). --Mathematical. J. W. SMITH.

Radioactivity. A. F. KOVARIK and L. W. MCKEEHAN (Bull. Nat. Res. Council, 1929, No. 51, 203 pp.).—A second revised printing of the Report of the Committee on X-rays and radioactivity first issued in 1925.

Search for element 87 by analysis of positive rays. K. T. BAINBRIDGE (Physical Rev., 1929, [ii], 34, 752-762) .- Previous searches are surveyed critically. Predictions of spectral values, and estimates for the sensitivity of detection and identification by at. wt. determinations, radioactive means, physiological effects, X-ray and optical spectrum analysis are given. An intense homogeneous source of positive ions, by means of a tungsten filament heated at 1200-1300° Abs., was incorporated into a mass spectrograph, and positive ions of mass number 223 or 224 were looked for in the product obtained after attempting the chemical separation of cæsium and eka-cæsium from pollucite and lepidolite ores. Ekaexsium was not present to an extent greater than 3.5×10^{-7} and 7.3×10^{-6} in the cæsium separated from the two ores, respectively. Measurements of the vapour pressures of the alkali metals by Langmuir and Kingdon (A., 1925, ii, 254) and by Killian (A., 1926, 653) by measurements of the positive ion current thermally produced from tungsten filaments in the vapour of these elements are shown to be highly accurate, and the method is applicable to the separation of isotopes and determinations of isotope intensity ratios. N. M. BLIGH.

Cathode drop in an electric arc. S. S. MAC-KEOWN (Physical Rev., 1929, [ii], 34, 611—614).— According to Langmuir's theory developed by Compton (cf. A., 1927, 926) the electrons emanating from the cathode in the mercury arc are due primarily to the high electric field and not to thermal emission. Values for the electric field at the cathode surface arc determined for varying percentages of current carried by positive ions. Assuming that the total cathode drop occurs in a distance less than one mean frce path from the cathode, the theory is shown to be consistent with available data. N. M. BLIGH.

Recombination of ions and of ions and electrons in gases. L. C. MARSHALL (Physical Rev., 1929, [ii], 34, 618—634).—By means of a new direct method, using constant radiation from a Coolidge tube as the ionising agent, together with a rotating commutator shutter, the X-ray exposure t', the initial ion concentration n_0 , and the time of recombination t could be varied independently over a wide range. Results in air show that the coefficient of recombination α varies as a function of t', t, and n_0 . The ions must therefore be non-uniformly distributed initially, and in pairs along the X-ray paths. As t', t, and n_0 increase, α approaches a constant value between 0.8 and 0.9×10^{-6} . Diffusion probably plays an important part in the initial stages of the mechanism of recombination. In argon α is nearly constant, due to rapid random distribution, at a value about half that for argon-oxygen mixtures. Values indicate that α is less for electrons and positive ions than for positive and negative ions, in agreement with the work of Kenty (cf. A., 1928, 1300). N. M. BLIGH.

Factors affecting the nature of ions in air. H. A. ERIKSON (Physical Rev., 1929, [ii], 34, 635— 643; cf. this vol., 483).—It was found that drying agents such as calcium chloride and phosphorus pentoxide were insufficient, and that cooling by liquid air is essential. In air thus dried the initial positive ion transforms into the final ion very slowly, if at all. The ionising process itself gives rise to impurities affecting the ions, confirming Tyndall and others (cf. this vol., 6). The effect of water is modified by the presence of the impurities due to ionisation.

N. M. BLIGH.

Relative probabilities of the ionisation of Kand L electrons of equal ionisation energy. G. L. PEARSON (Proc. Nat. Acad. Sci., 1929, 15, 658-664). -The intensities of X-ray lines were measured, using an X-ray tube on the target of which was a compound of two elements such that the values of the excitation voltage for the K series of one and the L series of the other were as nearly alike as possible. Lead selenide was used. Data were obtained on ratios of the values, for various sub-series, of the product of two factors, the probability that a cathode ray will produce an ionisation of the appropriate type, and the probability that the subsequent reorganisation will result in radiation of some line of the sub-series. Between two sub-series such as L_{21} and L_{22} , differing only in the inner quantum number, this product was proportional to the latter. A difference in azimuthal quantum number only between the K and L_{21} was found to have no appreciable effect; a difference in radial quantum number between K and L_{11} had a great effect. N. M. BLIGH.

Occurrence of ions in the decomposition of ozone and the ionisation of the stratosphere. H. HELLMANN (Ann. Physik, 1929, [v], 2, 707—731).— No ionisation is observed in the thermal decomposition of ozone, although the apparatus used is capable of detecting one ion pair for every 5×10^{15} molecules decomposing. The electrical conductivity of the upper layers of the atmosphere is therefore unlikely to be related to the presence of ozone.

R. A. MORTON.

Ultra-short waves and radiation from free electrons. D. S. KOTHARI and D. V. GOGATI (Indian J. Physics, 1929, 4, 175-178).—Theoretical.

W. E. DOWNEY.

Longitudinal distribution of photo-electrons. A. CARRELLI (Atti R. Accad. Lincei, 1929, [vi], 9, 1102-1110).—See this vol., 1121.

Hydrogen and the photo-electric emission from potassium. N. CAMPBELL (Physikal. Z., 1929, 30, 537-538; cf. Fleischer, this vol., 736).—Experiments as yet incomplete are consistent with the view that sensitisation is closely connected with two different processes. One is a gross change in the surface structure manifested by a change in colour and possibly arising from volatilisation of potassium. The other is in all probability a change in the atomic structure of the surface due to the formation (or possibly the removal) of monatomic gas layers. R. A. MORTON.

Electron scattering in atomic and molecular hydrogen. G. P. HARNWELL (Physical Rev., 1929; [ii], 34, 661-672; cf. this vol., 619).-By using an apparatus similar to that of Dymond (this vol., 368), electron scattering was investigated in hydrogen admitted from a discharge tube, containing more than 60% of atomic hydrogen. The electron energy spectrum was analysed into component peaks interpreted as due to elastic, inelastic, and ionising collisions. One inelastic loss at about 8 volts and several at about 12.5 volts were found. From the areas under the peaks the number of electrons scattered through a given angle was calculated and, plotted against scattering angle, gave similar results for atomic and molecular hydrogen, the former case agreeing well with the theoretical predictions of N. M. BLIGH. quantum mechanics.

Absorption coefficient for slow electrons in alkali metal vapours. R. B. BRODE (Physical Rev., 1929, [ii], 34, 673-678).—With the apparatus and method previously used for gases (A., 1925, ii, 617) the absorption coefficient for electrons was measured in the vapours of sodium, potassium, rubidium, and cæsium. The curves connecting absorption coefficient with electron velocity in each case increase monotonically from high to low velocity except in the regions of the critical potentials, where a sharp peak is superimposed on the monotonic rise, and in general resemble the curve deduced from wave mechanics for hydrogen. N. M. BLIGH.

Effective cross-section and molecular structure for the isosteric series: N_2 -(CH), and O_2 -[(NH),]-(CH₂), E. BRUCHE (Ann. Physik, 1929, [v], 2, 909-932).—The effective cross-section in cm.²/cm.³ for acetylene and ethylene has been determined for electron velocities from 0 to 7 volt! Acetylene shows a sharp maximum at 1.55-1.7 voltand an ill-defined maximum near 2.5 volt1. Ethylene exhibits a sharp maximum at 1.35 volt¹, a minimum about 2 volt¹, and a second broader maximum near 3 volt¹. The form of the effective cross-section curve depends on the electronic configuration in the isosteric series Ne, HF, H₂O, NH₃, CH₄, each of these molecules having a completed octet. The molecules N₂ and C₂H₂ are also isosteric, and the series O₂,(NH), [hypothetical], C.H. exhibits a similar relationship. Grimm's hydride displacement law is discussed in relation to the cross-section curves, and it is concluded that the results on the whole conform with expectations. The introduction of hydrogen (provided no dipole is formed) effects a simple magnification of the field, which is more pronounced when several hydrogen atoms occur, e.g., the field for acetylene is greater than for nitrogen, whilst the field for othylene is much greater than for oxygen. R. A. MORTON.

Conductivity of ions in crossed electric and magnetic fields. L. PACE (Physical Rev., 1929, [ii], 34, 763—771; ef. this vol., 619).—Theoretical. Collisions of ions with one another are shown to be without effect, the transverse current at right angles to the fields being the same as in absence of collisions. Collisions of free ions with neutral particles are investigated where the velocity of progression u is small compared with the speed v of thermal agitation. As the mean free path is increased the current parallel to the electric field increases to a maximum and then falls asymptotically to zero, the transverse current parallel to u rising from zero to a limiting value for infinite mean free path. Calculations of the Hall coefficient on the present theory, taking account of long free paths, show that the coefficient increases with increasing magnetic field. N. M. BLIGH.

Charges of mercury atoms in the canal-ray stream. W. JACOBI (Physikal. Z., 1929, 30, 568-575).-The stages of ionisation of the mercury atom have been studied by the simultaneous application of electric and magnetic fields to a mercury positive-ray stream (parabola method). In a hydrogen discharge containing a small quantity of mercury vapour, in addition to the hydrogen and Hg⁺ parabolas it is possible to record parabolas b, c, and d (a being the Hg⁺ parabola). The ratios $(e/m)_b$, $(e/m)_c$, $(e/m)_d$ are, respectively, equal to 7.9, 12, and 18.1 times $(e/m)_a$. These results are either due to the occurrence of multiply charged mercury atoms, Hg⁸⁺, Hg¹²⁺, and Hg¹⁸⁺ or to particles of smaller mass. Evidence is adduced which supports the hypothesis of multiple ionisation by definite stages rather than electron by electron. The results agree well with Stoner's scheme of electron distribution. R. A. MORTON.

Influence of surface layers on the electron emission from glowing metals. C. ZWIKKER (Physikal. Z., 1929, **30**, 578—580).—In Richardson's formula for the saturation current *i* in the emission of electrons from hot wires, $i=AT^{a}e^{-b/T}$, and the constants *A* and *b* depend on the surface condition of the metal. The relation between *A* and *b* for zirconium and hafnium wires covered superficially with various oxide layers follows the equation b= $c \log A+d$, *c* and *d* being constants. The change in *A* and *b* is probably due to gradual outgassing as the heating proceeds and adsorbed oxygen or nitrogen is set free. The line obtained by plotting log *A* against *b* for tungsten and platinum shows the same inclination as for zirconium and hafnium. This result is shown to follow from theoretical considerations.

R. A. MORTON.

Direct measurement of intensity distribution in molecular beams. J. B. TAYLOR (Z. Physik, 1929, 57, 242—248).—When an alkali-metal atom strikes a glowing tungsten wire, it parts with an electron and is re-emitted as a positive ion. By measuring the number of positive ions emitted from such a wire in various positions in the path of a molecular beam the number of alkali-metal atoms striking the wire per second can be determined, and hence the energy distribution in different parts of the beam deduced, with an accuracy of 1 in 10³.

J. W. SMITH. Electron emission and diffraction by a copper crystal. H. E. FARNSWORTH (Physical Rev., 1929, [ii], 34, 679—696; cf. A., 1928, 453).—A narrow beam of variable-speed electrons was incident normally on the face of a copper crystal, and measurements were made of the total secondary electron current under the

same conditions as the angular distribution of scattered electrons for bombarding potentials from 0 to 250 volts. The total secondary electron curve shows maxima at 3 and 10.5 volts and changes of slope at higher voltages. These correspond with intense electron beams issuing from the crystal, and to other beams normal to the crystal contributing to the total secondary current. The two types of diffraction beams found are discussed, and their respective refractive indices considered (cf. Davisson and Germer, A., 1928, 1173). The diffraction beams are composed entirely of full-speed electrons. Evidence of a selective angular distribution of emitted electrons, differing from that of the scattered electrons, was obtained. N. M. BLIGH.

Total radiation from nickel and cobalt. C. L. UTTERBACK (Physical Rev., 1929, [ii], 34, 785—790).— Using a platinum-tellurium thermocouple and a highsensitivity galvanometer at constant deflexion, measurements were made of the total radiation from nickel and cobalt for the range 630— 1600° and 672— 1590° Abs., respectively, measured by means of an optical pyrometer calibrated at the gold and palladium points, and by a platinum platinum-rhodium thermocouple. The value of n in the formula $E = cT^n$ is evaluated, and a logarithmic graph of energy against temperature is given. N. M. BLIGH.

Photo-ionisation of some alkali vapours. F. L. MOHLER and C. BOECKNER (Bur. Stand. J. Res., 1929, **3**, 303—314).—Relative measurements of photosensitivity as a function of wave-length have been made by the space-charge method, and absolute values at favourable wave-lengths measured by a direct method. The shape of the sensitivity curve for cæsium is similar to published results and is independent of pressure. The atomic absorption coefficient k is $2\cdot3 \times 10^{-19}$ at the principal series limit. The curve for rubidium is similar and the value of k at the limit is $1\cdot1 \times 10^{-19}$. For potassium the sensitivity is low at the limit 2856 Å, and rises rapidly from 2600 to 2200 Å. C. J. SMITHELLS.

Dissociation of nitrogen by electron impact. L. A. TURNER and E. W. SAMSON (Physical Rev., 1929, [ii], 34, 743—746; cf. Herzberg, A., 1928, 931). —Using Kondratjev's method (A., 1926, 989), the $2p^{2}3s^4P - 2p^23p^4P^0$ N I lines near 8200 Å. were produced by bombarding N₂ molecules with electrons having energies of 23 ± 1 volts or more. Variations of currents and pressures indicated that the rate of production of excited atoms depends on a single impact and not on successive double impacts. The possible emission of the lines following the recombination with electrons of N⁺ ions, shown by positive-ray experiments to be produced at this voltage, is discussed (cf. Kenty and Turner, this vol., 114). N. M. BLIGH.

Excitation potential of the negative bands of nitrogen. L. A. TURNER and E. W. SAMSON (Physical Rev., 1929, [ii], 34, 747—751).—The energy of the $0 \rightarrow 1$ negative band of nitrogen at 4278·1 Å. was found to be 19.0 volts, by comparison with the energy of excitation of neon lines. This gives 15.8 volts for the ionising potential of nitrogen and 8.4 volts for the heat of dissociation (cf. Birge, this vol., 7). Peculiar effects in the excitation of the 2s-2p lines of neon are discussed. N. M. BLIGH. Dependence of the photo-electric conductivity of red mercuric iodide on the temperature. L. PIATTI (Nuovo Cim., 1929, 6, 14—35; Chem. Zentr., 1929, i, 2513).—The change of photo-electric conductivity previously observed when a vessel of water is interposed between the source of light and the mercuric iodide cell is attributed to infra-red rays. The method is applicable to the determination of the temperature of transition into the yellow variety.

A. A. ELDRIDGE.

Ionisation potentials and conductivities of metals. B. B. RAY and D. P. R. CHAUDHURI (Nature, 1929, 124, 512—513).—For metals possessing the same crystal structure, the product of the electrical conductivity with the ionisation potential varies inversely as the atomic number. Magnesium, calcium, strontium, rhodium, and bismuth exhibit discrepancies. A. A. ELDRIDGE.

Absorption of ultra-violet light by organic substances. X. L. KWIECIŃSKI and L. MARCHLEW-SKI (Bull. Soc. chim., 1929, [iv], 45, 591-611; cf. this vol., 9).—Paraldehyde, metaldehyde, and aldehyde-ammonia show no selective absorption. Acetaldehyde and propaldehyde are characterised by absorption bands with maxima at 2780 and 2800 Å., respectively, and minima at 2260 and 2340 Å. Methylglyoxal shows considerable absorption in the ultraviolet with a maximum at 2640 and a minimum at 2260 Å. O. J. WALKER.

Absorption of ultra-violet light by benzene. L. KWIECIŃSKI and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1929, A, 255—263).—A re-investigation of the absorption spectrum of carefully purified benzene is described; the six bands had maxima at 2684, 2608, 2546, 2490, 2433, and 2390 Å. The absorption spectrum of benzene in various concentrations of alcohol has also been measured. A. I. VOGEL.

Structure of absorption-resonators of organic chromophors. I. Structure of absorptionresonators of halochromic complexes of quinones and quinhydrones. D. RADULESCU and F. BAR-BULESCU. II. Polarity of substituents as determining factor in displacement of bands. D. RADULESCU and A. GEORGESCU. III. Phenomena of halochromism in sulphonation. D. RADU-LESCU (Z. physikal. Chem., 1929, B, 5, 177-198, 301-303).-I. Absorption curves of naphthacene and its derivatives have been compared. Where the distribution of electrons characteristic of the unsubstituted hydrocarbon is retained (as in a halochromic complex compound of naphthacenediquinonc) the compound gives a spectrum very similar to that of the hydrocarbon, except for a displacement, the magnitude and direction of which depend on the polarity and strength of the substituent. Where the electronic skeleton is different (as in ketonic quinones and diquinones) the characteristic absorption spectrum of the hydrocarbon is not obtained. These observations are at variance with Pfeiffer's theory of local "absorption centres," but support the conception in which the resonator responsible for the characteristic selective absorption is assumed to be a complicated structure of linked valency electrons. Quinhydrones are complex compounds possessing the same absorption resonators

as the rest of the halochromic compounds of the corresponding quinones.

II. Alteration of the polarity of a substituent of a chromophor group displaces the characteristic absorption spectrum of the group and is unaccompanied by any appreciable distortion. By choosing a suitable chromophore group and graduating the polarity by the substitution of Cl, Me, OMe, etc. in the nucleus, it is found that the essential structure of the chromophore group remains unchanged. Increased negative polarity displaces the entire spectrum towards the red, sometimes by as much as 1000 Å. Conversely, the degree of displacement of a given spectrum affords a measure of the polarity of the substituent.

III. Preliminary. The transient colouring often observed during the sulphonation of hydrocarbons is due to the production of a complex compound. Spectroscopic observations show that the effect is quite general, but is especially marked with coloured hydrocarbons such as naphthacene and pyrene. Measurcments of the absorption bands of naphthacene and its intermediate product show that the latter has the characteristic spectrum of the hydrocarbon displaced toward the red. It therefore possesses the same resonator system. It is possible to recover the unchanged hydrocarbon quantitatively from the sulphuric acid. F. L. USHER.

Quantitative spectrographic studies in the ultra-violet. I. Hormones. W. GRAUBNER (Z. ges. exp. Med., 1928, 63, 527—551; Chem. Zentr., 1929, i, 2068).—Adrenaline, thyroxine, and the pituitary hormone give a specific band at 2800, 3250, and 2650—2670 Å., respectively. Thyroid extracts do not exhibit the thyroxine spectrum. Insulin preparations give a band at 2450—2850 Å., with a centre at 2750 Å. Ergotamine and ephedrine give absorption bands with heads at 3170 and 2570 Å., respectively. Combination of two hormones caused a shift of the absorption towards the red and disappearance of the characteristic bands.

A. A. ELDRIDGE.

Absorption of ultra-violet light by some hormones and allied substances. L. MARCHLEWSKI and B. SKARŻYŃSKI (Bull. Acad. Polonaise, 1929, **A**, 241—254).—Measurements of the absorption spectra of the following substances are described: *dl*-ephedrine hydrochloride in water (three bands with maxima at 2638, 2564, and 2508 Å.); *l*- and ψ -ephedrine hydrochloride in water (similar to the *dl*-compound); adrenaline hydrogen tartrate in water (one band, maximum at 2800 Å.); thyroxine in 0.01Nsodium hydroxide (broad band with maximum at 3110 Å.; cf. tyrosine, band with maximum at 2750 Å.); α -hydroxytyrosine in 0.1N-hydrochloric acid (one band, maximum at 2808 Å.). A. I. VOGEL.

Ultra-violet absorption of the carbonyl group. K. L. WOLF and W. HEROLD (Z. physikal. Chem., 1929, **B**, 5, 124—130).—The substances containing the carbonyl group the data for which were collected comprised acids, aldehydes, and ketones of the aliphatic, heterocyclic, and homocyclic series. The log k_{max} , values for the first ultra-violet absorption bands of these substances in various alcoholic solutions are discussed, and for the ketones a new series of values is

put forward. Experiments with propaldchyde are quoted which show that the aldehyde bands are normal. Any reaction between aldehyde and alcohol to form an acid can be followed optically. The formation of aldehyde hydrates and acetals can be followed by investigating the ultra-violet absorption.

A. J. MEE. Absorption spectrum of carbon disulphide in the near ultra-violet. E. D. WILSON (Astrophys. J., 1929, 69, 34-42).—The absorption spectrum of carbon disulphide vapour has been photographed under varied conditions favourable to the complete development of the band system between 2900 and 3800 A. The wave-lengths of about 650 lines have been measured and their intensities have been compared photometrically. Certain regularities in the band system are indicated and some of the lines have been L. S. THEOBALD. grouped into series.

Ultra-violet spectral absorption of lignin derivatives. E. HAGGLUND, F. W. KLINGSTEDT, and (in part) O. LUND (Svensk Kem. Tidskr., 1929, 41, 185-190).-By the action of alcohols and anhydrous hydrogen chloride on lignin from pine, birch, and beech woods various alkyl-lignins have been prepared (cf. Holmberg, B., 1926, 267) and their ultra-violet absorption spectra in alcoholic solution investigated. The absorption curves are all of the same type, consisting of a broad, continuous band, with minimum in each case about $\lambda = 2590$ Å., and a second band, not completely traced (x=about 2330 Å.), superimposed on a strong, continuous absorption. Comparison of these results with those of Herzog and Hillmer (this vol., 915) for coniferyl alcohol would seem to exclude a purely aliphatic character for the lignin unit which, the authors conclude, must contain at least one aromatic ring. The difference in the two sets of type-similar absorption curves depends on differences in the side chains attached to the ring system. The ultra-violet absorption spectrum of ligninsulphonic acid (from pine), which approximates in type to that of the isoamyl-lignins from birch and beech, shows that it contains the same unsaturated groups responsible for the selective absorption of the latter.

J. W. BAKER.

CH-band at 3143 Å. and a new NH-band at 2530 Å. T. HORI (Nature, 1929, 124, 480).—The CH-band at 3143 Å. appears to belong to a ${}^{2}\Sigma \longrightarrow {}^{2}\Pi$ system ; it has a common final level 2II with the bands at 3900 and 4300 Å. The nuclear distance in the $^{2\Sigma}$ state is $r_{0}'=1.12\times10^{-8}$ cm. A new simple NH-band at 2530 Å. of comparatively small intensity has band at 2500 A. of comparatively small intensity has been observed; the corresponding transition is of $1\Sigma \rightarrow 1\Pi$ type. The nuclear separations of the molecule in the initial and final states are $r_0'=1.03 \times 10^{-8}$ cm. and $r_0''=1.06 \times 10^{-8}$ cm., respectively.

A. A. ELDRIDGE.

Ultra-violet dispersion frequencies, measurable in air, of the alkali halides. R. HILSOH and R. W. POHL (Z. Physik, 1929, 57, 145-153).--A method for distilling substances on to surfaces as thin films is described. Curves are given for absorption in the region 180-250 mµ for alkali bromides and iodides and for reflexion from potassium iodide. If absorption is due to the removal of an electron from

the halogen anion and its return to the alkali cation, the lowest energy level should equal Q+E-J (Q is the "Coulomb grating energy," E the halogen electron affinity, and J the ionisation potential of the alkali metal). This relation leads to frequencies near those observed. A trace of iodide in the chloride crystal causes selective absorption at frequencies given by the above relation, except that Q is the chloride grating energy, whilst E and J refer to the iodide. A. B. D. CASSIE.

Influence of X-rays on the absorption spectra of alkali halide phosphors. (FRL.) A. ARSENJEWA (Z. Physik, 1929, 57, 163-172).-The intensities of the sharply-defined absorption bands of alkali halide phosphors containing lead as exciting ion are found to be diminished by exposure to X-rays, whereas in the case of phosphors containing thallium the intensities are increased. With potassium chloride phosphor containing lead, the maximum of the extreme shortwave excitation band is shifted slightly towards the short-wave side. Evidence has also been obtained of a doubling of the absorption bands in this case. In all cases irradiation by X-rays also develops a continuous absorption underlying the normal absorption bands, this continuum increasing in intensity towards the short-wave side. This abnormal absorption is not permanent, but disappears, recovery being slowest in the case of sodium chloride phosphors. The con-clusion is also reached that all the above-described effects of X-rays on the absorption spectra of phosphors are independent of whether the phosphors contain "foreign colouring of the first kind" or whether this foreign colouring is removed before the J. W. SMITH. investigation.

Cathodic luminescence spectra of rare earths extracted from samarskite, ishikawaite, and monazite of Ishikawa, Iwaki Province. Y. UZUMASA (Japanese J. Chem., 1929, 4, 7-9).

C. W. GIBBY.

Excitation of fluorescence in benzene at -183° by monochromatic light. J. STARKIEWICZ (Bull. Acad. Polonaise, 1929, A, 287-294; cf. Pringsheim and Reimann, A., 1925, ii, 181; Pringsheim, A., 1927, 186).—The fluorescence spectra excited in beuzene at -183° by the almost monochromatic radiation from electrodes of zinc (λ =2502 and 2558 Å.) and of cadmium (λ =2265 and 2313 Å.) are in all respects similar to each other and to that obtained in similar circumstances by Reimann with a mercury lamp. It is therefore concluded that this independence of fluorescence on wave-length cannot be due, as in the case of the vapour, to collisions, but, as supposed by Pringsheim, to some intramolecular mechanism.

C. A. SILBERRAD.

Thermoluminescence excited by X-rays. Further experiments on synthetically-prepared materials. F. G. WICK and (MISS) M. K. SLATTERY (Physical Rev., 1928, [ii], 31, 306).-Exposure of the sulphates of cadmium, calcium, sodium, and zinc containing a small amount of manganese to X-rays produces two types of thermoluminescence, one which appears quickly and is of short duration, and the other which appears more slowly and lasts longer. Both types are preserved at the temperature of liquid air, but are destroyed by exposure to ultra-violet light of a definite frequency. L. S. THEOBALD.

Oxidation of carbon monoxide. M. PRETTRE and P. LAFFITTE (Compt. rend., 1929, 189, 177— 179).—An apparatus for studying quantitatively and continuously the phenomena which occur during the period of violet-red luminosity below the ignition temperature of mixtures of dry air and carbon monoxide (20—43.5%) has been devised. The luminosity corresponds with slow oxidation of the monoxide (this vol., 771), and the fact that it disappears before oxidation is complete is shown by the ignition of the remaining mixture when the pressure is reduced to 8 mm. of mercury. On the other hand, after an interval of 10 min., reduction of pressure will not effect combustion and the luminosity reappears at a temperature within 10—20° of the ignition point.

J. GRANT.

Phosphorescent flame of arsenic. H. J. EMELÉUS (J.C.S., 1929, 1846—1848; cf. A., 1927, 497).—The spectrum of the glow produced by heating arsenic in a current of air at temperatures between 250° and 360° consists of a continuous band between 4300 and 4900 Å., similar to that of the ordinary flame. The glow is inhibited by the vapours of benzene, ethyl alcohol, hexane, acetone, chloroform, amyl acetate, methyl alcohol, and chlorobenzene, but reappears on removal of the organic vapour or on raising the temperature by 12—30°. C. W. GIBBY.

Light emission from phosphorescent flames of ether, acetaldehyde, propaldehyde, and hexane. H. J. EMELÉUS (J.C.S., 1929, 1733—1739; cf. A., 1927, 7).—The spectra of phosphorescent flames of acetaldehyde, propaldehyde, and hexane all give the same series of bands degraded towards the red between 5000 and 3360 Å. In each case the combustion of the substance was incomplete. Acetaldehyde was found in the products of combustion of ether, but not of propaldehyde or hexane. C. W. GIBBY.

Infra-red absorption spectrum of hydrogen sulphide. A. H. ROLLEFSON (Physical Rev., 1929, [ii], 34, 604-610).—Using a prism-grating spectrometer a narrow intense absorption band was observed at 4.2 μ , but could not be resolved. The 5.6 μ band observed by Coblentz was not found and was probably due to an impurity. Thirty-four lines of the band in the region of 8.0 μ were observed and tabulated. N. M. BLIGH.

Infra-red absorption spectra of organic nitrates. E. K. PLYLER and P. J. STEELE (Physical Rev., 1929, [ii], 34, 599-603).—Methyl, ethyl, propyl, and butyl nitrates were studied in the region $1\cdot0$ ---7.5 μ . Two absorption bands at $1\cdot4$ and $2\cdot96 \mu$ are attributed either to an O·H linking or to water. All other bands are attributed to the carbon-hydrogen linking, and as an additional CH₂ group is introduced the intensity of all bands decreases and a shift of from 0.01 to 0.06 μ to longer wave-length occurs. No characteristic absorption spectra of the NO₃ group were found. An intense absorption band was observed at 6.7 μ .

N. M. BLIGH.

Near infra-red absorption spectra of some halogen derivatives of ethane. B. J. SPENCE and M. A. EASLEY (Physical Rev., 1929, [ii], 34, 730– 742; cf. A., 1928, 1170).—Infra-red absorption spectra $(0.8-3 \mu)$ of 14 halogen derivatives of ethane were studied. A large number of new absorption bands were discovered, and full data are tabulated. Bands were not observed for compounds containing no hydrogen. The other spectra showed a close similarity, particularly when the halogens were interchanged. N. M. BLIGH.

Intensity measurements in the Raman effect and the distribution law of Maxwell and Boltzmann. L. S. ORNSTEIN and J. REKVELD (Physical Rev., 1929, [ii], 34, 720—725).—By considerations similar to Einstein's treatment of Planck's law a relation is deduced for the ratio of intensities between Stokes and anti-Stokes lines in the Raman effect, and is shown to give good agreement with experimental results on carbon tetrachloride. A precision measurement of the constant h/k can be developed.

N. M. BLIGH.

Vibrational selection principles in the Raman effect. J. H. VAN VLECK (Proc. Nat. Acad. Sci., 1929, 15, 754-764; cf. Manneback, this vol., 866).— Theoretical. A proof is given of the proposition of the usual absence of all displacements in the vibrational quantum number except the fundamental.

A. J. MEE.

Raman spectra of polyatomic gases. R. G. DICKINSON, R. T. DILLON, and F. RASETTI (Physical Rev., 1929, [ii], 34, 582-589; cf. Rasetti, this vol., 241, 627, 975; Wood, ibid., 627) .- Raman spectra of gaseous carbon dioxide, nitrous oxide, ammonia, methane, and ethylene were photographed using the mercury line a 2536 Å. for excitation. Vibrational transitions were observed for each gas, and rotational transitions for ammonia and methane. Values are listed for the frequency shifts due to vibrational transitions. Raman spectra for liquid ammonia were photographed, and gave the frequency shifts 3298.4 and 3214.5. For gaseous ammonia, pure rotational transitions gave the value $I_0 = 2.79 \times 10^{-40}$, and for methane the positive and negative branches of the 3022.1 band gave the value $I_0 = 5.17 \times 10^{-40}$ for the moment of inertia. The relations between these data and infra-red absorption data are discussed.

N. M. BLIGH.

Raman effect in liquids. A. S. GANESAN and S. VENKATESWARAN (Indian J. Physics, 1929, 4, 195-280).—Results for a number of representative compounds are given. The shifts below are given in wave numbers per cm. All the paraffins show a prominent band corresponding with shifts of 2850—2960, and resolved into five components; the relation of the constant of spacing, about 27, to the rotational frequency of the molecule is discussed. Carbon disulphide shows no correspondence between molecular frequencies from Raman and infra-red absorption measurements. Chloroform and bromoform illustrate the influence, among the halogen derivatives of methane, of the mass of the substituents on the positions of the Raman lines. For the alcohols, the structure of the band shifted about 2960, its development up the series, and the influence of isomerides are discussed. The fatty acids show a

general continuous spectrum, and glycerol a prominent one, the origin of which is discussed. A strong line is characteristic of the carbonyl groups and of the nitrocompounds, shifted by 1700 and 1347, respectively. Characteristic differences for aliphatic and aromatic compounds between 3 and 10 μ are pointed out. The Raman spectra of the xylenes illustrate the influence of substitution. The cases of ethyl ether and anisole are considered. cycloHexane illustrates the lines of open-chain and cyclic compounds; the aliphatic 2853-2935 band and the 800 band are very prominent. Pyridine and benzene lines are compared; in the former the additional line 1027 is the most prominent; corresponding lines in the two liquids are polarised to nearly the same extent, indicating molecular structural similarity. Quinoline gives a prominent fluorescence spectrum, the Raman spectrum being similar to that of naphthalene with 1370 most prominent in each. Sulphuric acid gives a continuous spectrum in addition to the lines; hydrochloric acid shows only water bands sharpening with the concentration; nitric acid shows a number of prominent lines in addition to the water band, which is resolved into three sharp components as in ice. Potassium and sodium carbonate solutions give a prominent line at 1064, identified with the inactive frequency of the CO_3 ion. The 3μ band of water consists of a prominent component 2.9 and also 2.77 and 3.13μ ; the structure of the band in ice, in hydrated crystals, and in electrolytes, and the effect of temperature on the band, are discussed. The noncorrespondence of molecular frequencies from Raman lines and direct infra-red measurements is discussed and explained on the wave-mechanical treatment of dispersion. Raman lines for aliphatic compounds are generally more polarised than for aromatic, indicating a close analogy to the classical scattering. Full tabulations of Raman lines are given.

N. M. BLIGH. Raman spectra from acetone. R. T. DILLON and R. G. DICKINSON (Proc. Nat. Acad. Sci., 1929, 15, 699—702).—The measurements of Williams and Hollaender (this vol., 866) on the Raman spectra from acetone do not agree with this redetermination. Seven mercury lines are concerned in the production of Raman lines. A table showing the frequency differences of the modified lines is given. A. J. MEE.

Raman spectra of some organic and inorganic compounds. A. PETRIKALN and J. HOCHBERG (Z. physikal. Chem., 1929, B, 4, 299–311; cf. this vol., 741, 865).—Measurements of the Raman spectra of 15 further organic compounds confirm the usefulness of these spectra in elucidating the nature of the interatomic linkings in organic molecules. The results are summarised along with those given in previous papers. The Raman spectrum of stannic chloride consists of two narrow doublets and is quite different from that of carbon tetrachloride. The cyanide radical in a concentrated solution of potassium cyanide gives a single line of wave-length 4:80 μ as compared with 4:41–4:48 μ obtained with organic compounds containing the 'CN group. The oscillator in this case is the free cyanide ion. O. J. WALKER.

Relation between Raman lines and infra-red bands. C. P. SNOW (Phil. Mag., 1929, [vii], 8,

369-379).-The Langer-Dieke account (cf. this vol., 379, 490) of the relation between Raman lines and infra-red bands is discussed. For oxygen, nitrogen, and carbon monoxide a similar scheme to that of Dieke for hydrogen chloride must be used, and for the three gases the position of the central Raman line should not coincide with the electronic vibration frequency. There is experimental evidence of vibration-rotation bands of oxygen and nitrogen. Evidence in favour of absorption by oxygen was obtained with an infra-red vacuum spectrometer; the intensity of absorption for a metre path of oxygen has 5% as its upper limit. The Raman effect for carbon dioxide is in agreement with the Langer-Dieke account, and some suggestions are advanced on the transitions to be expected; the effect for hydrogen gives results not N. M. BLIGH. yet explained by the theory.

Raman spectra of calcite, aragonite, and aqueous solution of potassium carbonate. M. KIMURA and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 199—204).—Raman lines of calcite are given for light incident (i) perpendicular and (ii) parallel to the optic axis. The inactive frequency $\lambda = 9 \mu$ always appeared strongly. The frequency $\lambda = 11.4 \mu$ appeared strong in i, weak in ii. The external frequency $\lambda = 36 \mu$ always appeared almost as strong as $\lambda = 9 \mu$. Aragonite was illuminated along and perpendicular to the acute bisectrix of the axes, but no peculiarities were noted. The intensity of the inactive frequency and of the external frequency ($\lambda = 36 \mu$) suggests that the oxygen atoms determine the field in which the calcium ion moves. A. B. D. CASSIE.

Raman spectrum of gypsum. R. G. DICKINson and R. T. DILLON (Proc. Nat. Acad. Sci., 1929, 15, 695-699).—The change of frequency on scattering at gypsum was determined and compared with that for a solution of ammonium sulphate. There are eight different frequency shifts for gypsum. The two largest are probably due to water of crystallisation, whilst the smaller ones are due to the sulphate ion. The multiplicity of lines found from gypsum may be explained on Brester's theory of the multiplication of characteristic frequencies due to removal of symmetry. A. J. MEE.

Raman spectra of crystals. K. S. KRISHNAN (Indian J. Physics, 1929, 4, 131—140).—The Raman spectra of quartz, calcite, topaz, and selenite have been observed. Selenite shows lines corresponding with ice and two lines of somewhat longer wave-length than the prominent line shown by solutions of sulphates in water. W. E. DOWNEY.

Raman effect in crystals. C. SCHAEFER, F. MATOSSI, and H. ADERHOLD (Physikal. Z., 1929, 30, 581—585).—The following wave-lengths correspond with Raman lines observed with crystals : calcite $62\cdot1$, $35\cdot4$, $13\cdot95$ (weak), $9\cdot18$, $6\cdot9\mu$ (weak); sodium nitrate 105 (weak), $53\cdot65$, $13\cdot7$ (weak), $9\cdot3$, $7\cdot17\mu$; gypsum 24.5 (weak), $9\cdot9$, $8\cdot85\mu$ (weak). Nitric acid solution gave $7\cdot8$, $9\cdot53$, $13\cdot9$, and $14\cdot3$, the alleged 12μ line being absent. Dilute sulphuric acid (1:4) gives $9\cdot4$ (weak), $15\cdot15\mu$. Infra-red investigations on calcite indicate two series of vibrations, "outer" and "inner." For the former poor agreement with Raman lines is obtained, whilst for the latter the 9·1 μ line is optically inactive and a line at 11·38 μ is missing from the Raman spectrum. The 9·1 μ vibration is the least and the 11·38 μ vibration the most symmetrical. The Raman lines for the CO₃ and NO₃ groups exhibit a fairly close analogy. Infra-red data on gypsum indicate bands at 8·74 and 14·84 μ . Raman lines at 2·84 and 2·95 μ observed with gypsum arise from the water of crystallisation. The relationship between the infra-red bands for carbon disulphide and the Raman lines remains obscure. R. A. MORTON.

Raman effect from powdered crystals. A. C. MENZIES (Nature, 1929, **124**, 511—512).—Raman lines were obtained by reflexion from powdered potassium nitrate. A. A. ELDRIDGE.

Primary photo-electric current in antimony glance. K. H. VOIGT (Z. Physik, 1929, 57, 154– 162).—The photo-electric primary current with antimony sulphide has been investigated with respect to its change with time, with the intensity of the light, and with the accelerating voltage applied. The decrease in the primary current after shutting off the light is in agreement with the views of Gudden and Pohl (cf. A., 1921, ii, 145; 1923, ii, 718; 1925, ii, 343). J. W. SMITH.

Photo-electric behaviour of salts. J. WERNER (Z. Physik, 1929, 57, 192-226).-It has been shown that cadmium iodide, lead chloride, and potassium nitrate are all photo-sensitive, and that the photoelectric effects to be observed are due to the salts themselves and not to photochemical decomposition products. Using an accelerating potential of 40 volts, the photo-electric current decreases rapidly with time, but finally reaches a constant value. This is analogous to the behaviour of metals, and is due to the lowering of the concentration of free electrons in the surface, the latter being determined by the ratio of the velocity of the liberation of electrons to the velocity of their emission. On screening off the light or on application of a retarding potential a recovery is observed. The recovery process differs in the two cases. Recovery in the light under the influence of a retarding field is brought about by the decrease in the surface concentration of free electrons being neutralised by the further liberation of electrons; this can also be partly effected by lowering the accelerating potential. Recovery in the dark is brought about by the return of previously emitted electrons to the surface.

As in the case of metals, outgassing at first increases the photo-electric sensitivity of cadmium iodide, but a maximum is soon reached, after which a decrease is observed. Very complete outgassing stops the effect completely. Water vapour seems to exert a specific influence in this respect, since, after a preparation has been rendered completely insensitive by thorough outgassing, the admission of dry gas causes no change, whereas when a little moisture is introduced recovery is rapid. J. W. SMITH.

Dielectric constants of argon and neon. A. B. BRYAN (Physical Rev., 1929, [ii], **34**, 615–617; cf. A., 1928, 1076).—Using the heterodyne beat method, the values found relative to 1.000589 for air were 1.000574 and 1.000148 for argon and neon, respectively, at N.T.P. (cf. Braunmühl's value for argon 1.000571; A., 1927, 294). N. M. BLIGH.

Dipole moment of hydrocyanic acid and of some nitriles. O. WERNER (Z. physikal. Chem., 1929, B, 4, 371-392).—The dipole moments of hydrocyanic acid, aceto-, propio-, butyro-, and benzo-nitrile have been determined by measuring the dielectric constants of dilute solutions of these substances in benzene. An improved resonance method is described which makes use of a piezoelectric quartz crystal for maintaining a constant frequency. The dipole moments of the nitriles in the aliphatic series increase with the length of the carbon chain. The dipole in these substances extends more over the whole molecule, whereas in the alcohols and amines the dipole is localised at the strongly deformed OH and NH, groups, respectively. It is calculated that the dipole moment would reach a limiting value in the nitrile series at the member C_6H_{13} CN. Hydrocyanic acid in its dielectric properties fits in regularly as the first member of the series and therefore has the nitrile structure. The dielectric constant and density of solid hydrogen cyanide have been redetermined (ε^{-40} = $3.4\pm0.2, d^{-40}=0.925\pm0.005$). O. J. WALKER.

Range of validity of the method of dilute solutions for the determination of dipole moments. O. WERNER (Z. physikal. Chem., 1929, B, 4, 312-320).—The importance of the three terms which go to make up the total polarisation of a molecule, as determined by the method of dilute solutions, is discussed. The polarisation due to the deformation of the atoms cannot be determined with certainty and, in the case of heteropolar substances with large molecular volume, can no longer be considered as a small correction factor to be added to the orientation polarisation of the whole molecule. Measurements of the dielectric constants of solutions of tetraisoamylammonium picrate in. benzene show that that substance is dissociated even in this solvent. The dilute solution method is therefore not applicable in such a case for determining dipole moment. O. J. WALKER.

Temperature variation of the dipole moment. O. WERNER (Z. physikal. Chem., 1929, B, 4, 393-400).-The distinction between rigid and non-rigid (flexible) dipoles is discussed (cf. Hojendahl, "Studies of Dipole Moment," 1928), and it is suggested that the two types of dipole may be distinguished by studying the temperature dependence of the dipole moment. A variation of the moment with the temperature would indicate the presence of an equilibrium, i.e., of a flexible dipole. This is illustrated by measurements of the dipole moment of benzonitrile (rigid dipole) and of quinol diethyl ether (flexible dipole) in dilute benzene solution at 20°, 40°, and 60°. The moment of benzonitrile is constant at the three temperatures, whereas that of the quinol ether increases by 16% from 20° to 60° . The application of the above view to the elucidation of the structure of pentaerythritol is indicated. O. J. WALKER,

Electric moments of aromatic *p*-diamines. A. WEISSBERGER and R. SANGEWALD (Z. physikal. Chem., 1929, B, 5, 237-240; cf. Williams, A. 1928, 1180).—The dipole moments of tetramethyl-pphenylenediamine and tetramethylbenzidine have been determined in N-benzene solution and found to be $1\cdot23\times10^{-18}$ and $1\cdot25\times10^{-18}$ e.s.u., respectively. These values support the general observation that corresponding disubstitution products of these types have similar dipole moments. The results further indicate that the figure given by Williams for the dipole moment of p-phenylenediamine is too low, and cannot therefore be used in favour of a "folded" formula for benzidine. F. L. USHER.

Influence of solvents and other factors on the rotation and rotation-dispersion of optically active compounds. XXVII. Derivatives of lactic acid. T. S. PATTERSON and A. LAWSON (J.C.S., 1929, 2042—2051).—The rotations of a number of esters of lactic acid have been determined in light of six different wave-lengths at temperatures from 0° to 140°. The results show that the lactic acid formerly described as *d*-lactic acid should be called *l*-lactic acid. The general behaviour of the lactates seems to be similar to that of the tartrates.

C. W. HART-JONES. Influence of position isomerism on specific properties. N. SCHOORL (Rec. trav. chim., 1929, 48, 935–937).—The molecular refractions (Gladstone-Dale; Lorentz-Lorenz), molecular coefficients of refraction (Eisenlohr, A., 1920, ii, 717), and parachors of o-, m. p. 29·3°, d_{1}^{20} 1·0465, n_{20}^{20} 1·5453, m-, m. p. 8°, d_{1}^{20} 1·0336, n_{20}^{20} 1·5398, and p-cresols, m. p. 33·6°, d_{1}^{20} 1·0341, n_{20}^{20} 1·5395, are calculated. The values for the m- and p-derivatives are in closer agreement in all cases, and the largest difference for the o-compound is for the parachor (o). H. BURTON.

Valency. XIII. Molecular structure of the quadrivalent derivatives of tellurium. T. M. LOWRY and F. L. GILBERT (J.C.S., 1929, 2076-2091). -The properties of the quadrivalent derivatives of tellurium are discussed in the light of the structure recently assigned to the β -compounds by Drew (this vol., 546). Drew's conclusion that the conversion of the α - into the β -dihalides involves the wandering of a methyl group from one tellurium atom to another is verified, but the contrast between these salts is not sufficient to class the β -salts as necessarily complex and the α -salts as always monomeric. There is strong a priori evidence for the view that the solid phase of the a-compounds may have a similar structure to that assigned by Drew to the β -compounds. According to this view, the solid may be a complex salt $[TcMe_3]^+[TeMeI_4]^-$ or an aggregate of the two components $TcMc_3I$, $TeMeI_3$. In the case of the complex salt all the atoms are covalently linked to tellurium and may be expected to contribute to the colour of the ion, but in the case of the double salt, one of the iodine atoms should be colourless as in TeMeI₃. The existence of a labile red and a stable purple solid form of the bromotri-iodide (Drew) TeMe₃Br,TeMeI₃ or [TeMe₃]+[TeMeBrI₃]- could be explained by formulating the red crystals as the double salt and the purple crystals as the complex salt. The existence of an orange high-temperature and a purple low-temperature form of cyclotelluripentane di-iodide (Morgan and Burgess, A., 1928, 435) is

similarly explained. The absorption spectra of many of the β -salts have been examined, and the molecular extinction coefficients determined from 2000 to 5000 Å. The conductivities of the β -methyl and -ethyl bases have been determined in aqueous solution, and those of various salts in the fused state and in non-aqueous solvents. The solubilities of α -dimethyltelluronium di-iodide in various organic solvents at 25° are given. The parachor of diphenyl telluride gives a value of 77.4 units per atom of tellurium. The values determined from the α - and β -dihalides of the methyl and ethyl series are considerably less.

C. W. HART-JONES.

Theory of the valency octet in the "torular" atom model. I—VII. D. RĂDULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 263—279, 280—291, 292—305, 306—311, 312—322, 323—325, 326—332; Chem. Zentr., 1929, i, 1783—1784).—Theoretical.

A. A. ELDRIDGE.

Para- and ortho-hydrogen. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, **B**, 5, 292).—An explanatory note regarding a passage in an earlier paper (cf. this vol., 982). F. L. USHER.

Homogeneity of water. K. F. BONHOEFFER and P. HARTECK (Z. physikal. Chem., 1929, B, 5, 293-296). -From consideration of the various terms in Nernst's expression for vapour pressure it is shown that the ortho and para modifications of a liquid should have different vapour pressures; hence fractional distillation, sublimation, or condensation should lead to a change in the proportion of the constituents and to the possibility of detecting a difference in their vapour pressures. Theoretical considerations, supported by some preliminary fractionation experiments with water, made it evident that fractions with different vapour pressures could not be expected with the usual experimental arrangement owing to the high velocity with which equilibrium between the ortho and para components is established. Single fractionations were therefore carried out with conductivity water at a low temperature as rapidly as possible and the vapour pressures of the distillate and residue measured quickly and accurately. Even under these conditions no difference could be detected. The negative result is attributed entirely to the high velocity of transformation of one modification into the other.

F. L. USHER.

General principles of oxidation-reduction reactions and of chemical combinations. II, III. B. JIRGENSONS (Z. Elektrochem., 1929, 35, 473-477, 477-483; cf. this vol., 896).—A discussion of the application of the electronic theory of valency to inorganic oxidation-reduction reactions and to the structure of various organic compounds.

H. T. S. BRITTON.

Numerical approximations neglected in both chemistry and physics. R. PANEBIANCO (Schola et Vita, 1929, 4, 163—172).—The errors introduced into chemical and physical data by the neglect or the incorrect application of the theory of approximations are pointed out and discussed with illustrative examples. L. S. THEOBALD.

Determination of the configuration of stereoisomeric ethylene derivatives. K. VON AUWERS and L. HARRES (Z. physikal. Chem., 1929, 143, 1—20). —The relationships between the b. p., densities, refractive indices, and specific elevations of the esters of stereoisomeric substituted acrylic acids correspond in general with those between o- and p-benzene derivatives of analogous structure, in accordance with Langseth's assumption. It is therefore legitimate in these cases to reach conclusions regarding configuration. Numerous exceptions, however, exist; the rule is not valid for the comparison of the esters of maleic and fumaric acids with those of o- and terephthalic acids, neither can the configuration of the oximes be deduced by comparison of the physical constants with those of phenols. H. F. GILLBE.

Molecular structure of triatomic gases. P. N. GHOSH and P. C. MAHANTI (Physikal. Z., 1929, 30, 531-537).-Triatomic molecules may possess a symmetrical linear structure, an unsymmetrical linear form, or a structure of the form of an isosceles triangle. From data on the dielectric constant and the refractivity of carbon dioxide $(\varepsilon - 1) \times 10^{-7}$ is equal to $(n_{\infty}^2 - 1) \times 10^{-7}$, indicating a symmetrical linear structure. The analysis of infra-red spectra and the Raman effect supports this conclusion. For sulphur dioxide $\varepsilon > n_z^2$, indicating an unsymmetrical structure. The dipole moment is large, so that the triangular model is more probable than the unsymmetrical linear form, a conclusion supported by the infra-red data. For carbon disulphide $\varepsilon = n_{\infty}^2$, indicating that the linear structure shown by carbon dioxide is reproduced in conformity with the spectroscopic data. For nitrogen peroxide $\varepsilon > n_{\infty}^2$ and the unsymmetrical molecule is more likely to exhibit the triangular than the linear form. R. A. MORTON.

Molecular energy and structure. G. BECK (Z. anorg. Chem., 1929, 182, 332-342).—Various regularities in the properties of molecules are derived on the assumption that the electrons in a molecule in the solid state comport themselves as a quasi-ideal gas. H. F. GILLEE.

Properties of salt-like compounds and atomic structure. A. HANTZSCH and H. CARLSOHN (Z. Krist., 1929, 69, 556; Chem. Zentr., 1929, i, 1889).— Polemical (cf. Fajans, A., 1928, 1170).

A. A. ELDRIDGE.

[Properties of salt-like compounds and atomic structure.] K. FAJANS (Z. Krist., 1929, 69, 557; Chem. Zentr., 1929, i, 1889—1890).—A reply to Hantzsch and Carlsohn (preceding abstract). A. A. ELDRIDGE.

Shell charge and proton migration. E. WI-BERG (Z. physikal. Chem., 1929, 143, 97—118).— Theoretical. It is assumed that when a proton is detached from one central atom to combine with another it moves from the atom with the greater effective repelling force, as measured by the charge contributed by the outer electron shell. General definitions of acidity and basicity are given, and the acidic or basic properties of various atomic groupings are discussed and explained on the assumption of proton migration in the direction indicated by this rule. Different stabilities are predicted for ammonium and oxonium compounds, and the hydrolysis of certain

sodium compounds, e.g., sodamide and sodium methide, is explained. F. L. USHER.

Evaluation and interpretation of parachors. S. A. MUMFORD and J. W. C. PHILLIPS (J.C.S., 1929, 2112-2133).—The mean CH₂ parachor increment adopted by Sugden (cf. A., 1924, ii, 662) is too small. New values calculated for the various atomic and structural constants have been obtained by the aid of a corrected increment, and lead to an improvement in the agreement between observed and calculated values, especially in the case of compounds of high mol. wt. They also afford a rational interpretation of parachor variations on the basis of intramolecular strain. The interatomic stresses in substituted ring systems, in branched-chain derivatives, and in compounds containing accumulated negative groups are considered. The departure of the parachor from additivity in such compounds is accounted for by the introduction of strain constants, the value of which is shown to give a measure of the alteration in the effective size of the central atom of the group. The parachors of hydroxycompounds and amines are brought into line with those of non-associated compounds by assuming the effective volume of the hydrogen atom to decrease with increasing electron affinity of the atom to which it is attached. By assigning a higher value to halogen ions than to bound halogen atoms, the apparent parachor anomaly of fused salts (Sugden and Wilkins, this vol., 983) is overcome. A method for estimating such ionic parachors is indicated. The conclusions of Sugden and co-workers with respect to different types of interatomic linkings are not invalidated.

C. W. HART-JONES.

Determination of molecular forces from the viscosity of a gas. H. R. HASSE and W. R. COOK (Proc. Roy. Soc., 1929, A, 125, 196-221; cf. A., 1927, 616).-The law of variation of viscosity of a gas with temperature has been determined on the basis of Lennard-Jones' molecular model (A., 1925, ii, 91), and an equation is derived for the special case where the mutual actions of the molecules are represented by repulsive and attractive forces of the types λr^{-9} and μr^{-5} , respectively. The calculated values for argon, hydrogen, nitrogen, carbon dioxide, air, and mercury vapour are in fair agreement with experiment over a limited range of temperature, but no agreement is found in the cases of helium and neon. The values of the force constants λ and μ are calculated and compared with those deduced from the equation of state, using the same molecular model; excellent agreement is obtained in the values of λ , but those of μ show a divergence. It is possible that the value of the index L. L. BIRCUMSHAW. m is incorrect.

Dimensions of diatomic molecules. J. K. SYRKIN (Z. physikal. Chem., 1929, B, 5, 156— 159).—Mathematical. Diatomic homopolar molecules are assumed to be rigid quadrupoles. Their moments can be calculated from the critical constants. From the size of the moment, the dimensions of the quadrupole can be obtained. Results are given for a number of diatomic gases, which are in good agreement with the nuclear distances obtained by a study of spectra. A. J. MEE. X-Ray diffraction by amorphous solids. P. KRISHNAMURTI (Indian J. Physics, 1929, 4, 99– 108).—The changes in the X-ray diffraction maxima of ordinary rosin, shellac, and a synthetic resin of composition $(C_7H_6)_n$ have been observed over the temperature range 28—120°. For shellac and the synthetic resin the contraction of the halo is greatest between 28° and 45°, whilst for rosin the maximum changes take place at about 65°.

W. E. DOWNEY.

Ionisation spectrometer for long-wave X-rays. H. KULENKAMPFF and B. WOERNLE (Physikal. Z., 1929, **30**, 551—554).—A preliminary account of a new instrument. R. A. MORTON.

Effect of X-rays on certain optical properties of liquids and glass. F. ALLISON (Physical Rev., 1928, [ii], **31**, 306).—In sucrose and tartaric acid solutions, X-rays increase the induced right-handed rotation approximately in proportion to the concentration. X-Rays induce in glass in a magnetic field a small rotation opposite to the Faraday rotation. L. S. THEOBALD.

Influence of crystal habit on the Debye-Scherrer diagram. J. BOHM and F. GANTER (Z. Krist., 1928, 69, 17-25; Chem. Zentr., 1929, i, 2013).

Isomorphism and homology. P. C. RAY (Nature, 1929, 124, 480–481).—Ammonium and potassium beryllium fluorides are complex salts having the bivalent anion BeF₄, although partly further dissociated. Double salts, X_2BeF_4 , YSO_4 , $6H_2O$ (X=K or NH₄, Y=Ni, Co, or Zu; X=K, Y=Cu; X=NH₄, Y=Fe, Mn, Mg, or Cd), have been prepared. These salts are isomorphous with the double sulphates and fluoberyllates. A. A. ELDRIDGE.

Favourable direction of growth of some metal crystals. S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 223—226).—The directions of growth of crystals of aluminium, lead, zinc, cadmium, and bismuth have been investigated, when crystallisation was made to take place in one direction by drawing up a wire from the molten metal. Aluminium and lead generally grew in a direction parallel to the (100) axis of their face-centred cubic crystals, and the other three metals nearly perpendicular to the principal axis of their hexagonal crystals. The most favourable direction is closely connected with the form of the crystal lattice. C. W. GIBBY.

Examination of ice crystals by X-rays. U. YOSHIDA and S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 203—207).—Ice formed on the surface of still water, in ice columns in the ground, and in icicles has been examined by means of X-rays. The direction of growth is in each case parallel to the basal plane of the hexagonal ice crystal. No such regularity is found in ice produced by sudden cooling.

C. W. GIBBY.

Method of producing long single crystals of metal. Factors influencing crystal orientation and perfection. A. GOETZ and M. F. HASLER (Proc. Nat. Acad. Sci., 1929, 15, 646-656).—General methods of producing large crystals are discussed. A two-stage method is described for the production of crystals of any desired length with a constancy of diameter to less than 2%; the progressive crystallisation of molten metal (bismuth) in a glass or quartz tube is followed by the remelting of the metal in the tube and starting a new crystallisation by drawing out the tube and metal together by means of a mechanical device effecting and controlling the speed of introduction of the tube into a furnace and its withdrawal. The zone of crystallisation is located and the effects of a strong magnetic field and the temperature gradient on the orientation were studied. Variation of gradient and of strain applied to the crystal influenced the orientation. N. M. BLIGH.

Theory of recrystallisation of pure metals. U. DEHLINGER (Ann. Physik, 1929, [v], 2, 749—793).— The recrystallisation temperature is found on the basis of experiment to be best defined as that temperature at which the velocity of recrystallisation undergoes a sudden change. Recrystallisation involves at least two successive processes. One is a loosening of inner forces (Verhakungen) which is not detectable by X-ray analysis, but nevertheless fixes the recrystallisation temperature and the time factors. The other is the recovery or grain-formation as a result of inner elastic forces persisting in the deformed state. An extended theoretical discussion is given. R. A. MORTON.

Morphological and structural relationships of meteoric iron in relation to its evolution. J. LEONHARDT (Neues Jahrb. Min., 1928, 58, A, 153– 212; Chem. Zentr., 1929, i, 1915–1916).—An X-ray, microscopical, and goniometric study shows that the structure of meteoric iron is affected by secondary processes of growth and metamorphosis.

A. A. ELDRIDGE.

X-Ray study of iron-nitrogen compounds. A. OSAWA and S. IWAIZUMI (Z. Krist., 1928, 69, 26– 34; Chem. Zentr., 1929, i, 2012).—In the nitride Fe_4N , cubic, a 3.86 Å., $d_{calc.} 6.57$, the iron atoms form a face-centred lattice with one nitrogen atom in the unit cell. In the nitride Fe_2N , hexagonal, a 2.743 Å., c: a = 1.59, $d_{calc.} 5.02$, the iron atoms form a closepacked hexagonal lattice with one nitrogen atom in the unit cell. A. A. ELDRIDGE.

Structural investigation of Heusler's alloy. S. VALENTINER and G. BECKER (Z. Physik, 1929, 57, 283—291).—X-Ray spectrograms of alloys of the composition Al(Cu,Mn)₃ were obtained, and combined with metallographic observations, including the change of length on tempering, lead to the result that the magnetic properties of Heusler's alloy cannot be attributed to any particular lattice arrangement.

A. J. MEE.

Internal strain of uniformly distorted aluminium crystals. K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 151–169; cf. this vol., 248).—X-Ray analysis shows that the internal strain within a uniformly distorted aluminium crystal is chiefly due to the elastic curvature of the crystal which is necessarily produced by slipping of a limited area on the slip plane, so long as the strain due to slip does not exceed about 0.2 or 0.3. The amount of rotation of the slip plane (cf. Taylor, A., 1928, 695) increases gradually and almost linearly with increasing amount of shear. Specimens with higher resistance to slipping are also the most strained internally for the same amount of shear, thus showing the close relationship of the internal strain and the work-hardening of the metal. J. W. SMITH.

Crystal structure of the chlorides of certain bivalent elements. L. PAULING (Proc. Nat. Acad. Sci., 1929, 15, 709-712) .- Results given by Bruni and Ferrari (A., 1926, 995) were used to deduce the atomic arrangement of the bivalent chlorides of cadmium, magnesium, nickel, and cobalt. It has also been shown that other representatives of the same class are manganese, zinc, ruthenium, rhodium, palladium, iridium, and platinum chlorides. The structure found is one closely resembling the cadmium iodide structure. Each cation is surrounded by six chloride ions approximately at the corners of a regular octahedron, six edges of which are shared with other octahedra so as to form a layer. It seems probable that the cadmium chloride structure is the stable one for substances of the type MX₂ where the cation M has a co-ordination number 6 and the anion has a small polarisability. A. J. MEE.

Crystal structure of strontium. F. SIMON and E. VOHSEN (Proc. Nat. Acad. Sci., 1929, 15, 695; cf. A., 1928, 694).—The higher value found by King (this vol., 749) than by the authors (*loc. cit.*) for the unit cube edge of strontium is due to the fact that King worked at the ordinary temperature, whereas the authors used liquid air temperatures. When this is corrected for, the values obtained by both sets of observers agree to within the experimental error, and also agree with those obtained by Ebert (this vol., 631). A. J. MEE.

Crystal structure of some binary compounds of the platinum metals. II. L. THOMASSEN (Z. physikal. Chem., 1929, **B**, **4**, 277–287; cf. this vol., 630).—Four further compounds have been investigated. The following have the pyrites structure: palladium diarsenide, $PdAs_2$ (a 5.970 \pm 0.004 Å.), platinum diphosphide, PtP_2 (a 5.683 \pm 0.004 Å.), rhodium disulphide, RhS_2 (a 5.574 \pm 0.005 Å.). Platinum monoantimonide, PtSb (a 4.130 \pm 0.004, c 5.472 \pm 0.005 Å.), has a nickel arsenide structure. None of these substances is ferromagnetic. A new determination of the structure of platinum diarsenide, $PtAs_2$, gave a value of $a=5.957\pm0.003$ Å.



X-Ray investigations of manganese nitrides. G. Hagg (Z. physikal. Chem., 1929, B, 4, 346-370).-X-Ray investigations of the system manganesenitrogen show the existence of four nitride phases. The manganese nitrides were prepared by heating powdered maganese in presence of gaseous ammonia. The phase with the lowest nitrogen content is homogeneous at about 2% N and can exist only above 500°. The manganese atoms are arranged in a face-centred tetragonal lattice (for 2.2% N a=3.765, c=3.684 Å.), but there is no indication of a regular arrangement of the nitrogen atoms. The next higher nitride phase is homogeneous between 6.0 and 6.5% N at 400° and below. The manganese atoms have a face-centred cubic lattice (a 3.855-3.860 Å. at 400°). In the third phase the manganese atoms are arranged in a 4 M

hexagonal lattice with most dense spherical packing, the nitrogen atoms being distributed at random in the spaces between them. At 400° the lattice dimensions increase from a 2.773, c 4.520 Å. for 9.2% N to a 2.828, c 4.528 Å. for 11.9% N. The fourth phase has a face-centred tetragonal arrangement of the manganese atoms, the dimensions increasing from a 4.194, c 4.031 Å. for 13.5% N to a 4.207, c 4.129 Å. for 14% N. The cubic and hexagonal phases are analogous to two phases in the system ironnitrogen. The manganese nitrides can exist in a stream of ammonia at atmospheric pressure even when their nitrogen fugacity is greater than 1 atm.

O. J. WALKER. Polymorphism of sodium sulphate. I. Thermal analysis. F. C. KRACEK (J. Physical Chem., 1929, 33, 1281–1303).—Heating and cooling curves for sodium sulphate over the range 190–280° indicate that five distinct modifications of this substance exist, but owing to hysteresis in the inversions the equilibrium temperatures cannot be definitely fixed. Approximate values are quoted, however, and the five phases are identified with those of previous workers. L. S. THEOBALD.

Polymorphism of sodium sulphate. II. Densities of anhydrous sodium sulphate at 25°. F. C. KRACEK and R. E. GIBSON (J. Physical Chem., 1929, **33**, 1304—1308; cf. preceding abstract).— Density determinations at $25^{\circ}\pm0.01$ show that sodium sulphate can exist in at least two modifications at the ordinary temperature and pressure. These forms are thenardite or Na₂SO₄–V, $d 2.664\pm0.001$, and Na₂SO₄–III, $d 2.697\pm0.001$, which is the modification finally left when thenardite is heated above 200° and then cooled. Persistent inclusions of air or liquid in the crystals of sodium sulphate limit the accuracy of d. L. S. THEOBALD.

Structural relations of alkali sulphates. B. GOSSNER and F. MUSSGNUG (Z. Krist., 1929, **69**, 446– 454; Chem. Zentr., 1929, i, 1891).—The lattice constants of sodium sulphate are: a 9.79, b 5.89, c 12.31 Å., the corresponding axial ratio being a:b:c=1.662:1:2.090. The unit cell contains 8 mols., d_{cale} , 2.673, space-group V_{5}^{*4} . Results for the molecules LiKSO₄, NaK₃(SO₄)₂, K₂SO₄, and Na₂SO₄ are compared. A. A. ELDRIDGE.

Lattice constants of copper sulphate. B. Goss-NER and K. BRUCKL (Z. Krist., 1929, **69**, 422-426; Chem. Zentr., 1929, i, 1891-1892).—The lattice constants are: $a \ 6.07$, $b \ 10.78$, $c \ 5.89$ Å., with 2 mols. of CuSO₄,5H₂O in the unit cell, the corresponding axial ratio being a:b:c=0.563:1:0.546 (goniometric, a:b:c=0.5721:1:0.5554).

A. A. ELDRIDGE.

Crystal structure of anhydrous alums $R'R''(SO_4)_2$. L. VEGARD and A. MAURSTAD (Z. Krist., 1929, **69**, 519–532; Chem. Zentr., 1929, i, 1892).—The following constants (Å.) for the hexagonal unit cells were obtained : $KAl(SO_4)_2$, a 4.706, c 7.960; $NH_4Al(SO_4)_2$, a 4.724, c 8.225; $NH_4Fe(SO_4)_2$, a 4.825, c 8.310; $KCr(SO_4)_2$, a 4.737, c 8.030. The unit cell contains 1 mol.; space-group D_3^2 .

A. A. ELDRIDGE.

Lattice constants and the space-groups of barium and strontium carbonates. T. A. WIL-SON (Physical Rev., 1928, [ii], **31**, 305).—The fundamental lattice for both carbonates is the simple orthorhombic Γ_0 , and the unit cell contains 4 mols. That of barium carbonate has a_0 5·252 \pm 0·001, b_0 8·828 \pm 0·002, c_0 6·544 \pm 0·001 Å., d_{calc} 4·291 \pm 0·004; the corresponding values for strontium carbonate are 5·118 \pm 0·003, 8·404 \pm 0·005, 6·082 \pm 0·004 Å., 3·722 \pm 0·006. The space-group of barium carbonate is 2Di-16 (X=a), and that of strontium carbonate probably the same. L. S. THEOBALD.

Cobaltammine chloratosulphates and perchloratosulphates, and a comparison of the lattice constants of cobaltiates and chromiates. O. HASSEL and H. KRINGSTAD [with I. OFTEDAL] (Z. anorg. Chem., 1929, 182, 281-288).-Hexamminocobaltic chloratosulphate, prepared from the corresponding chloride by liberation of the base with moist silver oxide and neutralisation with a mixture of sulphuric acid and chloric acid, is sparingly soluble in water and forms yellow octahedra. Pentammineaquo- and hexammino-cobaltic perchloratosulphates have been prepared in a similar manner. The lattice constants in A. of these three complexes, all of which crystallise in the cubic system, are 10.80+0.01, 10.89+0.01, and 10.95+0.01, respectively. Tetramminediaquocobaltic perchloratosulphate, obtained from the chloride, forms reddish-violet, hexagonal prisms, and the trihydrate of triamminotriaquocobaltic perchloratosulphate, prepared from triam-minotrinitritocobaltic chloride by direct treatment in acetic acid solution with a mixture of sulphuric and perchloric acids, forms deep reddish-violet prisms; although both substances crystallise in the hexagonal system, the elementary cell containing 4 mols., the X-ray diagrams differ considerably. Other lattice constants which have been measured are : pentamchloratosulphate, mineaquocobaltic 10.73 + 0.01;11.545 + 0.005; hexamminochromic perchlorate, pentammineaquochromic perchlorate, 11.47 + 0.00; pentammineaquochromic bromatosulphate, $10.535 \pm$ 0.005 Å. The approximately constant difference between the lattice constants of the hexammino- and pentammineaquo-compounds indicates a constant change of volume by substitution of ammonia by water, whereas by the substitution of cobalt by chromium more complex relationships exist. The larger lattice dimensions of the chromium compounds are to be expected in view of the greater nuclear charge.

H. F. GILLBE.

Fine structure of the chemical elements. J. BECKENKAMP (Zentr. Min. Geol., 1929, A, 65-79; Chem. Zentr., 1929, i, 1890).

Crystal structure. II. A. Nold (Z. Krist., 1929, 69, 427-445; Chem. Zentr., 1929, i, 1890).

Lattice constant of barium telluride. V. M. GOLDSCHMIDT [with E. BROCH and I. OFTEDAL] (Z. Krist., 1929, 69, 411-414; Chem. Zentr., 1929, i, 1891).—New values (± 0.002 Å.) are 6.986 and 6.984Å., in accord with the earlier value 6.986.

A. A. ELDRIDGE. Change [of crystal structure] of rubidium halides by pressure. L. PAULING (Z. Krist., 1928,

69, 35-40; Chem. Zentr., 1929, i, 2011).—The cæsium chloride structure for the high-pressure modifications of rubidium halides is supported.

A. A. ELDRIDGE.

Translation lattice of methylcellulose. X-Ray investigations on cellulose derivatives. II. C. TROQUS and K. HESS (Z. physikal. Chem., 1929, B, 4, 321-345; cf. A., 1928, 1225).-Two forms of trimethylcellulose, one preserving the natural fibre structure of ramie and the other corresponding with the mercerised fibre, have been studied. The diagrams for both agree with a 21.3, b 25.6, c 11.3 Å. The digonal helical axis is lacking in both. Within the limitations of technique the diagram to be expected from the net plane distances is reproduced experimentally. Reference is made to the uncertainty of conclusions connecting intensity measurements and constitutional problems regarding cellulose and also of the calculation of micellar magnitudes from the breadth of interference fringes. The interpretation of the digonal helical axis in the fibre diagrams of cellulose and cellulose hydrate in the sense of principal valency chains is scarcely to be reconciled with the methylcellulose diagram without recourse to special hypotheses. R. A. MORTON.

Reversible and irreversible lattice changes of cellulose triacetate. X-Ray investigations of cellulose derivatives. III. K. HESS and C. TROGUS (Z. physikal. Chem., 1929, B, 5, 161-176; cf. preceding abstract).-When fibrous cellulose triacetate is allowed to swell in cyclohexanone, methyl alcohol, benzene, pyridine, or a chloroform-methyl alcohol mixture, an expansion of the lattice at right angles to the fibre is observed, and the original dimensions are regained when the solvent is removed by drying or displacement. If, however, the material is completely dispersed in chloroform the lattice is destroyed, and on reprecipitation with methyl alcohol a different lattice is formed. The change in the lattice structure corresponds with a marked difference in external properties, the reprecipitated material consisting of doubly refracting crystalline needles, possessing when swollen a lower elastic limit, and incapable of forming a film on drying. The lattice of this second form remains unchanged when the substance is moistened with organic liquids. The nature of the process of dissolution is discussed in the light of the observations. F. L. USHER.

Silk fibroin. II. O. KRATKY (Z. physikal. Chem., 1929, B, 5, 297–300; cf. Brill, A., 1924, i, 102).—A preliminary account of the application of improved experimental methods (cf. Weissenberg, this vol., 493) to the X-ray examination of silk fibroin. F. L. USHER.

Crystal structure of tartaric acid, isohydrobenzoin, and rubidium tartrate. A. REIS and W. SCHNEIDER (Z. Krist., 1928, 69, 62-76; Chem. Zentr., 1929, i, 2524).—Tartaric acid and isohydrobenzoin crystallise in space-group C_2^2 , with 2 mols. in the unit cell. The following values, respectively, are recorded: $T_{(100)}$ 7.68, 12.40; $T_{(010)}$ 6.03, 7.92; $T_{(001)}$ 6.18, 5.81 Å.; β 100° 17', 92° 53'. Rubidium tartrate, Rb₂C₄H₄O₆, crystallises in space-group D_3^4 (D_3^6) with 6 mols. in the unit orthohexagonal cell; $T_{(010)}$ 7.17, $T_{(011)}$ 13.19 Å. A. ELDRIDGE.

Crystal structure of anhydrous mesotartaric acid and tartrates. W. SCHNEIDER (Z. Krist., 1929, 69, 49-61; Chem. Zentr., 1929, i, 2523-2524). -The smallest (triclinic) translation cell has $T_{(100)}$ 9·24, $T_{(010)}$ 6·33, $T_{(001)}$ 5·45 Å.; α 70·5°, β 78·0°, γ 79·5°, and contains 2 mols. of C₄H₆O₆. The thallium salt contains 4 mols. of Tl₂C₄H₄O₆; $T_{(100)}$ 13·66, $T_{(001)}$ 7·63 Å.; β 86° 37′. Potassium mesotartrate dihydrate has $a:b:c=1.019:1:1.600; \alpha 95^{\circ} 44'$. $\beta 102^{\circ} 52', \gamma 61^{\circ} 46'$; the unit cell contains 2 mols. of $K_2C_4H_4O_6, 2H_2O; T_{(100)} 7.02, T_{(001)} 11.02 A.$

A. A. ELDRIDGE. X-Ray studies on pentaerythritol. H. MARK and G. VON SUSICH (Z. Krist., 1928, 69, 105-117; Chem. Zentr., 1929, i, 2520-2521).-The following values were obtained : a 6.09, c 8.79 Å.; 2 mols. $C_5H_{12}O_4$ in the unit cell; space-group C_4^5 or S_4^2 .

A. A. ELDRIDGE.

Crystal structure of pentaerythritol, pentaerythrityl tetra-acetate, and dibenzylidenepentaerythritol. F. A. VAN MELLE and H. B. J. SHURINK (Z. Krist., 1928, 69, 1-16; Chem. Zentr., 1929, i, 2521).-Studies on the crystal structure of compounds CX_4 are discussed. Pentaerythrityl tetra-acetate has space-group $C_{\rm sh}$. Dibenzylidenepenta-erythritol has c:a=6.09; J_{0001} , 36.7 Å.; the unit cell contains 3 mols. A. A. ELDRIDGE.

Crystalline form of thiophen and its solid solutions with benzene. G. BRUNI and G. NATTA (Rec. trav. chim., 1929, 48, 860-863).—The axial ratios a:b:c=0.771:1:0.704 have been found for benzene crystals at about -170° in an X-ray examination using a calcium anticathode. These results confirm those of Cox (A., 1928, 1081). Thiophen crystallises with a tetragonal cell with an axial ratio c/a=1.32, containing 4 mols. At about -170° the dimensions of the cell are a 7.22, c 9.53 Å.; $v=497\cdot10\times10^{-24}$ cm³., d_{calc} 1.123. Benzene and thiophen are not isomorphous, but exhibit isodimorphism by reason of their similar crystalline form and dimensions. Solid solution crystals separating from mixtures containing 75-50% of thiophen give photograms identical with those of thiophen, the contractions in the lattice dimensions varying from 0.01 to 0.03 Å. F. G. TRYHORN.

Crystal structure of tysonite and some artificial lanthanide fluorides. I. OFTEDAL (Z. physikal. Chem., 1929, B, 5, 272-291).-Powder diagrams of tysonite ([Ce,La]F3), and of specimens of lanthanum, cerium, praseodymium, neodymium, and samarium fluorides prepared in the laboratory have been made. A common structure is proposed for all the substances named : a hexagonal elementary cell with c-axis of the order 7 Å. and axial ratio 1.77, containing two metal ions. From the Laue diagram of tysonite it is inferred that the above is a pseudo-cell, the smallest cell compatible with the diagram being three times as large, and containing 6 mols. of RF_3 . The axial ratio is about 1.023 for all the substances.

F. L. USHER.

Technique for X-ray examination of crystal structures with many parameters. W. L. BRAGG and J. WEST (Z. Krist., 1928, 69, 118-148; Chem. Zentr., 1929, i, 2012).

Structure of diopside, CaMg(SiO₃)₂. B. WAR-REN and W. L. BRAGG (Z. Krist., 1928, 69, 168-193; Chem. Zentr., 1929, i, 2013).

Fine structure of brookite. J. H. STURDIVANT and L. PAULING (Z. Krist., 1929, 69, 557-559; Chem. Zentr., 1929, i, 1892).-Schröder's results (*ibid.*, 1928, 67, 485) are based on an error.

A. A. ELDRIDGE.

Crystal structure of the A-modification of sesquioxides of the rare-earth metals. L. PAUL-ING (Z. Krist., 1929, 69, 415-421; Chem. Zentr., 1929, i, 1891) .- Contrary to Zachariasen's view, a structure having symmetry D_{2d}^3 is proposed.

A. A. ELDRIDGE.

Comparative X-ray examination of magnes-ium silicates. B. GOSSNER and F. MUSSCNUG (Neues Jahrb. Min., 1928, 58, 213–252; Chem. Zentr., 1929, i, 1892).—Prismatin (SiO₂ 33·20, Al_2O_3 42·36, Fe_2O_3 0·30, FeO 5·81, MgO 11·76, Na₂O 5·07, K₂O 0·83, H₂O 1·62%, d 3·280) forms a rect-angular parallelepiped, a 13·86, b 16·02, c 6·78 Å. (calc. a:b:c=0.865:1:0.423), and is considered to be 3ALO. 4MgSiO. with 4 mols in the unit cell be $3Al_2O_3, 4MgSiO_3$ with 4 mols. in the unit cell. Kornerupin has c 6.8 Å. Sapphirin has a:b:c= $0.667: 1: 0.691, \beta = 105^{\circ} 29'$ (approx.), with 8 mols. of $2Al_2O_3$, Mg_2SiO_4 (partial replacement of SiMg by Al_2) in the unit cell. Actinolite has a:b:c=0.536:1:0.290, $\beta=105^\circ$ 36'. Glaucophane, with 4 mols of NaAlSi_2O_6,2MgSiO_3 in the unit cell, has a:b:c=0.543:1:0.300, $\beta=104^\circ$ 10'.

A. A. ELDRIDGE.

Aenigmatite and its position in the silicate system. B. Gossner and F. Mussgnug (Zentr. Min. Geol., 1929, A, 5-11; Chem. Zentr., 1929, i, 1914).-The unit cell has a 18.3, b 18.3, c 10.6 Å., a 96.5°, β 96·5°, r 113·5°. A. A. ELDRIDGE.

Thortveitite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1929, 1-5; Chem. Zentr., 1929, i, 1915).—Thortveitite, monoclinic, $2\text{SiO}_2, \text{Se}_2\text{O}_3$, has a 6.56, b 8.58, c 4.74 Å., β 103° 8′, whence a:b:c=0.767:1:0.552. The unit cell contains 2 mols.; A. A. ELDRIDGE. space-group C_{2k}^3 .

Magnetic birefringence in solutions and its relation to crystal structure and properties. M. RAMANADHAM (Indian J. Physics, 1929, 4, 109-130).—Benzene, naphthalene, phenanthrene, azo-benzene, and anthracene show positive magnetic double refraction in ascending order of magnitude. Nitro-aromatic compounds, maleic acid, nitrates, and nitrites also give the effect. The known magnetic and optical properties of these various crystalline compounds have been related to the magnetic birefringence exhibited by them, on the assumption that the molecules inside the crystal are all parallel.

W. E. DOWNEY.

Anomalous diamagnetism of graphite. S. PARAMASIVAN (Indian J. Physics, 1929, 4, 141-146).—Seven varieties of amorphous carbon have been found to show specific diamagnetic susceptibility between 0.36×10^{-6} and 0.53×10^{-6} . Graphite gives values 3.5×10^{-6} to 4.2×10^{-6} , diamond 0.47×10^{-6} , and graphitic anthracite 0.97×10-6. W. E. DOWNEY.

Structure of the atomic magnet in ferromagnetic materials. R. FORRER (J. Phys. Rachum, 1929, [vi], 10, 247-262).-A fine metal wire is annealed, stretched to the breaking point, wound on a mandrel six times the wire diameter to give it a slight permanent curvature, and straightened by inserting it into a capillary tube. Such a wire gives a very simple magnetisation curve in which the reversible and irreversible components are almost completely separated. It is concluded from comparisons with models that in nickel there are two magnetic moments at right angles to each other. This doublet may be oriented without respect to the crystallographic axes and is influenced by a magnetic field. In ferromagnetic materials the hysteresis cycle results from a rotation and inversion of the magnetic multiplet. The multiplet is deformable, and may close up under the action of an intense field, resulting in saturation. Similar considerations lead to the assumption of a trirectangular triplet in electrolytic iron.

C. J. SMITHELLS. Degeneration of paramagnetism at high temperatures. A. SCHIDLOF (Helv. phys. Acta, 1928, 1, 578-600; Chem. Zentr., 1929, i, 2392).

Degeneration of electron rotation and magnetism at low temperatures. A. SCHIDLOF (Helv. phys. Acta, 1928, 1, 601-612; Chem. Zentr., 1929, i, 2392).

Fused paramagnetic salts. L. A. WELO (Nature, 1929, 124, 575–576).—Values of c and 0 for solid and fused hydrated salts are tabulated, and curves are given. Coalescence of the salts may be mistaken for fusion. A. A. ELDRIDGE.

Magnetic quadrupole moment of the iron atom. N. S. AKULOV (Z. Physik, 1929, 57, 249–256; ef. this vol., 248, 752).—Mathematical. Expressions are derived for the dipole energy density of a bodycentred lattice and also for its quadrupole energy density. These are applied to the case of the iron atom. The quadrupole moment of the iron atom is calculated by two entirely independent methods, the results being in satisfactory agreement (4.50×10^{-29}) and 4.54×10^{-29}). J. W. SMITH.

Hall effect, electrical conductivity, and thermoelectric power of the copper-tin series of alloys. E. STEPHENS (Phil. Mag., 1929, [vii], 8, 273-289; cf. this vol., 384) .- The resistance of the alloys was determined, with annealing, until a constant value was obtained. The temperature coefficient of resistance, thermo-electric power, and Hall effect were then determined for the alloys in this final state. Singular points corresponding with both Cu₃Sn and Cu,Sn were obtained in each of the curves relating these constants and the concentration of one metal in the alloy. The Hall effect, although negative for copper and tin, is positive for Cu₃Sn and Cu₄Sn and for alloys of composition ranging between 74% Cu, 26% Sn, and 4% Cu, 96% Sn. Cu₃Sn has the maximum positive Hall coefficient 0.000935, or approximately one half that of Cu₃Sh. The effect of annealing on the resistivity of the alloys depends on N. M. BLIGH. their composition.

Barkhausen effect in iron, nickel, and permalloy. I. Measurement of discontinuous

change in magnetisation. R. M. BOZORTH (Physical Rev., 1929, [ii], 34, 772-784).-The magnetic material was placed in a slowly and uniformly changing magnetic field, and the discontinuities in the magnetisation, characteristic of the Barkhausen effect, were followed through the E.M.F. created in a surrounding coil of wire. It was found that the changes in magnetisation taking place suddenly in large groups of atoms account quantitatively for the whole change in magnetisation which corresponds with the steeper part of the hysteresis loop. The magnetic moments of only a very small number of atoms are reversed in groups smaller than 10^{10} atoms, or a volume of 10^{-13} c.c. The maximum size of the discontinuities for each material was found to be about the same, corresponding with the complete reversals of the clementary magnets in a volume of about 10-6 c.c. Previous discordant results are attributed to different N. M. BLIGH. decay rates of eddy currents.

Theory of magneto-optical phenomena in crystals. J. BECQUEREL (J. Phys. Radium, 1929, [vi], 10, 313-320, and Z. Physik, 1929, 58, 205-216). —See this vol., 1134.

Paramagnetic properties of rare earths. B. CABRERA and A. DUPERIER (Anal. Fís. Quím., 1929, 27, 671-682).—See this vol., 982.

Magnetic susceptibility of nitric oxide at 296° and 216° Abs. F. BITTER (Proc. Nat. Acad. Sci., 1929, 15, 638—642).—By an improved form of the method of hanging a test body surrounded by the gas to be measured in an inhomogeneous magnetic field, results were obtained in good agreement with the theoretical calculations of Van Vleck (cf. A., 1928, 572). N. M. BLIGH.

Problem of magnetism. W. GERLACH (J. Phys. Radium, 1929, [vi], 10, 273-282).-Methods for the direct measurement of the moment of a free atom from photomicrographs of atomic rays under the influence of a magnetic field are described. Simple patterns are obtained for atoms having a magnetic moment of one Bohr magneton; more complicated patterns indicate the existence of atoms with more than one magneton. The orientation of the atoms appears to correspond with a maximum moment; birefringence expected for paramagnetic gases is not observed. Another method of atomic moment determination is that of Weiss from susceptibility measurements and the Curie constant. From calculations on the paramagnetic saturation of gadolinium sulphate it is shown that the moments of the gadolinium ion calculated with Langevin's theory by the method of atomic rays, and indirectly with the laws of space quantisation, respectively, are in the same numerical relation as the Weiss and Bohr magneton. Becquerel's magneto-optical measurements on paramagnetic saturation are a proof of space quantisation. Direct measurements of the susceptibility of potassium vapour were attempted, and the calculated Curie constant is in good agreement with that calculated from the Bohr magneton. It is concluded that the susceptibility of diamagnetic gases is independent of the temperature and pressure. Ferromagnetism and its relation to dia- and para-magnetism is briefly N. M. BLIGH. discussed.

Superstructure and magnetic susceptibility in the system copper-gold. H. J. SEEMANN and E. VOGT (Ann. Physik, 1929, [v], 2, 976-990).---The variation of diamagnetic susceptibility with concentration has been measured for the gold-copper mixed crystal series. Alloys of the composition Cu₃Au and CuAu in certain circumstances exhibit super-imposed structure lines consistent with a regular arrangement of the constituent atoms; e.g., the corners of the elementary cube may be occupied by gold atoms and the face-centres by copper atoms. The relation between susceptibility and the appearance of super-structure has been determined for alloys of the composition Cu₃Au and CuAu, and it is found that for the former an increase and for the latter a decrease in diamagnetic susceptibility accompanies the production of regular atomic distribution in the lattice. Control experiments on alloys differing in composition from the whole-number ratios indicated no difference in susceptibility for quenched and slowly-cooled specimens. No explanation is available for the difference in sign of the effect R. A. MORTON. with Cu₃Au and CuAu.

Magnetic susceptibility of cæsium in the solid and liquid state. C. T. LANE (Phil. Mag., 1929, [vii], 8, 354—362; cf. Crow, A., 1926, 14; Sucksmith, A., 1926, 782; McLennan, A., 1927, 1017).—Determinations were made with highly purified cæsium, using the Gouy method for the liquid and a modified form of this method for the solid metal. Cæsium was found to be paramagnetic; the values for the specific susceptibility were $4-0.22 \times 10^{-6}$ and 40.20×10^{-6} in the solid and liquid state, respectively, in good agreement with the value for the solid state calculated on Pauli's theory. N. M. BLIGH.

Electrical conductivities of liquid alkali-metal amalgams. D. BOOHARIWALLA, G. R. PARANJPE, and M. PRASAD (Indian J. Physics, 1929, 4, 147— 160).—The liquid sodium, potassium, and lithium amalgams show break points in the conductivityconcentration curves as pointed out by Hine (cf. A., 1917, ii, 287). The conduction has been shown to be metallic and not electrolytic. W. E. DOWNEY.

Specific resistance and purity of sodium electrolysed through soda-glass. J. R. NIELSEN (Physical Rev., 1928, [ii], 31, 304).—The specific resistance for solid sodium, containing 0.08% K as the only detectable impurity, between 30° and 90° is $4661 \times 10^{-9} \times (1+0.00484t)$ and for liquid sodium below 160° , $9828 \times 10^{-9} \times [1+0.00354(t-100)+$ $0.00000039(t-100)^2]$. L. S. THEOBALD.

Electrical conductivity of natural and artificial sodium chloride crystals. A. D. GOLDHAMMER (Z. Physik, 1929, 57, 173—185; cf. Salessky, this vol., 384).—Between 120° and 200° sodium chloride crystals obey Ohm's law up to 600 volts. The temporary production of polarisation and its magnitude are determined by the temperature and potential applied. Quantitative conductivity measurements show that crystals should be divided into two groups: (a) natural crystals and old synthetic crystals, and (b) synthetic crystals, with or without the addition of foreign ions. The conductivity of the crystals is shown to be strongly dependent on the presence of small quantities of foreign ions introduced into the crystal lattice during preparation of the crystal. J. W. SMITH.

Mechanism of metallic conduction. H. M. BARLOW (Phil. Mag., 1929, [vii], 8, 289-304).— The electron fluid theory of conduction recently proposed (cf. this vol., 496) is developed. It is shown that the application of an E.M.F. to a metal bar involves a distortion of the electron orbits; the larger is the number of valency electrons the greater is the work necessary for distortion and the higher is the resistance of the conductor. The new theory is developed mathematically with regard to the ordinary phenomena of conduction and their relation to thermal conductivity. N. M. BLIGH.

Internal specific heat. I. W. JAZYNA (JACYNO) (Z. Physik, 1929, 57, 341—344).—Theoretical. Using the assumption of uniform energy distribution, the "heat-mol. wt." and the "internal absolute" specific heat of gases are calculated. Results are given for sixteen common gases. A. J. MEE.

Recrystallisation of substances of low m. p. and of ice. G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1929, 182, 289-313).-The recrystallisation at constant temperature of transparent substances such as camphor, pinene hydrochloride, and ice has been studied by direct visual observation. The nature of the displacement experienced by the particles is determined by the orientation of adjacent crystals, but the velocity of this displacement is governed by the concentration of minute films of impurities which separate on the surface of the particles; such films have been isolated as honeycombed structures after removal of the crystal. This view is supported by the observation that decrease of the amount of impurities present results in an increase of the recrystallisation velocity, and that mechanical working causes the recrystallisation velocity to diminish on account of the more rapid separation of the impurities. H. F. GILLBE.

Alternation in the heats of crystallisation of the normal monobasic fatty acids. IV. W. E. GARNER and (MISS) A. M. KING (J.C.S., 1929, 1849-1861; cf. A., 1924, ii, 239; 1926, 1087).-The following values have been obtained for the heats of crystallisation of these acids : margaric, 12.22; tricosoic, 17.60; pentacosoic, 20.00; behenic, 18.75; lignoceric, 21.10; cerotic, 52.25 kg.-cal./mol. Q and Q/T when plotted against the number of carbon atoms give linear relationships for both the odd and even acids. The equation for the setting points of the odd acids is $T_s = (0.9651n - 4.49)/(0.002505n - 0.0071)$ and gives a convergence temperature of 112.2°. Cerotic acid is an exception, but X-ray analysis shows it to be a mixture of at least two acids. Detailed study of the transition of the α and β forms of the odd acids has been made, and the heats of transition $\alpha \longrightarrow \beta$ have been found to be constant for margaric, tricosoic, and pentacosoic acids at an average value of 1.55 kg.-cal./mol. There is a discontinuity in the curve of these heats plotted against number of carbon atoms per molecule between C₁₁ and C₁₃. For acids above C_{11} the $\beta \longrightarrow \alpha$ change does not easily take place. C. W. HART-JONES.

M. p. of chromium. C. J. SMITHELLS and S. V. WILLIAMS (Nature, 1929, 124, 617-618).—Preliminary determinations give 1920°, or a rather higher temperature, as the m. p. of chromium.

A. A. ELDRIDGE.

Intensively dried liquids. J. W. SMITH (Phil. Mag., 1929, [vii], 8, 380—383).—Experimental data on intensively dried liquids are reviewed. The work of Smits (A., 1928, 1189) and Lenher (this vol., 872) indicates that Baker's results for such liquids are not conclusive evidence of inner complexity of the liquid system, and that the abnormal effects may be due to a slowness in attaining an equilibrium state. The rate of distillation of super-dried nitrogen tetroxide gradually rose when determined after long undisturbed periods. N. M. BLIGH.

Vapour pressures of lead iodide, cuprous iodide, cuprous bromide, silver iodide, and silver bromide by a modified transference method. K. JELLINEK and A. RUDAT (Z. physikal. Chem., 1929, 143, 55—61).—The following latent heats of evaporation, in kg.-cal./mol., have been calculated from vapour-pressure measurements at 900—1200°: lead iodide, 27.70; cuprous iodide, 18.30; cuprous bromide, 18.10; silver iodide, 38.60, and silver bromide, 40.80. The vapour density of cuprous iodide at 900—1100° corresponds with the formula CuI, whereas the bromide possesses the double formula. H. F. GILLBE.

Vapour pressure of thallium and lead halides. F. VOLMER (Physikal. Z., 1929, **30**, 590-596).— The vapour pressures of thallium chloride, bromide, and iodide, lead chloride, and bromide at various temperatures have been measured in nitrogen by the streaming method. Lead iodide tends to decompose in nitrogen. The vapour pressures of silver halides are too small to be measurable by this method up to 750°, above which temperature decomposition occurs.

R. A. MORTON.

Vapour pressure of titanium tetrachloride. K. ARII (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8. 714—718).—The vapour pressure of titanium tetrachloride between 20° and 135° can be represented by log $p_{(mm.)}=7.64433-1974\cdot6/T$. The molecular latent heat of vaporisation is calculated to be 8960 g.-cal. at 25° and 8620 g.-cal. at the b. p.

C. W. GIBBY.

Vapour pressure of thionyl chloride. K. ARII (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 719— 722).—The vapour pressure of thionyl chloride between 20° and 75° may be expressed by $\log p_{(mm.)} =$ 7.60844—1648.21/T. The b. p. was found from the *p*-T curve to be 75.7°/760 mm., and the molecular latent heat of vaporisation was calculated to be 7553 g.-cal. at 25° and 7482 g.-cal. at the b. p.

C. W. GIBBY.

Constants of chlorine fluoride. O. RUFF and F. LAASS (Z. anorg. Chem., 1929, 183, 214–222).— The chlorine fluoride, prepared by a method previously described (this vol., 40) and purified by redistilling five times, had m. p. $-154^{\circ}\pm0.5^{\circ}$. Vapour pressures between -150° and -105° have been determined and the results are represented by the equation $\log p=15\cdot738-3109/T+1\cdot538\times10^5/T^2$. This gives $-100\cdot8^{\circ}$ as the b. p., approximately -14° as the critical temperature, and $-2\cdot27$ kg.-cal./g.-mol. as heat of vaporisation. The heat of formation of hydrogen fluoride has been found to be 62·3 kg.-cal. (cf. Wartenberg and Fitzner, A., 1926, 476) and the heat of reaction between chlorine fluoride and hydrogen 58·6 kg.-cal. From these values and the heat of formation of hydrogen chloride, 22·0 kg.-cal., the calculated heat of formation of chlorine fluoride is 25·7 kg.-cal. M. S. BURR.

General method of measuring the partial pressure of mercury [over any amalgam] at the ordinary temperature. L. L. HIRST and A. R. OLSON (J. Amer. Chem. Soc., 1929, 51, 2398—2403).— The vapour pressure is calculated from the pressure change which is produced in a mixture of ethylene, hydrogen, and mercury vapour by mercury resonance radiation at 2536 Å. which has traversed a layer of the mercury vapour. The activities at 26° of some thallium amalgams, calculated from the results, substantially agreed with those found by Richards and Daniels (A., 1920, ii, 34). The broadening of the absorption line of mercury for its own resonance light by hydrogen was investigated and the change in the atomic absorption coefficient of mercury in presence of hydrogen was determined. S. K. TWEEDY.

Vapour tensions and vapour densities of ethylene and nitrous oxide. G. T. BRITTON (Trans. Faraday Soc., 1929, 25, 520-525).—A method for the measurement of vapour tension and vapour density simultaneously is described. The measurement of the latter is carried out by determining the buoyancy correction to be applied when an aluminium weight of known volume is weighed in the vapour, using a McBain and Bakr sorption balance. The pressure-temperature equation of Batschinski fits the data well in the form $t+c=K \times p^{1/4}$.

F. J. WILKINS.

Limiting values for the expansion and pressure coefficients of helium, hydrogen, and nitrogen. W. HEUSE and J. OTTO (Ann. Physik, 1929, [v], 2, 1012-1030).-By means of a new method it is found that the isotherms of helium, hydrogen, neon, argon, nitrogen, and oxygen in the region 0.4-1 mm. of mercury follow a linear course, the inclinations being consistent with data obtained at higher pressures. From the expansion and pressure coefficients of helium, hydrogen, and nitrogen measured at different pressures the limiting value at p=0 is calculated. Thermodynamic relations applied to the isotherm inclinations at 0° and 100° for higher pressures lead to the values $\gamma = 0.0036609$ and $T_0 = 273.16$. The method of linear extrapolation to p=0 gives $\gamma=$ 0.0036610. Taking earlier data into account, the values $\gamma = 0.0036608$ and $T_0 = 273.16$ are obtained as means. R. A. MORTON.

Entropy of hydrogen. W. H. RODEBUSH (Proc. Nat. Acad. Sci., 1929, 15, 678—680; cf. Fowler, A., 1928, 469; Giauque and Johnston, this vol., 138).— If an equilibrium condition is assured between the two kinds of molecules of hydrogen (cf. Bonhoeffer, this vol., 479; Eucken, *ibid.*, 497) by making specific heat measurements on hydrogen which has been kept at a low temperature for a long time, the discrepancy can probably be removed between the entropy values as obtained from thermal data and indirectly from the equilibrium between hydrogen, oxygen, and water. A corrected value can be obtained theoretically when account is taken of rotational energy. N. M. BLIGH.

Isotherms of hydrogen, carbon monoxide, and their mixtures. G. A. SCOTT (Proc. Roy. Soc., 1929, A, 125, 330-344).—The isotherms of hydrogen, carbon monoxide, and mixtures of the two in the molecular proportions 2:1, 1:1, and 1:2 have been determined at 25° over a pressure range up to 170 atm. The method employed consists in filling a vessel of known constant volume at a known constant temperature with the gas or mixture under investigation up to a given measured pressure, and on releasing the gas, determining its volume at atmospheric pressure. Full details are given of the apparatus, comprising a high-pressure vessel, its filling system, a glass measuring system, an accurate pressure balance, and a water-bath. The isotherms are expressed by equations of the form $pv_{\Lambda} = a + bp + cp^2$, and the values of a, b, and c for hydrogen are calculated to be 1.09090, 0.6511×10^{-3} , and 0.033×10^{-6} , respectively; for carbon monoxide, $1.09196, -0.4393 \times$ 10^{-3} , and 3.55×10^{-6} ; for the 2:1 mixture, 1.09109, 0.4626×10^{-3} , and 0.947×10^{-6} ; for the 1:1 mixture, 1.09122, 0.3281×10^{-3} , and 1.28×10^{-6} , and for the 1:2 mixture, 1.09142, 0.1514×10^{-3} , and 1.88×10^{-6} . The mixtures show deviations both from the law of additive volumes and from that of additive pressures, and behave in general very similarly to the hydrogennitrogen mixtures studied by Verschoyle (A., 1926, 894). The constant b_{12} for the force acting between a molecule of hydrogen and a molecule of carbon monoxide at 25° has been calculated from the isotherms (cf. Lennard-Jones and Cook, A., 1927, 727), and is found to be 0.50, 0.51, and 0.62×10^{-3} for the three mixtures containing 66.3, 51.7, and 33.1%L. L. BIRCUMSHAW. of hydrogen, respectively.

Compressibilities and thermal pressure coefficients of certain liquids. J. H. HILDEBRAND (Physical Rev., 1929, [ii], 34, 649-651).—A small error is corrected in the values recently obtained by Westwater and others (cf. A., 1928, 228) for the compressibilities of a number of organic liquids, and the corrected values are found to be in good agreement with those found by Freyer and others (cf. this vol., 637). Values are given for a constant from which the coefficients of thermal pressure or of compressibility at various temperatures can be calculated by the aid of existing data for the densities and coefficients of expansion, and their values and those of the constant are listed for the eight organic liquids.

N. M. BLIGH. Compressibility of crystals. R. F. MEHL and R. H. CANFIELD (Nature, 1929, 124, 478-479).--- Raschevsky's views (this vol., 499) are criticised, the genuineness of the compressibility coefficient being regarded as established by consideration of (a) internal evidence from the inter-relationships of the generally accepted compressibility coefficients among themselves and with other physical properties, and (b) the possible volume of internal voids.

A. A. ELDRIDGE.

Viscosity, heat conductivity, and diffusion in gas mixtures. II. Viscosity of hydrogennitrogen and hydrogen-carbon monoxide mixtures. M. TRAUTZ and P. B. BAUMANN. III. Viscosity of hydrogen-ethylene mixtures. M. TRAUTZ and F. W. STAUF. IV. Viscosity of binary and ternary rare-gas mixtures. M. TRAUTZ and K. F. KIPPHAN (Ann. Physik, 1929, [v], 2, 733-736, 737-742, 743-748; cf. A., 1926, 118, 671; 1927, 194).-II. Measurements have been made of the viscosities of air, hydrogen, and nitrogen at a series of temperatures between -78° and 250° . The Sutherland formula applies when the constant is 101.1 for carbon monoxide and 102.7 for nitrogen. The viscosity isotherms for the systems hydrogencarbon monoxide and hydrogen-nitrogen have been determined. Maxima can appear only at very low temperatures, e.g., -100° to -150° ; at -78° the isotherms on the non-hydrogen side are nearly horizontal.

III. The viscosities of hydrogen and of ethylene have been determined and the results agree well with the Sutherland formula (when the constants are 82.8 and 238.9, respectively) for the range -40° to 250° , the agreement being less satisfactory from -40° to -78° . The isotherms in the viscosity/molar fraction curves exhibit a marked maximum which becomes flatter with rise of temperature. The position of the maximum is shifted in the direction of lower hydrogen content as the temperature rises.

IV. The viscosities at various temperatures have been measured for the binary systems hydrogenhelium, helium-neon, helium-argon, neon-argon, and the ternary system helium-neon-argon. The results conform very closely to theoretical requirements and it is shown to be possible to analyse mixtures of inert gases by measurement of viscosities and densities. R. A. MORTON.

Mixtures of alcohol and ethyl ether. DES-MAROUX (Mem. Poudres, 1928, 23, 198-229).-The densities of mixtures of ethyl alcohol and ether at 0° have been determined; there is always a contraction on mixing, which passes through a maximum at an equimolecular mixture. Mixtures of alcohol with a light essential oil showed a dilatation reaching a maximum at 40 mol.-% of oil. Only small variations in molecular volume were found in mixtures of ether with the essential oil. The partial vapour pressures of alcohol and ether over mixtures have been determined at 0°; they show positive deviations from Raoult's law. Similar measurements have been made with alcohol-oil and ether-oil mixtures. The heats of admixture of alcohol and ether at 0° are negative, showing a maximum cooling at about 66 mol.-% of ether. Mixtures of the oil with alcohol and with ether behave similarly. The electrical conductivity of mixtures of alcohol with the essential oil diminishes linearly as the oil content rises. In mixtures of alcohol and ether it diminishes as ether is added, at first slowly and then more rapidly. The f.-p. curve for mixtures of alcohol and ether shows three maxima, corresponding with compounds of 1 mol. of alcohol with 1, 3, and 5 mols. of ether.

C. W. GIBBY.

Viscosity isotherms of binary mixtures. I. Benzene-sulphur monochloride. II. Nitrobenzene-sulphur monochloride. F. DE CARLI (Gazzetta, 1929, 59, 495-501, 502-506).—I. The system benzene-sulphur monochloride has a euteetic point at -92° corresponding with about 4% of benzene. The viscosity isotherms at 15.5° and 20° are continuous and show neither maximum nor minimum. With increasing percentage of benzene the fall in viscosity at 20° is considerably more rapid than at 15.5°. It is inferred from Batschinski's rule that sulphur monochloride is associated, but that dissociation is promoted by the presence of benzene.

II. Evidence of an unstable compound, $PhNO_2,S_2Cl_2, m. p. -18^\circ$, is obtained from the thermal diagram for the system nitrobenzene-sulphur monochloride. The density in this system varies linearly with the composition at 20°. The viscosity isotherm at 20° is partly linear, but between 50 and 80% of nitrobenzene the viscosity is lower than that calculated from the mixture law; the divergence is less than in the 3° isotherm, in which the observed viscosity is lower throughout than the calculated. F. G. TRYHORN.

Partial pressures of binary solutions. R. W. DORNTE (J. Physical Chem., 1929, 33, 1309-1331).-Measurements of the partial pressures have been made for mixtures of ethyl alcohol and water at 25°, and for mixtures of benzene and carbon disulphide at 20°, 25°, and 30°, by the use of an interferometer. Bancroft's equation (this vol., 255, 638) holds over a wide range of concentration, especially in the second system, and it can be successfully applied to the data of Campbell (Trans. Faraday Soc., 1910, 10, 197) and others on various binary systems containing one volatile component. Data for the system ethyl alcohol-water obtained by a distillation method and by the interferometer method are compared and the latter is shown to be untrustworthy unless an empirical L. S. THEOBALD. calibration is used.

Reactivity of atoms and groups in organic compounds. IX. Vapour pressures, densities, and refractive indices of binary mixtures. S. W. PRENTISS (J. Amer. Chem. Soc., 1929, 51, 2825-2832) .- An apparatus for the measurement of vapour pressures by a static method is described. Determinations of the vapour pressures at 20° of binary mixtures of nitrobenzene, acetone, n-butyl alcohol, and benzene with pyridine or ethyl iodide, the densities at 25° of similar mixtures of nitrobenzene, acetone, tert.-butyl alcohol, and benzene with pyridine or ethyl iodide, and refractive indices at 25° of benzene and nitrobenzene with pyridine or ethyl iodide show that the deviations from the ideal solution laws bear no relation to the "adjuvance" of the solvent (Norris and Prentiss, this vol., 47). H. BURTON.

Physico-chemical measurements of azeotropic mixtures. W. HERZ and (MISS) M. LEVI (Z. anorg. Chem., 1929, 183, 340-346).—Some of the physicochemical properties of azeotropic mixtures of the following pairs of liquids have been determined at 20°, 30°, 40°, and 50°, and compared with the values calculated from the mixture rule : methyl alcoholethyl acetate, methyl alcohol-ethylene chloride, and ethyl alcohol-ethylene chloride. The b. p. of these mixtures all lie below the b. p. of their components. The density, viscosity, surface tension, and possibly also the heat of vaporisation are lower for the azeotropic mixture than is calculated by the mixture rule, whilst the specific heat is higher. M. S. BURR.

Glass. IV. Viscosity data for liquid dextrose and dextrose-glycerol solutions. G. S. PARKS and W. A. GILKEY (J. Physical Chem., 1929, 33, 1428—1437; cf. this vol., 980).—The viscosities of undercooled liquid dextrose have been measured by methods of shear at temperatures between 28° and 110°. Five different samples gave slightly different viscosity-temperature curves between 28° and 60°, probably owing to varying proportions of α - and β glucose in the samples and to variable but small amounts of water. The "hardening point" has been arbitrarily defined as the temperature at which $\eta = 10^{13}$ poises; this occurs at 25° with dextrose. The system dextrose-glycerol gives fairly stable organic glasses when correctly cooled, and the viscositics and hardening points for glasses of various compositions in this system have also been determined.

L. S. THEOBALD.

Critical state. IV. Solutions in ethyl ether. E. SCHRÖER (Z. physikal. Chem., 1929, 142, 365-390; cf. this vol., 498).—The limiting curves in the temperature-density and temperature-pressure diagrams have been determined for solutions of triphenylmethane, phenanthrene, benzil, and of resorcinol in ethyl ether. The temperature-density curves are made up of two parts corresponding with two distinct systems, viz., a small amount of dis-solved substance in a large amount of solvent phase, and a large amount of dissolved substance in a small amount of solvent. In the temperature-pressure diagrams the pressure increases linearly with the temperature up to the critical point, after which the curve begins to bend towards the temperature axis. The elevations of the critical temperature and of the critical pressure are directly proportional to the number of dissolved molecules up to fairly high concentrations. The critical opalescence is much more intense with the solutions than with pure ether. In certain cases the phenomenon of retrograde condensation was observed isothermally and quantitatively. Isothermals of some of the solutions have been determined and are found to be displaced in the direction of the liquid state compared with the isothermals of pure ether. This displacement is strongest in the region of high compressibility of pure ether. The isometric lines of solutions are linear, *i.e.*, $(\partial p/\partial t)_v$ is constant above the critical temperature. O. J. WALKER.

Demixing curves with more than one inflexion. P. A. MEERBURG (Rec. trav. chim., 1929, 48, 935959).—A second maximum in the miscibility curve of castor oil and 89.9 vol.-% of ethyl alcohol occurs on the addition of small amounts of sesamé oil. The critical solution temperature in the castor oilalcohol eurve occurs at 27.4° with a mixture containing 62.5% of castor oil. This critical solution temperature increases to about 40° at practically constant percentage of castor oil on the addition of sesamé oil. The new critical solution temperature occurs in mixtures containing 10-15% of castor oil and increases from 19° to 55° as the percentage of sesamé oil rises from 2.94 to 10.52%.

F. G. TRYHORN. Determination of temperature of completion of solidification of mixed crystal series by heating curves. R. RUER and K. KREMERS (Z. anorg. Chem., 1929, 183, 223-224).—For determining the completion of solidification of mixed crystals the breaks in the heating curve are more sharply defined than those of the cooling curve. It is therefore more satisfactory to employ the heating curve, especially in metallic systems which have high heat conductivity and fusion velocity. A correction of +3° should be applied to the temperature at which fusion begins. M. S. BURR.

Transition of austenite into martensite in hardened steel. E. SCHEIL (Z. anorg. Chem., 1929, 183, 98—120).—Dilatometric measurements have been made with hardened steel with the view of determining the conditions governing the transition of austenite into martensite during cooling. Since the transition velocity is very great over the whole temperature range of $+300^{\circ}$ to -200° the main factor cannot be diffusion. The measurements show that the transition is caused by internal mechanical stresses, since diminution of these forces, e.g., by keeping the steel at the ordinary temperature for several days, retards the formation of austenite. When viowed under the microscope the transition process resembles the formation of twin crystals under the influence of mechanical forces. H. F. GILLBE.

Absorption velocity of gases by liquids. II. Absorption of carbon dioxide by sodium hydroxide solution. S. HATTA (J. Soc. Chem. Ind. Japan, 1929, 32, 809-814; cf. this vol., 150).-With the apparatus used previously, the author has studied the velocity with which carbon dioxide mixed with air is absorbed by sodium hydroxide solution (N, 2.14N, 3.16N, and 4.15N) at 20° and 30° and sometimes under 1.53 atm. pressure. Under the same conditions, the rate of absorption is always less than that obtained with potassium hydroxide. The curves representing the relation between the absorption velocity and the concentration of the free alkali are quite different in the two cases. For sodium hydroxide the velocity decreases continuously as the free alkali decreases, but discontinuities are observed with potassium hydroxide. This is attributed to differences in the chemical reaction between carbon dioxide and the two alkalis. Although the method used is not very accurate, it would seem that the reaction velocity is proportional to p^n , where p is the pressure of the carbon dioxide and n < 1.

K. KASHIMA.

Solubility of iodine in gaseous carbon dioxide. H. BRAUNE and F. STRASSMANN (Z. physikal. Chem., 1929, 143, 225—243).—The vapour pressure of iodine, and the increased saturation concentration of iodine in the gas phase in presence of carbon dioxide at 1—50 atm. pressure, have been determined over the temperature interval $32.6-98.5^{\circ}$. The molecular attraction coefficient for iodine and carbon dioxide varies inversely as the temperature and decreases rapidly at high carbon dioxide concentrations; the heat change for the dissolution of iodine in carbon dioxide at *M*-concentration is about 1000 g.-cal./mol. The experimental results are correlated with those of Quinn (A., 1928, 470).

H. F. GILLBE. Solubility of sodium salicylate in alcohol. W. SCHNELLBACH (Amer. J. Pharm., 1929, 101, 586-587).—One g. of sodium salicylate dissolves in 7.52 g. of U.S.P. alcohol (d_1^{25} 0.8083) at 25°.

E. H. SHARPLES.

Calcium oxalate and its solubility in the presence of inorganic salts with special reference to the occurrence of oxaluria. (MLLE.) G. HAMMARSTEN (Compt. rend. Lab. Carlsberg, 1929, 17, No. 11, 1-85).-Neutral calcium oxalate forms three hydrates. The dihydrate and trihydrate are readily converted into the monohydrate, which is the stable form above 0°. The rate of conversion varies largely with the temperature, and, in the case of the trihydrate, is accelerated by oxalate ions. The solubility of calcium oxalate in water and in solutions of sodium, potassium, lithium, rubidium, and ammonium chloride, and of sodium and potassium sulphate at 37° has been determined. The results are not in good agreement with the Debye-Huckel theory. The solubilities have also been measured in solutions of primary and secondary sodium phosphates, in mixtures of the latter with sodium chloride, in magnesium chloride, and in mixed magnesium chloride-sodium chloride solutions.

C. W. GIBBY.

Solubility relationships and solvation in nonaqueous salt solutions. P. P. KOSAKEWITSOH (Z. physikal. Chem., 1929, 143, 216-224).—The alkali metal halides diminish the solubility of carbon dioxide in methyl, ethyl, and *n*-butyl alcohols and in acetone, the magnitude of the effect diminishing in the order : lithium, sodium, and iodine, bromine, ehlorine for ethyl alcohol, and lithium, sodium, and iodine, chlorine, bromine for methyl alcohol. In concentrated solution the salt molecules combine with 3—5 mols. of solvent, and in very dilute solution with 7—10 mols. H. F. GILLBE.

Solubility of sodium and calcium in their chlorides and in chloride mixtures. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, **183**, 121— 126).—The solubility of sodium in sodium chloride is $4\cdot2\%$ at 800° and 15—20% at 850°, whilst at higher temperatures the metal phase disappears. The total solubility of sodium and calcium at constant temperature in a fused mixture of sodium and calcium chlorides increases in an approximately linear manner with the calcium chloride concentration, and increases rapidly with rise of temperature. H. F. GILLBE.

Wo. Ostwald's "solid-phase rule" and the solubility of casein in sodium hydroxide. S. P. L. SøRENSEN and J. SLADEK (Kolloid-Z., 1929, 49, 16-35).—The authors' physico-chemical inter-pretation of the abnormal solubility relations of globulin and other proteins is compared with Wo. Ostwald's colloid-chemical explanation. Measurements of the solubility of casein in dilute solutions of sodium hydroxide show that with constant amounts of sodium chloride and hydroxide and increasing amounts of casein, the quantity of casein which dissolves increases so long as the proportion of casein to sodium hydroxide does not become very great; at the same time, the p_{π} of the solution falls. On the other hand, the percentage of casein which is dissolved by a constant amount of sodium hydroxide diminishes as the total quantity of casein increases. With a constant quantity of sodium chloride and of casein, the amount of casein which passes into solution is increased by using larger quantities of sodium hydroxide and the p_{π} of the solution increases. The distribution of the sodium hydroxide between the solution and the solid phase is such that the excess of sodium hydroxide in the solution (C_{NaOH}) increases with the amount of sodium hydroxide used more rapidly than the amount of dissolved case (C_N) , so that the relation falls with increasing p_n . Increase in the concentration of sodium chloride has the effect of raising the solubility of casein in dilute solutions of sodium hydroxide, and of decreasing the solubility in dilute hydrochloric acid. It seems that addition of increasing amounts of sodium chloride displaces the isoelectric reaction of casein in the acid direction. The increase in solubility brought about by sodium chloride in alkaline solutions becomes more pronounced until a concentration 2N is reached, and at higher concentrations the solubility falls again, probably as the result of the formation of compounds between casein and sodium chloride or its E. S. HEDGES. ions.

Solubility of oxygen in solid iron. W. KRINGS and J. KEMPKENS (Z. anorg. Chem., 1929, 183, 225-250).-The solubility of oxygen in solid iron has been determined by a kinetic method. Mixtures of hydrogen and water vapour of definite composition were passed over iron or iron oxide at 715° until no further change in weight of the solid took place. The pressure of oxygen in the gaseous phase was determined from the amount of water vapour by the equilibrium relation $2H_2O \Longrightarrow 2H_2 + O_2$ and the value plotted against percentage of oxygen in the solid. Starting with iron, for example, the percentage of oxygen present in the iron increases as the pressure of oxygen increases until a certain maximum limiting pressure is reached. This represents the pressure at which the iron is saturated with oxygen, and formation of ferrous oxide begins. The solubility is thus found to be $0.11 \pm 0.015\%$, which is greater than the values for technical iron based on metallographic observations or on the relation between oxygen content and physical properties. On the other hand, it is below that found by other investigators by a static method. It is claimed that the kinetic method possesses considerable advantages over the static. The suitability of a number of different materials for combustion boats has been tested.

M. S. BURR. Distribution equilibrium of silver between lead and aluminium. Test of the distribution law for condensed systems. R. LORENZ and F. ERBE (Z. anorg. Chem., 1929, 183, 311-339).-The system aluminium-silver-lead has been investigated at 750° and 1000° over a large concentration interval. Lead and aluminium are practically immiscible with one another and their great density difference facilitates the separation of the two phases. Silver is miscible with both, but does not appreciably influence their mutual solubility, except at very high concentrations. The results are tabulated and ternary diagrams showing weight percentages and atomic percentages at 1000° are given. At both temperatures the distribution ratio, silver in aluminium to silver in lead, remains approximately constant at low concentrations, *i.e.*, is in agreement with the ideal distribution law. It then slowly increases to a maximum, after which it falls rapidly. Values for 1000° are, throughout, smaller than for 750°. The results are discussed from the point of view of van Laar's distribution law. For lack of exact values for van der Waals' constants of the distributing material, the results cannot be made to agree quantitatively with van Laar's law, but they agree a little better with the latter than with the ideal distribution law. Some experiments have also been carried out using tin instead of silver, and the results recorded, but as all three metals become completely miscible at moderately high concentrations of tin, the results are useless for the purposes of the investigation.

M. S. BURR.

Sorption of sulphur dioxide, carbon dioxide, and nitrous oxide by activated carbon. D. O. SHIELS (J. Physical Chem., 1929, 33, 1386-1397).-The adsorption of carbon dioxide, nitrous oxide, and sulphur dioxide by an activated gas-mask charcoal at $25^{\circ}\pm0.03$ has been determined from 0 to 40 mm. pressure for the first two gases, and from 0 to 22 mm. for the last. In the case of carbon dioxide, adsorption is reversible, but with the other two gases, especially the last-named, hysteresis occurs. As is to be expected from their similar electronic configurations, carbon dioxide and nitrous oxide give isotherms which nearly coincide, whilst the curves obtained by plotting the volume of liquid adsorbed against the quotient p/P, where p is the equilibrium pressure observed during adsorption and P is the saturation pressure at 25°, coincide exactly for these two gases. The order of adsorption differs from that obtained with silica gel (Patrick and others, A., 1925, ii, 508), being greatest with sulphur dioxide and least with carbon dioxide. The adsorption of nitrous oxide and carbon dioxide can be represented by Patrick's equation, $V = K(p/P)^{1/n}$. L. S. THEOBALD.

Adsorption of mercury vapour by activated charcoal. D. O. SHIELS (J. Physical Chem., 1929, 33, 1398—1402).—The adsorption of mercury vapour by activated charcoal at the ordinary temperature in a vacuum is of the order of 0.2 mg. per g. of charcoal. No definite indication of adsorption in the presence of air was obtained. The results are of the same order of magnitude as those of Coolidge (A., 1927, 928), but differ from those of Zelinski and Rakuzin (A., 1926, 1090), whose method is shown to be untrustworthy. L. S. THEOBALD.

Calorimetric determination of heats of adsorption. A. MAGNUS and H. GIEBENHAIN (Z. physikal. Chem., 1929, 143, 265—277).—An extremely sensitive calorimeter whereby heats of adsorption may be experimentally determined is described. The heats of adsorption Q of carbon dioxide on silica and on carbon remain approximately constant over the pressure range for which Henry's law is valid; at higher pressures Q undergoes a linear decrease with increase of pressure, the rate of decrease diminishing at the highest pressures studied. With rise of temperature Q decreases. H. F. GILLBE.

Adsorption of phosphoric acid by stannic sulphide. R. CHANDELLE (Bull. Soc. chim. Belg., 1929, 38, 255—258).—There is a definite but small adsorption of phosphoric acid by stannic sulphide. If the phosphorus in a bronze is determined by removing the metal as sulphide and precipitating with magnesia mixture there is a loss of about 0.2%of the total phosphorus due to adsorption. The formation of basic compounds of tin should be avoided, since these increase the adsorption of phosphoric acid. O. J. WALKER.

Probable role of ammoniacal complexes in the adsorption of copper and nickel salts by ferric hydroxide. (MLLE.) L. S. LÉVY (Compt. rend., 1929, 189, 426—428).—Extension of earlier experiments (this vol., 1001) has shown that the influence of ammonia on the formation and stabilisation of complex salts depends on the concentration of the ammonia and that only the portion of the copper or nickel salt liberated by hydrolysis of the complex ion is capable of being adsorbed. An excess of ammonia has no influence except in so far as it alters the $p_{\rm H}$ value of the medium (cf. Geloso, A., 1927, 407). J. GRANT.

Adsorption of aerosols by solids. A. ASTROM (Svensk Kem. Tidskr., 1929, 41, 190-203).-The preparation and properties of aerosols are discussed. The degree of adsorption is determined by counting the number of particles in unit volume of the aerosol, before and after passage of the filter, the ultramicroscope being employed; it is necessary to take the mean of a large number of observations in order to secure trustworthy results. An alternative method is to measure the Tyndall effect, using the apparatus of Tolman and Vliet (A., 1919, ii, 180), the intensity being proportional to the concentration of the disperse phase. Particles of size ranging from 50 to 100 µµ are the most difficult to adsorb. Passage through cotton and woollen filters showed that the degree of adsorption increased with the thickness of material, but was not directly proportional to this; direct proportionality exists, however, between the rate of passage through the filter and the amount of unadsorbed solid. Adsorption is rendered more complete if the air charged with the aerosol is passed intermittently through the filter instead of in a steady

stream. The above experiments were made using aerosols formed by condensation of superheated vapours in a continuous current of air, as such are relatively homogeneous. Aerosols prepared by dispersion (e.g., by detonation) give untrustworthy results owing to the rapidity with which they aggregate. H. F. HARWOOD.

Determination of maximum adsorption of activated charcoal. H. BURSTIN and J. WINKLER (Przemysl Chem., 1929, 13, 114–119).—For the system activated charcoal-benzene the maximum adsorption is $A_{\text{max}} = kQ$, where Q is the heat of wetting; k was determined experimentally.

CHEMICAL ABSTRACTS.

Heterogeneous splitting reactions. H. DOHSE and W. KALBERER (Z. physikal. Chem., 1929, B, 5, 131-155).-The elimination of water from isopropyl alcohol at the surface of bauxite is investigated as an adsorption phenomenon, and the part reactions are discussed. The kinetics of the decomposition show that it may be regarded as a continuous reaction of a surface layer which becomes gradually diminished by the adsorption of reaction products. The heat of activation is 39,000 g.-cal. The inhibitive effect of water on the reaction is investigated. If water is removed the reaction is of zero order, and the heat of activation is then 26,000 g.-cal. The difference between these two quantities of heat corresponds with the heat of desorption of water. The adsorption isotherms of water, propylene, and isopropyl alcohol on the surface of bauxite were obtained at different temperatures in the neighbourhood of the reaction temperature. For small densities on the surface the unimolecular constant is independent of the quantity adsorbed, but it decreases rapidly with increasing densities. A. J. MEE.

Regional absorption of dyes by growing crystals. A. G. MILLIGAN (J. Physical Chem., 1929, 33, 1363-1373).-Crystals of potassium alum separating from a saturated solution coloured by chlorazol-sky-blue FF show a modified habit and an intense blue coloration in the centre of each cubic face. This regional deposition of the dye favours the development in area of the absorbing face by retarding the deposition of salt upon it. Croceine-scarlet 3B has a similar effect, but the absorption in this case is weaker and the inhibition of growth is less marked. Regional absorption also occurs with methyl-violet, but other dyes are either salted out by the saturated solution of alum or are not absorbed (methylene-blue, acid-green G, etc.). Sodium chlorate and phloxine or croceine-scarlet 3B, and oxalic acid and rhodamine B also showed this phenomenon, and Rochelle salt and croceine-scarlet 3B, chlorazol-sky-blue FF, and acid-green G showed it to a marked degree, but little or no alteration of habit occurred in these last three cases. Rochelle salt and acid-green G gave the only instance of absorption of the dye simultaneously on two forms of the crystal. An hypothesis to account for regional absorption is tentatively advanced.

L. S. THEOBALD. Adsorption phenomena in systems of several constituents. C. WAGNER (Z. physikal. Chem.,

1929, 145, 389-396).-From measurements of the surface tension of aqueous solutions of aniline-phenol mixtures the quantities of each of these substances adsorbed by powdered charcoal at an air-water interface have been determined. Below certain limiting concentrations at which blocking of the surface occurs, the presence of one constituent favours the adsorption of the other, showing that the mutual effect of the molecules is an important factor in the adsorption. The nature of this attractive force remains uncertain. In the case of aniline the ratio (amount of aniline adsorbed)/(concentration of aniline in solution) increases with increasing concentration of aniline. A qualitative explanation of these two results is given by taking into account the effect of the reciprocal action of phenol-phenol and anilincphenol molecules in the adsorption layer on the F. L. USHER. work of adsorption of phenol.

Frenkel adsorption isotherm. F. J. WILKINS and A. F. H. WARD (Nature, 1929, 124, 482).—An algebraic error is corrected (cf. Frenkel, Z. Physik, 1924, 26, 133). A. A. ELDRIDGE.

Theory of liquid film formation. C. W. FOULK (Ind. Eng. Chem., 1929, 21, 815-817).-It has been established that pure liquids do not foam; that some substance must be molecularly or colloidally dispersed in a liquid to make it foam; that foams can be produced whether the added substance is positively or negatively adsorbed at the surface; and that certain substances have the property of destroying foam and preventing its formation. A study of the mechanical aspects of liquid film formation leads to the view that liquid films are always the result of the approach to each other on the liquid side of two already formed surfaces. Several examples are given and the view is supported by energy considerations. A new theory of film formation is developed which aims at explaining why in the case of solutions two surfaces when very close to each other resist a mechanical push to bring them together, whilst there is no such resistance in the case of the surfaces of a pure liquid. Starting from the fact that in solutions the solute is either more or less concentrated in the surface layer than in the interior of the liquid, it is maintained that such a system will resist a force tending to bring about an equality of concentration, that is, it will resist a tendency to mix the surface layer with the rest of the liquid. A resistance will therefore be set up when two such surfaces are brought together by some small mechanical force. The theory explains why the effect is the same whether the surface tension is raised or lowered by the dissolved matter. The view is expressed that film formation and film stability are separate questions which have often been confused in the literature.

E. S. HEDGES. Growth of silver iodide films. U. R. EVANS and L. C. BANNISTEE (Proc. Roy. Soc., 1929, A, 125, 370-394).—A study has been made of the relation between the weight increment and the interference colour due to the iodide film which is formed on exposure of silver foil to solutions of iodine in chloroform. The experimental results do not support the assumption, made by previous investigators, that the

thickness of the film can be judged by dividing the thickness of the air film required to give the same colour by the refractive index of the film material: this method, in fact, gives values too low at great thicknesses and too high at small thicknesses. A new colour method is described which is more accurate for small specimens than direct weighing. A short pre-exposure to air at ordinary temperatures does not measurably affect the growth of iodide films, although exposure for 30 min. at 400° considerably retards film formation, and a preliminary heating in a vacuum, with hydrogen as the residual gas, accelerates it. Electrometric and nephelometric methods have been used to determine the film thickness, and are compared with the gravimetric procedure. The rate of growth of the film has been studied under different conditions of solvent, stirring rate, abrasive treatment, temperature, and concentration of solution. Other things being equal, violet solutions cause much quicker growth of films than brown solutions, and coarsely abraded surfaces are attacked more rapidly than finely abraded. The velocity of film growth is increased by stirring. The fact that the rate of thickening decreases with the thickness indicates that the process is essentially controlled by diffusion through the solid film. The concentration factor indicates that the molecular condition of the free iodine in the film is never less complex than I₂, but the small temperature coefficient excludes the possibility of gaseous diffusion through large apertures. The effect of varying the solvent makes it highly improbable that the solution, including the solvent, enters the pores. The mechanism of film growth which best fits the experimental data is that the iodine passes through pores of a few molecular diameters in loose union with the silver iodide of the walls, a process intermediate in character between gaseous diffusion and diffusion in solid solution. This conception is supported by previous work on films other than iodides.

L. L. BIRCUMSHAW.

Velocity of crystallisation. I. E. N. GAPON (Ukraine Chem. J., 1929, 4, 161-192).-The velocity of crystallisation of ammonium oxalate, sodium oxalate, potassium sulphate, potassium dichromate, sodium picrate, potassium alum, ammonium alum, and potassium nitrate was determined by two methods. The first consists in adding a known weight of a salt to 250 c.c. of a solution of the salt of known supersaturation, at either 0° or 25°, and stirring vigorously (1500-1800 r.p.m., at which velocity of stirring the velocity of crystallisation becomes independent of the intensity of stirring). A sample is withdrawn every $\frac{1}{2}$ min. The second ("compensation") method consists in determining the velocity of crystallisation of a solution of a degree of supersaturation C_1 and of three other solutions with supersaturation values $C_1/2$, $C_1/2^{1/2}$, and $C_1/2^{1/3}$ and in the presence of twice the number of crystallisation centres. From these experiments it appears that the two factors which determine crystallisation from a supersaturated solution are dehydration of the ions and adsorption, and also that for the majority of the salts the process of crystallisation consists of two stages, the initial and the normal. In the initial stage if the velocity is determined by adsorption its order will be unity as, for instance, in the first $\frac{1}{2}$ — $l\frac{1}{2}$ min. of the crystallisation of a supersaturated solution of sodium oxalate, and most of the other salts. If, however, the velocity is determined by dehydration of the ions, then the order of the reaction will be equal to the number of ions dehydrated, *e.g.*, crystallisation of sodium picrate at 25°. In the normal stage the order is always bimolecular. A. FREIMAN.

Trichloroacetic acid as a cryoscopic medium for organic compounds and binary salts. P. WALDEN (Rec. trav. chim., 1929, 48, 880-884).-The high cryoscopic constant (122) of trichloroacetic acid renders it a useful medium for mol. wt. determinations of organic compounds, especially for those in dilute solution. Typical organic compounds have normal mol. wt. in this medium. On the other hand, typical binary salts which in aqueous solution are classed uniformly as strong, may behave in trichloroacetic acid solution in different ways, ranging from double or triple association to complete dissociation. Both cation and anion have a marked influence on the mol. wt. Salts of a given cation, e.g., NMe₄, with a series of equivalent, strong anions, e.g., Cl', Br', I', NO₃', may behave quite differently, exhibiting molecular states between association (x=2) and complete dissociation. Salts of a given anion, e.g., I', Cl', or the picrate ion, change in molecular condition with change of cation. The degree of association of salts of alkylated ammonium bases varies with the size of the alkyl group and the degree of alkylation. In view of the low dielectric constant of trichloroacetic acid the high dissociation of many of these salts cannot be referred to high ionisation of the type $MA = M^+ + A'$, but must be attributed to acidolysis of the type $M^+A' + xCCl_3 \cdot CO_2H = M^+CO_2' \cdot CCl_3, (x-1)CCl_3 \cdot CO_2H \longrightarrow AH$. It appears that through the action of the solvent even strong acids may be driven out of combination with strong bases, and ions such as SCN', NO_3' , or $C_6H_2(NO_2)_3$.O' may be converted into non-ionising compounds. The results indicate that as a result of mass action and catalytic effects a solvent may completely alter the accepted affinity relationships F. G. TRYHORN. of acids and bases.

Apparent hydration of ions. III. Densities and viscosities of saturated solutions of ammonium chloride in hydrochloric acid. J. W. ING-HAM (J.C.S., 1929, 2059-2067).-The solubility of ammonium chloride in aqueous solutions of hydrochloric acid of concentrations up to 13N and the densities and viscosities of the saturated solutions have been determined at 25° . The density is a linear function of the acid and salt concentrations, and the solution volume of the ammonium ion is calculated to be 19.64. The effect of the chloride ion on the viscosity is approximately equal and opposite to that of the ammonium ion, and both effects remain practically constant over a wide range of concentration, indicating that neither ion is hydrated. From the viscosity data the solution volume of the ammonium ion is calculated to be 14. It seems probable that the viscosity is determined principally by the number of particles present in the

solution and on their sizes compared with that of the water molecule, the predominating species.

R. CUTHILL.

Dependence of equivalent refraction of strong electrolytes in solution on concentration. XI. Addition to "refractometric experiments" of Fajans and co-workers. W. GEFFCKEN (Z. physikal. Chem., 1929, B, 5, 81-123).—The dependence of equivalent refraction on concentration in the range from 2N to practically saturated solutions at 25° was investigated for a number of strong electrolytes. The solutions examined were potassium fluoride, sodium, potassium, rubidium, cæsium, and ammonium chlorides, sodium iodide, sodium and potassium nitrates, zinc sulphate, lithium, aluminium, and mercuric perchlorates. The expression for calculating the equivalent refraction of a dissolved substance can be written as $R = \text{const.} (\phi + \pi)$, where ϕ is a simple function of the density and concentration of the solution, and π is a function of the refractive index and concentration. It is possible to make use of this equation to obtain, graphically, the density of a solution from its concentration, and vice versa, with errors of 0.01% for the density, and 0.1% for the concentration. A useful control method for observations of density and refractive index is out-lined. A new method for the preparation of pure sodium iodide by the electrolytic reduction of sodium iodate is given. There is a very approximate linear relationship between refraction and concentration. Deviations are shown by sodium iodide and potassium fluoride. There is some confirmation for the assumption that with increasing concentration of electrolyte there are formed combinations of oppositely charged ions which are directly in contact with each other without the intervention of water molecules, thus giving rise to an undissociated fraction. A rough evaluation of the undissociated part on the basis of variation of refraction with concentration leads to reasonable results. The extrapolated values of the equivalent refraction of electrolytes at infinite dilution are shown to be strictly additive.

A. J. MEE.

Size of gas bubbles in liquids. R. SCHNUR-MANN (Z. physikal. Chem., 1929, 143, 456—474; cf. this vol., 903).—The size of the bubbles formed by forcing air through filters of various types into different liquids has been found to be determined by the viscosity of the liquid. In ionised liquids a subsidiary factor is the charge on the bubble, but this is effective only when the viscosity of the electrolyte solution is of the same order as that of water. The bubble size is independent of the nature of the filter used. These facts explain the author's results on the determination of the pore diameter of porcelain filters by the bubble pressure method. A picture of the process of formation of visible bubbles is given. F. L. USHER.

Velocity of elutriation and particle size. A. H. M. ANDREASEN and J. J. V. LUNDBERG (Kolloid-Z., 1929, 49, 48-51).—Experiments on the relation between elutriation velocity and particle size in the case of graded pulverised flint show that Stokes' law can be applied. E. S. HEDGES. BRITISH CHEMICAL ABSTRACTS.---A.

Theory and methods of ultracentrifuging. O. LAMM (Z. physikal. Chem., 1929, 143, 177-190).— The mathematical theory for the sedimentation and diffusion of a dissolved substance in a centrifugal field is developed. The optical refraction method of observing concentration changes has been applied to the experimental study of the ultracentrifuge, and experiments with solutions of starch and proteins demonstrate the usefulness of the method for the study of solutions containing two or more substances. H. F. GILLBE.

Interference colours of finely disperse precipitates in transmitted light. G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1929, 49, 1-3).---When water vapour from the air condenses on a glass slide cooled to -15° or -20° , or when the vapour of benzoic acid condenses on a cool glass slide, the film produced exhibits interference colours when viewed by transmitted light. A theory is advanced in explanation. E. S. HEDGES.

Nucleus formation in the condensation of vapours in non-ionised dust-free air. E. X. ANDERSON and J. A. FROEMKE (Z. physikal. Chem., 1929, **142**, 321—350).—A critical summary of earlier work dealing with nucleus formation in the condensation of vapour is given. An improved form of cloud condensation apparatus for the measurement of the expansion necessary for the various stages of condensation of a vapour is described. A volume of air saturated with water vapour must expand to $1.2006 \pm$ 0.0007 times its volume before condensation commences. The value of 1.252 found by Wilson is therefore too high. O. J. WALKER.

[Stability of coarse particles in solutions. IV. Formation and removal of liquid sheaths in suspensions of *Bulus alba*. Reversible sol-gel transformation; thixotropism.] H. WERNER (Ber., 1929, **62**, [B], 2474).—The author's experiments (this vol., 878) are in harmony with the conceptions of Ostwald (this vol., 137). H. WREN.

Theory of stability of disperse systems. II. Stability of hydrosols of Prussian-blue. E. N. GAPON (Ukraine Chem. J., 1929, 4, 155-159; cf. A., 1928, 949).—The stability at the ordinary temperature of dispersed systems of Prussian-blue in water for varying proportions of potassium ferrocyanide and ferric chloride has been found to decrease with increasing concentration of ferric chloride.

A. FREIMAN.

Emulsions and the effect of hydrogen-ion concentration on their stability. J. C. KRANTZ, jun., and N. GORDON (Coll. Symp. Mon., 1928, 6, 173—206).—The particle size and viscosity are affected by the $p_{\rm H}$ value for gum tragacanth emulsions, but not for gum arabic emulsions, except that for the latter the particle size increases at $p_{\rm H} > 7$. Fischer's hydrate theory appears to be substantiated by emulsions prepared with gum tragacanth. The stability of various emulsions has been determined. The surface tension of water-in-oil emulsions is unaffected by changes in $p_{\rm H}$ of the internal phase; unstable emulsions have a lower viscosity than stable emulsions. Variations in particle size, up to 30 μ , do not affect the stability. CHEMICAL ABSTRACTS.

Change of viscosity of sols and of precipitating concentrations of electrolytes with purity, and change of ratio of precipitating concentrations with temperature of coagulation. V. GORE and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 641-652; cf. this vol., 506).-The viscosity of ferric, stannic, ceric, zirconium, and thorium hydroxide sols increases steadily with the elimination of impurities, supporting the view that the increase of viscosity due to decrease of electric charge as a is result of the removal of adsorbed electrolyte. By reversing the process and adding electrolytes to the pure, unstable, and highly viscous sols of ferric, stannic, and zirconium hydroxides, stability and electric charge increase, owing to adsorption of electrolyte, whilst viscosity diminishes. The coagulum from an impure stannic hydroxide sol is white, but from a highly purified and viscous sol it is almost transparent, indicating that increase in hydration has accompanied purification. The ratio of the precipitating concentrations of uni- and bi-valent ions decreases as the purity and viscosity of the sols increase. On raising the temperature the ratio of the precipitating concentrations of uni- and bivalent ions with ferric, stannic, and ceric hydroxide sols becomes less, but the relative diminution in the ratio, as the temperature increases from 30° to 60°, is the same for any one sol no matter what its degree of purity may be. No definite relationship could be established between the viscosity and purity of the sols of arsenious and antimony sulphides, Prussianblue, cupric and uranium ferrocyanides, mastic, and gamboge, since they are all progressively hydrolysed M. S. BURR. on dialysis.

Relation of dielectric constant of emulsions to the concentration of the disperse phase and the degree of dispersion. A. PIEKARA (Kolloid-Z., 1929, 49, 97-102).—See this vol., 27.

Role of dielectric constants, polarisation, and dipole moment in colloid systems. VI. Swelling of cellulose acetate in binary mixtures. II. I. SAKURADA (Kolloid-Z., 1929, 49, 52-60).-Experiments have been made to determine the connexion between swelling and polarisation in binary mixtures consisting of benzene, carbon tetrachloride, or carbon disulphide as one component and one of the lower aliphatic alcohols as the other component. A binary system consisting of a dipole-free liquid and an aliphatic alcohol always gives a swelling maximum. Cellulose acetate swells more strongly in mixtures of alcohol with benzene than in those with carbon tetrachloride or carbon disulphide. Equimolecular concentrations of cellulose acetate swell to a practically equal extent in dilute solutions of alcohol in benzene, irrespective of the alcohol used, but at higher concentrations the swelling becomes less with increasing molecular complexity of the alcohol. Curves were constructed showing the deviations of the experimental values of total polarisation, dielectric constant, and swelling from the values calculated by means of the arithmetical mixture rule, and it is shown that all the curves take a similar course. E. S. HEDGES.

General solvation equation for colloid systems. Wo. OSTWALD (Kolloid-Z., 1929, 49, 60-74).- Measurements of the swelling of caoutchouc and gutta-percha in benzene, nitrocellulose in acetone, and isoelectric gelatin and hæmoglobin in water confirm Ostwald's equation $P = cRT/M + bc^n$, where Pis the observed osmotic pressure, c is the weight in g. of substance swelling in 1 c.c. of liquid, and b and n are constants. The solvation constant n generally has a value of approximately 2, whilst b is a characteristic colloid-chemical constant for each material. The view is confirmed that not only gels, but also sols can swell and that the "osmotic" pressure of a sol in a cell of micellar thickness is composed of the ordinary van 't Hoff pressure plus solvation pressure. E. S. HEDGES.

Effect of ultra-violet light on colloids. P. LAL and P. B. GANGULY (J. Indian Chem. Soc., 1929, 6, 547-556).—Since both negative and positive sols are coagulated by ultra-violet light the effect cannot be satisfactorily explained as the result of the generation of electrons by the radiation. A study of the $p_{\rm H}$ values of the clear filtrate from an ultra-filter, before and after coagulation, has shown that these change appreciably, increasing in some cases and decreasing in others. These variations in $p_{\rm H}$ value have been interpreted on the basis of known chemical and photochemical reactions, and the coagulation of colloids by the action of ultraviolet light is ascribed to the destruction of the stabilising agents in the chemical changes brought about by the light. M. S. BURR.

Action of X-rays on colloidal solutions. S. S. BHATNAGAR, R. S. GUPTA, K. G. MATHUR, and K. N. MATHUR (Z. Physik, 1929, 56, 684-693).--The velocity of cataphoresis of sols exposed to X-rays and those not so exposed, together with the stability of the two sets after the addition of electrolytes, have been measured. The exposures varied for different sols between 2 and 3 hrs. The following colloids were used: gold, silver, copper, copper hydroxide (positive and negative), and ferric hydroxide. To investigate the stability of the sols after addition of 0.02N potensium obligities addition of the solution of the solu of 0.02N-potassium chloride solution, and find whether it varied on exposure to X-rays, the optical transmission of the sols was determined by means of a thermopile. Only in the case of silver and copper (both prepared by Bredig's method) did the colour of the sol change after exposure. There was no change in the coagulation value of the copper sol. Except in the case of partly dialysed sols (ferric and copper hydroxides) there was no marked change in the velocity of cataphoresis before and after exposure. These results are discussed. A. J. MEE.

Preparation of jellies of some inorganic substances. S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 587—598; cf. A., 1926, 676; 1927, 934).—The conditions necessary for the formation of gels of the following inorganic substances are given, and their properties described : ferric borate, molybdate, and tungstate; thorium phosphate and molybdate; stannic arsenate, phosphate, tungstate, molybdate, and borate. M. S. BURR.

Silicic acid gels. I. Time of setting of gels. M. PRASAD and R. R. HATTIANGADI (J. Indian Chem. Soc., 1929, 6, 653-663).—Silicic acid gels

have been prepared by the action of ammonium acetate solution, with or without acetic acid, on solutions of sodium silicate. The time of setting has been determined by measuring the variation with time of the light scattered by the gel. The intensity of scattered light is found to increase more and more slowly until it reaches an approximately constant value. The time required for this is the time of setting. When there is no added acetic acid the time of setting decreases as the concentration of ammonium acetate increases up to a certain limit. At higher concentrations no gels, but only flocculent precipitates, are obtained. The gels are alkaline to litmus and no minimum value of the setting time is observed. The gels obtained with ammonium acetate acidified with acetic acid are alkaline, neutral, or acid to litmus; this depends on the concentration of ammonium acetate and acetic acid used, i.e., on the hydrogen- and hydroxyl-ion concentration. All mixtures set in a minimum time when they are slightly alkaline or neutral to litmus and the value of this minimum time is smaller the greater is the silica content of the mixture. Highly alkaline and highly acidic mixtures take a long time to set. The gels differ in appearance according as they are prepared from high or low concentrations of acidified ammonium acetate, the former being more transparent, and hence probably forming smaller aggregates, than the latter. M. S. BURR.

Diffusion in gels. V. MORAVEK (Kolloid-Z., 1929, 49, 39-46).—The diffusion of lead nitrate into dilute solutions of potassium dichromate contained in gels of gelatin, agar, and mixed gelatin-agar has been studied. The time course of the diffusion is in accordance with a parabolic equation, but certain irregularities were observed when the concentration of the diffusing lead nitrate was varied. In gelatin and in the mixed gels, the curve connecting rate of diffusion with concentration of the lead nitrate passes through two maxima. This behaviour is ascribed to the formation of compounds between gelatin and the potassium dichromate. The form of the curve also depends on the concentration of potassium dichromate in the gel. In agar gels the rate of diffusion is directly proportional to the concentration of lead nitrate in the superimposed solution and the rate was scarcely affected by increasing the concentration of agar. The formation of periodic structures in these experiments is related to a dynamic equilibrium between the gel and the aqueous phase.

E. S. Hedges.

Behaviour of swollen gelatin in water vapour. E. H. BUCHNER (Rec. trav. chim., 1929, 48, 1047— 1051).—Lloyd's observations (A., 1920, i, 452) on the behaviour of swollen gelatin (acid or alkali treatment) are confirmed. The loss of water from the swollen gelatin when kept in a saturated vapour (cf. *loc. cit.*) is due either to a change in the hydrogen-ion concentration of the gelatin or to surface forces.

H. BURTON.

Osmosis in ternary liquids through a membrane permeable to two of the three substances. F. A. H. SCHREINEMAKERS (Rec. trav. chim., 1929, 48, 926-930).—Theoretical. When demixing into two or more liquid phases does not occur in an osmotic system of the type $L_0|M(WY)|L$, osmotic equilibrium is possible only when L_0 and L have the same compositions. In the case of the systems $L_0(Y+W)|$ M(WY)|L(X+Y+W) and $L_0(W)|M(WY)|L(X+Y+W)$ osmosis will continue until the left-hand side has been completely absorbed by the right-hand side liquid. F. G. TRYHORN.

Donnan membrane equilibrium. Change of protein solutions by heating, its effect on the membrane equilibrium, and its relation to the viscosity. K. SHIGI (Kyoto J. Med., 1928, 25, 706—710).—N-Hydrochloric acid or sodium hydroxide was added to egg-white and the mixture was heated at 490° for various periods. With acid, no change of membrane potential occurs under 60 min. After 80 min. the potential gradually falls and becomes zero after 150 min. With sodium hydroxide a change in viscosity is observed after 10 min.

CHEMICAL ABSTRACTS. Use of flat membranes for dialysis and for the determination of the osmotic pressures of colloidal solutions. J. ZAKOWSKI (Chem. Fabr., 1929, 427—429).—It is practically impossible to prepare collodion membranes of the customary sacklike form which possess a uniform degree of porosity throughout. This condition is more easily attained if the membranes employed are flat, and types of apparatus are described in which membranes of this description are used. H. F. HARWOOD.

Cataphoretic migration velocity of zeolite suspensions. A. VON BUZAGH (Kolloid-Z., 1929, 49, 35-39).-Measurements have been made of the cataphoretic migration velocity of electrodialysed chabasito and electrodialysed synthetic aluminium silicate particles in presence of various electrolytes. Small concentrations of alkali hydroxides raise the ζ-potential, but higher concentrations lower it. Hydroxides of calcium and barium lower the ζ-potential at all concentrations. The chlorides of uni- and bi-valent cations have a discharging effect in the following order: Na<K<Ca<Ba. Aluminium and thorium chlorides discharge the particles at low concentrations, at higher concentrations they reverse the charge, and at still higher concentrations a further discharging effect in the positive region is observed. E. S. HEDGES.

Equilibrium constants of reactions involving hydroxyl. D. S. VILLARS (Proc. Nat. Acad. Sci., 1929, 15, 705—709).—Mathematical. The equilibrium constants are calculated from the heat of dissociation of the hydroxyl group. A. J. MEE.

Cryoscopic determination of molecular equilibria of resorcinol in aqueous solutions of potassium chloride and of sodium chloride. F. BOURION and C. TUTTLE (J. Chim. phys., 1929, 26, 291-311).—The view previously suggested (cf. this vol., 648, 759), that the higher cryoscopic constant obtained with solutions of resorcinol in aqueous alkali chloride solutions can be attributed to adsorption of water by the ions or molecules of the dissolved salt, is discussed and it is shown that there is a parallelism between the degree of hydration derived

from this assumption and that calculated by other methods. O. J. WALKER.

Chemical-kinetic and cryoscopic determination of equilibria in *p*-toluidine solution. Aminolysis. H. GOLDSCHMDT and E. OVERWIEN (Z. physikal. Chem., 1929, 143, 354-388; cf. A., 1907, ii, 244).—The behaviour of various inorganic and organic acids in the basic solvent p-toluidine has been studied. That the acids differ in strength just as in aqueous solution is shown by conductivity measurements and by the different velocities with which they catalyse the intramolecular reaction diazoaminotoluene \rightarrow aminoazotoluene. Although the reaction velocities and conductivities run parallel for a given series of catalysing acids, the velocity coefficients do not decrease as rapidly as the equivalent conductivities. Addition of bases decreases the re-action velocity and increases the conductivity to an extent depending on the amount of salt formation taking place between the acid and the added base. The aminolytic constant [salt]/[acid][base] obtained by the cryoscopic method is smaller than when calculated from reaction velocity measurements, but the series order for the acids used is the same for both. The amount of salt formation depends on the strength of the added base and of the acid used.

F. L. USHER.

Equilibrium between amylene and trichloroacetic acid in non-aqueous solvents. L. M. ANDREASOV (Ukraine Chem. J., 1929, 4, 143—148). —The equilibrium has been examined at 25° and 50° in benzene and carbon tetrachloride. The data are inconsistent with the supposed formation of double molecules of the acid. A. FREIMAN.

Electrolytic dissociation constant of hydrogen peroxide. V. A. KARGIN (Z. anorg. Chem., 1929 183, 77-80).—The difficulty of measuring the acid dissociation constant of hydrogen peroxide is discussed; by potentiometric titration with potassium hydroxide solution using the glass electrode the value $K=1.55 \times 10^{-12}$ at 20° is obtained. H. F. GILLBE.

Electrical dissociation of dibasic acids. V. Dissociation constants of the three hydroxybenzoic acids. E. LARSSON [with N. HOLMBERG] (Z. anorg. Chem., 1929, 183, 30-36).-The acidic and phenolic ionisation constants of salicylic and m- and p-hydroxybenzoic acids and the ionisation constants of their ethyl esters have been determined potentiometrically; the second constants for the o-, m-, and p-acids are 4×10^{-14} , 1×10^{-10} , and 4×10^{-10} , respectively, and the constants for the esters are 3×10^{-11} , 8×10^{-10} , and 5×10^{-9} , respectively. By consideration of the influence of the ionised carboxyl group on the hydroxyl group the values 1.1, 3.4, and 2.8 are derived as the distances in A. between the site of the electric charge and the hydroxyl hydrogen atom in the o-, m-, and p-hydroxybenzoate ions. H. F. GILBE.

Determination of the tertiary dissociation constant of phosphoric acid. I. N. KUGELMASS (Biochem. J., 1929, 23, 587–592).—Hydrolysis of the tertiary phosphates gives 1.02×10^{-12} at 20° and 1.48×10^{-12} at 38°. S. S. ZILVA. Dissociation of alkaloid salts (caffeine, colchicine). M. GOURSAT (J. Pharm. Chim., 1929, [viii], **10**, 263—267).—Potentiometric measurements of the $p_{\rm H}$ of mixtures of equivalent quantities of a solution of caffeine (14.98 g./litre) and 0.1N-solutions of sulphuric, hydrochloric, tartaric, oxalic, and benzoic (0.01N) acids show that the salts are completely dissociated in solution, the $p_{\rm H}$ value being the same as that of the free acid. Similar results are obtained with colchicine (3.99 g./litre) and 0.01Nsolutions of the same acids, and in agreement with this, both alkaloids are completely extracted with chloroform from their solutions in acids. J. W. BAKER.

Hydrolysis of aluminium salts of strong acids. V. CUPR (Coll. Czech. Chem. Comm., 1929, 1, 467— 476).—The hydrogen-ion concentrations of 0.5— 0.01M-solutions of aluminium sulphate, chloride, bromide, chlorate, perchlorate, and nitrate at 20°, of the sulphate, chloride, and bromide at 25°, and of 0.2—0.01M-solutions of aluminium potassium, aluminium sodium, and aluminium ammonium sulphate at 20° have been measured with the quinhydrone and hydroquinhydrone electrode. In dilute solutions the ratio [H]/[concentration] varies in approximately the same manner for the simple salts with the exception of the sulphate; differences appear in more concentrated solutions. A. I. VOGEL.

Germanium. V. Hydrolysis of sodium germanate and the dissociation constants of germanic acid. W. PUGH (J.C.S., 1929, 1994—2001; cf. this vol., 997).—The hydrolysis of sodium germanate at 20° has been determined over a concentration range of 0.001—0.100 g.-mol./litre, the hydrolysis constant at the highest dilutions having the value of about 0.054, which gives 1.9×10^{-13} for the second dissociation constant of the acid. Electrometric titration of sodium germanate with hydrochloric acid yields a titration curve of the form characteristic of dibasic acids and gives a value of 2.6×10^{-9} for the first dissociation constant of the acid. Roth and Schwartz' value (A., 1926, 350) therefore seems much too high. R. CUTHILL.

Electrolytic dissociation of some metal malonates. H. L. RILEY and (MISS) N. I. FISHER (J.C.S., 1929, 2006—2010).—If the degree of dissociation of an electrolyte is largely influenced by the readiness of the cation to accept electrons and of the anion to donate electrons, it would be expected that salts consisting of an anion which readily forms stable complex ions and a cation which departs considerably from the inert gas structure would not be very highly dissociated. In confirmation of this view it is found by conductivity measurements at 25° that the tendency to dissociation of magnesium, cadmium, zinc, and cupric malonates diminishes in this order. R. CUTHILL.

Physico-chemical studies of amino-acids. G. TAKAHASHI and T. YAGINUMA (Japan. J. Chem., 1929, 4, 15—31; cf. this vol., 141).—The b. p. of the *l*-ethyl ester of leucine at pressures between 4 and 480 mm., the solubility of *l*-leucine in water between -0.2° and 81°, and the densities of the solutions are recorded. The system *l*-leucine-HCl-H₂O has been investigated at 15° and 30°, establishing the exist-4 N ence of the compounds l-leucine hydrochloride hydrate, $C_6H_{13}O_2N$,HCl, H_2O , and β -l-leucine hydrochloride ethyl ester, $C_6H_{12}O_2N \cdot C_2H_5$,HCl. The optical rotation and dispersion of mixtures of l-leucine, hydrochloric acid, and water have been determined. C. W. GIBBY.

Lowest temperatures at which oxides show reduction by hydrogen. J. L. ST. JOHN (J. Physical Chem., 1929, 33, 1438—1440).—Reduction by hydrogen becomes appreciable at 140° in the case of copper oxide, at 185° with lead monoxide, at 280° with cadmium oxide, at 310° with zine oxide, and at 185° with arsenic trioxide. A connexion between the temperatures of initial reduction and the heats of formation of these oxides is suggested.

L. S. THEOBALD.

Hydrogen reduction equilibria of metal chlorides, bromides, and iodides at high temperatures, and the chemical constants of chlorine, bromine, and iodine. K. JELLINEK and A. RUDAT (Z. physikal. Chem., 1929, 143, 244-264).-The equilibria attained in the reduction of lead and manganous chlorides, and lead, silver, and cuprous bromides and iodides for temperatures at which the halides exert appreciable vapour pressures have been determined. Since the integration constants of the dissociation equilibria of the lead halides are considerably greater than the integration constants of the vapour-pressure equations of the corresponding condensed halogens, the conclusion is reached that the entropies of the crystalline halogens at 0° Abs. are appreciably greater than zero.

H. F. GILLBE.

Equilibrium $CO_2 + C \implies 2CO$. F. J. DENT and J. W. COBB (J.C.S., 1929, 1903—1912).—Investigation of the above equilibrium at 800°/1 atm., using various forms of carbon, has shown that the equilibrium composition depends on the character of the carbon and the pre-treatment which it has received. With graphite in presence of sodium carbonate as catalyst, the equilibrium mixture of gases contained 13.8% CO₂. Samples of coke impregnated with sodium carbonate and of coconut charcoal gave initially much smaller equilibrium concentrations of carbon dioxide, but repeated heating at 900° in a vacuum resulted in the concentration gradually rising to 13.8%, due apparently to progressive surface graphitisation, a change which was brought about with the coke more readily than with the charcoal. Sodium carbonate appears, below 1000°, to retard graphitisation. The reactivity of coke diminishes as reaction proceeds; the equilibrium composition of the gas phase before partial gasification is not the same as after, since the more active portions of the R. CUTHILL. coke gasify first.

Connexion between the different hydrates of a salt. W. BRÜLL (Z. anorg. Chem., 1929, 183, 347-352).—Theoretical. In the detection of the different hydrates of a salt by the dehydration method, it is necessary to carry out isothermal or isobaric dehydration at very varying temperatures and pressures, respectively, as, owing to the intersection of the $T-\log p$ curves, the region of stability of a given hydrate may not be realisable under the conditions of any single experiment. M. S. BURR. Equilibria between metals and salts in fluxes. XVIII. Equilibrium between calcium and sodium and their chlorides when lead and antimony are present in the metal phases. R. LORENZ and R. WINZER (Z. anorg. Chem., 1929, 183, 127–139).—Addition of lead to the metal phase displaces the equilibrium $Ca+2NaCI \implies CaCl_2+2Na$ to the right, but the effect does not conform to the law of mass action; the displacement increases until the ratio Pb/(Ca+Na) is about 8, after which further addition of lead produces no further change, and the mass action law is then applicable to the equilibrium. The influence of antimony resembles that of lead, but the magnitude of the maximum displacement is different. H. F. GILLBE.

Isotherms of the ternary system containing water, alkali sulphate, and a sulphate of the vitriol type. I. A. BENRATH (Z. anorg. Chem., 1929, 183, 296--300; cf. this vol., 650).—The isotherms for the system $MnSO_4-Na_2SO_4-H_2O$ at 50° have been determined, and also a certain amount of data at 11°, 25°, 30°, and 41° has been obtained. The results indicate the existence of the salt $MnSO_4, 3Na_2SO_4$, in addition to the compound $MnSO_4, Na_2SO_4, 2H_2O$ previously found (*loc. cit.*). M. S. BURR.

Uranyl formate. A. COLANI (Bull. Soc. chim., 1929, [iv], 45, 624–626).—The system uranyl formate-formic acid-water has been studied at 25°. A solution of uranyl formate monohydrate slowly deposits the basic formate $UO_3, 2H_2O, UO_2(HCO_2)_2, H_2O$, the solubility of which increases with the concentration of formic acid. The solubility of the monohydrate decreases with increase of acid concentration. O. J. WALKER.

Reciprocal salt pair MgSO₄-2NaNO₃-H₂O. II. W. SCHRÖDER (Caliche, 1929, **11**, 154-162).—See this vol., 267.

The general thermodynamical integrating factor of the entropy function. A. PRESS (Z. Physik, 1929, 56, 131-146).

Methods of calorimetry and the question of allotropy in the case of heats of dissolution of potassium nitrate and chloride. W. A. Roth and C. EYMANN (Z. physikal. Chem., 1929, 143, 321-353; cf. A., 1928, 22).—A review of the literature relating to the heat of dissolution of potassium nitrate in water reveals large discrepancies in the absolute values assigned to it by different workers, in spite of the good agreement between the results obtained by individuals. Fresh experiments have been undertaken in order to ascertain how far these discrepancies are to be attributed to defects in the calorimetric methods used and to inhomogeneity of the material. A specimen heated for a long time at 160° and then chilled at -16° gave a value about 1%lower than the values obtained when the salt had been cooled slowly from above its transition temperature, corresponding with an admixture of 8.5% of the β -modification, which, however, could not be prepared pure by this treatment. On the other hand, the results are influenced to a far greater extent by the type of calorimeter employed. If the course of the thermal change is different in the calibration and

the actual measurement, the usual method gives uncertain results, particularly if vacuum vessels or metal vessels of small size are used. A metal calorimeter completely immersed in water is the most satisfactory. These restrictions do not apply to adiabatic methods, which are, however, more difficult in use. The most suitable method is an adiabatic compensation method, in which the thermal effect is exactly neutralised by heat generated electrically within the calorimeter, an additional advantage being that the determination is made at a definite temperature. This method was therefore used, in conjunction with an immersed metal calorimeter, as a control in the measurement of the heats of dissolution of potassium nitrate and chloride. The following values are given: $KNO_3,350H_2O, -8.418$ kg.-cal. per mol./21.0°; $KCl,150H_2O, -4.322$ kg.-cal. per mol./21.0°; heat of neutralisation of 1 mol. of oxalic acid in 1170H₂O, +28.11 kg.-cal./20.0°. It is considered that many of the accepted thermo-chemical constants for solids are inexact. F. L. USHER.

Determination of heats of dilution of hydrated salts (second method). J. PERREU (Compt. rend., 1929, 189, 462—465; cf. this vol., 1014).—To determine the heats of dilution (L) and of addition (A) where these are very small the method adopted consisted in immersing a small bulb containing varying amounts of water (π) in varying amounts (P) of saturated solution of concentration p contained in a calorimeter, breaking the bulb, and measuring the heat evolved (q). This process is repeated until the total heat evolved is equal to that of dissolution in a large excess of water. The results are plotted on a πq curve, and A is determined as $(100M/p)(dq/d\pi)$. The values of A thus determined are : Na₂CO₃,10H₂O -0.95; BaCl₂,2H₂O -0.25; CuSO₄,5H₂O -0.10. L for CuSO₄,5H₂O deduced in this way is -2.48, agreeing well with -2.44 determined directly.

C. A. SILBERRAD. Adiabatic calorimetry. I. Temperature changes of the order of 1°. E. LANGE and E. O. ROUNSEFELL (Z. physikal. Chem., 1929, 142, 351— 364).—Improvements in calorimetric technique which have been evolved in the course of several years' work on heats of dilution and of dissolution (cf. Lange and others, 1925 onwards) are described. Amongst the points dealt with are the measurement of temperature changes of the order of 1° by means of mercury thermometers graduated to 0.01° and 0.001°, an electrical glass capillary heater for calibration purposes, and an electrically controlled speed regulator for maintaining constant speed of the stirring motor. The possibility and mode of prevention of errors due to heat exchange between the calorimeter contents and surroundings, and also of those due to evaporation and condensation effects, are discussed. O. J. WALKER.

Thermo-chemistry of hypochlorous acid and some of its salts in aqueous solution. B. NEU-MANN and G. MÜLLER (Z. anorg. Chem., 1929, 182, 235-254).—The heats of the reactions Cl_2+ 2MOH_{aq.}=MOCl_{aq.}+MCl_{aq.} and HOCl_{aq.}+MOH_{ad.}= MOCl_{aq.}+H₂O have been determined when M is

lithium, sodium, potassium, calcium, strontium, or barium. For the second reaction, the mean, value obtained is 8440 g.-cal./mol. and is lower than those given by Thomsen (9976 g.-cal.) and Berthelot (9600 g.-cal.). The heat of dilution of hypochlorous acid. increases with the concentration of the acid, and the heat of dissolution of chlorine monoxide (1 mol.) in water (2072 mols.) is found to have a mean value of 8737 ± 7 g.-cal. The heats of formation of aqueous solutions of hypochlorous acid and the hypochlorites of the above bases from their respective elements have been evaluated from these and other data. The values of [H, Cl, O, aq.] vary from 30,366 g.-cal. when calcium hydroxide is used to 30,550 g.-cal. with lithium hydroxide, the mean value from the six hydroxides being $30,439(\pm 0.1\%)$ g.-cal. The values for the hypochlorites are sodium 82,803, potassium 85,748, lithium 92,190, calcium 180,642, strontium 181,446, and barium 179,420 g.-cal./g.-mol. Other data are also evaluated.

Concentrated solutions of hypochlorous acid con-taining 16-22% HClO have been prepared by the addition of a slight excess of freshly-precipitated mercuric oxide to water saturated at 0° with chlorine and distillation at 18-20 mm. pressure. Addition of liquid chlorine monoxide to this product gave a chlorine-free solution containing 30% HClO. L. S. THEOBALD. Calorimetric researches. XVIII. The two

hydrobenzoins. P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1929, 48, 1031—1034).—The heats of combustion at 15° of d- and l-hydrobenzoin are respectively Q_v 1719.3, Q_p 1720.8, Q_v 1719.0, Q_p 1721.1 g.-cal. For the racemic compound obtained by the reduction of benzoin with aluminium ethoxide in boiling decalin the values Q_v 1718.6, Q_p 1720.0 were found. The heat of racemisation according to these data is 1.0 g.-cal. F. G. TRYHORN.

Transference of water and its dependence on concentration in the electrolysis of sodium chloride solutions. (MISS) M. TAYLOR and E. W. SAWYER (J.C.S., 1929, 2095-2106) .- Transport experiments have been made at 25° with 0.5N-solutions of sodium chloride containing carbamide, this substance having been shown by control experiments not to migrate under the influence of the electric field. A transportation of water towards the cathode was detected, the amount transported per faraday being rather greater than in Washburn's experiments with N-solutions (A., 1915, ii, 311). R. CUTHILL.

Electrical conductivity of salts of alkaloids in pure and in mixed solvents. J. N. RAKSHIT (J. Indian Chem. Soc., 1929, 6, 607-612).-Molecular conductivities of the hydrochlorides of morphine, codeine, narcotine, and cotarnine, in mixtures of alcohol and water varying in composition from pure alcohol to pure water, have been determined at 35° and at different dilutions. Molecular conductivity in all cases decreases as the water in the solution is replaced by alcohol, whilst the dilution of the salt remains constant. The relative variations are not the same for all the salts. M. S. BURR.

Conductivity measurements in very dilute alcoholic solutions. L. THOMAS and E. MARUM

(Z. physikal. Chem., 1929, 143, 191-215),-The conductivities of the sodium and piperidinium salts of trinitro-m-cresol and of hydrochloric and picric acids in dilute aqueous solution have been determined, the extrapolated values of λ_{∞} for the sodium salts being 80.3, 127.5, and 81.3, and for the piper-idinium salts 66.3, 113.5, and 67.3, respectively. The following values of λ_{∞} , in methyl and ethyl alcohol, respectively, have been extrapolated from conductivity measurements at dilutions up to 45,000 litres; sodium chloride 100.5, 43.0; sodium bromide 104.8, 44.9; sodium iodide, 110.3, 47.8; sodium picrate 94.7, 45.8; sodium trinitro-m-tolyloxide 92.7, 44.0; piperidinium chloride 112.6, 50.4; piperidinium picrate 106.8, 53.2; piperidinium trinitro-*m*-tolyloxide 104.8, 51.4.0 Measurement of the conductivity of very dilute solutions of hydrogen chloride in absolute and aqueous methyl and ethyl alcohols yields the values 0.25 and 0.06, respectively, for the equilibrium constant of the partition of the hydrogen ion between the alcohol and water; the difference of mobility of the alcoholated and hydrated hydrogen ion is in methyl alcohol 97.5 and in ethyl alcohol H. F. GILBE. 40.3.

Electrical conductivities of ammonia-water mixtures between 26 and 82% ammonia and from -30° to $+30^{\circ}$. M. DE K. THOMPSON and R. B. ATKINSON (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 19 pp.).—The electrical con-ductivities of ammonia and instance of the second ductivities of ammonia-water mixtures were measured in a glass cell. For solutions of lower ammonia content (from 26%) the specific conductance increases regularly and rapidly with rise of temperature, but with the more concentrated solutions the increase is comparatively slow and irregularities are observed which are attributed to action on the glass. At $+30^{\circ}$ solutions containing more than 50% of ammonia attack glass to such an extent as to interfere with the measurements. With regard to the possibility of using the data for the determination of the composition of ammonia-water mixtures in different parts of the circulatory system of a refrigerator, it is concluded that above 15° the composition of pure mixtures containing up to 50% of ammonia could be deter-mined to within 0.5%. At lower temperatures the accuracy becomes rapidly less and at -30° mixtures containing more than 32% of ammonia could not be analysed by this means. H. J. T. ELLINGHAM.

High-frequency conductivity and dielectric constants of aqueous solutions of electrolytes. H. RIECKHOFF (Ann. Physik, 1929, [v], 2, 577---615).—The change in conductivity of an electrolyte in a high-frequency field can be measured by the damping action on another vibrating system. The method is a substitution process with potassium chloride as the standard electrolyte. A wave-length of 1 m. is used. Data for twenty electrolytes with various valency combinations and different concentrations are in satisfactory agreement with the Debye-Falkenhagen theory of the dispersion effect. The principal deviations occur with the ions of higher valency. The effect of temperature conforms with theoretical requirements. Investigation of dielectric constants shows that the introduction of a dispersion

correction produces changes in the values of Hellmann and Zahn, but that such changes are generally quite small. Anomalous data obtained by Walden's resonance method are ascribed to an error in the indicator coupling, and a satisfactory indicator system is described. R. A. MORTON.

Dispersion of electrolytic conductivity. B. BRENDEL, O. MITTELSTAEDT, and H. SACK (Physikal. Z., 1929, 30, 576—578).—Preliminary. A method for measuring the conductivity of an electrolyte with high frequencies is described. Results with magnesium sulphate in relation to potassium chloride are in moderately good agreement with the Debye theory. R. A. MORTON.

Influence of pressure on the electrical conductivity of salt solutions. G. TAMMANN and A. ROHMANN (Z. anorg. Chem., 1929, 183, 1–29).— The percentage change of conductivity $\Delta\lambda$ with increase of pressure up to 3000 kg. per cm.² has been determined for aqueous solutions of sodium acetate, potassium cyanide, barium chloride, calcium chloride, mercuric chloride, ammonium cyanide, ammonium chloride, ammonium acetate, and hydrogen cyanide at 20-40°. The isothermal $\Delta\lambda/p$ curves for the strong electrolytes are all of the same type and exhibit maxima which with increase of concentration are displaced in the direction of higher pressure on account of the greater influence of pressure on the interionic friction at higher concentrations; with rise of temperature the maxima are displaced in the direction of lower pressures, and the curves become flatter. The isotherms for weak electrolytes are always concave to the pressure axis, and higher values are attained than for strong electrolytes; mercuric chloride is anomalous, since the isotherms for 0.1-0.3N-solutions resemble those for the weak electrolytes, for 0.01N are approximately linear, and for 0.001N-solutions become convex to the pressure axis. The variation of $\Delta\lambda$ with concentration at 500 kg. per cm.² approximates in general to that calculated from the influence of pressure on the volume and viscosity of the solution, the assumption being made that the influence of the interionic friction is equal to that on the viscosity of the solvent; at 300 kg. per cm.² the observed effect is greater than the calculated, although the curves are approximately parallel. The observed pressure effect affords evidence for the complete ionisation of strong electrolytes. The interionic friction of salt solutions, regarded as a function of pressure, passes through a minimum, the curves resembling that of the variation of the viscosity of water under pressure, but for acids the interionic friction diminishes continuously as the pressure rises. For the special case of zinc sulphate the variations with pressure of the interionic friction and the internal friction of the solution are very nearly equal on account of strong hydration. The influence of pressure on the hydrolysis of salts is discussed; although exact calculation of the effect is not possible, the experimental results are qualitatively in accord with theoretical requirements.

H. F. GILLBE.

Influence of pressure on the conductivity of solutions of acids. G. TAMMANN and W. TOFAUTE

(Z. anorg. Chem., 1929, 182, 353-381).-The influence of pressure on the conductivity of a number of solutions of weak and moderately strong electrolytes has been measured in relationship to the concentration and temperature. At constant temperature the percentage increase of conductivity, regarded as a function of concentration, reaches a maximum at a concentration which is the higher the greater is the dissociation constant of the acid. With ternary electrolytes the rate of increase of the influence of pressure on the dissociation constant with increase of concentration is less rapid, and lower maximum values are obtained, than for binary electrolytes. Increase of pressure causes an increase of interionic friction in all cases except that of the hydrogen and hydroxyl ions, for which the reverse holds true. The change of conductivity of water under pressure expressed as a function of the total ammonia and carbon dioxide concentration exhibits a well-defined minimum. H. F. GILLBE.

Standard electrode potentials in methyl alcohol. P. S. BUCKLEY and (SIR) H. HARTLEY (Phil. Mag., 1929, [vii], 8, 320—341).—In view of numerous sources of error and divergent values in the work of previous investigators, a study was initially made of reference electrodes, liquid-junction potentials, and activity coefficients in methyl alcohol. Measurements were made of the standard electrode potentials of hydrogen, sodium, thallium, silver, cadmium, and copper, and the results have been used for determining the solubilities of silver chloride, bromide, iodide, and thiocyanate and of thallium chloride, and the dissociation constant of methyl alcohol. The standard electrode potentials of chlorine, bromine, and iodine were found from the solubility products of the corresponding silver halides. The quinhydrone electrode was studied in aqueous and alcoholic solutions. N. M. BLIGH.

Quinhydrone electrode. A. E. BRODSKY and F. I. TRACHTENBERG (Z. physikal. Chem., 1929, 143, 287-300).—The general theory of the quinhydrone electrode is developed. The E.M.F. of the saturated quinhydrone electrode has been determined against that of the quinol electrode at various concentrations in water, and in absolute and aqueous methyl and ethyl alcohol solutions; the calculated solubilities agree with those determined analytically. The osmotic theory of electric cells is applicable to non-aqueous solutions. H. F. GILLBE.

Acidity and ionic potentials. J. N. BRÖNSTED (Z. physikal. Chem., 1929, 143, 301—312).—In general ionic potentials and electric potentials in chemical systems cannot be determined on the basis of ordinary thermodynamic considerations on account of the theoretical and practical inapplicability of the thermodynamic functions when passing from the concept of unchanged molecules to that of ions. A method is described for dealing with such functions by consideration of an electrically neutral isolated homogeneous phase. The measurement of acidity in terms of hydrogen-ion concentration is particularly discussed. H. F. GILLBE.

Electrode potentials of copper anodes and copper cathodes. E. F. KERN and R. W. ROWEN
(Amer. Electrochem. Soc., Sept., 1929. Advance copy, 14 pp.).-Measurements of the anodic polarisation at copper electrodes of various degrees of purity have been made in solutions of types used in copper refining, and of the cathodic polarisation during the deposition of copper from these solutions. All measurements were made at 1.6 amp./dm.² Agitation or circulation of the electrolyte decreased the polarisation, especially at the cathode, but the concentration of free acid in the electrolyte had no appreciable effect. Raising the temperature caused a slight decrease in anodic polarisation and a considerable fall in cathodic polarisation. The polarisation at the anode increased with increasing amounts of impurity in the copper. Addition of glue to the electrolyte produced a slight increase in anodic polarisation, but a considerable increase in cathodic polarisation, the latter actually increasing with rise in temperature. Addition of sulphite waste liquor residue ("goulao") caused a slight increase in polarisation at the anode, whereas that at the cathode was raised during only the first few minutes of electrolysis and then became normal. The effect of glue and goulac together was the sum of the separate effects. Equilibrium potentials were measured in all the above cases. These were slightly more positive for rolled than for cast anodes. The presence of glue made the equilibrium potential at the cathode slightly less H. J. T. ELLINGHAM. positive.

Cathode potentials and electrode efficiencies of copper in copper cyanide-sodium cyanide solutions. G. M. SMITH and J. M. BRECKENRIDGE (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).-Solutions of copper cyanide in sodium cyanide solution were electrolysed at various constant current densities between copper electrodes for periods of 3 hrs. and the cathode potential at the end of the period and the cathodic and anodic current efficiencies over the period were measured. The cathode potential becomes more negative with increase in current density or dilution of the electrolyte, and the higher the molar ratio of copper to sodium cyanide the greater is the change of potential with increase in current density. The cathodic current efficiency decreases with increasing current density, with dilution of the electrolyte, and with decrease in the molar ratio of copper to sodium cyanide. If this ratio is less than 1:4 the efficiency is practically zero or even negative. The anodic current efficiency decreases with increasing current density and with increase in the molar ratio of copper to sodium cyanide. H. J. T. ELLINGHAM.

E.M.F. of some molten salt cells. R. LORENZ and H. VELDE (Z. anorg. Chem., 1929, 183, 81–97). —The E.M.F. of lead, zinc, cadmium, and magnesium against their respective chlorides have been measured as functions of the temperature in the neighbourhood of 400–700°; for lead E=1.2467- 6.5×10^{-4} ($t-550^{\circ}$), for cadmium $E=1.3421-6.29\times$ 10^{-4} ($t-599^{\circ}$), and for magnesium $E=2.5112-6.73\times$ 10^{-4} ($t-700^{\circ}$), whilst for zinc, which is peculiar in that the E/T curve is parabolic, $E=1.6050-4.6\times$ 10^{-4} ($t-427^{\circ}$)- 8.93×10^{-7} ($t-427^{\circ}$). The E.M.F. of various combinations of the type M'[M'CI]M''CI]M''CI]M'' have been calculated on the assumption that there is no P.D, at the interface between the two chlorides, and in certain cases the results deviate considerably from those obtained experimentally. The theoretical significance of the results is discussed.

H. F. GILLBE.

Membrane potentials. J. M. ORT and W. G. FRANCE (J. Physical Chem., 1929, 33, 1374—1385). —A study of a modified form of Des Coudres' cell has shown the collodion membranes used to be specifically charged at zero pressure, the measured cell potentials differing from the values calculated by means of Des Coudres' equation; on the contrary, the potentials equal the algebraic sum of the specific charge and the calculated value. The effects of temperature, composition of electrolyte (mercurous nitrate in nitric acid), nature of the membrane, and time of exposure of the membrane to the electrolyte have been determined, and the origin of the specific charge is discussed. L. S. THEOBALD.

Electrolysis with a mercury cathode. II. Explanation of the anomalies on the electro-capillary curves. J. HEYROVSKY and R. SIMÓNEK (Phil. Mag., 1929, [vii], 7, 951-970).—Current-voltage curves obtained with the dropping mercury cathode when solutions exposed to the air are polarised are found to show definite reproducible maxima due to the electro-reduction of dissolved atmospheric oxygen. These anomalies, first noted by Kučera, are most prominent in approximately 0.001N-solutions. The fall of the current at the maxima is associated with a sudden fall at the interfacial tension at the polarised mercury dropping cathode and a sharp increase of the cathodic potential. The presence of surface-active substance, active anions, or high concentrations of electrolytes eliminates the current maxima and the changes in inter-facial tension; this may be explained on the basis of the preferential adsorption of the suppressing agencies. The discontinuous changes in current and interfacial tension are attributed to an effect of concentration polarisation which prevents the further adsorption of oxygen at the mercury-electrolyte interface. A. E. MITCHELL.

Overpotential of bismuth in acid solutions. W. V. LLOYD (Trans. Faraday Soc., 1929, 25, 525-529).—The overpotential of bismuth in acid solutions has been measured and the results have been compared with those obtained (A., 1927, 317) with antimony. Both the direct and the commutator methods were used. A bismuth cathode must be polarised for a longer time in order to attain the maximum overpotential at a given current density. The overpotential of bismuth in acid solutions is approximately 0.1 volt greater than that of antimony. The incidence of maximum commutator potential of bismuth indicates a constant degree of supersaturation of the electrode with hydrogen, which is independent of the hydrogen-ion concentration, and the anion of the electrolyte. F. J. WILKINS.

Theory of passivity. VI. Passivation of chromium at low current densities. W. J. MÜLLER and K. KONOPICKY (Monatsh., 1929, 52, 289-296).—Calculations based on the current density-time curves of Müller and Noack (A., 1927, 942) show the applicability of the equation given by Müller and Konopicky for the rate of growth of the surface film, viz., $t-t_0=B(1/i^2-1/i_0^2)$, where *i* and i_0 are the current densities at times *t* and t_0 (this vol., 146). *B* is a function of the potential applied to the chromium and the potential at which B=0 is identical with the electrode potential of active chromium. The passivation of chromium at low current densities is therefore held to be due to a surface film. J. A. V. BUTLER.

Circuit transmission and interference of activation waves in living tissues and in passive iron. R. S. LILLIE (Science, 1929, 69, 305-308; cf. this vol., 272).-Circuit transmission has been obtained in passive iron by suspending "Armco" wire in a circular trough containing nitric acid (75-80% by volume). Interference has been observed after touching the wire with zinc at any point when two activation waves are set up and travel in opposite directions until they meet and extinguish each other. Contact with platinum stops such an activation wave started by zinc. These and similar experiments are compared with wave transmission in living tissues, which is also discussed, and explanations based on surface oxidation and reduction phenomena are L. S. THEOBALD. advanced.

Photo-voltaic cells with silver-silver bromide electrodes. II. S. E. SHEPPARD, W. VANSELOW, and V. C. HALL (J. Physical Chem., 1929, 33, 1403-1414; cf. this vol., 653).—Photographic records of the photo-potential changes which occur during the first second of illumination in cells with Ag AgBr electrodes in various electrolytes have been obtained by means of a system containing an amplifier-oscillograph. The factors studied include the age of the electrode, the Svensson-Bccquerel effect, halogen acceptors, electrolytes, and intermittent exposure to light. With potassium bromide solutions, saturated with silver bromide, as electrolyte, no photopotentials are produced by exposure of this electrolyte to the quartz-mercury vapour arc. Small differences in potential were observed with electrodes of different age, but the maximum value is reached in all cases in approximately the same time, 0.06 second. In the presence of a halogen acceptor, such as acetonesemicarbazone, this time becomes greater and the negative potential is also increased. The maximum negative photo-potential also varies with the nature of the electrolyte. The results support the theory previously advanced (loc. cit.). L. S. THEOBALD.

Influence of temperature on photo-electric E.M.F. G. ATHANASIU (Compt. rend., 1929, 189, 460-462).—The electrodes of the cells investigated were: (a) Ag-AgI, (b) Ag-AgBr, (c) Ag-Ag₂S, (d) Cu-oxidised Cu, and (e) Hg-Hg₂I₂. No satisfactory results were obtained with (e). In (a), (b), and (c) the electrolyte was sulphuric acid, in (d) potassium chloride. One electrode was illuminated with mono-chromatic light from the region of the spectrum giving maximum photo-electric effect for that electrode. In all cases this effect increases as the temperature falls. The following results are given: $(T=\text{temperature limits}; \lambda=\text{wave-length}; E=\text{corre}$

sponding E.M.F. in volts $\times 10^5$): (a) T 13—1°, $\lambda 0.420 \ \mu, E$ 43—81; (b) T 16—2°, $\lambda 0.430 \ \mu, E$ 38—47; (c) T 18·5—2·5°, $\lambda 0.650 \ \mu, E$ 46·7—125; $\lambda 0.800 \ \mu, E$ 97·0—256; $\lambda 1.000 \ \mu, E$ 170—480; (d) T 12—3°, $\lambda 0.540 \ \mu, E$ 17—38. The temperature coefficient of (c) is thus practically constant (1·60— 1·68) for the wave-lengths used. These results support the author's conclusions (cf. this vol., 514) that the E.M.F. is the algebraic sum of E.M.F. due to (i) photochemical reaction but little affected by temperature, and (ii) thermal reaction favoured by rise in temperature. C. A. SILBERRAD.

Reduced equations in chemical kinetics. W. SWIENTOSLAWSKI and J. G. ZAWIDZKI (Bull. Acad. Polonaise, 1929, A, 295-315).—See this vol., 770.

Influence of indifferent gases on the thermal decomposition of ozone. E. H. RIESENFELD and E. WASSMUTH (Z. physikal. Chem., 1929, 143, 397-434).—The rate of decomposition of ozone at 90° and 100° has been measured by the static method in the presence of oxygen, nitrogen, carbon dioxide, helium, or argon, at different total pressures between 100 and 1000 mm. The decomposition proceeds in two ways simultaneously, viz., by a bimolecular reaction which is independent of the partial pressure of oxygen (cf. Riesenfeld and Bohnholtzer, A., 1928, 24), but is accelerated by the other gases named, and by a unimolecular reaction which is retarded by all the gases except helium. For the usual velocity coefficients of the unimolecular and bimolecular reactions must be substituted $A_1 + B_1 p$ and $A_2 + B_2 p$, respectively, where A_1 and A_2 are constants independent of the nature of the indifferent gas, B_1 and B_2 are specific proportionality factors, and p is the partial pressure of the indifferent gas. To B_1 are assigned the values -6, -3, -10, 0, -6 for the different gases in the order named above, and to B_2 the values 0, 4, 10, 3, 3. The temperature coefficient of the unimolecular reaction between 90° and 100° is 1.8, that of the bimolecular 3.0, and neither is appreciably changed by admixture of the gases studied. The temperature coefficient of the unimolecular reaction corresponds with a heat of activation insufficient to account for a spontaneous change $O_3 = O_2 + O_3$, and it is therefore concluded that the primary reaction is initiated by traces of some foreign material in the gas or on the walls of the containing vessel, this substance being subsequently regenerated. The retarding effect of indifferent gases is due either to a specific action in breaking the ensuing "chain," or to their protecting the ozone against the action of the foreign material. The latter explanation receives support from the observation that the retarding effects are in the same order as the adsorbabilities. The bimolecular reaction is also to be regarded as a chain reaction, viz., (1) $O_3^* + O_3 = 3O_2^*$, (2) $O_2^* + O_3 = O_3^* + O_2$, etc. The molecules of an indifferent gas act as energy carriers, and the differences observed are due to variations in the time of conservation of the energy carried, the latter being dissipated most rapidly by oxygen and least F. L. USHER. rapidly by carbon dioxide.

Ignition of phosphorus vapour in oxygen. A. KOWALSKY (Z. physikal. Chem., 1929, B, 4, 288– 298).—Measurements have been made of the lower and upper pressure limits, p_1 and p_2 , respectively, beyond which phosphorus vapour does not undergo oxidation in oxygen, and the relation between these two pressures and the partial pressure, $p_{\rm P}$, of the phosphorus vapour has been determined. From Semenov's chain reaction theory of the oxidation of phosphorus vapour (cf. A., 1928, 483) the two expressions $p_1 p_r = k_1$ and $p_r / p_2 = k_2$ are derived. These are verified experimentally and the values 3.2×10^{-4} and 2.8×10^{-5} are found for k_1 and k_2 , respectively. From these constants the minimum partial pressure of phosphorus vapour below which reaction will not take place under any conditions can be calculated and is found to be 1.9×10^{-4} mm., in good agreement with the experimental result, which lies between 1.0 and 2.0×10^{-4} mm. Experimental support is therefore obtained for Semenov's theory. O. J. WALKER.

Quenching of flames in atmospheres of a certain composition and at the limits of explosion regions. W. P. JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1929, 48, 1069-1074). -From a comparison of the quenching of flames at the limits of explosion regions and the corresponding phenomena in a closed space or on plunging the flame into gas mixtures of various oxygen contents it is shown that a combustible gas or vapour will burn only in atmospheres with oxygen contents above a certain limit which is definite for each gas or vapour. The correspondence between the quenching of Bunsen flames and that of other flames is discussed from this point of view. Except with carbon dioxide the oxygen contents of atmospheres in which flames are quenched are in the same order as those of mixtures in which explosion limits have coincided.

F. G. TRYHORN.

Oxidation of phosphine at low pressures. R. H. DALTON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1929, A, 125, 294-308).-It has long been known that mixtures of phosphine and oxygen explode when the pressure is reduced, and it is now found that, in addition to the higher pressure limit, there is also a lower pressure limit below which the rate of combination is negligible but above which explosion occurs. The nature of this limit has been investigated by compressing the gases at low pressure until explosion takes place. The phenomenon is explained by the theory that the oxidation is a chain reaction, the chains being broken only when they reach the walls of the vessel. The limiting pressure is that at which the rate of initiation of chains just begins to exceed the rate at which they are broken. The simple development of this theory leads to the following relation between the partial pressures of the various gases at the explosion point : p_{o_s} . p_{PH_s} . $d^2[1+p_{N_s}/(p_{o_s}+p_{PH_s})]=$ constant, where d is the diameter of the containing tube and p_{N_s} the pressure of nitrogen or any other inert gas present. This formula is analogous to that used by Semenov for the oxidation of phosphorus vapour (this vol., 514). It describes the results qualitatively in that (a) there is an inverse relationship between the pressures of oxygen and phosphine at the explosion point, (b) the critical partial pressures are lowered by the presence of nitrogen or argon, and (c) in the absence

of inert gases the product $p_{O_1} \cdot p_{PH_2}$ is approximately inversely proportional to the square of the diameter of the tube. To obtain quantitative agreement the theory needs elaboration. In the absence of an inert gas, $p_{O_1} \cdot p_{PH_2}$ is not constant but passes through a maximum when $p_{O_2} = p_{PH_2}$. The effect of inert gases is smaller than that calculated, although the theory predicts the correct order of magnitude. Further, in wide tubes the product $p_{O_2} \cdot p_{PH_2} \cdot d^2$ tends to rise. These quantitative deviations are attributed to the fact that some of the chains may be broken in the gas and not solely at the walls of the reaction vessel. L. L. BIRCUMSHAW.

Kinetics of the oxidation of ethylene. H. W. THOMPSON and C. N. HINSHELWOOD (Proc. Roy. Soc., 1929, A, 125, 277-291).-The rate of reaction of oxygen with ethylene has been measured between 400° and 500° by the method previously described (A., 1928, 483). Although the rate of increase of pressure is not an exact measure of the rate of disappearance of the ethylene, it is sufficiently nearly so for the mixtures $C_2H_4 + O_2$, $C_2H_4 + 2O_2$, and $C_2H_1 + 3O_2$ to enable it to be used in an investigation of the effect on the reaction velocity of the total pressure, the temperature, and the relative proportions of the two gases. The influence of the total pressure on the rate is roughly that corresponding with a reaction of the third order, the effect depending much more on the partial pressure of the ethylene than on that of the oxygen. In certain regions of pressure the rate is proportional to about the third power of the ethylene concentration. The oxidation is assumed to take place by a chain mechanism, and it is suggested that the first stage in the reaction is the formation of an unstable peroxide, $C_2H_4:O_2$. If this collides with another ethylene molecule, two active hydroxylated molecules, e.g., CH2:CH-OH, are produced which continue the chain, but if the peroxide collides with oxygen it is either decomposed or oxidised to stable products. The reaction is considerably retarded by increasing the surface of the vessel exposed to the gas. A consideration of the temperature coefficient and the influence of nitrogen and argon on the velocity of reaction leads to the conclusion that the chains are L. L. BIROUMSHAW. comparatively short.

Thermal decomposition of gaseous ethylene oxide. W. W. HECKERT and E. MACK, jun. (J. Amer. Chem. Soc., 1929, 51, 2706-2717).—The thermal decomposition of gaseous ethylene oxide in a pyrex vessel at $380-444^{\circ}$ is a homogeneous unimolecular reaction : $\log_c k=34\cdot02-52000/RT$. There is a period of induction during which the velocity increases. In the later stages the velocity is diminished owing to the accumulation of reaction products, methane and carbon monoxide. Other indifferent gases have the same effect, but hydrogen behaves otherwise. A mechanism is suggested in which isomerisation to active acetaldehyde, with consequent interference with the formation of activating reaction chains (Christiansen and Kramers, A., 1924, ii, 28), is the first stage. S. K. TWEEDY.

Irreversible transformations of organic compounds under high pressures. P. W. BRIDGMAN and J. B. CONANT (Proc. Nat. Acad. Sci., 1929, 15. 680-683),-Under a pressure of 10,000 atm. for 24 hrs. the following substances were not appreciably affected : amylene, pinacone, tert.-amyl alcohol, diacetone alcohol, aniline acetate dissolved in aniline, solid maleic acid, benzoquinone in *iso*propyl alcohol, and phenol in 20% aqueous formaldehyde. Under 9000 atm. for 24 hrs. isoprene, $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ butadiene, styrene, and indene were partly polymerised; isobutaldehyde and n-butaldehyde under 12,000 atm. for 40 hrs. were converted into unknown polymerides which passed to a liquid in 24 hrs. The rate of polymerisation of isoprene was investigated at pressures up to 12,000 atm. Carboxyhæmoglobin under pressure gave a red precipitate resembling the "denatured" product obtained by the action of alcohol. N. M. BLIGH.

Velocity of esterification of bromobenzoic acids in glycerol and ethyl alcohol solutions containing hydrochloric acid. A. KAILAN and K. HEXEL (Monatsh., 1929, 52, 260-288).-The velocities of esterification of o-, m-, and p-bromobenzoic acids have been determined at 25° in dry and moist ethyl alcohol and glycerol solutions, with hydrogen chloride as catalyst. In the dry media the unimolecular velocity coefficients are proportional to the catalyst concentration, but the addition of water causes a more rapid rise. The velocity coefficients in all cases except that of p-bromobenzoic acid in glycerol can be represented as functions of c and w(c being the concentration of hydrogen chloride, w that of water in g.-mol. per litre) by interpolation formulæ of the same type. The addition of water retards the reaction in glycerol much less than in alcohol solutions. The velocity coefficients of o-, m-, and p-bromobenzoic acids for $c=\frac{1}{2}$ and w=0.03are in the ratio 0.29: 0.69: 0.54 in ethyl alcohol and 0.54: 1.15: 0.92 in glycerol solutions, the value for benzoic acid in a similar solution being taken as unity in each case. The solubilities of the bromobenzoic acids in ethyl alcohol and glycerol have been determined. J. A. V. BUTLER.

Velocity of esterification of chloro- and fluorobenzoic acids, ethyl hydrogen phthalate, and abietic acid in ethyl alcohol solutions containing hydrochloric acid. A. KAILAN and W. ANTROPP (Monatsh., 1929, 52, 297-338).-The velocities of esterification of o-, m-, and p-chloro- and -fluorobenzoic acids, ethyl hydrogen phthalate, and abietic acid have been determined at 25° in dryand moist ethyl alcohol solutions, with hydrogen chloride as catalyst. The unimolecular velocity coefficients are proportional to the catalyst concentration in dry alcohol, but rise more rapidly in solutions containing water. They can be represented by interpolation formulæ similar to those previously employed (see preceding abstract). The velocity coefficients of o., m., and p-fluorobenzoic acids for $c = \frac{1}{6}$, w = 0.03 are in the ratio 0.95 : 0.69 : 0.54and those of the corresponding chlorobenzoic acids in the ratio 0.38: 0.69: 0.66, the value for benzoic acid in a similar solution being taken as unity. With the exception of anthranilic acid, the rate of esterification of abietic acid is smaller than that of any other organic acid investigated. The hydrolysis of the correspond-

ing neutral ester is apparent only in the case of ethyl hydrogen phthalate. J. A. V. BUTLER.

Reactivity of atoms and groups in organic compounds. VIII. Relative reactivities of hydroxyl groups in certain alcohols. J. F. NORRIS (Rec. trav. chim., 1929, 48, 885–889; cf. A., 1925, i, 626; 1927, 1166).—A summary of results to be published later in more detail. The (second order) velocity coefficients for the reaction between hydrogen bromide (1 mol.) and various alcohols (25 mols.) at 100° and 60% conversion (appreciable quantities of ethers are formed towards the end of the reaction) are: methyl, 0.0056; ethyl, 0.0022; n-propyl, 0.0029; n-butyl, 0.0039; isopropyl, 0.0004; isobutyl, 0.001; sec.-butyl, 0.0017. Water has a marked effect on the velocity (particularly for secondary alcohols), and the change of velocity with changes in concentration of water and temperature has been studied. The temperature coefficients for the reactions are high. The data support the view that the mechanism of the reaction involves the direct addition of the two reactants and subsequent elimination of water. H. BURTON.

Kinetics of the hydrolysis of certain glucosides. III. β-Methylglucoside, cellobiose, melibiose, and turanose. E. A. MOELWYN-HUGHES (Trans. Faraday Soc., 1929, 25, 503–520).—The critical increments for the acidic hydrolysis of β -methylglucoside, cellobiose, melibiose, and turanose, deter-mined by following the reaction polarimetrically at 60° and 80°, are 33,730, 30,710, 38,590, and 23,450 g.-cal. per mol., respectively. From a survey of the velocity coefficient and critical increment data for seventeen glucosides, it is shown that the relative stability of the disaccharides towards acids is governed, not by the α - or β -nature of the biose linking, but by the position of attachment of the glucosidic monose unit to the second monose unit. Attachment of the oxygen atom of the biose linking at position 4 gives a biose less stable than when the junction involves position 6. The most stable type of disaccharide is that in which attachment of the monoses takes place through position 1.

Calculation of the number of degrees of freedom of the molecule which are associated with the critical increment, according to the method of Hinshelwood (A., 1927, 26), gives values of 45 for hydrolysis of glucosides by acids, 48 for the hydrolysis of galactosides by acids, 52 for the hydrolysis of sucrose by invertase, and 121 for the hydrolysis of starch by amylase. F. J. WILKINS.

Effect of cohesion of medium on reaction velocity. Velocity of interaction of N-chloroacetanilide and hydrobromic acid in aqueous solutions. M. RICHARDSON and F. G. SOPER (J.C.S., 1929, 1873—1884).—The surface tension of a medium is taken as a measure of its cohesion, and it is shown from collected data that, in general, if the products of a reaction are substances of higher cohesion than the reactants, then the reaction is accelerated by solvents of high cohesion, and if the products are substances of lower cohesion than the reactants, the reaction is retarded by such solvents. When products and reactants have like cohesion, the solvent has relatively little influence on reaction velocity. It is suggested that these results are connected with the influence which the solvent may exert on the critical complex of the two reactants.

The mechanism of the interaction of N-chloroacetanilide and hydrobromic acid has been investigated. The products have smaller cohesion than the reactants. The velocity of reaction was studied in various aqueous solutions, the relative cohesions of which are deduced by two independent methods.

The activities of the chloroamine and hydrogen bromide in the media were measured. The activity velocity coefficient was almost constant in sucrose solutions, where the surface tension is nearly the same as in water. In solutions of sodium and potassium nitrates the cohesion was increased and the activity velocity coefficient was decreased. The converse effects were observed in aqueous solutions of methyl and ethyl alcohols. The results agree with the theory. J. G. A. GRIFFITHS.

Rate of corrosion of magnesium and ultralight alloys. A. PORTEVIN and E. PRETET.—See B., 1929, 780.

Corrosion phenomena on aluminium sheet. R. WESENBERG.—See B., 1929, 779.

Theory of chemical reactions in concentrated solution of electrolytes. M. BOBTELSKY (Z. anorg. Chem., 1929, 182, 93—96).—A discussion of catalysis and the neutral salt effect in the light of recent experimental work (cf. this vol., 1149).

H. F. GILLBE.

Acid and salt effects in catalysed reactions. XXI. Catalytic effects associated with oxalic acid in first and second stages of dissociation. H. M. DAWSON, C. R. HOSKINS, and J. E. SMITH (J.C.S., 1929, 1884—1895).—The catalytic effects of oxalic acid, in the first and second stages of dissociation, on the acetone-iodine reaction are in accord with the general relationships discovered by recent work with monobasic acids. The effective catalysts during the first stage are the hydrogen and hydrogen oxalate ions and the oxalic acid molecule. The respective catalytic constants are 465×10^{-6} , 13×10^{-6} , 210×10^{-6} . The coefficient for the hydrogen oxalate ion is much greater than is expected from results for anions of moderately strong monobasic acids and indicates its tendency to produce hydrogen ions by dissociation.

The action of oxalic acid is similar to that of other acids (cf. Dawson and others, this vol., 36), and it is suggested that the interionic force effect in salt-free solutions of such acids is relatively very small. Results with oxalic acid-potassium hydrogen oxalate solutions indicate an increase of ionisation constant K_1 with salt concentration, and observations with potassium chloride-oxalic acid solutions show that the inert salt effect is similar to that found for other acids (Dawson and Lowson, this vol., 889).

The catalytic action of oxalic acid in the second stage of dissociation has been studied by means of mixtures of normal and acid potassium oxalates. The results are due to the combined effects of the hydrogen, hydrogen oxalate, and oxalate (catalytic constant= 1.0×10^{-6}) ions and undissociated oxalic acid. J. G. A. GRIFFITHS. Esterification of formic acid in ethyl alcohol solution. H. GOLDSCHMIDT, H. HAALAND, and R. S. MELBYE (Z. physikal. Chem., 1929, 143, 278— 286).—A study of the catalysis by hydrogen chloride, pieric acid, and trinitro-*m*-cresol of the esterification of formic acid with ethyl alcohol shows the velocity of the reaction to be proportional to the hydrogen-ion concentration; for the autocatalysis of the reaction by the formic acid hydrogen ions the same law is valid, but addition of a formate considerably retards the esterification velocity. Neutral salts at 0.025 to 0.25N-concentration cause retardation, but at higher concentrations acceleration is produced.

H. F. GILLBE.

Theory of heterogeneous catalytic reactions. Model of dehydrogenation catalysis. A. A. BALANDIN (J. Russ. Phys. Chem. Soc., 1929, 61, 909-937; cf. this vol., 772, 774).-The action of catalysts is ascribed to attachment of the substrate to groups of multiplets on their surface, the products of reaction being then removed by thermal impulses of the Boltzmann type taking place in the mass of the catalyst. The above conception explains the specificity of action of contact catalysts, the space lattice of which must possess dimensions and a configuration corresponding with those of the substrate. This conception is illustrated by the dehydrogenisation of cyclohexane in the presence of platinum catalyst. In this case, each multiplet consists of six atoms of the catalyst (platinum); three atoms adsorb and bind two atoms each of carbon, whilst the remaining three atoms each bind two atoms of hydrogen.

R. TRUSZKOWSKI.

Catalytic activity of carriers of platinum. I. E. ADADUROV and K. I. BRODOVITSCH (Ukraine Chem. J., 1929, 4, 123—127).—The authors have investigated a number of substances used, or entering into the composition of materials used, as platinum carriers in the catalysis of sulphur dioxide to sulphur trioxide as to their own catalytic effect in that reaction. Asbestos, under specified conditions of flow etc. and at 470°, had a catalytic effect of 47%, silica gel precipitated by nickelous chloride had an activity of 67%, the substance precipitated by ferrous chloride 64% at about 450°, whilst refractory material itself had an activity of 73%. When moistened with a mixture of 3 vols. of aluminium sulphate and 1 vol. of chromium sulphate it had at 454—470° an activity of between 91.4% and 100%. A. FREIMAN.

Dissociating action of catalyst carriers. I. E. ADADUROV and K. I. BRODOVITSCH (Ukraine Chem. J., 1929, 4, 129—141).—Some of the substances investigated as catalyst carriers in the reaction $SO_2 \implies SO_3$ had no dissociating effect, e.g., silica gel precipitated by nickelous chloride; others had only a very slight effect (0.06—0.22%), e.g., porcelain, glass spheres, aluminium oxide, etc., whilst some had a quite appreciable effect, e.g., magnesium oxide 0.67%, silica gel precipitated by ferrous chloride 4—3%, refractory material moistened by a mixture of 3 vols. of chromium sulphate and 1 vol. of aluminium sulphate 7—1.5%. It is concluded that there exists no direct or inverse proportionality between the catalytic activity of a material and its dissociating activity, that a rise in temperature does not necessarily cause an increase in dissociation, and that for each substance there exists a separate maximum of its catalytic and dissociating activity in a given reaction. The catalytic and dissociating activities of the substances are attributed to light radiation emitted by the substance, and by applying Brodsky's equation (A., 1927, 705) giving the relation between the intensity of a spectral line and temperature, an attempt is made to explain the differing behaviour of the various substances. A. FREIMAN.

Catalytic dissolution of copper in sulphuric acid. J. B. EVTUSHENKO (J. Chem. Ind. Moscow, 1929, 6, 429-430).—The dissolution of copper in sulphuric acid is accelerated by the addition of a catalyst consisting of 1 part of chromic sulphate and 0.5 part of nitric acid per 100 parts of sulphuric acid. The product contains only a trace of chromium.

CHEMICAL ABSTRACTS. Relative activation of a nitrogen-hydrogen mixture by electrons and by K⁺ ions in the formation of ammonia. C. H. KUNSMAN (Physical Rev., 1928, [ii], **31**, 307).—Without an applied *P.D.*, the iron-potassium catalyst used as the source of K⁺ ions is much more active in synthesising ammonia from the nitrogen-hydrogen (1:3) mixture at pressures less than 1 mm. than is the tungsten filament used as the electron source. At electron speeds greater than 17 volts, however, a large increase is observed with tungsten whilst the rate with the K⁺ ions remains unchanged up to 330 volts. L. S. THEOBALD.

Action of iron catalysts on mixtures of carbon monoxide and hydrogen. E. AUDIBERT and A. RAINEAU.—See B., 1929, 840.

Activation of halogens and carbon monoxide. N. C. JONES (J. Physical Chem., 1929, 33, 1415-1427) .- The activation of chlorine, bromine, and carbon monoxide by charcoal and by hopcalite has been investigated. Chlorine and bromine, but not carbon monoxide, hydrogen, or oxygen, are activated. by charcoal. Hydrobromic acid is formed when hydrogen containing bromine is passed over charcoal, the conversion of bromine into the acid being 13.2% at 100°, 49.1% at 150°, and 99.3% at 200°. In the synthesis of carbonyl chloride over charcoal, chlorine but not carbon monoxide is activated, since neither formaldehyde nor methyl alcohol could be synthesised from carbon monoxide and hydrogen, nor could carbon dioxide be formed from the monoxide and oxygen by passage over activated charcoal. Hopcalite activates oxygen, but not carbon monoxide or hydrogen, to such an extent that benzene vapour is completely oxidised at 78°. Carbon monoxide is shown to be a more powerful reducing agent than hydrogen, and is considered to be essentially electropositive in nature, since it reacts more readily with oxygen and chlorine than it does with hydrogen even when all three gases are activated. The above results support the theory of Fischer and Tropsch (B., 1926, 475) on the mechanism of the hydrogenation of carbon monoxide.

L. S. THEOBALD.

Platinised silica gels as catalysts for oxidation of sulphur dioxide. H. N. HOLMES, J. RAMSAY, and A. L. ELDER.—See B., 1929, 849.

Poisoning of the hydrogen electrode. A. H. W. ATEN and M. ZIEREN (Rec. trav. chim., 1929, 48, 944-948).-The effect of traces of arsonic trioxide on the potential of a platinum-black electrode (measured against a standard hydrogen electrode) immersed in various media and in contact with differing mixtures of hydrogen and oxygen has been determined. In 0.1N-sulphuric acid solution the potential of the platinum electrode is negligible until the gas mixture contains approximately 50 equiv .- % of oxygen. Then the potential suddenly increases to about 0.7 volt, after which with increasing oxygen the potential gradually rises to about 1.0 volt. The addition of small amounts of arsenic trioxide (up to 0.066%) causes the sudden increase in potential to occur at lower oxygen concentrations, but the maximum finally attained in pure oxygen is lower by about 0.3 volt. The results in 0.1N-sodium hydroxide solution are similar with the exception that the maximum potential finally attained is unaltered. The shift of the vertical portion of the potential-oxygen concentration curve is attributed to a retardation of the reaction $H_2 \longrightarrow 2H$, and the lowering of the final potential to an inhibition of the reaction between atomic hydrogen and oxygen. It is suggested that the retardation of the reaction $H_2 \longrightarrow 2H$ is due to the increase in the diffusion velocity of the electrolytic hydrogen into the electrode in the presence of the poison. These views are supported by the fact that addition of arsenic trioxide or mercuric chloride promotes the diffusion of electrolytic hydrogen in a thin polarised electrode of iron. F. G. TRYHORN.

Removal of gold from cathode metals in the glow discharge. T. ASADA and K. QUASEBARTH (Z. physikal. Chem., 1929, 143, 435-455; cf. Haber, Jaenicke, and Matthias, A., 1926, 699).-When a copper plate containing a small proportion (1 in 10⁶ to 107) of gold is used as cathode in a glow discharge the metal is gradually deprived of gold. It is shown that the effect is not due to thermal evaporation, but that it depends on the disintegration of the cathode surface under bombardment by positive ions, the gold being sprayed away far more rapidly than the copper. The disintegration is about 25 times more rapid, and the loss of gold relatively greater, in mercury vapour than in air. When the surface of the cathode has been deprived of gold the resulting diffusion gradient becomes operative, and in the course of time the whole of the gold is brought to the active surface and there dissipated. From the initial and final gold content, assuming that the concentration of gold at the surface is constant and zero, the coefficient of diffusion of gold in copper is shown to be of the order 10⁻⁶ cm.²/day, at an estimated temperature of 200°. F. L. USHER.

Influence of the silent electric discharge on hydrogen sulphide. R. SCHWARZ and W. KUNZER (Z. anorg. Chem., 1929, 183, 287-295).—An apparatus in which the behaviour of hydrogen sulphide under the silent electrical discharge may be studied at different temperatures and compared with the simple thermal effect is described. With rise in temperature the amount of decomposition by the discharge diminishes, and above the b. p. of sulphur re-formation of the hydrogen sulphide from the products of thermal decomposition takes place. This is ascribed to the activation of gaseous sulphur by the discharge as observed by Schwarz and Schenk (this vol., 1151).

M. S. BURR. Electrolytic deposition of chromium from aqueous solutions of chromic acid. J. ROUDNICK (Bull. Soc. chim. Belg., 1929, 38, 276-294).---Oxidation and reduction during electrolysis of 20% chromic acid solutions containing 1% of sulphuric acid have been investigated, confirming the equation : Reduction %-oxidation %=yield ($Cr^{v_{I}} \rightarrow Cr_{metal}$) +yield($Cr^{v_{I}} \rightarrow Cr^{u_{I}}$). The influence of the nature of the electrodes and of the concentration of chromic acid has been studied. C. W. GIBBY.

Combination of alkali metals and nitrogen under the influence of electrical discharges. W. MOLDENHAUER [with H. MOTTIG] (Ber., 1929, 62, [B], 1954-1959).-Nitrogen, activated by exposure to the dark electric discharge, unites with the alkali metals with production of azides. In the cases of cæsium, rubidium, and potassium, the products of the action contain small amounts of nitrides which result secondarily from the azides. Sodium does not appear to yield any nitride. With lithium, azide formation is not observed and nitride production to only a slight extent. H. WREN.

Fibrous structure in metals deposited through difference in electrolytic solution pressures. II. S. TSUBOI (Mem. Coll. Sci. Kyoto, 1929, A, 12, 209-215; cf. A., 1928, 1175).-When lead is deposited by zinc from 2% and 5% solutions of lead acetate, dendritic crystals are obtained, of which the (111) planes are generally nearly parallel to the flat surface of the deposit. In the spongy deposit of cadmium similarly obtained from 1% and 3% solutions of cadmium sulphate, the (0001) parallel to the surface. C. W. GIBBY. cadmium sulphate, the (0001) plane of the hexagonal

Chemical action of electric discharge. I. Effect of nature of electrodes on production of nitric oxide in electric arc. E. BRINER and A. RIVIER (Helv. Chim. Acta, 1929, 12, 881-893).-In synthesising nitric oxide by the arc process, coating the electrodes with oxides of the alkaline-carth metals, particularly barium oxide, depresses the P.D. of the arc and at the same time increases the efficiency very considerably. The alkali silicates have a similar but much less marked effect. Beryllium, magnesium, zinc, and aluminium oxides are practically indifferent, and ferric oxide reduces the yield. Zirconium oxide slightly increases the P.D. and decreases the yield, whereas thorium oxide has the reverse effect. The rare-earth oxides distinctly reduce the P.D., but have only a slight and variable effect on the yield. In general the results show that the effect of the various compounds on the yield runs parallel with their thermionic emissive power, suggesting that the activation of the reacting molecules is effected by electrons. In a particular group of oxides, the property of increasing the yield becomes more marked with increase in the atomic number of the metal.

R. CUTHILL.

Anodic relationships of aluminium. A. GUN-THER-SCHULZE (Z. physikal. Chem., 1929, 143, 62-

68).-The theory of Muller and Konopicky (this vol., 770) is regarded as untenable owing to errors in the experimental work. H. F. GILLBE.

Oxidation of salts of monobasic fatty acids with potassium percarbonate and potassium persulphate. F. FICHTER and H. LAPIN (Helv. Chim. Acta, 1929, 12, 993-1002).-The mechanism of the action of inorganic salts in the electrolytic synthesis of alcohols by Hofer and Moest's method (A., 1902, i, 736) has been investigated. The action of carbonates is to be ascribed primarily, it would appear, to their alkaline reaction, although there may also be formation of percarbonates. Perchlorates certainly do not depend for their effect on the formation of ozone, for ozone does not produce methyl alcohol from acetates. Sulphates possibly owe their activity to the formation of persulphate, for potassium persulphate produces methyl alcohol from mixtures of acetate and carbonate, ethyl alcohol and ethylene from mixtures of propionate and carbonate, propylene from mixtures of butyrate and carbonate, and isobutylene and isobutyl isovalerate from mixtures of isovalerate and carbonate. R. CUTHILL.

Peroxide theory of Kolbe's electrosynthesis. F. FICHTER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 8 pp.).-Recent work on the oxidation of fatty acids by the action of fluorine or persulphates or by anodic treatment is reviewed and discussed, with special reference to evidence for the intermediate formation of per-acids (cf. preceding abstract). H. J. T. ELLINGHAM.

Cathodic halogen : electrolysis of N-halogenoamides. H. R. L. STREIGHT and E. G. HALLON-QUIST (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 9 pp.).-Solutions of a number of N-halogenated amides and imides in ethyl alcohol, nitromethane, acetonitrile, and pyridine have been electrolysed between silver electrodes. From pyridine solutions a deposit containing the halogen was always obtained at the cathode and the free halogen was detected in the catholyte in many cases, but with N-iodopropionamide and N-iodo-n-butyramide (m. p. 97°) anode deposits containing halogen were also obtained on prolonged electrolysis. From acetonitrile solutions several of the compounds give halogen at both electrodes, but from ethyl alcohol or nitromethane solutions the halogen is liberated only at the anode. Cathodic chlorine was obtained for the first time by electrolysis of pyridine solutions of N-chlorosuccinimide, N-dichlorocarbamide, and N-chlorophthalimide. It is concluded that the N-halogenoamides behave as electromerides, the halogen being negative in most solvents but entirely positive in pyridine (cf. A., 1928, 1197; this vol., 407). H. J. T. ELLINGHAM.

Electrochemical preparation of phenylhydrazine. R. E. MCCLURE [with A. LOWY] (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 11 pp.).—The influence of various factors on the current efficiency of production of phenylhydrazine by the electrolytic reduction of aqueous solutions of certain benzenediazonium compounds has been studied. With benzenediazonium chloride the best current efficiency (36.5%) was obtained by electrolysis at $0-8^{\circ}$ with 5·12 amp./dm.² at a mercury cathode and maintaining an excess of free hydrochloric acid in the solution. The current efficiency could not be increased by raising the temperature, since this caused decomposition of the diazonium salt. With potassium isodiazobenzenesulphonate, however, much higher temperatures could be used and the best current efficiency (47·6%) was obtained at 90—95° with 1·9 amp./dm.² at a mercury cathode, the solution containing acetic acid and sodium acetate during electrolysis, and afterwards being treated with hydrochloric acid and boiled. Some chemical reduction also occurred. It is observed that mercuric phenyl chloride is produced by stirring finely divided mercury with benzenediazonium chloride solution.

H. J. T. ELLINGHAM. Chemical action of light. M. BODENSTEIN (Naturwiss., 1929, 17, 788-795).—A lecture.

A. J. MEE. Action of ultra-violet radiation on inorganic compounds. II. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 708—709).—In the manner previously described (this vol., 1152) the action of ultra-violet radiation on thirty different salts has been examined qualitatively. C. A. SILBERRAD.

Photosensitised decomposition of ozone. A. J. ALLMAND and J. W. T. SPINKS (Nature, 1929, 124, 651).—The transmission for the mercury line 3650 Å. of a mixture of ozone and chlorine containing a low concentration of chlorine increases appreciably during the early stages of the reaction. When gases dried with sulphuric acid are used a distinct mist is formed on insolation. Further, if chlorine dioxide, dried with phosphorus pentoxide, is mixed with dry ozone, a red liquid is produced; on admission of moist air a mist is formed and the liquid is hydrolysed with formation of chloric and perchloric acids. These observations suggest that the following processes take place: (1) production of chlorine atoms by light, (2) formation of ClO_3 groups by union of chlorine atoms and ozone molecules, (3) a short chain reaction, probably terminated by adsorption of intermediate atoms or groups on the walls, (4) union of some ClO₃ groups to form chlorine hexoxide, immediately hydrated in presence of water to chloric and perchloric acids, (5) formation from chlorine atoms and oxygen molecules of ClO₂ molecules, these reacting with ozone molecules to give ClO₃ groups and oxygen molecules. A. A. ELDRIDGE.

inhibited by admixture of hydrogen, and much less by carbon monoxide, carbon dioxide, nitrogen, or argon, and in such cases the velocity is equal to $k_1I/(1+k_3[G]/k_2[C])$, where G and C represent the foreign gas and the pentacarbonyl vapour, respectively, I is the light intensity absorbed per sec., and k_2 and k_3 are the respective velocity coefficients of reactions (2) and (3) in the following scheme: (1) $Fe(CO)_5 + E =$ $Fe(CO)_5^*$; (2) $Fe(CO)_5^* + Fe(CO)_5 = Fe_2(CO)_9 + CO$; (3) $Fe(CO)_5^* + G = Fe(CO)_5 + G^*$. In the presence of oxygen a different reaction occurs and ferric oxide is formed, and traces of air or of moisture give rise to a period of induction. The vapour pressures of the pentacarbonyl between -14° and $+20^\circ$ have also been determined and found to differ considerably from those given by Dewar and Jones.

F. L. USHER.

Photodichroism and photoanisotropy. IV. Colour selectivity of photochloride. F. WEIGERT and E. ELVEGARD (Z. physikal. Chem., 1929, B, 4, 239-257; cf. this vol., 871, 894).-The phenomenon of colour selectivity in the photochloride layer was investigated, using more accurate apparatus than had been used previously. The primary photodichroism was investigated with excitation with monochromatic light. Christiansen's universal filter was used, the incident light being purified by an ordinary monochromator. The existence of a selective effect of the dichroism in the excited layer varying with the wavelength of the light used was shown with certainty. The curves obtained for long wave-length light were quite different from those obtained with short wavelength light, whilst between the two ranges is an indifferent region in which the layer shows only very weak dichroism. This opposite action of short and long wave-length light is discussed from the point of view of micelle deformation. A. J. MEE.

Photodichroism and photoanisotropy. V. Colour selectivity in dye systems. F. WEIGERT and M. NARASHIMA (Z. physikal. Chem., 1929, B, 4, 258—276; cf. this vol., 871, 894).—By means of the method already described (cf. preceding abstract) different light-sensitive colour layers were investigated. The form of the dichroism curve for these systems shows that polarised light can effect two different actions. For weak excitation there is a very sharp colour selectivity. The special form of the extinction curve for any particular colouring matter does not influence the dichroism. For strong excitation this no longer holds. The extinction curve of the colouring matter is, in this case, important. For strong excitation, the spectral distribution of the optical changes is dependent on the form of the absorption spectrum of the colouring matter and independent of the colour of the exciting radiation. It must be concluded that in light-sensitive colouring matters, two quite different phenomena occur by the action of light; they can be separated from each other by the method of dichroism. The relationship between the new effects and previously known photochemical properties of colouring matters is discussed. A. J. MEE.

Effect of X-rays on crystalline and dissolved sucrose. M. C. REINHARD and K. L. TUCKER (Radiol., 1929, 12, 151-153).—Sucrose crystals are coloured reddish-brown by exposure to X-rays, measurable amounts of invert-sugar being formed. The amount of invert sugar formed by exposure of sucrose solutions to X-rays is, for a given quality of radiation, proportional to the time of exposure, but not to the concentration of sucrose.

CHEMICAL ABSTRACTS.

Uranyl oxalate method of daylight photometry and its photo-electric standardisation. W. R. G. ATKINS and H. H. POOLE (Sci. Proc. Roy. Dublin Soc., 1929, 19, 321-337).-The photo-sensitivity of uranyl oxalate solution has been used to study the intensity of daylight illumination along the coast and at sea. 10 C.c. samples of a solution containing 6.3 g. of crystalline oxalic acid and 4.27 g. of uranyl sulphate diluted to I litre were placed in quartz tubes 13 cm. long and 1.3 cm. in diameter. During the exposure the tubes were arranged either to swing about a mean vertical position or to rest slightly inclined from the horizontal in order to allow the gas to escape. The extent of the decomposition was determined by titration with 0.1N-permanganate solution, using 10 c.c. of the mixture, 10 c.c. of sulphuric acid (1:3), and 100 c.c. of boiling water. By deducing the mean illumination acting on the tubes from readings of a photometer containing a potassium vacuum cell, the rate of decomposition was found to be 0.225 c.c. of 0.1N-acid for an illumination of 1000 metre-candles. A comparison between glass and quartz tubes showed that the former required 1.14 times as long an exposure as quartz to produce equal amounts of decomposition. Figures are given for the mean horizontal and vertical illumination values at sea.

H. J. DOWDEN.

Antioxygenic action of cholesterol and ergosterol. IX. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 709—710).—The anti-oxygenic effect (Moureu's method) of the addition of 1% of ordinary and irradiated cholesterol and ergosterol to benzaldehyde, furfuraldehyde, and turpentine is shown to be practically the same and very slight in all cases. This is held to support the view that irradiation affects an impurity only in ergosterol. C. A. SILBERRAD.

Effect of X-rays on cholesterol. A. BACHEM and R. P. MACFATE (Strahlentherapic, 1927, 25, 476—478; Chem. Zentr., 1929, i, 1789).—If dissolved in chloroform or carbon tetrachloride, but not if dissolved in benzene, toluene, alcohol, acetone, butyl ether, or carbon disulphide, cholesterol is decomposed when exposed to X-radiation. Chloroform and carbon tetrachloride are themselves decomposed by X-rays. A. A. ELDRIDGE.

Action of high-speed cathode rays on acetylene. J. C. MOLENNAN, M. W. PERRIN, and H. J. C. IRETON (Proc. Roy. Soc., 1929, A, 125, 246—262).—By means of an apparatus similar to that described by Coolidge (A., 1926, 989), the kinetics of the reaction taking place when acetylene is bombarded with high-speed electrons have been investigated in detail. During each experiment the voltage applied to the cathoderay tube and the current through it were kept constant, and the pressure was read at different times. No change in pressure occurred during the bombardment until the voltage across the tube exceeded 85 kilovolts, when a slight mist formed throughout the reaction cell and a pale yellow amorphous solid $(d_4^{25} 0.97, n_{\rm D}^{25} 1.625)$ was deposited on the walls. This reaction was accompanied by a decrease in pressure. The product had no measurable vapour pressure and on bombarding it there was no increase of pressure. No X-ray spectrum could be obtained from it. The reaction is apparently unimolecular, the rate of change of pressure being proportional to the pressure for any given voltage, and the velocity coefficient increases directly as the voltage. A direct measure of the electron current outside the cathode-ray tube was made by collecting the electrons passing through the window in a Faraday cylinder placed close to the window and measuring the current with a microammeter. It is found by calculation that the number of molecules of acetylene reacting is of the same order as the number of ions formed by each electron passing through the window, and the observed facts are explained on the hypothesis that the reaction takes place between molecules of which some have been ionised by the cathode rays. L. L. BIRCUMSHAW.

Salt-like compounds of sodium and their change into intermetallic phases. E. ZINTL (Naturwiss., 1929, 17, 782-783).-Compounds of sodium with a number of metallic and non-metallic elements were prepared and their decomposition was investigated. For following the changes quantitatively an electrometric titration method was used. All elements of the long periods of the periodic system occupying places 1—4 away from a rare gas, and forming liquid hydrides, will combine in liquid ammonia with sodium to give polysulphide-like compounds which have the characteristics of salts, and to which the name "polyanionic" salts is given. By treating sodium with lead iodide compounds of the type Na₄Pb₇ and Na₄Pb₉ can be obtained. Their constitution is probably of the form Na⁺₄[Pb⁴⁻(Pb)₈]. These polyanionic salts are soluble in ammonia, the solutions being deeply coloured and capable of being electrolysed, the sodium going to the cathode, and other metals to the anode. Elements which occupy positions in the periodic table more than four places away from a rare gas will not form these polyanionic salts, but form instead typical intermetallic phases of another structural type, insoluble in liquid ammonia. Polyanionic salts may also be obtained by extracting alloys of the elements concerned with liquid ammonia. The solution contains negatively-charged sub-microns. The salts crystallise from ammonia in the form $[Na(NH_3)_y]^+_n[X^{n-}(X)_x]$. X-Ray experiments show that Na_4Pb_7, yNH_3 and Na_4Pb_9, yNH_3 cannot exist in the polyanionic state in the ammonia-free form. The latter changes into an intermetallic phase with a cubic structure and four atoms in the elementary cell, of which the homogeneity range extends from 28% to 35% of sodium; it contains no chemical compound. The substance Na₄Pb₇, yNH₃ decomposes into two intermetallic phases. The introduction of a little sodium into the lead lattice causes a contraction, whereas an expansion would be expected; the contraction is due to the distorted symmetry of the charge distribution between neighbouring particles. A. J. MEE.

Double carbonates of alkalis and alkaline earths. W. EITEL and W. SKALIKS (Z. anorg. Chem., 1929, 183, 263-286).-By heating together the simple carbonates in a bomb, in which it was possible to obtain a pressure of 1200-1300 atm. at 800-900°, the following double carbonates have been prepared : Na₂Ca(CO₃)₉, m. p. 812°; K₂Ca(CO₃)₂, m. p. 813°; Na₂Mg(CO₃)₂, m. p. 677° (p=1240 kg./ cm.²); K₂Mg(CO₃)₂; NaLiCO₃, m. p. 514°; KLiCO₃, m. p. 515°. When calcium and lithium carbonates are heated together in equimolecular proportions an eutectic mixture only is obtained. The magnesium salts had not previously been produced in the dry way, because of the high dissociation pressure of magnesium carbonate. The sodium lithium carbonate had not been prepared before. All the compounds are optically negative and belong to the hexagonal or trigonal crystal system. The potassium magnesium carbonate can be super-cooled and obtained in the vitreous form at the ordinary temperature, suggesting a relationship between carbon and silicon such as might be expected from their neighbouring positions in the periodic table. The refractive indices and specific volumes of the compounds are not additive. The following heats of formation from the simple carbonates are given: NaLiCO₃, +0.54 kg.-cal. per mol.; Na₂Ca(CO₃)₂, -2.07 kg.-cal. per mol.; K₂Ca(CO₃)₂, +0.72 kg.-cal. per mol. The lattice structure of the sodium compounds and of the potassium calcium carbonate has been examined. Substitution of potassium for sodium in the calcium compound has a marked morphotropic effect in the direction to be expected from the respective ionic dimensions. M. S. BURR.

Preparation of pure cupric sulphide. K. FISCHBECK and O. DORNER (Z. anorg. Chem., 1929, 182, 228-234).-Pure cupric sulphide has been prepared by heating under pressure finely-divided copper, obtained by the reduction of copper oxalate with hydrogen at 220-260°, and sulphur precipitated from solution in carbon disulphide by means of light petroleum. The copper was covered with carbon disulphide, and then carbon disulphide containing sulphur in excess of that required to form the lower sulphide was added gradually with constant stirring. After transference to the bomb-tube, double the quantity of sulphur required to form the higher sulphide was added, and the tube was filled with carbon disulphide and heated, with rotation, in a current of steam for 4 hrs. The excess of carbon disulphide was removed and the product dried at 90-100° at a pressure of 0.1-1 mm. The dark blue cupric sulphide is soluble in potassium cyanide and is a good electrical conductor. The formation of a higher sulphide by this method is improbable.

L. S. THEOBALD. New antipyrine co-ordination compounds of metal perchlorates. E. WILKE-DÖRFURT and O. SCHLIEPHAKE (Z. anorg. Chem., 1929, 183, 301-310; cf. A., 1928, 494).—The general method of preparation of the antipyrine compounds of the metal perchlorates is to mix together, at the ordinary temperature, the corresponding metal salt solution, chloride, nitrate, or sulphate, and solutions of antipyrine and pure ammonium perchlorate. In this way hexa-antipyrine perchlorates of magnesium. calcium, strontium, zinc, cadmium, lead, manganese. iron, cobalt, and nickel, of the general formula $[M(COC_{10}H_{12}N_2)_6](ClO_4)_2$, have been obtained. The barium salt can be obtained only by the use of barium perchlorate itself. Hexa-antipyrine perchlorates of aluminium, iron, and chromium, general formula [M(COC₁₀H₁₂N₂)₆](ClO₄)₃, and of quadrivalent thorium, as well as penta-antipyrine perchlorates of copper and uranyl, and silver tri-antipyrine perchlorate, have also been prepared. Solubilities, m. p., and densities are recorded in all cases, as well as the densities of the compounds previously obtained (loc. cit.). In every case the thermal stability of the perchlorate is increased by the introduction of antipyrine into the rotomaily ni .my St b.M. S. BURR, molecule.

Displacement of cadmium from its solutions by aluminium. P. G. Porov (Ukraine Chem. J., 1929, 4, 281—284).—Aluminium displaces cadmium from solutions of cadmium sulphate or nitrate also in the absence of cobalt or chromium nitrate, contrary to the observations of Goldschmidt (A., 1906, ii, 581). The solution requires, however, prolonged heating and the aluminium should preferably be in the form of a powder or dust. The reaction also proceeds with aluminium powder in presence of sodium or potassium hydroxide. A. FREIMAN.

Action of gaseous ammonia on mercuric bromide and mercuric chloride. M. FRANÇOIS (Bull. Soc. chim., 1929, [iv], 45, 616—621).—Contrary to statements by earlier experimenters, mercuric chloride and mercuric bromide combine with dry gaseous ammonia to give the compounds $HgCl_2,2NH_3$ and $HgBr_2,2NH_3$; respectively, and therefore behave similarly to mercuric iodide. The above two compounds appear to be additive compounds. They are fairly stable and do not lose ammonia appreciably at the ordinary temperature. O. J. WALKER.

Boron. I. Reaction of boron trifluoride with ammonia and alkylamines. C. A. KRAUS and E. H. BROWN (J. Amer. Chem. Soc., 1929, 51, 2690-2696).—Monoamminoboron trifluoride, BF_3 , NH_3 , is very conveniently prepared by saturating an ethereal solution of boron trifluoride with ammonia in the cold. It is a true compound and forms a white solid which fuses and sublimes in a vacuum at about 180° and is soluble in liquid ammonia, ethylamine, diethylamine, and triethylamine containing excess of ammonia, ammonolysis occurring in the first two liquids. Alkyl derivatives of the monoammino-compound may be prepared as white solids by treating a cooled ether solution of boron trifluoride with the corresponding alkylamine. Triethylamminoboron trifluoride, NEt3, BF3, m. p. 29.5°, becomes brown on keeping, is soluble in benzene and ether but insoluble in water. Diethylamminoboron trifluoride, NHEt₂, BF₃, m. p. 150-160°, is insoluble in benzene and ether but soluble in water. Ethylamminoboron trifluoride, NH₂Et,BF₃, m. p. 89°, decomposes in air above its m. p., and is soluble in benzene and slightly soluble in ether. Other methods of preparing these compounds are given. S. K. Tweedy.

Ultramarine. J. HOFFMANN (Z. anorg. Chem., 1929, 183, 37-76).-Methods of formation of ultramarine, and the reasons for the production of the colour and its variations, have been studied. The blue colour of boron ultramarines is primarily due to the presence of sulphur and is independent of the presence of water, but physical factors are at least as important as chemical. The colour is partly dependent on the nature of the alkali metal, and its production depends on a change of the borate beginning at the stage $R_2B_6O_{10} \longrightarrow R_2B_{10}O_{16}$. Replacement by boron trisulphide of part of the boron trioxide which is in excess of that required for the presence of alkali tetraborate yields orange-red to brown substances, the blue colour appearing only when a sulphide of the alkali metal is present; thiosulphate is not necessarily present in the blue substances, but may be formed as an intermediate substance in certain types of ultramarine. The chemical and physical action of the sulphur is discussed. Since ultramarine is formed much more slowly when sulphur is heated with anhydrous borax than with alkali sulphide or polysulphide, the latter is probably formed as an intermediate. Conditions necessary for the formation of ultramarine are discussed, with particular reference to the part played by auxiliary valencies and the structure of the compounds formed. All the blue polysulphide ultramarines contain a structure analogous to diborates bridged by alkali monosulphide to the boric acid part of a higher borate which may range from tri- to octa-borate. The old idea that ultramarine synthesis depends on solubility phenomena is disproved. Ultramarines may be classified under five types : inorganic, including the ordinary ultramarines; organic, including a variety of organic dyes containing sulphur; inorganic-organic, including certain hydrocarbon ultramarines and compounds such as ethyl and butyl alumina ultramarine; temporary inorganic, such as phosphate and certain borate varieties; temporary organic, such as cyanoultramarine. The formation in nature of the mineral ultramarines is discussed. H. F. GILLBE.

Behaviour of alkali fluoborates in tungstenfilament lamps. J. H. DE BOEB (Rec. trav. chim., 1929, 48, 979-983).-Alkali fluoborates introduced into electric lamp bulbs can react with tungsten spattered from the filament during burning. In the case of the potassium salt a tungsten compound with a W: F atomic ratio of 1:3 is formed. The intensity of blackening of the bulb wall with the introduction of other alkali fluoborates shows that the amount of reaction is in the decreasing order cæsium, rubidium, potassium. This is confirmed by the amount of tungsten extracted in these cases by sodium hydroxide and by hydrofluoric acid. Reaction is negligible with sodium fluoborate owing to the decomposition of this salt at temperatures above 320° during the evacuation of the lamp. F. G. TRYHORN.

Attack of aluminium by ammoniacal solutions. J. CALVET (Compt. rend., 1929, 189, 485-486).— The action of ammonia solutions of different concentrations on aluminium of different degrees of purity has been investigated. Very pure aluminium (99.96%) is attacked just as readily as less pure specimens: Dilute solutions attack the metal to a greater extent than concentrated ones,

C. W. GIBBY. **Complex scandium oxalato-compounds.** J. STÉRBA-BOHM and J. SKRAMOVSKÝ (Časopis Českoslov. Lék., 1928, 8, 211—215; Chem. Zentr., 1929, i, 2399).—Sćandium oxalate crystallises $+6H_2O$. The *compounds* HSc(C₂O₄)₂, H₄Sc₂(C₂O₄)₅, and H₃Sc(C₂O₄)₃ have been prepared, and their relative stability has been observed. A. A. ELDRIDGE.

Oxidisability of silicon as a function of its state of division. A. SANFOURCHE (Compt. rend., 1929, 189, 533-535).—A reply to Bedel's criticism (cf. this vol., 997, 1030). The author's experiments on pyrophoric silicon may be reproduced if the silicon is in a sufficiently fine state of division, e.g., if it is obtained from the aluminium-silicon alloy "alpax." The presence of impurities exerts only a secondary influence. J. GBANT.

Hydrates and hydrogels. XII. Mono- and di-silicic acids. R. WILLSTATTER, H. KRAUT, and K. LOBINGER (Ber., 1929, 62, [B], 2027-2034; cf. A., 1926, 36; this vol., 39).-By shortening the time of action and exercising greater precautions with regard to the optimal acidity (0.002N-0.001N) of the solution, it has been found possible to prepare monosilicic acid $(M=62; \text{ calc. for } SiO_2, M=60)$ in greater purity. The stability of the acid and the subsequent members of the series depends greatly on the acidity of the solution. The mono- and di-acids are most stable in feebly acid solution and condense most rapidly in nearly neutral or incipiently alkaline solution. The variability of condensation with acidity causes silicic acids of mean mol. wt. 200-300 to vary irregularly in their properties, as shown by their behaviour towards egg-albumin. The gradual condensation of monosilicic acid in solutions of differing $p_{\rm H}$ is illustrated by a series of time-mol. wt. graphs, the most remarkable feature of which is the indication of the existence of a structural change in disilicic acid during the process without alteration of mol. wt. The condensation of silicic acid is delayed by addition of small amounts of ethylene glycol, glycerol, and other polyhydric alcohols, whereas ethyl alcohol is inactive.

The volatility of silicic acid during distillation of its solutions has been re-investigated, using monosilicic acid and the apparatus of Kraut, Lobinger, and Pollitzer (this vol., 1261). It has not been found possible to increase the mere trace of acid volatilised or to conduct the distillation without such volatilisation. Under the same conditions, distillation of a 0.4% solution of boric acid from 400 to 70 c.c. at 11° gave no trace of boric acid in the distillate.

H. WREN. Action of the alkali carbonates on lead bromide, iodide, and nitrate in aqueous solutions. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189, 428-430).—These reactions have been followed by chemical analysis of the precipitates and by conductivity measurements. The bromide and iodide behave analogously to lead chloride (this vol., 1154), whilst the nitrate gives only lead carbonate.

J. GRANT.

Action of the alkali oxalates on the halogen salts of lead in aqueous solution. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189, 535-536).— Further experiments (cf. preceding abstract) have shown that analogous results are obtained by the use of the alkali oxalates. A lead chloro- or bromooxalate is first produced which is subsequently transformed by an excess of reagent into lead oxalate (cf. following abstract). J. GRANT.

X-Ray study of some halogen salts. MATHIEU (Compt. rend., 1929, 189, 536—537; cf. preceding abstract).—X-Ray measurements of the dimensions of the lattice confirm the conclusion that the salts obtained by Demassieux contain the PbCl or PbBr ion. In general, isomeric similarity between salts is much closer when the substituted element enters a complex group than when it plays an ionic rôle.

J. GRANT.

Union of nitrogen and sulphur under the influence of electrical discharges. W. MOLDEN-HAUER [with A. ZIMMERMANN] (Ber., 1929, 62, [B], 2390—2392).—Under the influence of the dark electrical discharge, pure nitrogen at 10—1 mm. readily combines with sulphur at 80—100°, yielding a dark-coloured product from which extraction with ether and carbon disulphide yields nitrogen pentasulphide and nitrogen tetrasulphide. The residue left after treatment with these solvents is heated at 90—93°/vac. and then exhaustively treated with the same media, whereby the bluish-black nitrogen disulphide, $(NS_2)_x$, is isolated. The compound decomposes above 100° into nitrogen pentasulphide and tetrasulphide. It is decomposed by alkali hydroxide with evolution of ammonia and by concentrated hydrochloric acid into ammonium chloride and sulphur. H. WREN.

Constitution of nitrogen sulphide, N_4S_4 . A. MEUWSEN (Ber., 1929, 62, [B], 1959-1969).--Nitrogen sulphide in benzene is converted by stannous chloride in 96% alcohol into the compound (HSN)₄ (cf. Wolbling, A., 1908, ii, 272), decomp. about 145° after becoming discoloured at about 100°. The product is moderately stable towards dilute acids, but completely hydrolysed by hot, concentrated alkali hydroxide mainly with formation of thiosulphate and complete evolution of nitrogen as ammonia, thus showing the absence of the N-N linking. The presence of the -SH group is indicated by the yellow colour which is observed when the colourless solution of $(HSN)_4$ in acetone is treated with neutral, alcoholic ethyl nitrite. Further, when the substance (HSN)4 is dissolved in boiling formaldehyde, preferably in the presence of alkali, the compound (NS·CH₂·OH)₄ is obtained. It follows, therefore, that all the hydrogen atoms in (HSN)₄ are united to sulphur atoms, but they cannot be present as simple sulphydryl, SH, groups, since this would involve the presence of N-N linkings. It is therefore probable that the sulphur is quadrivalent, and this hypothesis is confirmed by the oxidative fission with bromine which requires 4×4 atoms of the halogen instead of 4×6 atoms required by the -SH group. The constitution $N \ll_{SH=N=SH}^{SH=N=SH} N$ is therefore deduced

and the compound is regarded as the inorganic analogue of hydrocyanic acid. Treatment of nitrogen sulphide with bromine shows that the four sulphur atoms exert twelve valencies towards nitrogen without indicating the number of valencies of the sulphur atoms to one another. Hydrolysis of nitrogen sulphide by alkali occurs almost quantitatively according to the scheme $S_4N_4+6NaOH+3H_2O=$ $Na_2S_2O_3+2Na_2SO_3+4NH_3$. The reaction thus closely resembles the hydrolysis of sodium hyposulphite, strengthening the conception that nitrogen sulphide is the cyclic nitrile of 2 mols. of hyposulphurous acid, $N \ll_{S-N=S}^{S-N=S}N$. The constitution of the compounds PbN₂S₂,NH₃ and HgN₂S,NH₃, described by Ruff and Geisel (A., 1904, ii, 396), is discussed. H. WREN.

[Glow produced by] oxidation of phosphorus vapour. E. J. Bowen and A. C. CAVELL (J.C.S., 1929, 1920-1926).-Intensity measurements are made by a photographic method incorporating special precautions. Within the range $60-380^{\circ}$ and for oxygen pressures between 40 and 350 mm. the intensity of the glow does not vary appreciably. This is in agreement with the "chain" mechanism of oridation (Becksträm A 1927 1151). Or one at oxidation (Backstrom, A., 1927, 1151). Ozone at low concentrations has no effect on the glow, but with more than 0.14% of ozone the intensity is increased linearly with concentration. Sulphur dioxide diminishes the glow and the effect is linear with respect to sulphur dioxide : oxygen ratio. Chlorine is a more efficient inhibitor and the intensity of glow decreases linearly with increase of chlorine: oxygen ratio over a large range, until the glow is less than one fifth of the maximum intensity. Further addition of chlorine has not the same quenching effect. It is suggested that chlorine can stimulate reaction chains involving oxygen. Ether vapour has no effect on the glow intensity even when present at a partial pressure fifty times that of the dry J. G. A. GRIFFITHS. oxygen.

Action of gaseous hydrogen chloride on phosphorus pentoxide. (MLLE.) J. M. A. HOEF-LAKE (Rec. trav. chim., 1929, 48, 973—978).—The curve for the absorption by phosphorus pentoxide of hydrogen chloride dried by distillation at low temperatures is autocatalytic in type. The rapid absorption of further hydrogen chloride confirms the formation of a catalyst in the initial stages of the absorption. A comparison of the effects of the compounds HPO₃, POCl₃, and of mixtures of PO₂Cl₂ and P₂O₃Cl₄ on the rate of absorption indicates that one or both of the latter intermediate chlorides is the catalyst. The initial period of delay in the reaction between hydrogen chloride and phosphorus pentoxide may be prolonged to 7 days by previously drying the gas with phosphorus pentoxide in two stages.

F. G. TRYHORN.

Dichlorophosphoric acid. H. MEERWEIN and K. BODENDORF (Ber., 1929, 62, [B], 1952—1953; cf. Lange, this vol., 662, 764).—If phosphoryl chloride or phosphorus pentachloride is treated with ice-water until dissolution is just complete the product requires almost exactly two or four equivalents of barium hydroxide for neutralisation in the presence of thymolphthalein, thus showing the production of dichlorophosphoric acid as a recognisable intermediate. An oily product consisting mainly of dichlorophosphoric acid remains after treatment of phosphoryl chloride with the requisite quantity of water in ether; a crystalline ammonium or oxonium salt could not be prepared. H. WREN.

Tantalum. V. SPITZIN and L. KASCHTANOV (Z. anorg. Chem., 1926, 182, 207-227).-Tantalum containing not more than 5% O as impurity has been prepared by the reduction of potassium fluotantalate with sodium in an atmosphere of hydrogen. The action of magnesium on tantalum pentoxide yields a product containing combined magnesium and having the formula TaO_2Mg or Ta_2O_4Mg . The behaviour of the pure metal and some of its compounds on being heated in a stream of hydrogen chloride has also been investigated. The pure metal reacts at 700°, forming the pentachloride and hydrogen, whilst the metal containing some oxygen reacts at a slower rate, giving the pentachloride and possibly two oxychlorides, one of which has the formula TaO₂Cl. The impure dioxide reacts at 850° with hydrogen chloride, forming hydrogen, a sublimate of the pentachloride, and a residue of the pentoxide and magnesium chloride. Above 500°, tantalum pentoxide is markedly volatile in hydrogen chloride and the reaction which takes place with the formation of water and the pentachloride is quantitatively reversed at lower temperatures. With a low concentration of water vapour, the black oxychloride, TaO₂Cl, and a less stable, white substance, possibly of the composition TaOCl_a, can be obtained by hydrolysis of tantalum pentachloride at suitable temperatures. Sodium metatantalate when heated in hydrogen chloride is decomposed at 850° into sodium chloride, tantalum pentoxide, and water. L. S. THEOBALD.

Action of air on flowers of sulphur and ground sulphur. J. E. STEPHENSON and S. W. BRIDGE (Analyst, 1929, 54, 590—591).—A known volume of air was passed over sulphur maintained at a constant temperature and then through standard iodine solution. At temperatures below 90° air had little or no action on ground sulphur (99.45% through 100-mesh), but appreciable and increasing quantities of sulphur compounds were evolved from flowers of sulphur from 17° and upwards. D. G. HEWER.

Preparation of hydrogen sulphide. H. GFELLER and K. SCHAEFER (Schweiz. Apoth.-Ztg., 1929, 67, 109-110; Chem. Zontr., 1929, i, 1970).—A mixture of paraffin (25 g.), sulphur (15 g.), and asbestos fibre (5.g.) is heated. A. A. ELDRIDGE.

Action of hydrogen sulphide on solutions of nitric acid. H. B. DUNNICLIFF and S. MOHAMMAD (J. Physical Chem., 1929, 33, 1343—1362).—Solutions containing up to 5% of nitric acid are not attacked by hydrogen sulphide even if nitrogen peroxide be added. Solutions containing up to 40% of nitric acid are attacked after an interval of time. This interval is removed when nitrous fumes are added or when slight decomposition of the acid is produced by insolation. The addition of sulphuric acid lengthens the period of induction. The products of the reaction are sulphuric and nitrous acids, ammonia, nitrous and nitric oxides, and nitrogen. The presence of sulphuric acid appears to influence the formation of the last-named, the evolution of which in the later stages of the reaction may be due to the formation of ammonia by secondary reactions and its subsequent decomposition. Sulphuric acid affects the course and the final products of the reaction, which ceases when the concentration of nitric acid falls to 23%and the total sulphuric acid content is 15%. A compound inert to the action of hydrogen sulphide is probably formed between the two acids. The mechanism of the formation of sulphuric acid and of the other products of the reaction is discussed.

L. S. THEOBALD. Decomposition of thiosulphuric acid. J. SCHEFFER and F. BOHM (Z. anorg. Chem., 1929, 183, 151-188).-Earlier work on the mechanism of the reaction $H_2S_2O_3 \longrightarrow H_2O + SO_2 + S$ is critically reviewed, and further study has been made of the reaction by nephelometric observation, measurement of the iodine titre, and the decolorisation of methyleneblue in the solution. At hydrogen-ion concentrations below 2.5×10^{-5} decomposition does not take place. the necessary condition for decomposition being the appearance of the labile HS₂O₃' ion; the ion SO₃" and the non-ionised molecule are relatively stable. Decomposition of an acidified solution commences before cloudiness appears, as is evidenced by the increase of the iodine titre and the presence of pentathionic acid. On acidification of a thiosulphate solution containing methylene-blue rapid decolorisation ensues, but if methylene-blue be added to the solution 3 hrs. after acidification only partial decolorisation ensues; the dye is adsorbed readily by freshlyprecipitated sulphur, but by the action of sulphur dioxide the sulphur loses this property.

H. F. GILBE.

Preparation of pure uranium. E. BOTOLFSEN (Bull. Soc. chim., 1929, [iv], 45, 626-627).—Uranium oxide is reduced by means of sublimed calcium by heating in an iron tube in a vacuum : $U_3O_8+8Ca=$ 3U+8CaO. The temperature is kept above the m. p. of calcium, the excess of which volatilises into the upper cold part of the tube. The uranium is separated through a sieve from most of the coarser calcium oxide, washed with 2% acetic acid solution and then with water, and finally dried with alcohol and ether. The powder obtained in this way contains 99.95% U. Uranium does not sublime in a high vacuum below its m. p. O. J. WALKER.

Reaction between ferric oxide and hydrogen sulphide at temperatures between 120° and 830°. L. A. SAYCE (J.C.S., 1929, 2002—2006; cf. Pearson and Robinson, A., 1928, 606).—Pure ferric hydroxide was dried at 50° to constant composition and was then treated with hydrogen sulphide at various temperatures between 120° and 830°. Iron disulphide was the principal product between 120° and about 400° and was accompanied by gradually diminishing proportions of ferrous and ferric sulphides up to 250°. Above 400° the composition of the product was markedly different. The iron disulphide almost disappeared and at the same time the presence of free sulphur was first noted. The product behaved as a mixture of ferrous and ferric sulphides. J. G. A. GRIFFITHS.

Fluorides of group VIII of the periodic system. O. RUFF and E. ASCHER (Z. anorg. Chem., 1929, 183, 193—213).—Pure cobalt trifluoride, CoF_3 , has been prepared by the action of fluorine on cobalt dichloride in a quartz tube at 150°. It is a light brown, crystalline, hygroscopic powder belonging to the hexagonal system; d (X-ray) 4.14; d (pyknometer) 3.88. By heating in a current of carbon dioxide it is completely decomposed to the difluoride at 350°. The previously known fluorides, FeF_3 and NiF_2 , may also be prepared by this method, whilst FeF_2 and CoF_2 may be obtained by the reduction of the higher fluorides at 400° and 200—300°, respectively. *Rhodium* trifluoride, RhF₃, has been obtained by heating the metal in chlorine and then in fluorine at 500-600°. The product was not perfectly pure. It forms a red crystalline powder belonging to the rhombic system; d (X-ray) 5.67; d (pyknometer) 5.38. It is very stable towards water, acids, and bases. By heating the metal or the trifluoride in fluorine at 600° a red. sublimate which may be either RhF4 or RhF5 is obtained. It is very reactive. Contrary to expectation, the compound obtained when palladium, or preferably the dichloride, is heated with fluorine is palladium trifluoride and not the difluoride. Sometimes brown crusts of the latter are obtained as the result of local heating. The trifluoride is a black, hygroscopic, crystalline powder belonging to the rhombic system, d (X-ray) 5.19; d (pyknometer) 5.06. Its chemical behaviour is similar to that of cobalt trifluoride. Impure palladium difluoride has been obtained by the action of reducing agents on the trifluoride or of hydrogen fluoride on the dichloride. Examined by the X-ray spectrograph it appears to be isomorphous with the other difluorides of the eighth group. The physical and chemical properties of all the fluorides mentioned have been tabulated.

M. S. BURR.

Cobalti-pentammines and a new case of isomerism. C. DUVAL and (MME.) DUVAL (Compt. rend., 1929, 189, 537-538).-The following new compounds were obtained by the action of freshly-prepared silver hydroxide on the compound [CoCl(NH₃)₅]Cl₂, the compound $[Co(H_2O)(NH_3)_5](OH)_3$ being formed as an intermediate product and decomposed at 70–100° by the appropriate acid or its alkali metal salt : boratopentamminecobaltic chloride, [CoBO2(NH3)5]Cl2; dichromatopentamminecobaltic chloride,

[CoCr₂O₇(NH₃)₅]Cl; cobalt phosphatopentammine, $[CoPO_4(NH_3)_5]$; sodium cobaltipentamminopyrophos-phate, Na $[CoP_2O_7(NH_3)_5]$; sodium cobaltipentamminobenzenepentacarboxylate, $Na_{2}[CoC_{6}H(CO_{2})_{5}(NH_{3})_{5}];$ sodium cobaltipentamminomellitate,

Na₃[CoC₆(CO₂)₆(NH₃)₅]. The two following pairs of complexes have the same compositions but different electrolytic valencies (radical isomerism): cobalt persulphatopentamminecobaltic sulphate,

[CoSO₄(NH₃)₅]SO₄ (orange); and sulphatopentamminecobaltic chloride, [CoSO4(NH3)5]Cl (rose); cobalt ferricyanopentammine, $[Co{Fe(CN)_6}(NH_3)_5]$ (brown), and potassium cobaltiferrocyanide, $K[Co{Fe(CN)_8}(NH_3)_5].$ J. GRANT.

Ferrocyanomolybdates and analogous compounds of ruthenium and osmium. G. A. BAR. BIERI (Atti R. Accad. Lincei, 1929, [vi], 9, 1015-1019) .- The canary-yellow, crystalline compound formed by the action of ammonium acetate on the reddish-brown, gelatinous precipitate obtained by the interaction of a molybdate and a ferrocyanide in acid solution (A., 1928, 160) is readily convertible into the corresponding silver compound, $Ag_4Fe(CN)_6,2MoO_3,H_2O$, the existence of the com-plex [Fe(CN)_6,2MoO_3] being thus indicated. The ammonium compound probably has the structure

[MoO₃(CN)₃Fe(CN)₃MoO₃](NH₄)₄. The corresponding ammonium ruthenocyanomolybdate,

(NH₄)₄Ru(CN)₆,2MoO₃,3H₂O, and osmiocuanomolybdate were also prepared. T. H. POPE.

Modification of Glocker's method of quantitative analysis by means of X-ray absorption. N. H. MOXNES (Z. physikal. Chem., 1929, 144, 134-136; cf. A., 1925, ii, 270).-Preliminary. The original method of Glocker and Frohnmayer has been modified by substituting for a continuous X-ray spectrum a line spectrum as the basis of the absorption measurements. F. L. USHER.

Simple sensitive method of spectrographic chemical analysis. E. VITERBO (Annali Chim. Appl., 1929, 19, 329-333).-A small drop of the solution to be examined is placed between the smooth, plane ends of two horizontal metal rods 2 mm. in diameter placed about 1 mm. apart. When the liquid has evaporated a condensed spark is passed between these electrodes, which may be of zinc, cadmium, or, better, magnesium. With a quartz spectrograph with a 0.01 mm. slit, the exposure used is a few seconds. The method is highly sensitive and permits of the detection, for example, of less than T. H. POPE. 6.4×10^{-10} g. of silver.

Rapid qualitative analysis. II. Spot tests for the commoner cations and anions. G. GUTZEIT (Helv. Chim. Acta, 1929, 12, 829-850).-The use of the reactions previously described (this vol., 898) and of some supplementary reactions as spot tests is explained, and a scheme for systematic R. CUTHILL. analysis in this way is given.

Photographic method for the determination of coloured solutions with special reference to the visual purple. R. J. LYTHGOE and K. TANSLEY (J. Physiol., 1929, 68, 45-48).-The photographic effect of light passing through the unknown solution is compared with that passing through a neutral tint wedge. E. BOYLAND.

Theory of physical titration. E. N. GAPON (Ukraine Chem. J., 1929, 4, 149-153).-Physical titration is defined as titration in the course of which neither the titrated nor the titrating substance undergoes any change. Examples are the titration of a mixture of ethyl alcohol and water with benzene until separation into two layers occurs, and the titration of benzene with a mixture of ethyl alcohol and water until the whole becomes homogeneous. Using the data of Lincoln (A., 1900, ii, 392) and the formula of Bancroft (J. Physical Chem., 1897, 1, 786), the physical method of titration is found to be quite satisfactory. A. FREMAN.

Dilution in colorimetric hydrogen-ion measurements. I. Isohydric indicator methods for accurate determination of $p_{\rm H}$ in very dilute solutions. E. H. FAWOETT and S. F. ACREE (J. Bact., 1929, 17, 163—204).—Dilution curves reveal three types of variation from electrometric $p_{\rm H}$ values : buffer dilution effects, the effect of carbon dioxide and alkaline impurities in the water, and differences in $p_{\rm H}$ values of the indicator solutions. The incidence of these variations is examined. By the use of indicators adjusted at various $p_{\rm H}$ values the isohydric indicator method can be used at the usual and at extreme dilutions. CHEMICAL ABSTRACTS.

Determination of hydrogen-ion concentration in surgery. E. SIMENAUER (Arch. klin. Chir., 1928, 150, 193-201; Chem. Zentr., 1929, i, 1972).

Potentiometric titration of acids and bases. L. KAHLENBERG and A. C. KRUEGER (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 11 pp.; cf. A., 1928, 1203) .- An investigation has been made of the possibility of carrying out the potentiometric titration of hydrochloric acid with N-sodium hydroxide by using as electrodes two simple plates of dissimilar metals. The electrodes were mercly immersed in the acid solution, which was mechanically stirred, and the variation in the P.D. between these plates during the addition of alkali was followed by means of a potentiometer. With the majority of pairs of metals used there was a marked inflexion of the titration curve at the end-point. Tungsten used in conjunction with most other metals gives a particularly sharp change of P.D. at the end-point and this change involves a reversal of polarity when the other electrode is nickel, cobalt, copper, silicon, chromium, or tin. In these latter cases the end-point can be determined to within about 0.1 c.c. by using only a voltmeter graduated in tenths of a volt to follow the change in P.D. In order to obtain the most rapid establishment of equilibrium it is recommended that copper, nickel, silicon, or cobalt should be used in conjunction H. J. T. ELLINGHAM. with tungsten.

Oualitative microanalysis of acids. F. FEIGL and P. KRUMHOLZ (Mikrochem., 1929, Pregl Fest., 77-86).-Small amounts of boric acid may be detected by the change in colour (violet to blue) which occurs on warming a 0.01% solution of quinalizarin in concentrated sulphuric acid with the substance dissolved in 1 c.c. of concentrated sulphuric acid. Nitrates, oxidising substances, and fluorides must be absent. Purpurin and alizarin-S may be used in place of quinalizarin, but the reaction is less sensitive. Traces of chromic acid may be detected by the reddish-violet colour given with diphenylcarbazide; mercuric salts and molybdates give similar colours, but the addition of sodium chloride in the former case and oxalic acid in the latter prevents interference by these metals. Traces of silica can be detected by warming a few drops of a slightly acid solution of the material with a drop of a nitric acid solution of ammonium molybdate, followed by addition of an acetic acid solution of benzidine and a saturated

solution of sodium acetate. A blue colour develops if only 0-0001 mg. of silica is present; arsenates and phosphates must be absent. The foregoing test can also be utilised for the detection of fluorine, the substance being warmed with concentrated sulphuric acid and quartz sand, the evolved silicon tetrafluoride being collected in a drop of water, and this solution tested for silica as above. The test may be used for the examination of mineral waters, and will detect 0-001 mg. of fluorine. Nitrates and halogens interfere, and should be previously removed.

H. F. HARWOOD.

Limits of applicability of indicators in simple p_H determinations. II. J. EISENBRAND (Pharm. Ztg., 1929, 74, 1287-1289; cf. this vol., 1157).-The application of indicators to p_{π} determinations in nonaqueous solutions on the basis of the mathematical equations previously given for aqueous solutions is not possible. Errors are caused by the alteration in the degree of dissociation of the indicator, and the absence of hydroxyl ions from many solvents. The presence in the solution of albumin and other substances of high mol. wt. also affects the p_{π} determination. The equations can be utilised only in the special case of a mixture of water with another solvent, the concentration of which varies within only narrow limits. Rapp's attempt to utilise $p_{\rm H}$ determinations as a means of affording a more accurate criterion of the degree of purity of various pharmaceutical products is adversely criticised, and the results are shown to be valueless for that purpose. The conclusion is reached that in the examination of pharmaceutical products the determination of the approximate limits of the $p_{\rm H}$ value by means of litmus paper is all that is H. F. HARWOOD. necessary.

Simple micro-analytical separation of chlorine and bromine. L. MOSER [with R. MIKSCH] (Mikrochem., 1929, Pregl Fest., 293—295).—The greater thermal dissociation of hydrogen bromide and iodide as compared with hydrogen chloride has been utilised for an indirect determination of chlorine and bromine. The precipitate of silver chloride or bromide (about 5 mg.) is filtered on a micro-Munro crucible, dried at 150°, and weighed. Six times the quantity of pure dry ammonium bromide is added and the crucible heated at 250—300° until all ammonium salt has volatilised. A second treatment is usually sufficient to ensure complete conversion of the chloride into bromide. Silver bromide may be converted into silver iodide in a similar way by treatment with ammonium iodide. H. F. HARWOOD.

Determination of perchlorate. O.S. FEDOROVA (Z. anal. Chem., 1929, 78, 249—268).—The colorimetric method of Hahn (cf. B., 1926, 404) for the determination of perchlorate in saltpetre has been extended to the determination of small amounts in electrolytic baths containing chlorate, perchlorate, and chloride. Contrary to Hahn's statement, the presence of chlorates was found to have an appreciable effect on the colour of the methylene-blue reagent; hence it is necessary that the standard solutions used for comparison should contain an amount of chlorate approximately similar to that in the solution under examination. To 0.1—0.2 c.c. of the solution is added 0.1 c.c. of 40% potassium nitrate solution, the whole is diluted to 0.3 c.c., and 5 c.c. of the zine sulphate-methylene-blue reagent are added, the resulting liquid being matched against standards. Not more ad than 0.75% of potassium nitrate, 0.9% of chlorate, or 0.5% of chloride should be present in the final test solution, and under these conditions 0.0004% of perchlorate can be detected. Chromates if present must be previously removed by precipitation with su load acetate. The above method is considered more at a statement for the determination of grandle guardities and the second statement of the second se

satisfactory for the determination of small quantities of perchlorate than the titanous chloride volumetric method of Spitalski and Jofa, which consumes considerable time. Attempts to utilise α -phenyl- β diethylaminoethyl *p*-nitrobenzoate hydrochloride as a reagent for perchlorates yielded no satisfactory results. H. F. HARWOOD.

Determination of iodine, especially in minute quantities [in organic substances]. J. SOHWAI-BOLD (Z. anal. Chem., 1929, 78, 161-180).-Numerous published methods for the determination of iodine have been tested for their usefulness in determining minute amounts such as occur in soils, plants, and various other organic materials. Direct combustion of organic materials in oxygen combined with absorption of any iodine volatilised by potassium carbonate, heating the carbonate and the ash together until white, and extracting the residue with water yields a solution containing all the iodine as potassium iodide together with only small quantities of alkali salts. The iodine can be determined colorimetrically after extraction with chloroform; a modification of this method is described in detail. Alternatively, the iodide may be oxidised to iodate by boiling with chlorine water or with 0.1N-chloroamine solution; the iodate is then determined by addition of iodide and hydrochloric acid and titration of the liberated iodine. Periodate may be determined in the presence of iodate by treating the neutral solution with boric acid and iodide, whereby reduction to iodate is effected with liberation of iodine; after titration with thio-sulphate hydrochloric acid may be added and the total iodate determined by again titrating with thiosulphate. A. R. POWELL.

Apparatus for micro-determination of sulphur dioxide in air. A. C. RÖTTINGER (Mikrochem., 1929, Pregl Fest., 313—314).—An apparatus which permits of the determination of sulphur dioxide when using only 1—2 litres of air is described. The air is aspirated through 0.01N-iodine solution, which is subsequently titrated with 0.01N-thiosulphate.

H. F. HARWOOD.

Micro-determination of selenium and tellurium in organic compounds. H. D. K. DREW and C. R. PORTER.—See this vol., 1323.

Drop method for detection of nitrite ions in presence of other anions. N. M. RONSHINA (J. Russ. Phys. Chem. Soc., 1929, 61, 897-898).-0.004 Mg. of nitrite ion contained in 0.05 c.c. of solution can be detected by the use of test-papers dipped in solutions in acetic acid of benzidine, a rose-yellow to deep red coloration being obtained according to the concentration of nitrite. The solution examined should be made alkaline before applying the test.

Cations and other anions, with the exception of chromate, do not interfere with this test; in the presence of chromate, barium chloride should first be added in excess. R. TRUSZKOWSKI.

Determination of nitrates in bismuth carbonate. G. J. W. FERREY.-See B., 1929, 850.

Availability of the isomeric aminonaphtholsulphonic acids for the colorimetric determination of phosphorus. B. VASARHELYI (Mikro-chem., 1929, Pregl Fest., 329-337).—The action of a number of different aminonaphthol-sulphonic acids and -disulphonic acids in reducing the complex phosphomolybdic acid to blue molybdenum oxides has been investigated, and compared with that of 1-amino-\beta-naphthol-4-sulphonic acid. With the latter acid the maximum blue colour develops more rapidly than when other isomeric acids are used, but some of the latter give a deeper colour. The rapidity of development of the blue colour with the different isomerides depends mainly on the relative positions of the sulphonic and amino-groups in the molecule, and to a smaller extent on the positions of the amino- and hydroxyl groups. The presence of large amounts of many salts, such as sodium chloride, ammonium sulphate, etc., hinders the reduction, and with 1-aminoβ-naphthol-4-sulphonic acid silica (as potassium silicate) interferes. H. F. HARWOOD. silicate) interferes.

Determination of degree of oxidation of some insoluble phosphates. A. COLANI (Bull. Soc. chim., 1929, [iv], 45, 621-623).-The amount of metallic oxide in uranous, molybdous, and ferrous phosphates is determined as follows. The phosphato is dissolved by heating at 200° in a scaled tube with a known volume of standard potassium dichromate solution (3-6 g. per litre) to which 4 vol.-% of sulphuric acid has been added. After complete dissolution the unreduced dichromate is titrated by one of the usual methods, the difference giving the amount of dichromate necessary for the oxidation of the metallic radical to the higher valency stage. In the case of uranous chlorophosphate, where the above procedure is inapplicable, the substance is melted in a vacuum with a large excess of sodium pyrophosphate, dissolved in water in an atmosphere of carbon dioxide, and the solution is then titrated with permanganate.

O. J. WALKER. O. J. WALKER. Accuracy of the Gutzeit method for [determining] arsenic. J. R. NELLER (J. Assoc. Off. Agric. Chem., 1929, 12, 332—341).—In a series of determinations of arsenic residues on fruit sprayed with lead arsenate, observations were made of the effects on the accuracy of such factors as size of the aliquot portion, absorption and evolution temperatures, method of preparing the mercuric bromide strips, and the point in the procedure at which the stannous chloride is added. The variations in the results were within the normal limits of accuracy of the method. H. J. DOWDEN.

Polarographic studies with the dropping mercury cathode. V. Electro-reduction in acidic solutions of arsenious oxide. K. Kačía. ková (Coll. Czech. Chem. Comm., 1929, 1, 477–492). —A polarographic investigation with the dropping

mercury cathode of solutions of arsenious oxide in 0.1N- and N-hydrochloric acid has been made. The current-voltage curve exhibits four sudden rises and two maxima. The first rise in the curve is due to the electro-reduction of arsenious acid to arsenic, probably by the primarily deposited hydrogen, the second rise is due to the formation of arsine, the third increase, which is followed by a prominent maximum, is ascribed to the absorption of positively-charged dissociation products of arsenious acid, whilst the fourth rise is attributed to the evolution of hydrogen from hydrogen ions of the acid. Similar results were obtained with sulphuric and nitric acid of various concentrations, and the form of the curve was unchanged by the addition of 6N-calcium chloride and of 3N-potassium chloride. The addition of acetic acid and of propionic acid to a solution of arsenious oxide in N-hydrochloric acid resulted in a marked change in the shape of the curve, whilst the addition of 0.001M-solutions of methylene-blue and of fuchsin hydrochloride suppressed the dissociation of the arsenious acid as indicated by the practical disappearance of the second maximum.

A. I. VOGEL. Potentiometric titrations with potassium ferricyanide in alkaline solution. I. Vanadium and hyposulphite. II. Arsenic, antimony, tin, and thallium. C. DEL FRESNO and L. VALDÉS (Z. anorg. Chem., 1929, 183. 251-257, 258-262).--I. Vanadyl sulphate may be titrated potentio-metrically with potassium ferricyanide in presence of sodium hydroxide at the ordinary temperature, but if ammonia, sodium carbonate, or borax is added a higher temperature (70°) must be used, or constant values of the potential will not be reached sufficiently quickly. An attempt has been made to determine vanadium and chromium in a mixture, but the first jump in the potential comes too soon. Potassium ferricyanide can be satisfactorily titrated with vanadyl sulphate if the ferricyanide is first warmed to 50-60° in a vacuum to remove dissolved air before making alkaline. Sodium hyposulphite may also be titrated by alkaline ferricyanide, but it must be kept in a current of nitrogen.

II. Solutions of stannous chloride, sodium arsenite, and antimony trichloride may be satisfactorily titrated in alkaline solution with potassium ferricyanide by the potentiometric method. The titration of stannous chloride must be carried out in an atmosphere of nitrogen. The titration of thallium gave results about 1% too low. With a high alkali content the potential reaches a constant value too slowly, and with a low one oxidation is incomplete.

M. S. BURR.

Micro-determination of carbon by Nicloux' method in dilute aqueous solutions. A. BOIVIN (Compt. rend. Soc. Biol., 1929, 100, 273-276; Chem. Zentr., 1929, i, 1842) .- Loss of carbon due to formation of carbon monoxide is avoided by dissolving the substance in water with sodium sulphate and drying in a vacuum to produce a large surface. Solutions poor in carbon are evaporated with sodium sulphate in a vacuum over sulphuric acid, and the residue is "washed" with dry sodium sulphate into Nicloux' apparatus. A. A. ELDRIDGE.

Determination of carbon in iron and iron alloys. N. A. ZIEGLER.-See B., 1929, 854.

Determination of carbon dioxide in carbonates which may contain sulphides. R. CHANDELLE (Bull. Soc. chim. Belg., 1929, 38, 248-254).—In a modification of the ordinary direct gravimetric method, the carbonate sample is dissolved by means of phosphoric acid containing potassium dichromate to oxidise any sulphide present. Accurate results are obtained even in presence of large amounts of sulphide. O. J. WALKER.

Detection of alkali metal salts in mixtures of soluble salts and in silicates. N. A. TANANAEV (J. Russ. Phys. Chem. Soc., 1929, 61, 815-822).-A method for detecting alkali metals (sodium and potassium) in the presence of salts of tin, antimony, lead, silver, bismuth, cadmium, copper, aluminium, chromium, iron, cobalt, nickel, zinc, manganese, barium, strontium, calcium, and magnesium is described. If the salts are chlorides or nitrates their solutions are directly evaporated with an excess of oxalic acid, but if they are sulphates they are first converted into chlorides by treating with barium chloride. The solution is evaporated to dryness and ignited, when the metals remain either as carbonates or oxides or in the metallic state (Herschkovitsch, A., 1921, i, 495). On boiling with water the solution will be alkaline if either sodium or potassium is present. Potassium is detected by Cuttica's method and sodium by Kolthoff's method (A., 1927, 436). In the case of silicates the powdered silicate is first heated with hydrofluoric acid. A. FREIMAN.

Detection of sodium with potassium anti-monate. W. BOTTGER (Mikrochem., 1929, Pregl Fest., 14-19).-Under the microscope 0.001 mg. of sodium can be detected by the reaction with potassium antimonate. For microchemical tests a solution of the reagent is best made by treating 0.05 g. with 5 c.c. of water at 50° for several minutes, and decantation of the solution from undissolved material. Large amounts of potassium salts do not affect the reaction, but magnesium salts interfere and must be removed before making the test.

H. F. HARWOOD.

Volumetric determination of silver in the presence of halides and cyanides. H. BAINES (J.C.S., 1929, 2037-2041).-Previous methods are inapplicable to cases where silver halides are dissolved in the presence of unknown quantities of potassium cyanide. In this procedure iodine is added until a faint opalescence of silver iodide is produced and thus the potassium cyanide in excess of that necessary to keep the silver in solution is determined. The silver is determined by the further amount of iodine which has to be added to decompose the potassium argentocyanide into the metallic iodides and cyanogen iodide. Starch is used as indicator. The solution must be neutral or slightly alkaline and of a dilution at which the final end-point is not interfered with by cyanogen iodide. The method is shown to be accurate to within 0.14%.

J. G. A. GRIFFITHS.

Complex-chemical determination of silver. F. FEIGL and J. TAMCHYNA (Ber., 1929, 62, [B],

1897-1901) .- The solution of the silver salt is heated to boiling with 2% mercuric cyanide solution and 0.1N-sodium hydroxide is gradually added until phenolphthalein is rendered pink; after cooling, the silver cyanide is collected, washed with water and very dilute nitric acid, dried at 110°, and weighed. If lead is present, the silver and part of the lead are precipitated [as AgCN and Pb(OH)2] by excess of alkali hydroxide; lead hydroxide is extracted from the filtered precipitate by 1% nitric acid. In neutral solution silver is determined volumetrically after addition of mercuric cyanide by titration with 0.1N-sodium hydroxide in presence of phenolphthalein or Congo-red. In acid solution preliminary neutralisation by barium carbonate is necessary. Alternatively, sodium hydroxide may be added to the solution at 70-80° until a slight permanent turbidity results and the titration may be completed as usual or the solution may be neutralised by sodium hydroxide in presence of methyl-red previous to addition of mercuric cyanide. The process is not complicated by the presence of thallium. Lead, if present in neutral solution, is precipitated by addition of sodium H. WREN. sulphate.

Radiometric micro-analysis. R. EHRENBERG (Mikrochem., 1929, Pregl Fest., 61-68).—An account of the methods of determining small quantities of calcium, potassium, sodium, ammonium, sulphate, phosphate, and carbonate by the radiometric method, thorium-*B* being employed as the radioactive material. H. F. HARWOOD.

Determination of calcium carbide in technical calcium cyanamide. D. STROHAL.—See B., 1929, 775.

Determination of strontium and barium. L. SZEBELLÉDY (Z. anal. Chem., 1929, 78, 198-206).-At 17°, 1 part of strontium bromide dissolves in 12.4 parts of anhydrous isobutyl alcohol, whereas 1 part of barium bromide requires 10,800 parts of the alcohol for complete dissolution. A method for separating the two elements is based on this difference in solubility; the solution containing about 0.5 g. of the two nitrates is evaporated to dryness with 50 c.c. of hydrobromic acid and the bromides are dried at 100° for 1 hr. The dried salts are ground with 2-3 c.c. of isobutyl alcohol, a further 10 c.c. of alcohol are added, the mixture is heated at 110° for 10 min., and, after settling, the clear liquor is decanted through a small filter. The filtrate is evaporated to dryness, the residue moistened with a few drops of water, about five times its weight of ammonium sulphate added, the mixture heated gently at first, then to bright redness, and the residue weighed as strontium sulphate. The barium bromide on the filter is dissolved in 25 c.c. of hot water, the solution evaporated to a syrup, treated with 2-3 c.c. of hydrobromic acid, and heated to obtain the dry bromide as before. The alcohol treatment is repeated and the weight of strontium sulphate added to that already obtained. The barium bromide residue is repeatedly treated as before until the weight of strontium sulphate obtained in an extraction is less than 5 mg. The barium salt is then dried at 180° and weighed. From the total weight of strontium sulphate obtained 0.5 mg. is

subtracted for every extraction made and added to the weight of barium bromide. A. R. POWELL.

Detection and determination of minute amounts of magnesium. F. L. HAHN (Mikrochem., 1929, Pregl Fest., 127—139).—Small amounts of magnesium may be detected and determined colorimetrically by means of an alkaline solution of 1:2:5:8-tetrahydroxyanthraquinone, the colour changing from reddish-violet to cornflower-blue; 0.001 mg. of magnesium in 1 c.c. of solution can be detected by this reaction. In applying the method to the determination of magnesium in aluminium alloys the greater part of the aluminium must be removed by saturating the solution with hydrogen chloride at 0° after addition of ether before the magnesium is determined. Amounts of magnesium of the order of 0.000001 mg. may be detected by carrying out the reaction in capillary tubes, special precautions being necessary to ensure accuracy; details of the procedure are described.

H. F. HARWOOD.

Micro-determination of magnesium with 8-hydroxyquinoline, and its separation from calcium. R. STREBINGER and W. REIF (Mikro-chem., 1929, Pregl Fest., 319-322).—The ammoniacal solution of the magnesium salt containing ammonium chloride is heated at 70°, and an excess of a 1% alcoholic solution of the reagent added. After 20 min. the liquid is filtered through a Pregl filter tube, the precipitate washed with hot water containing ammonia, then with alcohol, dried at 105° for 20 min., and weighed as $Mg(C_9H_6ON)_2, 2H_2O$. In the separation from calcium, the latter is first precipitated as oxalate in acetic acid solution, the filtrate neutralised with ammonia, ammonium chloride added, and the magnesium precipitated as above. When only minute amounts (0.04 mg.) of calcium are present with 5 mg. of magnesium, no precipitation of calcium oxalate takes place, even after the solution has been H. F. HARWOOD. kept for several days.

Identification of lead in any form by means of three successive microcrystalline tests. G. DENIGÈS (Bull. Soc. chim., 1929, [iv], 45, 678—680; cf. A., 1919, ii, 523).—The lead compound is converted successively by means of potassium bromide and potassium iodide solutions into lead bromide, potassium lead iodide, and lead iodide. The crystals of these three substances can be identified microscopically. The method is applicable to all soluble and insoluble compounds of lead, except lead sulphate, which requires a modified procedure.

O. J. WALKER.

Determination of lead peroxide. A. V. PAM-FILOV and others.—See B., 1929, 850.

Separation of lead and bismuth. H. BLUMEN-THAL (Z. anal. Chem., 1929, 78, 206—213).—The nitrate solution of the two metals is treated with an excess of 10% sodium carbonate solution until a heavy precipitate of lead carbonate is obtained, nitric acid is added drop by drop until the solution is just acid to methyl-orange, and, after boiling to expel carbon dioxide, an emulsion of freshly-precipitated mercuric oxide is stirred in until a slight excess is present whereby all the bismuth is precipitated as

basic nitrate. The solution is diluted with 100 c.c. of cold water, set aside over-night, and filtered. The precipitate is washed with a cold 0.1% solution of potassium nitrate and dissolved in dilute nitric acid; the bismuth is precipitated as phosphate for weighing. For the determination of bismuth in impure lead the metal is dissolved in nitric acid, the solution rendered slightly alkaline with sodium carbonate, just reacidified with nitric acid, treated with 6 c.c. of 5% manganous nitrate solution, and boiled with 4 c.c. of N-permanganate. The precipitate of manganese dioxide contains all the antimony, arsenic, tin, and bismuth; it is dissolved in hydrochloric acid, the solution treated with hydrogen sulphide, the bismuth separated by digestion of the sulphides with sodium sulphide, dissolved in nitric acid, and separated from the remaining lead by the mercuric oxide method.

A. R. POWELL.

Detection of thallium. A. J. STEENHAUER (Mikrochem., 1929, Pregl Fest., 315—318).—Photomicrographs are given of the crystalline precipitates given by solutions of thallium salts with sodium thiosulphate, ammonium molybdate, pieric acid, ammonium thiocyanate, ammonium dichromate, mercuric thiocyanate, and tartaric acid. Of the above, the last four are the most suitable for the detection of thallium. H. F. HARWOOD.

Rapid microchemical determination of copper. G. SPACU and J. DICK (Z. anal. Chem., 1929, 78, 241–244).—An adaptation of the authors' previous method (cf. A., 1927, 746) to the determination of minute amounts of copper. The copper is precipitated as the compound $[Cu(C_5H_5N)_2](SCN)_2$, and weighed after drying for 10 min. in a vacuum at the ordinary temperature. H. F. HARWOOD.

Electrometric determination of copper. I. Müller and Rudolph's method. II. Application of Volhard's method to electrometric analysis. M. E. PRING and J. F. SPENCER (Analyst, 1929, 54, 509—516, 576—581).—I. Müller and Rudolph's method (A., 1923, ii, 880) of reducing the solution of cupric salt by sodium hydrogen sulphite, heating at 70°, and titrating with potassium thiocyanate, using a copper electrode, is very sensitive to changes of temperature, concentration of hydrogen sulphite, and time taken for the operation; since no constant error was found no correcting factor could be used. The possibility of obtaining concordant results is regarded as remote. Sulphur dioxide was not satisfactory as a reducing agent, as reduction was incomplete even on boiling.

II. The copper solution (not more dilute than 0.04N) is saturated with sulphur dioxide, and 0.1N-potassium thiocyanate solution is added, whereby cuprous thiocyanate is precipitated, and the solution boiled to expel all sulphur dioxide. Water is added, and when cold a silver plate and a 0.1N-calomel electrode are inserted and the excess of thiocyanate is titrated with 0.1N-silver nitrate solution. To obtain a sharp end-point the rate of change of E.M.F. with changing amount of silver nitrate is plotted against the volume of silver nitrate added, and the titration is finished slowly. The presence of iron and zinc does not interfere with the accuracy of the titration,

and the experimental and calculated values agreed very closely. D. G. HEWER.

Application of the thiocyanate method for the precipitation of copper in the confirmatory tests for cadmium and antimony [in Noyes' scheme of qualitative analysis]. A. F. DAGGETT (J. Amer. Chem. Soc., 1929, 51, 2758—2759).—The part of the ammoniacal solution remaining after confirming copper is slightly acidified and 5 c.c. of N-potassium thiocyanate solution are added; the solution is boiled, then 0.5 g. of sodium sulphite is added, and the cuprous thiocyanate precipitate, coagulated by further boiling, is filtered off and the filtrate examined for cadmium by means of hydrogen sulphide. A similar procedure may be used to prevent copper interfering with the test for antimony. S. K. TWEEDY.

Rapid microchemical determination of mercury. G. SPACU and G. SUCIU (Z. anal. Chem., 1929, 78, 244—247).—The method previously described (this vol., 901) for the precipitation and weighing of mercury in the form of its compound $(HgI_4)(Cu en_2)$, has been applied to the determination of minute amounts of the metal. It offers the advantage that the determination can be carried out directly in solutions containing aqua regia after neutralisation with ammonia and ethylenediamine.

H. F. HARWOOD.

Electrometric titration of iodomercurates. L. MARICQ (Bull. Soc. chim. Belg., 1929, 38, 259– 264).—The iodomercuric ion can be accurately determined by electrometric titration with mercuric chloride, in the presence or absence of iodides, the reaction being $HgI_4''+Hg^{++} \rightarrow 2HgI_2$. C. W. GIBBY.

Use of Nessler's reaction for the rapid characterisation of mercury oxycyanide and its detection in mercuric cyanide. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1928, 66, 209–211; Chem. Zentr., 1929, i, 2088).—A 1% solution of the substance (2 c.c.) is treated with 5% potassium iodide solution (5 c.c.), ammonia solution (1 c.c.), and sodium hydroxide solution (1 c.c.), when a brown precipitate is obtained owing to the intermediate formation of potassium mercuri-iodide : $HgO+4KI+H_2O=K_2HgI_4+2KOH$. A. A. ELDRIDGE.

Use of potassium iodide for the rapid detection of mercury [ions] in mercuric cyanide. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1928, 66, 206—209; Chem. Zentr., 1929, i, 2087).—In presence of sulphuric acid, potassium iodide is a satisfactory reagent for concentrated solutions of mercuric cyanide; for dilute solutions antipyrine is added to produce a precipitate or an opalescence in the potassium mercuri-iodide solution. A. A. ELDRIDGE.

Gravimetric analysis with Kuhlmann's microbalance. [Determination of aluminium.] A. BENEDETTI-PICHLER (Mikrochem., 1929, Pregl Fest., 6—13).—Aluminium may be determined by precipitation with 8-hydroxyquinoline in the presence of ammonium acetate. The precipitate is washed with cold water and dried in a current of air for 5 min. at 140°. A special form of drying tube for use with this and other micro-precipitates is described.

H. F. HARWOOD.

Use of 8-hydroxyquinoline in separations of aluminium. G. E. F. LUNDELL and H. B. KNOWLES (Bur. Stand. J. Res., 1929, 3, 01-96).-Aluminium alone is precipitated by 8-hydroxyquinoline from ammoniacal solutions containing in addition phosphorus, arsenic, fluorine, and boron; from ammoniacal solutions (to which hydrogen peroxide has been added) containing in addition vanadium, tantalum, niobium, titanium, and molybdenum; and from ammonium carbonate solutions containing in addition uranium. For separation from beryllium, Kolthoff and Sandell (A., 1928, 981) precipitate in acctic acid solution with 8-hydroxyquinoline. The precipitate in each case has the formula $Al(C_9H_6ON)_3$, and may be weighed as such after drying at 110° (Berg, A., 1927, 436, 639, 674, 745, 847, 848; 1928, 39; this vol., 286), but it is preferable to destroy the organic matter with nitric and sulphuric acids and precipitate the aluminium C. HOLLINS. with ammonia as usual.

Quantitative analysis of gallium. III. A. BRUKL (Monatsh., 1929, 52, 253-259; cf. this vol., 670).-Methods, depending on the precipitation of gallium by "cupferron" after the removal of interfering metals, for the quantitative separation of gallium from titanium, zirconium, thorium, vanadium, molybdonum, tungsten, and the rare-carth metals J. A. V. BUTLER. are described.

Microchemical permanganate determinations. J. MIKA (Z. anal. Chem., 1929, 78, 268-297).-In microchemical titrations with permanganate a correction for the excess of solution used is always necessary. This may be obtained by titrating in all cases to a definite tint, a solution of cobalt ammonium sulphate being utilised as a comparison liquid, and subtracting the amount of a similar titration carried out on pure water. The 0.01N-permanganate used can be directly standardised microchemically against sodium oxalate; the factor so obtained is about 0.3%less than that given by the macrochemical standardisation with either sodium oxalate or sodium thiosulphate, hence special care must be taken that all the materials used are free from reducing substances. If the permanganate be standardised against 0.01N-thiosulphate the results agree, whether obtained in the microchemical or macrochemical way. The microchemical determination of manganeso by the Fischer-Volhard method requires the titration to be carried out in the presence of zinc acetate and acetic acid, preferably in a solution of p_{π} 5.0. The excess of permanganate used must be determined by centrifuging the solution after titration, and withdrawing a portion of the clear liquid, which is then titrated with 0.01N-thiosulphate after addition of potassium iodide. Details are given of a form of micro-weight-burette which is also suitable for the titration of hot solutions, and of a device for effecting the removal of a known amount of the clear solution after titration.

H. F. HARWOOD.

Determination of manganese and iron by successive titrations with permanganate. J. TELETOV and (MME.) N. ANDRONIKOV (Bull. Soc. chim., 1929, [iv], 45, 674-677).-Ferric hydroxide and hydrated manganese dioxide are precipitated from the solution containing ferrous and manganous

salts by means of sodium hydroxide and hydrogen peroxide. The precipitate is collected and well washed, and the manganese is determined by treatment with oxalic acid in presence of sulphuric acid and titration of the excess oxalic acid with permanganate solution in the usual way. The iron is then reduced to the ferrous state by filtering the solution slowly through a layer of electrolytic cadmium, and is titrated in turn with permanganate solution. O. J. WALKER.

Iodometric determination of [ferric] iron. E. H. SWIFT (J. Amer. Chem. Soc., 1929, 51, 2682— 2689).—The conditions essential for the accurate (0.2%) determination of ferric iron by addition of potassium iodide and acid and titration with thio. sulphate are elucidated experimentally. Sulphuric acid is less suitable than hydrochloric acid. The accuracy of the method is only apparent, however, since the reaction is incomplete and this is com-S. K. TWEEDY. pensated by an oxygen error.

Potentiometric determination of iron with permanganate solution. T. HECZKO (Z. anal. Chem., 1929, 78, 247-249).-A suitable comparison electrode (which permits of the end-point being marked by a reversal of the direction of the current) for use in the potentiometric titration of ferrous salts by permanganate consists of a 0.5% solution of vanadium pentoxide in dilute phosphoric acid containing a few drops of 0.1N-ferrous sulphate. The solution is employed in an Emich filter tube in the manner previously described (A., 1928, 1345). H. F. HARWOOD.

Two new reversible oxidimetric indicators, and their use with permanganate. J. KNOP (Chem. Listy, 1929, 23, 366-375).-See this vol., 670.

Volumetric determination of iron, using potassium permanganate in the presence of the oxidimetric indicators erioglaucin A and eriogreen B. J. KNOP and (MILE.) O. KUBELKOVÁ (Chem. Listy, 1929, 23, 399–402).—See this vol., 670.

Oxamide, a reagent for nickel. J. LISKA (Chem. Listy, 1929, 23, 402-403).-The presence of 0.1 mg. of nickel in 1 c.c. of solution can be demonstrated by the addition of crystalline oxamide, after which the solution is heated to boiling and 20% sodium hydroxide solution added, when an intense yellow coloration is obtained. This reaction, which is less delicate than that of Tschugaev, is not adapted to the determination of nickel. R. TRUSZKOWSKI.

Identification of vanadium and cerium, using hydrogen peroxide. J. LUKAS and A. JILEK (Chem. Listy, 1929, 23, 417-419).-30% Hydrogen peroxide solution produces a brown coloration on addition to solutions of vanadium in dilute sulphuric acid. A yellowish-green coloration, discharged by boric acid, is given under these conditions by solutions containing molybdenum. Neutral solutions of cerium salts give a yellow or orange coloration in the presence of 30% hydrogen peroxide solution and of quinine hydrochloride. R. TRUSZKOWSKI.

Quinhydrone electrode. G. E. CULLEN (J. Biol. Chem., 1929, 83, 535-538).-A modification of the electrode of Cullen and Biilmann (A., 1925, i, 1201) which eliminates errors due to loss of carbon dioxide is described. C. R. HARINGTON.

Apparatus for continuous purification of mercury. E. BOTOLFSEN (Bull. Soc. chim., 1929, [iv], 45, 782—784).—The mercury is drawn by a water pump up a long tube standing in a reservoir; an inlet tube drawn to a fine point admits air at the bottom of this tube so as to break up the column of mercury into small portions. The tube is bent twice at right angles, thus delivering the mercury into a funnel with narrow end through which it passes in a finely-divided state into a column of purifying liquid, at the bottom of which it collects and is thence passed back into the reservoir. A diagram and dimensions are given. C. A. SILBEBRAD.

Graduated burette with calibrated globe attached for accurate volumetry. A. TIAN (Bull. Soc. chim., 1929, [iv], 45, 778—782).—For very accurate volumetric work, e.g., when the result depends on the difference between two much larger measurements, a burette with very open scale (20 cm. for 10 c.c.) is surmounted by a calibrated globe containing 40 c.c. It is shown that for maximum accuracy (i) 5 min. should elapse before reading; (ii) the precision of reading is considerably increased by such a scale; but (iii) correction for dilatation must be made if the temperature of reading differs from that of calibration by more than 0.5°. *

C. A. SILBERRAD.

Improved stopcock for gas analysis burettes. W. E. KUENTZEL (J. Amer. Chem. Soc., 1929, 51, 2759—2760).—The improved four-way cock has provision for connecting the absorption pipette to the under-side of the barrel. S. K. TWEEDY.

Laboratory ozoniser. A. L. HENNE (J. Amer. Chem. Soc., 1929, 51, 2676—2677).—An inexpensive, efficient ozoniser which is a simplified form of that described by Smith (A., 1925, ii, 896) is described. S. K. TWEEDY.

Measurement of vacuum during distillation under reduced pressure. P. WALTHER (Pharm. Ztg., 1929, 74, 1289—1290).—Attention is directed to the error involved in the preparation of a manometer by filling with mercury a tube previously evacuated by means of a water-pump, and a number of manometers suitable for use in vacuum distillations are described. H. F. HARWOOD.

Apparatus for the distillation of sensitive solutions in a vacuum. H. KRAUT, K. LOBINGER, and F. POLLITZER (Ber., 1929, 62, [B], 1939—1941).— An apparatus is figured and described in which local superheating of the solution is avoided by causing a circulation of the liquid by the bubbles of vapour. Its application to the concentration of enzyme solutions is discussed. H. WREN.

which contains a few grams of metallic calcium (or magnesium when carbon dioxide is used), is heated at about 800° . The gases are completely absorbed and a pressure of 0.05 mm. may be obtained.

S. COFFEY. Apparatus for distillation at very low pressures. H. I. WATERMAN and E. B. ELSBACH (Chem. Weekblad, 1929, 26, 469).—An apparatus in which 1-bromonaphthalene may be distilled at the ordinary temperature, and dibromoisosafrole may be distilled without decomposition, is described. S. I. LEVY.

Still heads and laboratory rectification columns. V. LONGINOV and A. PRIANISCHNIKOV (Trans. Inst. Pure Chem. Reagents, Moscow, 1929, No. 7, 54 pp.).—A study of the effect of height, diameter, isolation, rate of distillation, reflux ratio, and the nature of the filling material on the efficiency of the Hempel column. CHEMICAL ABSTRACTS.

Centrifuge tube with detachable bottom. A. FRIEDRICH (Mikrochem., 1929, Pregl. Fest., 103-105).—A new form of tube, the lower portion of which consists of a small glass cap with ground joint, is described; the cap can be removed after centrifuging together with the precipitate it contains.

H. F. HABWOOD.

Apparatus for determination of m. p. under the microscope. G. KLEIN (Mikrochem., 1929, Pregl Fest., 192-203).—An improved form of apparatus for the determination of the m. p. of substances under the microscope has been devised. The apparatus is heated electrically, and is available for temperatures between 50° and 350°. The m. p. temperature is read directly on a thermometer, no correction being necessary. H. F. HARWOOD.

Pump for circulating gas of various kinds through a closed system. M. Dolor and K. GIESELER (Chem. Apparatur, 1928, 15, 229-231, 268-269; Chem. Zentr., 1929, i, 1722).

Removal of dissolved gases from liquids by vacuum sublimation. J. H. HIBBEN (Bur. Stand. J. Res., 1929, 3, 97-104).-The liquid is introduced by means of a pipette through a side-tube (which is then sealed) into the space between the walls of a Dewar vessel, the space being connected through a liquid-air trap to a McLeod gauge and mercuryvapour pump, drying tubes, and oil-pump. The space is then evacuated and the liquid frozen. The inner walls are then cooled by solid carbon dioxide and ether and the frozen liquid sublimes on to the cooled under-surface, the released gases being removed by the evacuating pump. At the end of the operation the inner wall is warmed and the melted sublimate falls back to its original position at the bottom of the space between the walls, the last traces being transferred by reversing the sublimation. During the operation the frozen liquid may be warmed to accelerate sublimation; for water a jacket at 50-80° may be used without melting the ice, so rapid is the sublimation. The temperature gradient, the temperature of the cooling surface, and the pressure in the space must be adjusted so that (a) the vapour pressure of the sublimate at the temperature of the inner wall is negligible, (b) there is direct condensation to solid without liquid phase, (c) the vapour pressure of each gas in the sublimate must be greater than its partial pressure in the evacuated space. The application of the method to water containing ammonia, hydrogen chloride, carbon dioxide, or oxygen is described. For hydrogen chloride condition (c) is not fulfilled; part of the sublimed ice melts and dissolves hydrogen chloride, and there is no removal of the dissolved gas. Oxygen and carbon dioxide are completely removed by one sublimation; for ammonia several repetitions are required. C. HOLLINS.

Apparatus for the analysis of small samples of gas. H. R. AMBLER (Analyst, 1929, 54, 517— 522).—The apparatus, which can conveniently deal with samples of gas from 1 to 15 c.c., consists of two three-way taps connected with a glass, waterjacketed measuring bulb (C), absorption bulb (B) fitted with platinum electrodes and spark gap, or a platinum spiral, or both. The sample is introduced into B, then transferred to C for measuring, by observing the pressure at which the constant volume of bulb (or bulbs) is filled on a mercury manometer attached to a scale, C being scaled against any leak by running mercury to a marked point. After introducing the absorbent solution into B, the gas is returned, and after absorption again passed to C and measured.

D. G. HEWER.

Cæsium-magnesium photo-cell. V. ZWORYKIN and E. D. WILSON (J. Opt. Soc. Amer., 1929, 19, 81—89).—Cæsium is retained on the surface of freshly-distilled magnesium without any change in photo-electric properties. Colour-sensitivity curves are given for vacuum cells, and for cells containing argon, helium, and ncon. The behaviour of the cells is practically independent of temperature.

C. W. GIBBY. Photo-electric smoke recorder. E. H. VEDDER (Elec. J., 1929, 26, 199-201).

CHEMICAL ABSTRACTS.

Use of photo-electric cells for polarimetric measurements. G. TODESCO (Nuovo Cim., 1928, 5, 376-390; Chem. Zentr., 1929, i, 2084).

Thermionic valve potentiometer for the determination of $p_{\rm II}$ with the glass electrode. W. C. STADIE (J. Biol. Chem., 1929, 83, 477-492).-A null method for the measurement of the potential of glass electrodes by a valve potentiometer is described. The grid, filament, and plate circuits of two valves are connected in parallel, the plate circuits being arranged as a Wheatstone bridge which may be balanced by variable resistances permitting a highsensitivity galvanometer to be inserted in the plate circuit. The potential of a glass electrode in the grid circuit of one valve may then be measured to within 0.001 volt. The apparatus is very steady in action and is free from electrostatic disturbances. Its sensitivity in measuring potentials through resistances of from 20 to 600 megohms is 1-4 mm. of deflexion per millivolt. F. G. TRYHORN.

Electrically conductive antimony mirrors on glass. S. MILLER (J. Opt. Soc. Amer., 1929, 19, 101—102).—Electrically conducting mirrors of antimony may be prepared by the thermal decomposition of stibine. They are stable in air, and do not sublime in a vacuum at 300°, but do so below the softening point of pyrex glass. C. W. GIBBY.

Pressure-controlled McLeod gauge. N. UNDERWOOD (J. Opt. Soc. Amer., 1929, 19, 78).— The mercury in a McLeod gauge is caused to rise by pressure applied to it in the reservoir by means of an atomiser bulb. Releasing the pressure brings the mercury back to its normal position.

C. W. GIBBY. Voltage regulator for gas discharge X-ray tubes. F. E. HAWORTH (J. Opt. Soc. Amer., 1929, 19, 79-80).—An improvement on the regulator described by Bozorth (A., 1927, 502).

C. W. GIBBY. Universal stand for electrolysis with rotating electrode. A. I. GUNDER (Ukraine Chem. J., 1929, 4, 293-295). A. FREIMAN.

Scopometer. W. G. EXTON (J. Amer. Med. Assoc., 1929, 92, 708—712).—A simple apparatus for the measurement of turbidity and colour is described. CHEMICAL ABSTRACTS.

Sources of error and calculation in the measurement of surface tension by the ring method and micro-balance. G. ORBÁN and L. REINER (Biochem. Z., 1929, **211**, 487–490).—In the determination of surface tension by the ring method, the weight required to detach the ring depends, not only on the surface tension and radius of the ring, but also on the ratio of radius (r) to square root of specific cohesion (a). This cannot be neglected when r is small. When r/a>3, F(r/a) is unity.

J. H. BIRKINSHAW.

Micro-polarimeter tubes with matt inner surface. H. NAUMANN (Biochem. Z., 1929, 211, 239—243).—By the action of hydrofluoric acid a matt inner surface is produced in black glass micropolarimeter tubes. Errors in polarimetric readings due to reflexion from the inner surface of the tubes are thus avoided. The tubes can be cleaned without difficulty. W. MCCARTNEY.

Measurement of vapour pressures at high temperatures by a transference method. K. JELLINEK and G. A. ROSNER (Z. physikal. Chem., 1929, 143, 51-54).—A convenient apparatus is described for measuring the vapour pressure of solids at high temperatures by determination of the quantity of vapour carried over when a current of inert gas is passed over the material, which is contained in an electrically heated porcelain tube.

H. F. GILLBE.

Nomography. O. LIESCHE (Chem. Fabrik, 1929, 437—438).—A diagram is given by which analytical results may be read, the weight of material taken, the final weight, the appropriate factor, and the percentage determined being each read on a separate vertical axis. S. I. LEVY.

Geochemistry.

Atmospheric ozone. G. M. B. DOBSON (J. Phys. Radium, 1929, [vi], 10, 241-246).-Observations made during 1920-1928 on the distribution of ozone in the atmosphere in different parts of the world show certain regularities. At a height of 50 km. there is a layer in which the concentration of ozone is equivalent to 2 mm. thickness at atmospheric pressure. The height of this layer is nearly constant, but the concentration varies. It is greater to the west of a cyclone and less to the east, the distribution being reversed for an anticyclone. Whilst the concentration of ozone at 50 km. is related to the meteorological conditions, that near the earth's surface appears to be unrelated. There is a marked variation of concentration in the 50 km. layer with latitude, the value being least at the equator and greatest at the poles. The polar concentration is greatest in the spring and least in the autumn. Atmospheric ozone cannot therefore be formed by solar radiation, but probably results from magnetic disturbances like the aurora. C. J. SMITHELLS.

Height of the ozone in the upper atmosphere. II. F. W. P. Görz and G. M. B. DOBSON (Proc. Roy. Soc., 1929, A, 125, 292—294).—Measurements made previously (A., 1928, 1209) have been corrected, and the average thickness of the ozone layer over Arosa is now found to be about 50 km., in good agreement with the values obtained by other investigators. There are indications that the height is greater in spring than at other times of the year and is also greater when there is much ozone present than when there is little. L. L. BIRCUMSHAW.

Origin of helium-rich natural gas. R. C. WELLS (J. Wash. Acad. Sci., 1929, **19**, 321-327).-Measurements have been made of the rate of separation of hydrogen from carbon dioxide by fractional diffusion through a plug of ball clay and it is shown to be possible to obtain a product containing 90% H₂ from one containing only 2.6% H₂ in seven stages. The bearing of these results on the accumulation of helium in natural gas deposits is discussed briefly and a programme of further work to establish the value of this theory is outlined. A. R. POWELL.

Hydro-chemistry of the upper Kama and its tributaries. A. TRIFONOV (Bull. inst. res. biol. univ. Perm, 1927, 5, 147-156).—A study of the water of the R. Kama between Perm and the mouth of the Wischera and at the mouths of seven tributaries supports the theory of universal chemical heterogeneity in the cross-section of a flowing stream.

CHEMICAL ABSTRACTS.

Thermal water of the military station at Acqui. 8. CORTASSA (Annali Chim. Appl., 1929, 19, 297-306).—The composition of the slightly radioactive water, which contains sulphide, sodium chloride, lithium, bromide, iodide, and borate, is recorded. T. H. POPE.

Precipitation of limestone by submarine vents, fumaroles, and lava flows. J. E. A. KANIA (Amer. J. Sci., 1929, [v], 18, 347-359).—A possible explanation is given for the occurrence of nonfossiliferous limestone beds intercalated between submarine lava flows. Limestone is precipitated on account of the removal of carbon dioxide from seawater by the heating and agitating action of submarine lava flows. The occurrence of limestone beds is often associated with times of great volcanic activity. C. W. GIBBY.

Application of X-rays in the classification of fibrous silicate minerals commonly termed asbestos. H. V. ANDERSON and G. L. CLARK (Ind. Eng. Chem., 1929, 21, 924—933).—The effects of acid and heat treatment on thirty samples of "asbestos" are described. X-Ray diffraction patterns are given and discussed: they constitute a rigorous method of specification. C. W. GIBBY.

Alkaline character of lavas from volcanoes at Antiparos (Cyclades). C. A. KATENAS (Compt. rend., 1929, 189, 489–491).—Analyses of lavas from Antiparos are given. With one exception they all contain an excess of potassium over sodium.

C. W. GIBBY. Constitution of mica. V. Pegmatitic muscovite. VI. Non-pegmatitic muscovite. J. JAKOB (Z. Krist., 1929, 69, 403–410, 511–515; Chem. Zentr., 1929, i, 2295).—Analyses are recorded and considered. A. A. ELDRIDGE.

Chemical relationships of rock-forming pyroxenes and amphiboles to one another and to the matrix. F. ANGEL (Z. Krist., 1929, 69, 455-475; Chem. Zentr., 1929, i, 2296).

Fahl ore. V. V. NIKITIN (Z. Krist., 1929, 69, 482-502; Chem. Zentr., 1929, i, 2296).—The formula $(Cu_2^{I}, Ag_2, Zn, Fc, Hg)_3(As, Sb, Bi)_2S_6$ is suggested. A. A. ELDRIDGE.

Ore-lead and rock-lead and the origin of certain ore deposits. A. HOLMES (Nature, 1929, 124, 477-478).-Although the average lead produced and accumulated in rocks during the earth's geological history cannot have an at. wt. higher than 206.9, the at. wt. of ore-lead never differs significantly from 207.2. Hence no appreciable part of ordinary lead can have been derived from the radioactive elements during their terrestrial history, and the hypothesis that within the earth the proportions of uranium and thorium diminish and become negligible is supported. Rock-lead, being a mixture in approximately equal parts of ore-lead and lead generated within the rocks, should have at. wt. 207.05, a mean value obtained by Piutti and Migliacci (A., 1924, ii, 181, 859) for lead from the Vesuvian sublimate cotunnite.

A. A. ELDRIDGE.

Meteoric stone of Lake Brown, Western Australia. G. T. PRIOR (Min. Mag., 1929, 22, 155-158).—This stone, found in 1919 and weighing 21½ lb., is an intermediate hypersthene-chondrite of the Baroti type. Separate analyses of the magnetic portion and of the unattracted portion (also of the part insoluble in hydrochloric acid) give the bulk composition: Fe 6·10, Ni 1·08, Co 0·06, Fe 3·98, S 2·28, SiO₂ 39·43, TiO₂ 0·35, Al₂O₃ 2·00, Cr₂O₃ 0·18, Fe₂O₃ 3.65, FeO 11.99, MnO 0.25, NiO 0.32, MgO 25.15, CaO 1.88, Na₂O 0.81, K₂O 0.10, H₂O(+110°) 0.50, H₂O(-110°) 0.08, P₂O₅ 0.31, total 100.50. This corresponds approximately with the mineral composition : nickel-iron 7, troilite 6, olivine 36, pyroxene 38, felspar 8, ferric oxide, water, etc. 5%. The ratio Fe : Ni in the nickel-iron is about 5.5 and in conformity with this the ratio MgO : FeO in the ferromagnesian silicates is about 3.5. The composition is very close to that of the Warbreccan (Queensland) stone (A., 1916, ii, 633). L. J. SPENOEE.

Analysis of allanite from Hagata-Mura, Iyo Province. Y. MINAMI (Japan. J. Chem., 1929, 4, 1-5).—Analyses of allanite lead to the formula $4R^{II}O,3R^{II}{}_{2}O_{3},6SiO_{2},H_{2}O$, where R^{II} may be Ca, Mn, Fo, and R^{III} Al, Fe, Ce, Y. The arc spectrum and the absorption spectrum of a solution of the rare earths extracted from allanite have been measured. C. W. GIBBY.

Geological age of ishikawaite from Iwaki Province. Y. UZUMASA (Japan, J. Chem., 1929, 4, 11-14).—Ishikawaite from Iwaki contains 0.069%Pb and 19.289% U, whence its age is calculated to be about 3×10^7 years (cf. Sasaki, A., 1927, 225). C. W. GIBBY.

Manganese diaspore and manganophyll from Postmasburg, Griqualand West. K. CHUDOBA (Zentr. Min. Geol., 1929, A, 11—18; Chem. Zentr., 1929, i, 1914).—Manganese diaspore, d^{20} 3·328, n_a 1·7023, n_β 1·7219, n_γ 1·7502, having the composition SiO₂ 0·11, Al₂O₃ 78·58, Fc₂O₃ 1·96, Mn₂O₃ 4·32, Mo (spectr.), CaO trace, H₂O 14·65%, is described. A. A. ELDRIDGE.

X-Ray study of the domeykite group. L. S. RAMSDELL (Amer. Min., 1929, 14, 188–196).—The copper-arsenic system contains only Cu_3As and copper-arsenic solid solutions. Whitneyite, Cu_9As , is a mixture of algodonite and copper-arsenic solid solution; algodonite, Cu_8As , a definite compound, breaks down at the m. p. into Cu_3As (domeykite) and the solid solution. Near the m. p., domeykite is converted into a form corresponding with the artificial compound. CHEMICAL ABSTRACTS. Mooreite, a new mineral, and fluoborite from Sterling Hill, N.J. L. H. BAUER and H. BERMAN (Amer. Min., 1929, 14, 165–172).—Mooreite, $7R(OH)_2$,RSO₄,4H₂O, where R=Mg : Mn : Zn (4:1:2), monoclinic, has d 2.470, H 3, α 1.533, β 1.545, γ 1.547. δ -Mooreite, $6R(OH)_2$,RSO₄,4H₂O, where R=Mg : Mn : Zn (5:3:4), granular, has d 2.665, H 3, α 1.570, β 1.584, γ 1.585. Fluoborite, $6MgO,B_2O_3,3(F_2,H_2O)$, with H₂O: F=2:3, hexagonal, has d 2.88. CHEMICAL ABSTRACTS.

Loseyite, a new Franklin mineral. L. H. BAUER and H. BERMAN (Amer. Min., 1929, 14, 150–153).—Loseyite, $2\text{RCO}_3,5\text{R}(\text{OH})_2$, where R= Mn: Zn: Mg (5:4:1), monoclinic, has d 3.27, H3, α 1.637, β 1.648, γ 1.676. CHEMICAL ABSTRACTS.

Hydrophilite. C. B. SLAWSON (Amer. Min., 1929, 14, 160–161).—Artificial hydrophilite is probably orthorhombic with pseudo-tetragonal development; $\alpha 1.600, \beta 1.605, \gamma 1.613 (\pm 0.003).$

CHEMICAL ABSTRACTS.

Radioactivity of the coals and anthracites of the Donetz coal basin. E. S. BURKSER, M. J. SCHAPIRO, and K. G. BRONSTEIN (Ukraine Chem. J. [Tech.], 1929, 4, 95-100).-The radioactivity of samples of different Donetz coals and anthracites was measured by determining their ionising activity by means of an Engler-Sieveking apparatus, whilst their α -ray activity was measured by means of an α -ray electroscope. The emanation formation was measured under reduced pressure. The samples were then burnt and the ash was submitted to the same tests; the ash was next fused with sodium or potassium hydroxide, treated with hydrochloric acid, and the acid and alkali solutions were tested for emanation. The potassium content of the ash was determined by Berzelius' method. Anthracites were also examined for their β - and γ -ray activity. Only the upper layers covering the coals and the middle coal layers have a high radioactivity, much higher than that observed by Joly for granites $(2.7 \times 10^{-12} \text{ g. Ra per g.})$. Other coals and anthracites have a radium content characteristic of limestones (according to Joly and Fletcher 0.5×10^{-12} g. per g.). Å A. FREIMAN.

Organic Chemistry.

Chemical effects of semi-corona discharge in gaseous hydrocarbons. S. C. LIND and G. GLOCKLER (J. Amer. Chem. Soc., 1929, 51, 2811-2822).-Methane, ethane, propane, butane, and ethylene condense to liquid and solid hydrocarbons in the semi-corona discharge (central aluminium rod in pyrex glass cylinder) (cf. A., 1928, 988). With the saturated hydrocarbons condensation is brought about by elimination of hydrogen and some methane; the reactions have the same general character as those produced in the same gases by α -radiation. The liquid products from different hydrocarbons (or from the same hydrocarbon in different tubes) have similar physical properties when obtained at the same trap temperature. The physical properties of these products can be varied by changing the temperatures of the discharge region and traps. H. BURTON,

Action of oxygen atoms on hydrocarbons. P. HARTECK and U. KOPSCH (Naturwiss., 1929, **17**, 727). —With the exception of methane, which is inert, hydrocarbons react with oxygen atoms, a bluish-violet flame being noticed in the zone of the reaction. The colour is ascribed to CH bands, and the OH bands are also found to be emitted strongly, so that the formation in the flame of the hydroxyl radical is proved. The relative intensities of the CH and OH bands, using benzene and ethylene, exhibit marked differences corresponding with different carbon contents. Carbonic acid is found among the products of the reaction. R. A. MORTON.

regramme of further work to establish

Action of high-speed cathode rays on acetylene. J. C. McLENNAN, M. W. PERRIN, and H. J. C. IRETON.—See this vol., 1249.

Use of substituted epidibromohydrins for the preparation of acetylenic hydrocarbons. Ay-Hexene and Ay-hexinene. R. LESPIEAU and WIEMANN (Bull. Soc. chim., 1929, [iv], 45, 627-635). -With bromine at 0° in absence of solvent a-bromo-Δ^β-pentene (Bouis, A., 1928, 1112) yields, in addition to αβγ-tribromopentane, m. p. 2.5-3°, d²¹ 2.0682, n_p 1.5583, a little $\alpha\beta\gamma\delta$ -tetrabromopentane, m. p. 114°, b. p. 152°/115 mm., and ay-dibromopentane, b. p. 73-75°/14 mm., d²⁵ 1.681, n_p 1.509, also obtained by addition of hydrogen bromide to α -bromo- Δ^{β} -pentene, a reaction which, together with its b. p., indicates its ay-structure. With zinc dust and alcohol ay-dibromopentane yields a hydrocarbon, b. p. 35.8-36°, d" 0.666, np 1.377, either ethyltrimethylene or dimethyltrimethylene. Under atmospheric pressure $\alpha\beta\gamma$ -tribromopentane yields with potassium two fractions, b. p. 72.5–73.5°/13 mm., d^{10} 1.745, $n_{\rm D}$ 1.53079, and b. p. 75-76°/13 mm., d 1.7475, np 1.5329, of Bouis' epidibromohydrin, which from a comparison of its b. p. with that of $\alpha\beta$ -dibromopentane, b. p. 68°/14 mm., and the formation of the bromides CH, Br. CH: CHR by the action of phosphorus tribromide on the alcohols CH2:CH-CHR.OH, is regarded as $\alpha\beta$ -dibromo- $\Delta\beta$ -pentene and not $\beta\gamma$ -dibromo-Δ°-pentene. The latter, b. p. 56°/11 mm., d 1.711, $n_{\rm p}$ 1.5182, is obtained when $\alpha\beta\gamma$ -tribromopentane is treated with potassium under reduced pressure. Zinc dust and alcohol convert it into ethylallene, b. p. 43-45°, whilst on repeated distillations a fraction, b. p. 72°/11 mm., is always obtained, indicating the progressive isomerisation of the By- into aB-dibromo- Δ^{β} -pentene. β_{γ} -Dibromo- Δ^{α} -pentene is also obtained by addition of bromine to ethylallene and in smaller amounts from potassium and apy-tribromopentane under normal pressure. With magnesium methyl bromide $\alpha\beta$ -dibromo- $\Delta\beta$ -pentene is converted into γ -bromo- Δ^{γ} -hexene, b. p. $34^{\circ}/16$ mm., d^{21} 1-197, n_{D} 1.459, yielding with cold bromine in absence of solvent mainly $\beta_{\gamma\gamma}$ -tribromohexane, b. p. 105—106°/ 9 mm., d^{20} 1.9434, $n_{\rm D}$ 1.5508, together with $\beta\gamma$ -dibromohexane, b. p. 73-74°/10 mm., d²⁰ 1.5995, n_D 1.5042, giving with zino dust Δr -hexene, b. p. 64°/753 mm., d¹⁹ 0.6807, n_p 1.394, and a tetrabromohexane, b. p. 151°/12 mm., d 2.225, np 1.586. βγγ-Tribromohexane is converted by sodium ethoxide into y8-dibromo-Δ^γ-hexene, b. p. 60-61°/9 mm., d²⁰ 1.6128, n_D 1.514, which with zine dust in alcohol yields Δr -hexinene b. p. 79–80°/770 mm., m. p. -51° , d^{20} 0.724, n_{ν} 1.4115, together with a fraction, b. p. $65-70^{\circ}/770$ mm., yielding a silver salt, probably γ -methyl- Δ^{α} -pentinene, and possibly due to the presence of $\beta\gamma$ -dibromo- Δ^{α} -pentene in the $\alpha\beta$ -isomeride. As in the case of the heptinenes and octinenes, the b. p. of the Δ^{γ} -hexinenes lies between those of the Δ^{α} - and Δ^{β} -isomerides.

Magnesium ethyl bromide and $\alpha\beta$ -dibromo- Δ^{β} pentene similarly yield propylallene and δ -bromo- Δ^{δ} -heptene, b. p. 53·5°/25 mm., 44·5—45°/12 mm., $d^{2\pm35}$ 1·1742, $n_{\rm D}$ 1·463, which with alcoholic potassium hydroxide gives a little γ -ethyl- Δ^{α} -pentinene, b. p. 87—88·5°, d^{25} 0·7246, $n_{\rm D}$ 1·4043 (cf. Prévost, this vol., 46), and, chiefly, Δ^{γ} -heptinene, b. p. 105—106°, d^{25} 0·7337, $n_{\rm D}$ 1·415. α -Bromo- Δ^{β} -butane with bromine yields $\alpha\beta\gamma$ -tribromobutane, b. p. 101—101·5°/13 mm., m. p. —19°, converted by potassium into $\alpha\beta$ -dibromo Δ^{β} -butene, b. p. $58 \cdot 5 - 59 \cdot 5^{\circ}/12 \text{ mm.}, d^{z_5} 1 \cdot 88, n_D$ 1 $\cdot 5392, \text{ and } \beta\gamma$ -dibromo- Δ^{α} -butene, b. p. $50 - 52^{\circ}/12 \text{ mm.}, d^{z_5} 1 \cdot 8698, n_D 1 \cdot 536$. The latter, which is also obtained by addition of bromine to methylallene, is slowly transformed into the $\alpha\beta$ -isomeride even at the ordinary temperature. R. BRIGHTMAN.

Pseudohalogens. IV. Hydrolysis constants of bromotricyanomethane and of chloro-, bromo-, and iodo-trinitromethanes. L. BIRCKENBACH and K. HUTTNER (Ber., 1929, 62, [B], 2065-2075; cf. this vol., 302).-An extension of the nomenclature proposed previously (loc. cit.) is advocated to chlorotrinitromethane etc., which is therefore designated chlorotrinitromethyl. The chemical properties of chloro-, bromo-, and iodo-trinitromethane are in complete harmony with those of bromotricyanomethane. In chlorotrinitromethane the trinitromethyl group is the more electronegative com-ponent; the decomposition potential of potassium trinitromethyl in 0.1N-aqueous solution is about 2.0 volts, thus approximating closely to that of 0.1Npotassium chloride. Hydrolysis of the compounds is represented by the equation $K = [H^{\bullet}] \times [pseudohal.'] \times$ [hal. OH]/[hal-pseudohal.] and is determined by conductivity measurements. Among halogenotrinitromethane compounds, the iodo-compound is most completely hydrolysed, thus resembling iodine monochloride. In extent of hydrolysis, bromotricyanomethane shows a similarity to bromine which is not observed with bromotrinitromethane. In general, the relationships observed during hydrolysis support the similarity of the halogenotrinitro- and halogenotricyano-methane compounds with the halogens, but exceptions exist, since the chlorine in chlorotrinitromethane is much less labile than in the chlorine molecule itself. H. WREN.

Spectrochemistry of aliphatic nitro-compounds. K. von Auwers and L. HARRES (Ber., 1929, 62, [B], 2287—2297).—Spectroscopical examin-ation of the compounds $CHCl_3$, CCl_4 , $CHBr_3$, CBr_4 , $CH(CO_2Et)_3$, $(CO_2Me)_2C(CO_2Et)_2$, $C(CO_2Et)_4$, and (CO,Et),C.CO.CO,Et does not give a perfectly uniform picture, but shows that, in general, accumulation of negative substituents at a carbon atom does not cause marked deviations from the normal spectrochemical behaviour, although small local irregularities are observed. With aliphatic polynitro-compounds, spectrochemistry has not a firm basis. All mononitroderivatives investigated are spectrochemically normal, but deviations occur as the nitro-groups accumulate, and it is doubtful whether these are due to structural changes or are to be regarded as optical anomalies. On spectrochemical grounds there is no support for the three-ring formula. If it is assumed that, since the spectrochemical behaviour of polynitro-compounds does not correspond with the hypothesis of pure nitro-forms, these compounds must contain groups of another kind, it is probable that the isomerisation of the true nitro-compounds occurs according to a definite general scheme leading either to nitrites or nitrones; the balance of the evidence is in favour of the nitrone formulation, since irregularities are observed for the nitrite structure for which there appear to be no adequate reasons. The case of

tetranitromethane is discussed in detail. The following data, amongst others, are recorded : carbon tetrachloride, d_4^{30} 1.5933, $n_{\rm He}^{30}$ 1.45881; bromoform, d_4^{213} 2.8833, $n_{\rm He}^{215}$ 1.59632; carbon tetrabromide, d_4^{365} 2.9609, $n_{\rm He}^{905}$ 1.59998; bromopicrin, d_4^{156} 2.7922, $n_{\rm He}^{41}$ 1.45800; ethyl bromonitromalonate, d_4^{174} 1.4835, $n_{\rm He}^{21}$ 1.45800; dichlorodinitromethane, d_4^{305} 1.6606, $n_{\rm He}^{308}$ 1.45871; nitroform, d_4^{413} 1.5967, $n_{\rm He}^{214}$ 1.44511; trinitroethane, d_4^{477} 1.4223, $n_{\rm He}^{117}$ 1.42005; chlorotrinitromethane, d_4^{477} 1.4223, $n_{\rm He}^{117}$ 1.42005; bromotrinitromethane, d_4^{472} 1.6810, $n_{\rm He}^{419}$ 1.45050; bromotrinitromethane, d_4^{412} 1.6810, $n_{\rm He}^{410}$ 1.48175; tetranitromethane, d_4^{412} 1.6377, $n_{\rm He}^{31}$ 1.42766; ethyl nitroacetate, b. p. 94°/11 mm., d_4^{131} 1.2115, $n_{\rm He}^{131}$ 1.42692; ethyl acinitroacetate ethyl ether, b. p. 88°/3.5 mm., d_4^{161} 1.1680, $n_{\rm He}^{61}$ 1.45799. H. WREN.

Thermal decomposition of primary aliphatic alcohols. K. KASHIMA (Bull. Chem. Soc. Japan, 1929, 4, 177-190).-The relative amounts of ethers and olefines produced when methyl, ethyl, propyl, butyl, and amyl alcohols are being dehydrated over Japanese acid clay at 200-400° are recorded. The amounts of ether formed decrease with increase of mol. wt. of the alcohol and also with higher reaction temperatures, being almost zero at 400°. Above 300° almost quantitative decomposition into the olefine takes place. Butyl alcohol gives a mixture of Δ^{a} - and Δ^{β} -butene, the latter being formed from the former by movement of the double linking under the catalytic influence of the clay. Methyl alcohol gave small amounts of hexamethylbenzene in addition to the main products. From considerations of the heats of formation it is concluded that ethers are first formed and are further decomposed by the action of the catalyst. A. A. GOLDBERG.

Determination of ethyl alcohol by chromic oxidation. L. SEMICHON and M. FLANZY (Ann. Falsif., 1929, 22, 414—415; cf. B., 1929, 449).— Boidin's method is considered to be longer, less sensitive, and to require greater attention to avoid loss of aldehyde than the method recommended by the authors (*loc. cit.*). H. J. DOWDEN.

Configurative relationships of heptan-y-ol and octan-&-ol to lactic acid. Effect of unsaturation on optical activity. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 579-589).- Δ^{β} -Octen- δ -ol, from crotonaldehyde and magnesium butyl bromide, has b. p. $78\pm1.5^{\circ}/20$ mm.; the l-carbinol (hydrogen phthalate, $[\alpha]_D - 7.7^\circ$ in alcohol, the resolution being made with cinchonidine) has $[\alpha]_{D}^{24}$ -3.0° without solvent, and is dextrorotatory in ethereal solution. When reduced with hydrogen and palladium it gave d-octan-8-ol, b. p. 79°/20 mm., [a] $+0.27^{\circ}$ in alcohol (lævorotatory in ether). With ozone it yielded d-a-hydroxyhexaldehyde, b. p. 60-64°/ 1 mm., $[\alpha]_D^{24} + 19.9^\circ$ in alcohol, reduced with sodium amalgam to d-hexane-ab-diol, b. p. 85-90°/1.5 mm., $[\alpha]_{D}^{\infty}$ +5.7° in alcohol (naphthylcarbamate, m. p. 165 168°, $[\alpha]_D^{25}$ -7.1 in acetic acid). Δ^{α} -Hepten- γ -ol hydrogen phthalate, m. p. 66-67°, was resolved with strychnine; from the insoluble salt was obtained the 1-carbinol, b. p. 65°/20 mm., [a] -22.2° without solvent, which, on reduction, gave d-heptan- γ -ol, b. p. 66-67°/20 mm., $[\alpha]_{\rm b}$ +6.7° without solvent, $n_{\rm b}^{25}$ 1.4198, and, with ozone, yielded 1-a-hydroxyhexaldehyde, $[\alpha]_{15}^{*} -28 \cdot 8^{\circ}$ in alcohol. $l \cdot \Delta^{\circ}$ -Hexen- γ -ol was treated with ozone, and the crude α -hydroxyvaleraldehyde, $[\alpha]_{15}^{**} +23 \cdot 0^{\circ}$, was reduced to d-pentane- $\alpha\beta$ -diol, b. p. 88—90°/2 mm., $[\alpha]_{15}^{**} +16 \cdot 8^{\circ}$ in alcohol (phenylcarbamate, m. p. 108—110°, $[\alpha]_{15}^{**} +16 \cdot 2^{\circ}$ in alcohol). d-Octan- δ -ol and d-heptan- γ -ol are therefore related to one another and to $l \cdot \alpha$ -hydroxy-*n*-hexoic acid; further, d-hexan- γ -ol is related to $l \cdot \alpha$ -hydroxy-*n*valeric acid. The optical relationships here observed between corresponding saturated and unsaturated carbinols are in disagreement with those recorded by Kenyon and Snellgrove (A., 1925, i, 771). The effect of introduction of a double linking on the optical activity of a carbinol depends both on its distance from the asymmetric carbon atom and on whether it is situated in the lighter or heavier radical.

C. R. HARINGTON.

Secondary citronellol [$\beta\zeta$ -dimethyl- Δ^{β} -octenn-ol]. J. DEUVRE (Bull. Soc. chim., 1929, [iv], 45, 710-715).-Magnesium methylheptenyl bromide (this vol., 907) and acetaldehyde yield a fraction, b. p. 119—120°/760 mm., containing a mixture of hydro-carbons, C_8H_{16} and C_8H_{14} (this vol., 1038), a methyl ketone, b. p. 84—87°/13 mm., probably $\beta\zeta$ -dimethyl- Δ^{β} -octen- η -one, by reaction of the secondary magnesium derivative, CMe,:CH. [CH,]; [CHMe], OMgBr, with excess of aldehyde, and, mainly, secondary citronellol (βζ-dimethyl-Δ^β-octen-η-ol), b. p. 101-103°/13 mm., d_4^{16} 0.857, n_D^{16} 1.4570, which on quantitative ozonisation (this vol., 542) affords 7% of formaldehyde, 13% of formic acid, and 78% of acetone, indicating that the sec.-citronellol is a mixture of 20% of the a(methylenic)form ($\beta\zeta$ -dimethyl- Δ^{α} -octen- η -ol) and 78% of the β-form. The original methylheptenyl bromide contained 22% of the α - and 76% of the β -form. Similarly, the sec.-citronellol, b. p. 106-108°/19 mm., d_4^{18} 0.858, n_D^* 1.4557, obtained from natural methylheptenone, by conversion into its glycidic ester, b. p. 143-145°/18 mm., d_4^{18} 0.978, n_D^{18} 1.454 (Verley, A., 1924, i, 865), hydrolysis with alcoholic potassium hydroxide to $\beta\zeta$ -dimethyl- Δ^{β} -hepten- η -al (yield 30%), b. p. 80°/19 mm., d475 0.853, nb75 1.4447 (together with products of b. p. above 145°/19 mm.), and condensation of the aldehyde with magnesium methyl iodide (yield 60%), is probably a mixture of the α - and β -forms essentially in the proportion in which they are present in the natural methylheptenone. On dehydrogenation at 250°/15 mm. in presence of reduced copper catalyst, sec.-citronellol is converted (yield 50%) into $\beta\zeta$ -dimethyl- Δ^{β} -octen- η -one, b. p. 87°/13 mm., d_4^{152} 0.851, n_D^{152} 1.4461, probably a mixture of the α - and β -forms. β -Dimethyl- Δ^{β} -nonen- η -ol, from magnesium methylheptenyl bromide and propaldehyde, has b. p. $114-116^{\circ}/16 \text{ mm.}, d_4^{18} 0.856, n_D^{15} 1.4543.$

R. BRIGHTMAN.

Action of potassium mercuri-iodide in alkaline medium on polyhydric alcohols and related substances. Analytical applications. P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 10, 241—258).—Various polyhydric alcohols, mannitol, dulcitol, inositol, erythritol, glycerol, and glycol, and related polysaccharides, both reducing and nonreducing, dextrose, sucrose, raffinose, stachyose, and glycogen, are oxidised by potassium mercuri-iodide in alkaline solution at 100°, and the effect of con-

centration and time of heating on the course of the reaction has been studied. The amount of oxidation. measured by the quantity of the reagent which is reduced, increases, towards a limit, with increasing concentration of alkali, with increasing concentration of mercuri-iodide if this is also accompanied by a corresponding increase in the volume of sodium hydroxide added, and with time; but after 30-40 min. for a given concentration of mercuri-iodide it is almost independent of time and is fixed at various limits depending on the alkalinity. Under the conditions given below the maximum quantity of oxygen taken up by the polyhydric alcohols studied slightly exceeds I atom for each atom of carbon. Similar results are obtained with the polysaccharides, but these are more resistance to attack the greater is their mol. wt. On the other hand, various hydroxy-acids, glycollic, lactic, gluconic, malic, tartaric, saccharic, mucic, citric, and salicylic, are unattacked or only very slightly attacked, the protective influence of the carboxyl group being evident in the greater resistance of dibasic than of monobasic acids. On the basis of these results the method has been applied to the determination of the alcohols mannitol, dulcitol, inositol (anhydrous), and glycol, the iodometric method of Baudouin and Lewin (A., 1927, 476) and of Rupp (A., 1905, ii, 484) being followed, but with the addition of 8-10 c.c. of a 10% aqueous suspension of precipitated barium sulphate. This absorbs the precipitated mercury and keeps it in a fine state of division so that it is readily soluble in the known volume of standard iodine solution which is added. The excess of the latter is titrated, after a few minutes, with standard sodium thiosulphate solution. Under these conditions (described in detail in the original) 10 mg. of the above alcohols are equivalent, respectively, to 7.31, 6.86, 7.34, and 7.15 c.c. of 0.1N-J. W. BARER. iodine solution.

Action of hydrogen bromide and bromine on a glycol of the ethylenic series. J. SALKIND and S. SABOJEV (Ber., 1929, 62, [B], 2169—2176; cf. A., 1927, 443).—Treatment of β e-dimethyl- $\Delta \nu$ -hexene- β e-diol (β -variety) with saturated, aqueous hydrobromic acid at the atmospheric temperature affords 2:2:5:5-tetramethyl-2:5-dihydrofuran, b. p. 102—103°, and a very unstable, liquid dibromide, C₈H₁₄Br₂, b. p. 117—120°/18 mm., which is completely resinified in 2—3 days. If the diol is added very gradually to the well-cooled hydrobromic acid and the product is worked up after $\frac{1}{2}$ hr., an isomeric dibromide, m. p. 55—57°, stable in anhydrous ether, but very easily resinified if exposed to air, is obtained. The liquid compound is converted by cold 10% potassium hydroxide into 2:2:5:5-tetramethyl-2:5-dihydrofuran, whereas the solid substance regenerates the original glycol. They are regarded as the cis- and trans- β e-dibromo- β e-dimethyl- $\Delta \gamma$ -hexenes. They add bromine in chloroform solution, giving tetrabromodimethyl- $\Delta\beta$ -hexene. When the diol is treated with hydrobromic acid at 40—50°, 3-bromo-2:2:5:5-tetramethyl- $\Delta\beta$ -hexene. When the diol is treated with hydrobromic acid at 40—50°, 3-bromo-2:2:5:5-tetramethyletrahydrofuran, b. p. 115—120°/14 mm., is produced. Addition of the diol to hydrogen bromide in glacial acetic acid leads to the formation of the

stable Byz-tribromo-Bz-dimethylhexane, b. p. 135-140°/13 mm., hydrolysed with difficulty to 3-bromo. 2:2:5:5-tetramethyltetrahydrofuran (cf. supra), and a product of m. p. 52-55°. Tetramethyldihydrofuran is transformed by bromine in chloro. form into 3:4-dibromo-2:2:5:5-tetramethyltetrahydrofuran, b. p. 100-101°/15 mm., m. p. 32-33°. Tetramethylbutenediol and bromine in ether afford y8-dibromo-BE-dimethylhexane-BE-diol, m. p. 98.5-99.5°, and a heavy oil which could not be purified, but passes when treated with steam into a resin and 3:4-dibromo-2:2:5:5-tetramethyltetrahydrofuran. The dibromo-glycol is hydrolysed by potassium carbonate to the dioxide, $\begin{pmatrix} CMe_2 \\ O \end{pmatrix}$, b. p. 73-74°/20 mm., 172-173°/atm. press., d₄²⁰ 0.9506, $n_{\rm D}^{20}$ 1.42632, converted by hot water into βε-dimethylhexane-βyδε-tetraol, m. p. 153-154°, and by hydrobromic acid into BE-dibromo-BE-dimethylhexane-ys-diol, m. p. 119-120°. H. WREN.

Action of chlorosulphonic acid on aldehydes. K. FUCHS and E. E. KATSCHER (Ber., 1929, 62, [B], 2381-2386; cf. A., 1928, 43).-Acetaldehyde and paracetaldehyde react vigorously with chlorosulphonic acid, yielding dark products which are soluble in water and not analogous to those derived from formaldehyde. Trichloroacetaldehyde yields up to 65% of octachlorodiethyl ether, $(CCl_3 \cdot CHCl)_2O$, b. p. 130–131°/11 mm., m. p. 47°, which separates when the reaction mixture is cooled to -50° ; hydrogen chloride and traces of carbonyl chloride are evolved. The filtrate from the ether yields chloralide, m. p. 114—115°, after long preservation. Tetrachloro-ethyl hydrogen sulphate appears to be the primary product of the action, since water-soluble compounds are initially obtained which are hydrolysed to chloral hydrate, sulphuric and hydrochloric acids. Similar results are obtained with metachloral and chloral hydrate. Fluorosulphonic acid and polymeric formaldehyde even at 90° yield compounds soluble in water and possibly containing fluoromethyl alcohol. Chloral and fluorosulphonic acid afford octachlorodiethyl ether in 20-25% yield.

Octachlorodiethyl ether reacts with aromatic and aliphatic Grignard reagents, but the isolation thereby of α -alkylated or -arylated hexachlorodiethyl ethers has not been effected. H. WREN.

XX. Poly-Highly-polymerised compounds. ethylene oxides. H. STAUDINGER and O. SCHWEIT-ZER (Ber., 1929, 62, [B], 2395-2405).-Polymerisation of ethylene oxide in the presence of tertiary amines, alkali metals, or stannic chloride gives ethercompounds, $\cdot [CH_2 \cdot CH_2 \cdot O]_n$. Polymerisation like occurs somewhat irregularly and is sometimes autocatalytically accelerated so as to give rise to violent explosions, thus indicating a possible danger in the technical use of ethylene oxide compressed in steel flasks. Sunlight, ultra-violet light, and Florida earth do not induce the change. Gaseous ethylene oxide and stannic chloride vapour give a solid polymeride and dioxan.

The polyethylene oxides are more stable than the polyoxymethylenes, but are decomposed above 300°, not into monomeric ethylene oxide, but into unsaturated products of higher b. p. and readily volatile materials containing acctaldehyde and acraldehyde. They dissolve readily in water, alcohol, benzene, and chloroform, but not in light petroleum or ether.

The polyethylene oxides can be separated by addition of ether to the benzene solution into a series of polymeric homologues, the m. p. and viscosity in water and benzene of the individual fractions increasing with increase in mean mol. wt. The relative viscosity is greater in water than in benzene, so that the viscosity of solutions of highly polymerised compounds depends, not only on the length of the molecules, but also on the solvent.

When cooled, the molten polyethylene oxides crystallise, the process commencing at individual nuclei and spreading concentrically in all directions. The operation thus resembles that in paraffin wax. The polyethylene oxides, like the polyoxymethylenes and the paraffins, are röntgenographically well crystallised. It is therefore established that the power to crystallise is not confined to completely homogeneous substances, but is also possible with molecules of unequal length but similar mode of structure. The crystallisation of cellulose derivatives, for example cellulose acetates, is not a proof that the product is composed of small, homogeneous molecules, but thread molecules of cellulose acetates can separate from a solution in such a manner that lattice-like arrangement of the molecules results. Similarly, the crystallisation of caoutchouc is not evidence of its structure from uniform, small fundamental molecules. H. WREN.

Determination of organic peroxides. S. MARKS and R. S. MORRELL (Analyst, 1929, 54, 503-508).-A quantitative result is obtained by adding potassium iodide (2 c.c. of concentrated solution or $\hat{2}$ g. of powder) to 0.2 g. of the peroxide dissolved in 25 c.c. of glacial acetic acid, and after a few minutes, diluting with about 100 c.c. of water and titrating with 0.1N-sodium thiosulphate solution. The result of a blank test is deducted. The method is applicable to straight-chain compounds. In the case of oxidised oils I g. is dissolved in 25 c.c. of acetic acid, and 1 c.c. of 50% sulphuric acid and 2 c.c. of cold saturated potassium iodide solution are added; after keeping in the dark for 24 hrs. in a closed vessel the mixture is diluted and titrated as before, a benzoyl peroxide control and two blanks D. G. HEWER, being made.

Alkyl peroxides. III. Methyl hydrogen peroxide. A. RIECHE and F. HITZ (Ber., 1929, 62, [B], 2458—2474; cf. A., 1928, 734; this vol., 292).— Dilute solutions of methyl hydrogen peroxide may be prepared by the action of methyl sulphate and potassium hydroxide on 10% hydrogen peroxide followed by distillation of the acidified solution. For the preparation of the homogeneous compound, b. p. 38—40°/65 mm., d_1^{15} 0.9967, n_5^{15} 1.36408, the aqueous distillate is exhaustively extracted with ether and the extract is dried for a protracted period over anhydrous copper sulphate and distilled over sodium sulphate. Methyl hydrogen peroxide is a colourless liquid with an intensely unpleasant odour. It explodes violently when heated, and is very sensitive to shock when hot.

The oxidising action of methyl hydrogen peroxide exceeds that of the dialkyl peroxides, but is inferior to that of hydrogen peroxide. With hydrogen iodide reaction is complete only after some hours, and does not lead to the quantitative production of methyl alcohol. It reacts rapidly but incompletely with titanium trichloride or sulphurous acid. It does not react with acid permanganate. With excess of hot, strongly alkaline permanganate the peroxide is completely transformed into carbon dioxide and the residual permanganate can be titrated, but elementary analysis is the most certain criterion of homogeneity. In freezing benzene the peroxide is associated, but normal values for the mol. wt. are obtained in water. Aqueous solutions freely dissolve barium and calcium hydroxides, giving readily soluble salts. In alkaline solution, methyl hydrogen peroxide vigorously evolves hydrogen mixed with a little oxygen and leaves mainly formate. Since the change is greatly accelerated by addition of formaldehyde, monohydroxydimethyl peroxide, MeO·O·CH2·OH, is regarded as an intermediate product, and since hydrogen is liberated in the atomic state, the change is represented by the scheme: $2MeO \cdot OH \longrightarrow 2H \cdot CHO + 2H_2O;$

 $2MeO \cdot OH + 2H \cdot CHO \longrightarrow 2MeO \cdot O \cdot CH_2 \cdot OH;$ $2\mathrm{MeO}{\cdot}\mathrm{O}{\cdot}\mathrm{CH_2}{\cdot}\mathrm{OH} \longrightarrow 2\mathrm{MeO}^-{+}2\mathrm{H}{\cdot}\mathrm{CO_2H}{+}2\mathrm{H};$ $2MeO^- \longrightarrow MeOH + H \cdot CHO \xrightarrow{+MeO \cdot OH} MeO \cdot O \cdot CH_{2} \cdot OH,$ etc. Ethyl hydrogen peroxide decomposes when warmed in alkaline solution, evolving very little hydrogen. After addition of formaldehyde to the concentrated solution almost explosive evolution of hydrogen is observed. Ethyl alcohol is formed in rather more than the calculated amount, and the production of acetaldehyde is betrayed by the brown colour of the solution; the presence of acetic acid can be detected. In presence of spongy platinum methyl hydrogen peroxide decomposes vigorously, mainly into carbon dioxide and methyl alcohol; formaldehyde and formic acid are produced in minor amount. Methylene-blue is decolorised by methyl hydrogen peroxide in alkaline solution in presence or absence of formaldehyde. Dinaphthylene dioxide 4:4'-quinone is reduced by methyl or ethyl hydrogen peroxide, alkali, and formaldehyde, but not by methyl hydrogen peroxide and alkali. Indigotin and anthraquinone are not reduced by methyl hydrogen peroxide and formaldehyde, although ethyl hydrogen peroxide reacts with anthraquinone in presence of formaldehyde and alkali. In very weakly alkaline solution at the ordinary temperature leucomethylene-blue immediately becomes coloured by methyl or ethyl hydrogen peroxide in presence or absence of formaldehyde; the last-named compound does not function as activator. If an alkaline solution of potassium ferricyanide is added to an ethereal solution of methyl hydrogen peroxide, potassium ferrocyanide is formed and a peroxide can be extracted from the aqueous solution, which contains nearly the whole of the active oxygen originally present in the methyl hydrogen peroxide.

Monohydroxydimethyl peroxide, which does not boil below 50°/20 mm., is a colourless, fairly mobile liquid of unpleasant odour which explodes violently when heated. It is associated in benzene. It evolves hydrogen when treated with alkali at the ordinary temperature.

Ethyl hydrogen peroxide, b. p. $41-42^{\circ}/55$ mm., $d_1^{45} 0.955, n_D 1.3833$, is obtained analogously to methyl hydrogen peroxide. Constancy of d and n are the most trustworthy criteria of homogeneity, since the determinations with titanium trichloride or iodometrically are untrustworthy and combustion in a stream of nitrogen gives results about 1.7% low for carbon. H. WREN.

β-Chloroethyl carbonate and sulphate. V. NEKRASSOV and J. F. KOMISSAROV (J. pr. Chem., 1929, [ii], **123**, 160—168).—Treatment of anhydrous ethylene chlorohydrin with carbonyl chloride at 0° affords β-chloroethyl chloroformate (I), b. p. 152·5°/ 752 mm., d_2^{∞} 1·3825, n_D^{∞} 1·4465, also obtained in presence of water and calcium carbonate. When I is treated with ethylene chlorohydrin at 130—150° β-chloroethyl carbonate, b. p. 240—241°, 115°/8 mm., m. p. 8·5°, d_2^{∞} 1·3506, n_D^{∞} 1·4610, is obtained. The same ester is formed by the action of ethylene chlorohydrin on trichloromethyl chloroformate (II), and also when I is boiled with β-chloroethyl nitrite (III). Carbonyl chloride and III at 65° yield I, whilst II and III give I and a small amount of the carbonate.

Ethylene chlorohydrin and sulphuryl chloride at 165° afford β -chloroethyl sulphate, b. p. 150—152°/7 mm., m. p. 11°, d_2^{39} 1.4801, n_D^{39} 1.4622, also formed from sulphuryl chloride and III. Appreciable amounts of di- β -chloroethyl ether are formed during these reactions. H. BURTON.

Synthesis of mixed fatty and amino-acid glycerides. M. WEIZMANN, L. HASKELBERG, and S. MALKOWA (Z. physiol. Chem., 1929, 184, 241-245).-Allylphthalimide, m. p. 65-65.5°, is brominated in chloroform solution to By-dibromopropylphthalimide, m. p. 107-108°, which is hydrolysed by 48% hydrobromic acid to $\beta\gamma$ -dibromo- α -aminopropane hydrobromide, m. p. 164°. Resolution of the base and successive conversion into the d-dibromohydrin and epibromohydrin is effected by Abderhalden and Eichwald's method (A., 1914, i, 801). d-Glycerol a-monobromohydrin (obtained by hydrolysis of the epibromohydrin with cold hydrochloric acid) gives with palmityl chloride in presence of pyridine and chloroform the 1- $\beta\gamma$ -dipalmitate, m. p. 62-63°, $[\alpha] -32.5^{\circ}$ in 95% alcohol. An inactive α -leucylβy-dipalmitylglyceride, m. p. 216°, is obtained in 32% vield when the dry sodium salt of leucine is heated with the d-dipalmitate at 150-160°. H. BURTON.

Conversion of alkyl sulphites into chlorosulphonates and normal sulphates. R. LEVAIL-LANT (Compt. rend., 1929, 189, 465–467).—Chlorine acts on alkyl sulphites, in a freezing mixture, to give good yields of the corresponding alkyl chlorosulphonate : $R_2SO_3+Cl_2 \longrightarrow RCl+RO\cdotSO_2Cl$, and thus are prepared methyl (90% yield), ethyl (87%), and *n*-propyl chlorosulphonates. By the action of thionyl chloride on ethylene chlorohydrin first at 0° and finally at 100°, a 75% yield of β -chloroethyl sulphite, b. p. 133°/12 mm., d_1^{20} 1·422, n_1^{20} 1·481, is obtained, similarly converted by the action of chlorine into β -chloroethyl chlorosulphonate, b. p. 92°/14.5 mm., d_9^{20} 1·580, n_1^{20} 1·4578, in 87% yield. By the action of alkyl sulphites on alkyl chlorosulphonates at 120— 190°, alkyl sulphates are obtained: RO·SO₂Cl+ $R_2SO_3 \longrightarrow RCl+SO_2+R_2SO_4$, and hence these are the main products of the action of chlorine on alkyl sulphites at 120— 140° . J. W. BAKER.

Interaction of alkyl sulphides and mercury salts. W. F. FARAGHER, J. C. MORRELL, and S. Сомах (J. Amer. Chem. Soc., 1929, 51, 2774-2781). -When finely-divided mercurous nitrate (or its aqueous solution) is treated with methyl, ethyl, n-propyl, n- and iso-butyl, and isoamyl sulphides, mercury is precipitated and the additive compound $R_2S,Hg(NO_3)_2$, formed. Mercurous chloride is not acted on except by methyl sulphide in presence of water. With mercurous acctate and the above sulphides mercury is formed in presence of water; methyl sulphide causes precipitation in absence of water. Mercury is formed from mercurous sulphate or iodide and the above sulphides even in absence of water. The compound Et₂S,Hg(NO₃)₂ has m. p. 63°. Thiophen reacts with mercurous nitrate only in presence of water. Each of the above sulphides furnishes two of the three following types of mercuric

furnishes two of the three following types of mercuric chloride additive compounds: $(R_2S)_2, HgCl_2,$ $R_2S, HgCl_2$, and $R_2S, 2HgCl_2$. The following are described: Et₂S, HgCl₂, m. p. 76·5—77°; Et₂S, 2HgCl₂, m. p. 119—119·5°; Pr^a₂S, HgCl₂ (I), m. p. 87·5—88°; Pr^a₂S, 2HgCl₂ (II), m. p. 121—122°; Bu^a₂S, HgCl₂ (III), m. p. 116°; Bu^β₂S, 2HgCl₂ (IV), m. p. 131°; Bu^a₂S, 2HgCl₂, m. p. 112—113°; $(Bu^a_2S)_2, HgCl_2, an oil; (iso·C_5H_{11})_2S, 2HgCl_2, and [(iso C₅H_{11})_2S]_2, HgCl_2, an oil. Various factors (molecular$ proportions, crystallisation solvent) decide the typeformed and the various discrepancies in m. p.recorded in the literature are readily explained. Theinterconversions I = II and III = IV are broughtabout by crystallisation. The additive compoundsfrom the sulphides and mercuric salts of oxy-acidsare soluble in water. H. BURTON.

Action of chloropicrin on mercaptans. V. NEKRASSOV and N. N. MELNIKOV (Ber., 1929, 62, [B], 2091—2094; cf. Ray and others, J.C.S., 1919, 115, 1308; 1922, 121, 323).—Chloropicrin behaves as an oxidising agent towards the simple mercaptans, thus converting potassium ethyl sulphide into ethyl disulphide, b. p. $151.5-153^{\circ}/745$ mm., d_4^{20} 1.9982, n^{29} 1.5030, potassium phenyl sulphide into phenyl disulphide, m. p. 60°, and potassium p-tolyl sulphide into p-tolyl disulphide, m. p. 46°. Reaction is accompanied by considerable evolution of gas, mainly carbon dioxide and nitrogen with smaller, approximately equal, quantities of nitric oxide and carbon monoxide, thus indicating the following changes: $2(SR)_3C\cdot NO_2=3RS\cdot SR+2CO_2+N_2$ (and $+2CO_+$ 2NO). The production of phenyl disulphide from potassium phenyl sulphide and chloropicrin in aqueous solution is a very sensitive test for the nitrohalide. Chloropicrin reacts very slowly with free mercaptans. H. WREN.

 β -n-Butyl sulphide. O. HINSBERG (Bcr., 1929, 62, [B], 2166—2168; cf. this vol., 310).—n-Butyl sulphide (now termed " α -variety") is slowly converted by warm 70% perchloric acid into β -n-butyl sulphide perchlorate, [Bu₂S]₂,HClO₄,H₂O, decomposed

by potassium hydroxide or potassium acetate into β-n-butyl sulphide, b. p. 190-230° (slight decomp.). Physically, it closely resembles the a-sulphide, from which it is distinguished by its immediate conversion by perchloric acid into the perchlorate described above and by yielding a yellow solution in concentrated sulphuric acid, in which the α -variety is colourless. Oxidation of either sulphide by hydrogen peroxide affords α -n-butyl sulphone, m. p. 44°. H. WREN.

Diethyl triselenide, sulphodiselenide, and disulphoselenide. G. R. LEVI and A. BARONI (Atti R. Accad. Lincei, 1929, [vi], 9, 1019-1024; cf. this vol., 1039).-Diethyl triselenide, Et₂Se₃, b. p. $100^{\circ}/26$ mm., d_4^{13} 1.7805, n_D^{128} 1.60919, is formed by the action of selenium oxychloride on selenomercaptan or by that of selenium on diethyl diselenide; diethyl sulphodiselenide, Et_2SSe_2 , b. p. 98°/26 mm., d_4^{13} 1.7070, n_D^{128} 1.60244, by the action of selenomercaptan on thionyl chloride or that of sulphur on the diselenide; and diethyl disulphoselenide, Et₂S₂Se, b. p. 94°/26 mm., d_4^{13} 1.4094, n_D^{128} 1.57914, from either mercaptan and selenium oxychloride, or mercaptan and selenium chloride, or diethyl disulphide and selenium. T. H. POPE.

Preparation of fatty acids from their higher homologues. F. ROCHUSSEN (Ber. Schimmel, 1929, 179-186).- a-Halogeno-fatty acids (or their esters) may be degraded directly to saturated fatty acids containing two atoms of carbon less by fusion with potassium hydroxide. After the first vigorous reaction is over the mixture is heated to 300-350° until gas evolution ceases. Acids containing C_{n-1} and C_{n-3} are sometimes obtained as by-products, the quantity of the former produced increasing as the series of fatty acids is descended and depending on the period of heating. Their formation is explained by the scheme $2CHRBr \cdot CO_2 K \xrightarrow{-3KBr} 0 < CHR \cdot CO_{CO} \cdot C$ $\xrightarrow{-200}$ 2R·CHO $\xrightarrow{2KOH}$ 2R·CO₂K+H₂. Thus ethyl α -bromomyristate gives a 77% yield of lauric acid. Ethyl α -bromolaurate is similarly degraded (72%) total yield) to equal quantities of decoic and undecoic acids, whilst the α -chloro-ester gives (72.8%) a mixture containing 34.5 and 65.5%, respectively, of these two acids. Only poor yields are obtained when free α -bromolauric acid is used. Methyl α -chloro-undecoate gives a mixture (69.7%) containing octoic (23.7), nonoic (35.3), and decoic (41%) acids. Ethyl a-bromo-octoate gives (80.4%) a mixture of hexoic (29.7) and heptoic (70.3%) acids when heating is con-tinued for 1.5 hrs. at 340-350°, but with short heating the proportion of the products is 15.6 and 84.4%, respectively (total yield 84.4%).

J. W. BAKER.

Catalytic action of cupric salts in promoting oxidation of fatty acids by hydrogen peroxide. M. A. BATTIE and I. SMEDLEY-MACLEAN (Biochem. J., 1929, 23, 593-599).-Oleic acid is sometimes but not always rapidly attacked by hydrogen peroxide in the presence of ferrous iron with the formation of carbonic, formic, acetic, and succinic acids. The addition of small amounts of nickel, manganese, or zinc does not influence the reaction, but that of copper salts does. The addition of cupric salts to succinic acid catalyses

the degradation of the acid in acid but not in alkaline solution. After the mixture has been kept for 1/2 hr. at 60° about 75% of the succinic acid has been decomposed into carbon dioxide, formic acid, and acetic acids. Neither in acid nor in alkaline media did ferrous salts influence the oxidation of succinic acid, whilst cupric chloride, cuprous chloride, or cupric sulphate did. Cuprous salts are more effective in decomposing hydrogen peroxide, but cupric salts are more active in catalysing the oxidation of the aliphatic acids by hydrogen peroxide. The effect of the above oxidising agent on some acids which might possibly occur as oxidation products of succinic acid was investigated. Dihydroxymalcic acid is much less readily oxidised to carbon dioxide than is tartaric acid, although the former acid is the first product of oxidation when the latter is oxidised by means of hydrogen peroxide in the presence of ferrous iron. Pyruvic and dihydroxymaleic acids were oxidised by hydrogen peroxide in the absence of the cupric salt. Alcohol, acetone, and glycol were not oxidised by the above reagents. S. S. ZILVA.

Organic molecular compounds with co-ordination centres. II. Co-ordination numbers of alkyl esters of fatty acids in cholic acids.-See this vol., 1293.

Preparation of acid chlorides. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 523-531).— Yields of 80-90% of acid chlorides are obtained by the reaction $\text{R-CCl}_3+\text{R'-CO}_2\text{H} \longrightarrow \text{R-COCl}+$ $R' \cdot COCI + HCl$, where R represents an aromatic and R' an aliphatic radical. The reaction proceeds at 70-80°, and is catalysed by zine chloride. Aliphatic acid anhydrides may also be used in place of acids. R. TRUSZKOWSKI.

Differing behaviour of a- and B-chlorobutyric acids during catalytic hydrogenation. C. PAAL and H. SCHIEDEWITZ (Ber., 1929, 62, [B], 1935-1939; cf. A., 1927, 646).-r-α-Chloro- and r-β-chlorobutyric acids in alcoholic solution are only slightly attacked by hydrogen in the presence of palladised barium sulphate and reaction soon ceases owing to the liberated hydrogen chloride. Under similar conditions, calcium a-chlorobutyrate (+2H,0) is almost quantitatively transformed into calcium butyrate, whereas with the generally more unstable calcium β-chlorobutyrate very little hydrogen is absorbed. Silver a-chlorobutyrate and the unstable silver B-chlorobutyrate are incidentally described. H. WREN.

Modes of addition to conjugated unsaturated systems. II. Reduction of conjugated unsaturated acids by metals dissolving in aqueous media. H. BURTON and C. K. INGOLD (J.C.S., 1929, 2022-2037; cf. A., 1928, 634).-A study has been made of the reduction products of vinylacrylic, sorbic, β -methylsorbic, and $\beta\delta$ -dimethylsorbic acids, dealing with the relative proportions of the 1:2- and 1:4-dihydro-isomerides produced in each case. Three cases of conjugative addition are discussed : (a) in which both parts are stable as anions, (b) in which one part is stable as an anion and the other as a cation, (c) in which both parts are stable as cations. The experimental work relates to the last case.

It is assumed that the reduction takes place in three

stages : (i) the unsaturated molecule, polarised in the electric field at the surface of the metal, extracts a proton from the aqueous solution; this proton becomes attached to that atom (Ca) which most readily tolerates the negative polarisation charge developed

to co-ordination $C_{\beta} \xrightarrow{\frown} C_{a} \longrightarrow X + \overset{\oplus}{H} =$ prior

 C_{β} CH X; (ii) the cation possesses an electron sextet at C_{β} and its electron affinity exerted in the region of the metallic surface locally breaks down, the electrostatic potential barrier inhibiting the escape of the metallic electrons. The successive absorption of the two electrons necessary to complete the octet converts the

cation into an anion, C_{β} C_aH X. (iii) The anion extracts a second proton from the solution, giving CgH·CaH·X. The theory shows that in the cases investigated 1:2 and 1:4 reduction products should be formed, and the proportion in which these appear will depend on the distribution of the charge in the electromeric anion, as determined by the relative degrees of electron absorption of the groups terminating the system. The results obtained are in general agreement with the theory given.

New methods are given for the preparation of vinylacrylic, β -methylsorbic, and β -methyl- $\Delta \gamma$ -hexenoic J. W. PORTER. acids.

Lower olefinic acids. I. n-Hexenoic acids. E. N. ECCOTT and R. P. LINSTEAD (J.C.S., 1929, 2153-2165).-" Hydrosorbic acid " (the acid mixture obtained by the reduction of sorbic acid) is shown to contain $\beta\gamma$ - and $\gamma\delta$ -hexenoic acids; these have also been prepared synthetically.

A mixture of $\alpha\beta$ - and $\beta\gamma$ -hexenoic acids was prepared. by equilibration of Δ^{α} -hexenoic acid by means of 40% potassium hydroxide at 100°. The mixture of the isomerides when distilled under reduced pressure, and the distillate cooled in ice, yields a liquid richer in the $\beta\gamma$ -isomeride, which is completely freed from the $\alpha\beta$ isomeride by repeated controlled esterifications with cold alcoholic hydrogen chloride. The By-isomeride (purity determined by iodometric analysis) had b. p. 105°/13 mm., m. p. 4-5°, d14 0.9626, n14 1.4397 (anilide, m. p. 75°).

The y8-isomeride was synthesised from crotonaldehyde, which was reduced to the alcohol, and this converted into the bromide, which by the action of ethyl malonate furnished ethyl Δ^{β} butenylmalonate. The corresponding acid when heated at 140° is converted into $\gamma\delta$ -hexenoic acid. This synthesis leaves no doubt of the position of the double linking, and gives a pure product, which is shown to be the β-form of Δ^γ-n-hexenoic acid, b. p. 111—112°/20 mm., d_{1}^{167} 0.9584, n_{1}^{167} 1.4367. This differs from the α-form described by Fichter (A., 1904, i, 547) in b. p., density, and refractivity, but gives a similar anilide, toluidide, J. W. PORTER. and cadmium salt.

Mechanism of the degradation of fatty acids by mould fungi. III. H. B. STENT, V. SUBRAMANIAM, and T. K. WALKER (J.C.S., 1929, 1987-1993; cf. A., 1928, 804) .- Acetone is one of the products of the growth of Aspergillus niger in calcium n-butyrate solution. The non-volatile products consist of succinic acid which is further degraded to a mixture

of *dl*- and *l*-malic acids. When the mould is grown in *dl*-malic acid, the *l*-acid is converted into fumaric acid, thus rendering the solution dextrorotatory. It is postulated that the acetone is produced from *n*-butyric acid by β -oxidation, and that the acetone is oxidised to succinic acid by a process comparable with the production of the latter from acetone by the action of hydrogen peroxide. J. W. PORTER.

Acidity measurements of the higher fatty acids by the iodometric method. W. RUZICZKA (J. pr. Chem., 1929, [ii], 123, 61-73).—Kolthoff's method for determining the acidity of weak acids can be employed in the case of the higher fatty acids, using emulsions of these. It is necessary to use an initial excess of thiosulphate, and to keep the experimental conditions constant; the values so obtained are inversely proportional to the number of carbon atoms present, but are independent of the degree of unsaturation. Acids containing hydroxyl groups yield higher values, dependent on the number of such groups present. H. F. HARWOOD.

Separation of glycerides. VI. Linseed oil, soya-bean oil, and whale oil. VII. Herring oil. VIII. Cod-oil. IX. Sardine oil. X. Sand-eel oil. XI. Oil from Theragra chalcogramma. XII. Cuttle-fish oil. XIII. Red salmon oil. XIV. Shark-liver oil. B. SUZUKI. XV. Two new fatty acids from fish oils. B. SUZUKI and Y. Yокоуама (Proc. Imp. Acad. Tokyo, 1929, 5, 265-271, 272-273).-VI. Bromination in light petroleum and separation of the soluble bromo-glycerides by fractional precipitation with alcoholic calcium chloride solutions of increasing concentration affords the following bromides in addition to those previously described (A., 1928, 152, 736). Linseed oil: bromides of linoleo-diolein (I), f. p. 5°, of an isomeric linoleodiolein, f. p. -2°, stearo-linoleo-olein (II), f. p. -4°, and of stearo-linoleno-olein, f. p. -7° ; soya-bean oil : I, and oleo-dilinolenin bromide, f. p. 6° ; whale oil : bromides of stearo-dizoomarin, f. p. 1° , stearo-linoleozoomarin, f. p. -3° , stearo-linoleno-zoomarin (III), f. p. -6° , and of palmito-stearidono-gadolein, f. p. -3° , and a substance (IV), f. p. -4° , which is either trierucein or tricetolein bromide.

VII. Bromination of herring oil by the method previously described (A., 1928, 152) gives zoomaro-stearidono-arachidonin bromide, m. p. 148°, zoomaro-arachidono-clupanodonin bromide, m. p. 150° (decomp.), gadoleo-diarachidonin bromide, m. p. 180°, and two compounds derived from a new acid, C22H36O2 (see below), gadoleo- $C_{22}H_{35}O$ -linolenin bromide, m. p. 104°, and zoomaro- $C_{22}H_{35}O$ -stearidonin bromide, m. p. 150°; linoleo-digadolein bromide (VI), m. p. 6°, linoleo-dizoomarin bromide (V), m. p. 2°, III, dieruceo- or dicetoleo-gadolein bromide, m. p. 5°, and IV, are also obtained by the precipitation method described above.

VIII. The oil is a mixture of oils from various organs other than the liver of cod. The following are obtained : zoomaro-linoleno-clupanodonin bromide, m. p. 131°, zoomaro-linoleo-arachidonin bromide, m. p. 255° (decomp.), V, linoleno-dizoomarin bromide, m. p. -2° , stearidono-dizoomarin bromide, m. p. -4° , and dieruceo- or dicetoleo-stearin bromide, m. p. -7°.

IX. By application of the foregoing methods,

sardine oil affords the following, some of which are derived from the new acids $C_{18}H_{28}O_2$ and $C_{22}H_{36}O_2$ (see later): bromides of di- $C_{22}H_{35}O$ -arachidonin, m. p. 85°, of zoomaro- $C_{22}H_{35}O$ -stearidonin, m. p. 120°, of di- $C_{18}H_{27}O$ -arachidonin (VII), m. p. 110°, of stearidono- $C_{18}H_{27}O$ -zoomarin, m. p. 135°, of triarachidonin (VIII), m. p. 205° (decomp.), of triolein, m. p. 6°, VI, of dieruceo- or dicetoleo-olein, m. p. -2°, II, and of dieruceo- or dicetoleo-arachidonin, m. p. -3°.

X. Sand-eel oil yields the following : IV, V, VII, bromides of di-C₁₈H₂₇O-clupanodonin, m. p. 124°, of linoleo-C₁₈H₂₇O-arachidonin, m. p. 153°, of arachidono-C₁₈H₂₇O-clupanodonin, m. p. 230°, of dieruceo- or dicetoleo-clupanodonin, of dilinoleo-zoomarin, of dioleozoomarin, and of palmito-zoomarin.

XI. The oil yields the bromides of diclupanodonoarachidonin, m. p. 95°, of stearidono-diclupanodonin, m. p. 125°, of diclupanodono-linolenin, m. p. 165° (decomp.), VIII, of arachidono-dizoomarin, and of zoomaro-linoleo-stearin.

XII. The oil affords VIII, the bromides of $(C_{18}H_{27}O)_3$, m. p. 74°, of $(C_{18}H_{27}O)_2$ -linolenin, m. p. 81°, of $C_{18}H_{27}O$ -distearidonin, m. p. 125°, of linoleno-dizoomarin, and of trizoomarin (IX).

XIII. Red salmon oil yields the bromides IV, V, IX, and dilinoleno-arachidonin, m. p. 103°, and linoleno-diarachidonin, m. p. 115°, bromides.

XIV. Shark-liver oil yields the bromides VIII, IX, and those of arachidono-diclupanodonin, m. p. 110° (cf. above), clupanodono-diarachidonin, m. p. 140° and 112°, clupanodono-arachidono-linolenin, m. p. 117°, digadoleo-linolenin, dizoomaro-linolenin, palmito-diolein, and of triolein.

XV. The acid $C_{22}H_{36}O_2$, obtained as the octabromide, m. p. 96°, by hydrolysis of the bromoglyceride (cf. above) with 20% hydrochloric acid, by debromination in acetic acid suspension with zine dust and catalytic hydrogenation of the product with platinum-black in amyl-alcoholic solution furnishes behenic acid. The acid, $C_{18}H_{28}O_2$, isolated as the octabromide, m. p. 104—105°, isomeric with stearidonic acid octabromide, m. p. 200° (decomp.), by debromination and hydrogenation in a similar manner yields stearic acid, and is probably an isomeride of stearidonic acid. C. W. SHOPPEE.

Preparation of α -ketonic acids. V. TSCHELIN-OEV and W. SCHMIDT (Ber., 1929, 62, [B], 2210—2214). —Acyl cyanides are obtained in 58—80% yield by heating a mixture of 1 mol. of acyl bromide with 1 mol. of cuprous cyanide on the water-bath for $1\frac{1}{2}$ —2 hrs. and distilling the cyanide. The following compounds have been prepared: acetyl cyanide, b. p. 93°, d_4^{30} 0.9745, n^{30} 1.3743, and thence pyruvic acid in 73·2% yield by hydrolysis with concentrated hydrochloric acid; propionyl cyanide, b. p. 108—110°, n^{30} 1.3225, and thence propionylformic acid, b. p. 74—78°/ 25 mm., n^{30} 1.3972; *iso*butyryl cyanide, b. p. 116— 118°, d_4^{30} 0.9860, and the very unstable *iso*butyrylformic acid, d_4^{30} 0.9968, n^{30} 1.3790; *iso*valeryl cyanide, b. p. 145—149°, from which the corresponding acid could not be obtained. H. WREN.

Reaction of bromine with aliphatic acids. III. [Keto-enol tautomerism in] α - and y-ketonic acids. E. D. HUGHES and H. B. WATSON (J.C.S., 1929, 1945—1954).—Evidence of the existence of keto-enol tautomerism in α - and γ -ketonic acids, corresponding with that in β -diketones and β -diketonic acids, is given in the cases of pyruvic and lævulic acids. A study of the kinetics of the bromination of these acids in aqueous solution shows that the speed of the reaction is constant throughout, and independent of the initial concentration of the halogen. The absence of an enolide in appreciable quantities in pure pyruvic acid is demonstrated by the fact that in none of the experiments has a measurable quantity of bromine been found to be absorbed instantaneously. The results show clearly that the bromination is preceded by a change of the acid to its enolic form, which reacts readily with the halogen.

In chloroform solution the bromination commences only after a latent period of variable duration, which is compared with the arrest of mutarotation observed by Lowry and Richards (A., 1925, i, 886). The mechanism of the enolisation is discussed in terms of the electronic theory of valency. J. W. PORTER.

Configurative relationships of α -, β -, and y-chloro- and -hydroxy-aliphatic acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1929, 83, 591-600). Δ^{α} -Hexen- γ -ol was resolved by the phthalate method, yielding an l-carbinol, b. p. 133-134°, $[\alpha]_{0}^{25} - 23.4^{\circ}$ without solvent; with phosphorus trichloride this gave d- γ -chloro- Δ^{α} -hexene, $[\alpha]_{\nu}^{25} + 17.85^{\circ}$ without solvent, which, with ozone, furnished 1-chloron-valeric acid, b. p. 80–84°/1 mm., $[\alpha]_{1}^{25}$ –11.6° in ether (sodium salt, $\lceil \alpha \rceil_{10}^{25} - 3 \cdot 0^{\circ}$). When reduced with hydrogen and palladium the above hexenol gave d-hexan-y-ol, b. p. 130-132°, [a]²⁵ +2.75° without solvent. 1- Δ^{α} -Hepten- γ -ol, $[\alpha]_{D}^{25}$ -22.2° without solvent, gave d- γ -chloro- Δ^{α} -heptene, $[\alpha]_{11}^{25}$ +14.60° without solvent, which yielded 1-a-chloro-n-hexoic acid, b. p. 80-95°/1 mm., $[\alpha]_D^{30}$ -2.1° in ether. d- Δ ^e-Hexenβ-ol (cf. Levene and Haller, A., 1928, 1353) gave 1-δ-chloro-Δa-hexene, b. p. 119-122°, [a]25 -38.75° without solvent, which yielded 1-y-chloro-n-valeric acid, b. p. $95-100^{\circ}/1$ mm., $[\alpha]_0^{22} - 40.9^{\circ}$ in ether (sodium salt, $[\alpha]_{D}^{22}$ -27.4°). *l*- γ -Chloro-n-valeric acid is thus related to $d-\gamma$ -hydroxy-*n*-valeric acid, since the latter has already (loc. cit.) been related to the d-hexenol; this conclusion is contrary to that previously reached, and it is now thought that the rule of the change of direction of rotation on passing from the non-ionised to the ionised state is generally applicable as a guide to configuration only among the α -substituted acids; in β - and γ -substituted acids the rule is applicable only when the substituent is the hydroxyl group. C. R. HARINGTON.

Formation of lactic acid from sucrose under pressure. H. WOLF (Biochem. Z., 1929, 210, 458-465).—By the action of lime under pressure on sucrose 73%, and on invert-sugar only 38% is obtained as lactic acid. The amounts of formic acid obtained are inversely. It is suggested that the labile modification of lævulose present in sucrose breaks down almost quantitatively into lactic acid.

P. W. CLUTTERBUCK.

Preparation of the enolic form of ethyl acetoacetate. G. MINGASSON (Bull. Soc. chim., 1929, [iv], 45, 716-718).—The sodium derivative obtained in the usual way by condensation of ethyl acetate in presence of sodium ethoxide is decomposed with acetyl chloride in ether, and the enolic *acetate*, b. p. 90—91°/10 mm., d^{17} 1.0989, n^{17} 1.46906, when hydrolysed with boiling 1% oxalic acid for $\frac{1}{2}$ hr., furnishes the pure enol, d^{17} 1.0379, n^{17} 1.444, which yields ethane quantitatively with magnesium ethyl bromide (cf. Rumeau, A., 1924, i, 939; Grossmann, *ibid.*, 834).

R. BRIGHTMAN.

Walden inversion. P. NEBBELING (Chem. Weekblad, 1929, 26, 462—469).—The various theories postulated to explain the mechanism of the conversion of d- into l-malic acid by the successive actions of phosphorus pentachloride and moist silver oxide are discussed, and inconsistencies between the arguments pointed out. No one theory can be said effectively to explain the inversion. S. I. LEVX.

Hydroxydialkylsuccinic anhydrides. P. COR-DIER (Compt. rend., 1929, 189, 538—543; cf. Bougault, A., 1925, i, 921, 1152; 1926, 725).—Treatment of α -methoxybenzylidene- β -phenylethylsuccinic acid with acetic anhydride at 100° for short periods yields the normal anhydride, m. p. 155°, which is also obtained by heating the acid at 160°. Prolonged treatment, however, with boiling acetic anhydride yields α -hydroxy- α -methoxybenzyl- β -phenylethylsuccinic anhydride, m. p. 70° (corresponding methyl ether, m. p. 46°). A. A. GOLDBERG.

Keto-lactol tautomerism. III. Influence of bulky substituents on the tautomerism of α -carboxy- γ -acetyl- β -methyl- β -ethyl- and $-\beta\beta$ -diethyl-butyric acids. M. QUDRAT-I-KHUDA (J.C.S., 1929, 1913—1920; cf. this vol., 295, 698).—The above acids have been prepared and found to yield dilactones and keto-monobasic acids when heated a few degrees above their m. p. In the case of the former acid the dilactone conversion amounts to 32%, whilst in the latter it amounts to 45%. The conversion into dilactones also takes place when the acids are heated in benzene solution, the latter acid changing the more readily. The acids give normal keto-esters on esterification, and react in the lactol form in the presence of dehydrating agents or concentrated hydrochloric acid.

Methyl β -methyl- Δ^{β} -butenyl ketone condenses with cyanoacetamide to give 6-hydroxy-2-keto-3-cyano-4: 6dimethyl-4-ethylpiperidine, m. p. 240°, which on alkaline hydrolysis yields α -carboxy- γ -acetyl- β -methyl- β -ethylbutyric acid, m. p. 89° (semicarbazone, m. p. 166°; diethyl ester, b. p. 154°/10 mm., d_1^{62} 1.0414, n_D^{62} 1.44873, and its semicarbazone, m. p. 89°). The acid when heated gives the dilactone, m. p. 82°, and γ -acetyl- β -methyl- β -ethylbutyric acid, b. p. 150°/10 mm., d_1^{62} 1.0425, n_D^{62} 1.45773 (semicarbazone, m. p. 152°, ethyl ester, b. p. 112°/10 mm., d_1^{174} 0.967526, n_D^{174} 1.43899, and its semicarbazone, m. p. 94°). The substituted butyric ester when treated with sodium and absolute alcohol gives 5-methyl-5-ethyldihydroresorcinol, m. p. 106°.

Methyl β -ethyl- Δ^{α} -butenyl ketone condenses with cyanoacetamide to give 6-hydroxy-2-keto-3-cyano-6methyl-4: 4-diethylpiperidine, m. p. 251°, which by alkaline hydrolysis yields α -carboxy- γ -acetyl- $\beta\beta$ -diethylbutyric acid, m. p. 97° (semicarbazone, m. p. 158°; ethyl ester, b. p. 167°/12 mm., d_1^{176} 1.0405, n_{17}^{176} 1.4553, and its semicarbazone, m. p. 88°). The acid when heated gives the dilactone, m. p. 113°, and γ -acetyl-ββ-diethylbutyric acid, b. p. 158°/10 mm., d_4^{142} 1.04214, n_{17}^{142} 1.46639 (semicarbazone, m. p. 155°; ethyl ester, b. p. 125°/11 mm., d_4^{186} 0.966424, n_{17}^{186} 1.44392, and its semicarbazone, m. p. 93°).

The lactones of δ -hydroxy- β -methyl- β -ethyl- Δ^{ν} hexenoic acid, b. p. 90°/10 mm., $d_4^{18'4}$ 0·991443, $n_D^{18'4}$ 1·4622, and δ -hydroxy- $\beta\beta$ -diethyl- Δ^{ν} -hexenoic acid, b. p. 106°/10 mm., $d_4^{17'2}$ 0·996021, $n_D^{17'2}$ 1·46867, are also described. J. W. PORTER.

Double citrates of bismuth and quinine. H. LENORMAND (J. Pharm. Chim., 1929, [viii], 10, 162— 168).—The preparation and properties of the following compounds are described :

 $\begin{array}{l} C_{6}H_{6}O_{7},BiOH,2(C_{6}H_{8}O_{7},C_{20}H_{24}O_{2}N_{2}),2H_{2}O\ ;\\ C_{6}H_{6}O_{7},BiOH,2(C_{6}H_{8}O_{7},C_{20}H_{24}O_{2}N_{2})\ ;\\ (C_{6}H_{6}O_{7},BiOH)_{2},C_{6}H_{8}O_{7},C_{20}H_{24}O_{2}N_{2}\ ;\\ C_{6}H_{6}O_{7},BiOH)_{2},C_{6}H_{8}O_{7},C_{20}H_{24}O_{2}N_{2}\ ;\\ C_{6}H_{6}O_{7},BiOH)_{2},C_{6}H_{2}O_{2}N_{2}O_{2}\ ;\\ G_{7},BiOH,C_{20}H_{24}O_{2}N_{2}. \end{array}$

 $C_{6}H_{6}O_{7}$, BiOH, $C_{20}H_{24}O_{2}N_{2}$. They are micro-crystalline powders insoluble in the usual organic solvents. E. H. SHARPLES.

Pectin substances. Tetragalacturonic acids and d-galacturonic acid from the pectin of the sugar beet. F. EHRLICH and F. SCHUBERT (Ber., 1929, 62, [B], 1974-2027).-The pectin of sugar beet (Beta vulgaris) is present in the root in a form insoluble in water and forms about 50% of the residue left after extraction of the shavings with cold water, alcohol, and ether. The genuine pectin (urpectin, protopectin) cannot be isolated as such, since treatment with warm water causes more or less extensive hydrolysis to water-soluble hydratopectin, obtained in gelatin-like sheets by evaporation of the solution, and separated by 70% alcohol into araban and the calcium magnesium salts of pectic acid. Since the araban cannot be extracted directly from the shavings by 70% alcohol, it does not exist uncombined therein; it is a mixture of anhydrides of l-arabinose, from which almost quantitative yields of arabinose are obtained by the aid of boiling, dilute acids. Pectic acid, isolated from the calcium magnesium salt, appears to be a homogeneous product, C41H60O36, formed by loss of 9 mols. of water from 4 mols. of galacturonic acid, 1 mol. of arabinose, 1 mol. of galactose, 2 mols. of acetic acid, and 2 mols. of methyl alcohol. It is identical with the pectic acid derived from other sources and, except for greater homogeneity, with the pectin of other investigators. It exists probably in different states of hydration, since $[\alpha]_{D}$ varies from $+110^{\circ}$ to $+160^{\circ}$ for different preparations and can reach $+220^{\circ}$ if solutions in dilute hydrochloric acid are preserved. It is an acid ester in which two carboxyl groups are esterified with methyl alcohol. Its main component is galact-uronic acid, present to the extent of 68.70%, according to the Tollens-Lefèvre method. Treatment of pectic acid with 2-5% hydrochloric acid on the water-bath causes the separation of tetragalacturonic acid A, which can also be prepared in about 15% yield directly from hydratopectin. It is a white, amorphous powder which absorbs 10-15% of water from

the air without apparent change. In acid, neutral, or slightly alkaline solution it has $[\alpha]_D^{\infty} + 275^{\circ}$. With salts of the heavy metals or alkaline earths it gives gelatinous precipitates, but not with magnesium salts. It reduces Fehling's solution slightly, strongly after hydrolysis. Analyses of the acid and its salts and determinations of mol. wt. show that it is a tetraanhydrotetragalacturonic acid, $C_{24}H_{32}O_{24}$, with four free carboxyl groups. With 12% hydrochloric acid it affords furfuraldehyde and carbon dioxide quantitatively: $C_{20}H_{28}O_{16}(CO_2H)_4=4C_5H_4O_2+4CO_2+$ $8H_2O$. It is oxidised by protracted action of 5% hydrochloric acid and bromine at 75° to mucic acid (yield 60.5%) and oxalic acid; under these conditions mucic acid is considerably oxidised to oxalic acid and other products.

The mother-liquors from the preparation of tetragalacturonic acid from pectic acid or hydratopectin contain tetragalacturonic acid B, isolated by pre-cipitation with alcohol. The yield of the acid increases with increasing duration of hydrolysis, whereas that of the A acid diminishes, so that the former is a degradation product of the latter, as confirmed by the direct conversion in presence of dilute acid or water, preferably under pressure. The acid B is an amorphous powder closely resembling the acid A. It has $[\alpha]_{\overline{D}}$ about +250° in water. Its alkali salts are soluble in water (sodium salt +H₂O, $[\alpha]_{\overline{D}}^{3}$ +217.7° in water) and the solutions give granular or slimy but not gelatinous precipitates, which are partly soluble in excess of precipitant, particularly in the cases of the alkaline-carth salts. The acid reduces hot Fehling's solution. Analyses and determinations of mol. wt. indicate the composition $C_{24}H_{32}O_{24}$. Three carboxyl groups are directly titratable, the fourth only after hydrolysis with excess of alkali hydroxide. The compound is therefore regarded as trianhydrotetra-galacturonomonolactone. With hydrochloric acid it evolves furfuraldehyde and carbon dioxide in amount exactly corresponding with its galacturonic acid content. With hydrochloric acid and bromine it yields

mucic acid (yield 68.2%) and oxalic acid. Tetragalacturonic acid C is obtained by the alkaline hydrolysis of pectic acid and is invariably produced by the acid hydrolysis of pectic acids of higher optical activity ($[\alpha]_{\rm p}$ +170° to +220°) which have received preliminary treatment with cold hydrochloric acid. It can be obtained as transformation product of acid A, which it resembles in physical and chemical properties. It has $[\alpha]_{D} + 285^{\circ}$. It contains 1 mol. of water more than the A acid, which is not lost at $100^{\circ}/$ vac., and hence it is regarded as monohydratotetraanhydrotetragalacturonic acid. It has four titratable carboxyl groups and gives a sodium salt identical with that derived from the A acid, from which hydrochloric acid invariably liberates the C acid, thus giving a ready transformation from A to C. Protracted ebullition of A or C with water or dilute mineral acids, particularly under pressure, results in conversion into B. The A acid when treated with an excess of sodium or potassium hydroxide immediately yields an intensely yellow solution, which, after a time, suddenly becomes turbid and slowly colourless with separation of the alkali salt. Under similar conditions, acid Cbecomes only faintly yellow and rapidly colourless

again with separation of the salt. The constitutions I, II, and III are assigned to acids A, B, and C.



The presence of the free aldehydic group in acid B appears to be established by its oxidation by hypoiodite in amount corresponding with one •CHO group, whereas the acids A and C are not oxidised by this reagent.

The three tetragalacturonic acids are converted by prolonged acid hydrolysis into d-galacturonic acid, which is best prepared by heating a suspension of acid A in 1% sulphuric acid for 10-20 min. under 4-5 atm. Sulphuric acid is precipitated with a minimal excess of barium hydroxide, the filtrate is evaporated in a vacuum, the residue extracted with alcohol, and the extract allowed to evaporate (yield 35%). Crystalline a-d-galacturonic acid has m. p. 156-159° (decomp.) after softening at 110°, becoming red at 130-140° and brown at 150°. It gives the orcinol and naphtharesorcinol reactions. . It is converted by hydrochloric acid into furfuraldehyde and carbon dioxide. It reduces Fehling's solution strongly when heated, but not when cold. With nitric acid and cold bromine water, respectively, it gives 76%

and quantitative yields of mucic acid. With hypoiodite it absorbs the oxygen required for one .CHO group. Its carboxyl group can be titrated directly with alkali. Attempts to obtain crystalline galacturone from it were unsuccessful. a-d-Galacturonic acid, $C_6H_{10}O_7, H_2O$, has $[\alpha]_{D}^{20} + 97.9^{\circ}$ to $+50.9^{\circ}$ in aqueous solution $(+107.0^{\circ} \text{ to } +55.6^{\circ} \text{ for the anhydr-}$ ous substance). β-d-Galacturonic acid, C₆H₁₀O₇, crystallises anhydrous and has $\left[\alpha\right]_{p}^{20} + 27.0^{\circ}$ to $+55.3^{\circ}$ in water (time 2 hrs.). In the preparation of d-galacturonic acid from pectin substances, the α - and β modifications are obtained in varying proportion, depending on the degree of concentration of the syrups and the concentration of the alcohol used for extraction and crystallisation. Evaporation of hot aqueous or dilute alcoholic solutions invariably yields only the α -variety, whereas the β -modification, m. p. 160°, is obtained from the α -form by ebullition with a large excess of absolute alcohol and rapid evaporation of the solution. The reverse transformation takes place in warm, aqueous solution, from which the α -variety is isolated by evaporation. The water in the α -acid is very firmly retained, but it appears possible, although difficult, to effect its removal by desiccation with consequent production of the *β*-acid. Aqueous solutions of the a-acid give a violet colour with magentasulphurous acid after ½ min., whereas the colour develops only slowly in solutions of the β -acid, indicating the presence of the aldehydic group in the α - but not in the β -acid. The constitutions (I) and (II) are assigned to the α - and β -acids.



The following salts of *d*-galacturonic acid are described: sodium, $C_6H_9O_7Na$, $[\alpha]_{ji}^{33} + 36.02^{\circ}$ in water (non-mutarotatory); cinchonine,

 $C_{6}H_{10}O_{7}, C_{19}H_{22}ON_{2}, H_{2}O, m. p. 178^{\circ}$ (decomp.) after darkening at 176°, $[\alpha]_{10}^{\infty} + 139 \cdot 0^{\circ}$ in water; brucine, $C_{6}H_{10}O_{7}, C_{23}H_{26}O_{4}N_{2}, m. p. 180^{\circ}$ after darkening above 170°, $[\alpha]_{20}^{\infty} - 7.70^{\circ}$ in water; anhydrous morphine salt, m. p. 162—163° (decomp.) after darkening at 158° and softening at 160°, $[\alpha]_{20}^{\infty} - 56 \cdot 6^{\circ}$ in water. H. WREN.

Humic acids. W. FUCHS (Kolloid-Z., 1929, 49, 47).—A discussion of the methods of investigating the constitution of humic acid. E. S. HEDGES.

Solubility of humic acids in phenol. M. SOUM and F. PODBREZNIK (Bull. Inst. Pin, 1929, 61-64; Chem. Zentr., 1929, i, 2194).—The humic acids can be dissolved in phenol in presence of a small quantity of hydrochloric acid; certain more highly condensed humin substances are also soluble in phenol. The solubility can be employed in the determination of humin substances in fossil fuels. A. A. ELDRIDGE.

Humic acids in coal and lignite. F. POD-BREZNIK (Bull. Inst. Pin, 1928, 193-196, 209-214, 237-238; Chem. Zentr., 1929, i, 1701).—Humic acids from Siorac-de-Belves (Dordogne) lignite, by repeated treatment with sodium hydroxide followed by hydrochloric acid, were obtained as a brownish-black powder; extraction with alcohol afforded hymatomelanic acid, which can also be obtained by treatment of coal with acetone. The calcium and barium salts are amorphous. The mol. wt. of humic acid is about 1120, and that of hymatomelanic acid (if tetrabasic) about 720. Two samples of coal contained 38.32 and 48.72%, respectively, of humic acids. The composition of humic acid corresponds with the formula $C_{51}H_{58}O_{26}$. The relation of the humic acids to the age and coking properties of the coal is discussed. A. A. ELDRIDGE.

Condensation of aliphatic aldehydes with malonic acid and formation of new ab-unsaturated fatty acids. B. ZAAR (Ber. Schimmel, 1929, 297-308).-Condensation of aliphatic aldehydes with malonic acid in the presence of primary and secondary bases (Knoevenagel's method) yields only By-unsaturated acids, whilst the use of tertiary bases as condensing agents (Harding and Weizmann, J.C.S., 1910, 97, 299) gives mainly $\alpha\beta$ -unsaturated acids together with 5-10% of the $\beta\gamma$ -compound. The presence of the latter is due to small amounts of primary and secondary bases in the pyridine used as a condensing agent and not to migration of the double linking under the influence of sulphuric acid during the conversion of the $\beta\gamma$ -acid into the lactone. Thus condensation of *n*-heptaldehyde with malonic acid in the presence of piperidine or diphenylamine gives Δ^{β} -octenoic acid, b. p. 114—115°/2 mm., d^{x_1} 0.929, n²⁰ 1.44842, solidification point -4.4° (chloride, b. p. 80-81°/4.5 mm., d²⁰ 0.9550; amide, m. p. 74.5-75°), which is converted by 85% sulphuric acid at 80° into the corresponding lactone, b. p. 113-114°/ 4 mm. With pyridine as a condensing agent the product is Δ^{α} -octenoic acid (86.24% yield), b. p. 130—132°/2 mm., d^{15} 0.9316, n_D^{20} 1.45942, solidification point -0.9° , together with only 5% of the Δ^{β} -acid (determined as the lactone). Similarly, from the appropriate aldehyde are obtained Δ^{a} -nonenoic acid, b. p. 148-149°/4.5 mm., d15 0.9280, n2 1.46161, solidification point 8.5° (chloride, b. p. 95-97°/2.5 mm., d²⁰ 0.9640; amide, m. p. 122-122.5°), and a small yield of the Δ^{β} -acid isolated as the corresponding lactone, b. p. 125-127°/3.5 mm.; △ª-undecenoic acid, b. p. 164-165°/2 mm., d²⁰ 0.9130, n²⁰ 1.46390, solidification point 18° (chloride, b. p. 122-124°/2.5 mm., d²⁰ 0.9430; amide, m. p. 113.5-114.5°); and Δ^{a} -dodecenoic acid, b. p. 169—171°/2 mm., d^{30} 0.8995, n³⁰ 1.46121, solidification point 27.9° (chloride, b. p. 131°/3 mm., d²⁰ 0.9380; amide, m. p. 116°).

J. W. BAKER.

New homologues of crotonaldehyde. B. ZAAR (Ber. Schimmel, 1929, 309-316).—Homologues of crotonaldehyde are prepared by condensation of higher saturated aliphatic aldehydes with acetaldehyde in the presence of anhydrous zinc chloride under pressure at temperatures varying between 125° and 190°. Thus *n*-heptaldehyde furnishes α -ethylidenen-heptaldehyde (20-25% yield), b. p. 57-59°/3 mm., d¹⁵ 0.8584, n_D^{∞} 1.45362, purified through its semicarbazone, m. p. 168-168.5° (oily oxime; p-bromophenylhydrazone, m. p. 63-64°; p-nitrophenylhydrazone, m. p. 102-103°), and is oxidised by silver oxide to a-ethylidene-n-heptoic acid, b. p. 118-124°/ 3.5 mm. (amide, m. p. 100°), and reduced with zinc and acetic acid to the acetate, b. p. 74.5-77°/2.5 mm. of a-ethylidene-n-heptyl alcohol, b. p. 82.5°/4.5 mm., Similarly from the appropriate aldehyde are obtained : a-ethylidene-n-butaldehyde, b. p. 34-38°/14 mm., d¹⁵ 0.8723, np 1.44762 (semicarbazone, m. p. 194-195°; p-nitrophenylhydrazone, m. p. 154.5-155.5°; m-nitrobenzhydrazone, m. p. 144-145°); a-ethylidene-n-octaldehyde, b. p. 70-75°/2.5 mm., d15 0.8630, np 1.45412 (semicarbazone, m. p. 162-163°); a-ethylidene-n-decaldehyde, b. p. 99-103°/3 mm., d15 0.8640, np 1.45712 (semicarbazone, m. p. 163-163.5°). J. W. BAKER.

Magnesium compounds derived from propargyl acetal. J. GRARD (Compt. rend., 1929, 189, 541-543).—'The action of magnesium methyl bromide on propargyl acetal gave magnesium yy-diethoxy- Δ^{a} -propinenyl bromide (I) and magnesium γ -ethoxy- Δ^{a} -butinenyl bromide (II). Interaction of I with acetaldehyde gave β -hydroxy- ε -diethoxy- Δ^{γ} -pentinene, d²² 0.995, n²⁵ 1.446, which reacted with urethane to give the compound OH·CHMe·C:C·CH(NH·CO₂Et)₂, m. p. 168-168.5°. With iodine I yielded a-iodoyy-diethoxy-ƻ-propinene, m. p. 7-8°, d[™] 1.533, n^{22} 1.502, which when heated with alcoholic iodine yielded aß stri-iodoacraldehyde, m. p. 129-130°. aaδδ-Tetraethoxy-Δ^β-butinene, b. p. 102-105°/3 mm., m. p. 18°, d^{22} 0.9526, n^{30} 1.431, which with urethane yielded a product, m. p. 300°, is described. The action of water on II gave γ -ethoxy- Δ^{α} -butinene, b. p. $87-88^{\circ}, d_4^{22} 0.8075, n_p^{23} 1.402$, which with ammoniacal silver nitrate yielded a monosilver derivative (III) and with iodine $\alpha\alpha\beta$ -tri-iodo-y-ethoxy- Δ^{α} -butene, m. p. 47-48°. With carbon dioxide II gave γ -ethoxy- Δ^{α} -pentinenoic acid, b. p. 107-108°/4 mm., d_4^{α} 1.0514, $n_{\rm D}^2$ 1.458, the *potassium* salt of which, when treated with silver nitrate, loses carbon dioxide to give III. Treatment of the potassium salt with aqueous copper sulphate gave a *dicuprous* derivative of β-hydroxy- γ -ethoxy- Δ^{α} -butene and carbon dioxide. Sodium γ -ethoxy- Δ^{α} -pentinenoate reacted with ethyl iodide to give ethyl γ -ethoxy- Δ° -pentinenoate, b. p. 68-70°/ 3 mm., d^{22} 0.842, n_{D}^{22} 1.444, which was also obtained by treatment of II with ethyl carbonate.

A. A. GOLDBERG.

Structure of bimolecular lactolides. M. BERG-MANN and A. MIEKELEY (Ber., 1929, 62, [B], 2297-2303).-Chemical evidence in favour of the main valency conception of certain bimolecular lactolides is afforded by the catalytic hydrogenation of lactol acetates of β -lactaldehyde and aldol to acetals of the type I, which is best explained by the following scheme : $0 < CHR \cdot CH_2 \cdot CH(OAc) > 0 \xrightarrow{+H_*} OCH(OAc) \cdot CH_2 \cdot CHR > 0$

$$0 < CHR \cdot CH_2 \cdot CH(OAc) > 0 - CH_2 - CH_2 - CH_2 - CHR > 0 - CHR = CHR + CH$$

(I) OAC•CHR•CH₂•CH $<_{O-CH_2}^{O-CHR}$ >CH₂ (R=H or Me).

Further, Bergmann and Weil (unpublished work) have prepared a methyl-lactolide of benzoin, m. p. 297°, and a transformation product therefrom, the production of which is most readily explained on the basis of the bimolecular, main valency structure,

 $CHPh < CPh(OMe) \cdot O > CHPh.$ A fundamental error has been discovered in the proof of unimolecular structure based on measurements of vapour density. The use of porcelain fragments, asbestos, or silver vessel in the Bleier-Kohn apparatus leads to the catalytic decomposition of the small amounts of lactolide, thus giving a far too low mol. wt. This decomposition is not observed in control experiments in which larger amounts of lactolide are heated in glass vessels for considerable periods at the temperature of the determination, frequently even if asbestos is present. In the case of acetomethyllactolide the decomposition leads to methyl alcohol and a substance, C7H12O3, m. p. 60-61°/15 mm. Analogously, methyl alcohol is obtained from the methyl-lactolide of oxycyclohexanone and acetic acid from the lactol acetate of acetaldol. If the determinations of the vapour densities of lactolides are made in the absence of catalysts which cause rapid decomposition and at a sufficiently low temperature, values are obtained for the lactolides of glycollaldehyde, acetol, β-lactaldehyde, aldol, and oxycyclohexanone which indicate the bimolecular form. The methyl- and ethyl-lactolides of salicylaldehyde appear unique, since they are unimolecular in phenol. H. WREN.

Determination of the configuration of oximes. T. P. RAIKOWA (Ber., 1929, 62, [B], 2142-2149; cf. this vol., 911).—The "nitrile method" for the determination of configuration is applicable only to those aldoximes which do not pass by desmotropic change into *\psi*-aldoximes, and hence, according to the Hantzsch-Werner hypothesis, exist in two stereoisomeric forms. Aldoximes which do not contain a methyl or methylene group in juxtaposition to the oximino-group belong to this class. Aldoximes of the type R·CH2·CH:N·OH (in which R is any simple or compound radical) which can isomerise to ψ -aldoximes and therefore, contrary to the Hantzsch-Werner theory, exist only in one form, cannot be examined by the nitrile method. The "Beckmann transformation" method can be applied to the determination of the configuration of ketoximes which cannot undergo desmotropic change and therefore exist in two stereoisomeric forms, but not to those in which desmotropic change is possible and of which only one form exists. There is no method of determining the configuration of aldoximes and of ketimines which, contrary to the Hantzsch-Werner theory, H. WREN. exist in only one modification.

Electrolytic reduction of acetone at a mercury cathode. C. J. HAGGERTY (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 5 pp.).-By the electrolysis of acetone dissolved in 40% sulphuric acid solution using a mercury cathode, varying amounts of mercury diisopropyl were obtained and very little isopropyl alcohol seemed to be formed (cf. Tafel, A., 1902, ii, 442; 1906, i, 941).

H. J. T. ELLINGHAM.

Reduction of acetone by magnesium in presence of anhydrous aluminium chloride. M. I. USCHA-KOV (Z. anorg. Chem., 1929, 183, 140-150).-By treatment of an ethereal solution of anhydrous
aluminium chloride with dry acetone the compound $Al_3Cl_9,5COMe_2$, m. p. 110—114°, has been prepared. Dilute solutions of anhydrous aluminium chloride in acetone contain the ions Cl' and $AlAc_6$ ^{···} and exhibit a conductivity maximum at about 10 mol.-% of aluminium chloride; the chlorine ion may be quantitatively precipitated by sodium iodide solution, and from the resulting solution the compound $AlI_3,COMe_2$ has been prepared. In dilute acetone solutions of aluminium chloride magnesium reduces the

 $[Al(COMe_2)_6]^{\cdots}$ ion, but in more concentrated solutions (25 mol.-% of aluminium chloride) the ion $[Al_2(COMe_2)_6Cl_3]^{\cdots}$ is reduced; by treatment of the

reaction products with water pinacol is obtained. H. F. GILLBE.

Ketals of hydroxyketones. V. V. EVLAMPIEV (Ber., 1929, 62, [B], 2386-2389).-The action of ethyl orthoformate on acetol in presence of hydrogen chloride gives the corresponding crystalline ethyllactolide, $\left(\text{OEt-CMe} < \stackrel{\text{CH}_2}{O}\right)_2$, m. p. 73-2-73-5°, whereas in presence of sulphuric acid a compound, $C_5H_{10}O_2$, was obtained, the molecular constitution of which could not be established by observations in freezing benzene. Chloroacetone, ethyl orthoformate, ethyl alcohol, and a little sulphuric acid yield a-chloroββ-diethoxypropane, b. p. $52-53^{\circ}/14$ mm.; α-bromo- $\beta\beta$ -diethoxypropane, d_0° 1.1075, is similarly obtained, whereas in the preparation of α -iodo- $\beta\beta$ -diethoxy-propane, b. p. 69°, the addition of moist silver oxide is advisable. Attempts to replace the halogen atoms of these compounds by OH or OAc were unsuccessful, since reaction either could not be caused to occur or proceeded with rupture of the molecule. B-Ketopropyl acetate is converted by ethyl orthoformate, ethyl alcohol, and a trace of sulphuric acid into $\beta\beta$ -diethoxypropyl acetate, b. p. $78.5-79.5^{\circ}(\text{corr.})/8$ mm., d_0° 0.9990, hydrolysed by aqueous calcium hydroxide at 80-90° to BB-diethoxypropyl alcohol (acetol ethylketal), b. p. $68-68\cdot5^{\circ}(\text{corr.})/9 \text{ mm.}, d_0^{\circ}$ 0.9828, mol. wt. 138.0 in freezing benzene; acetic anhydride in ether re-converts the alcohol into its acetate. The ketal is stable in neutral and alkaline aqueous solution, but is readily hydrolysed by traces H. WREN. of acid.

Form and size of highly complex molecules by spreading of unimolecular layers on a water surface. II. Comparison of polysaccharides and degraded polysaccharides. J. R. KATZ and P. J. P. SAMWEL (Annalen, 1929, 474, 296-300; cf. A., 1928, 937).—The observation of Bergmann, Herzog, and Jancke (A., 1928, 822) that biosan and alkali-soluble cellulose have the same X-ray spectra is confirmed. Although the work of Hess and Friese (A., 1927, 861) indicates that biosan is the anhydride of a disaccharide, complete agreement is found between the figures for area per C₆H₁₀O₅ unit and the thickness of unimolecular films given by derivatives of biosan and cellulose. Inulin acetate degraded by heating in tetrahydronaphthalene, normal inulin acetate, and the acetate of a cellulose degradation product described by Pringsheim (A., 1928, 1226) which cryoscopically appears to consist of a single $C_6H_{10}O_5$ unit, give the same values for area

per $C_6H_{10}O_5$ unit, thickness, compressibility, and resistance to fracture, which are similar to those obtained for cellulose triacetate. It appears that the space occupied by a $C_6H_{10}O_5$ unit and its side-chains in a unimolecular layer is largely unaffected, whether the $C_6H_{10}O_5$ units are united in large molecules by polymerisation or association, or whether they are present (in the unimolecular layer) as freely mobile individuals. The agreement found between the foregoing properties and the forms of the compressibility curves of biosan derivatives and maximally degraded polysaccharides is unexpected, and it is suggested that the latter are not degraded to the degree indicated by their cryoscopic behaviour.

C. W. SHOPPEE.

Oxidation of carbohydrates, fats, and nitrogenous substances by hydrogen peroxide and ferric salts. S. N. CHAKRABARTI and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 617-626).-Oxidation of a 1% solution of potassium stearate, oleate, and palmitate, dextrose, starch, alanine, and lactic acid with 12% hydrogen peroxide in presence of a small amount of ferric sulphate at 37° gives in all cases some reducing substances. Determinations of the volatile acetone-like products formed during similar oxidation of seven sugars, dextrin, inulin, glycogen, egg-white and -yolk, butter, and cholesterol, by titration with iodine show that varying amounts are produced from all the substances quoted. Oxidation of carbohydrates in presence of nitrogenous compounds or fats, fats in presence of nitrogenous substances, and a mixture of fats, carbohydrates, and nitrogenous compounds causes a decrease in the amount of reducing substances formed. The oxidation of a group of compounds is, therefore, retarded by the addition of a second group of substances. The amounts of acetone-like substances produced during the oxidation of mixtures of fats and carbohydrates are decreased further with increase in the added carbohydrate; retardation of the oxidation is greatest with starch and sucrose.

The disappearance of the acctone substances from the body after injection of insulin is considered to be due to a more complete oxidation of fats following the primary oxidation of the dextrose. H. BURTON.

Degradation of *l*-arabinose. V. DEULOFEU and R. J. SELVA (Anal. Asoc. Quím. Argentina, 1929, **17**, 13—24).—See this vol., 427.

Deoxyribose and deoxyxylose and their bearing on thyminose. P. A. LEVENE and T. MORI (J. Biol. Chem., 1929, 83, 803-816).—The deoxypentose obtained by hydrolysis of the thymonucleosides is designated thyminose. Although this compound titrates as a β -deoxyaldopentose and yields lævulic acid when heated with dilute sulphuric acid it is not identical with deoxyribose or with deoxyxylose. Thyminose (cf. this vol., 590) has m. p. 150° after softening at 78°, $[\alpha]_{D}^{\alpha} -90.6°$ to -40.0° in pyridine, -60.0° to -50.0° in water (as.-phenylbenzylhydrazone, m. p. 128°, $[\alpha]_{D}^{\alpha} -17.5°$). Acetobromoxylose yielded, with zinc and acetie acid, d-diacetylxylal, b. p. 103-107°/1.5-1.8 mm., m. p. 40°, $[\alpha]_{D}^{\alpha} -314.7°$ in chloroform, which was hydrolysed with barium hydroxide to d-xylal, b. p. 109112°/1·2 mm., m. p. 49—50°, $[\alpha]_{11}^{31}$ —254·5° in water; with dilute sulphuric acid this yielded d- β -deoxyxylose, m. p. 92—96°, $[\alpha]_{15}^{35}$ —40·25° to +50·75° in pyridine, —22·5° to —2·0° in water (as.-*phenylbenzylhydrazone*, m. p. 116—118°, $[\alpha]_{15}^{35}$ +13·5° in pyridine). Similarly from acetobromoarabinose there was obtained 1- β deoxyribose, m. p. 80·5—90°, $[\alpha]_{15}^{35}$ +2·75° to +2·13° in pyridine, +2·88° to 2·13° in water (as.-*phenylbenzylhydrazone*, m. p. 115—117°, $[\alpha]_{15}^{35}$ +7·8° in pyridine).

C. R. HARINGTON.

Determination of pentosans. C. KULLGREN and H. TYDÉN (Handl. Ing. Vetenskaps-Akad. Stockholm, 1929, No. 94, 62 pp.).-A very detailed investigation of the Tollens method of determining pentoses and pentosans by conversion into furfuraldehyde is recorded. The 12% hydrochloric acid used in the older method is open to objection, since as the distillation proceeds the composition tends to approach the azeotropic mixture, 20.2%. It is replaced by 13.15% hydrochloric acid saturated with sodium chloride, a mixture of constant b. p. This change leads also to a quicker distillation of the furfuraldehyde, since the distillation factor (ratio of furfuraldehyde in the vapour to that in the liquid phase) rises from 6.0 to 14.7. Under these conditions 96.9% of the furfuraldehyde formed can be distilled. Precipitation of the distillate with phloroglucinol or barbituric acid is replaced by the much quicker titration with potassium bromate-bromide mixture. The excess of bromate is titrated by thiosulphate after the addition of potassium iodide (cf. Powell and Whittaker, A., 1924, ii, 354). In a solution with a slight excess of acid each molecule of furfuraldehyde is initially equivalent to 2 atoms of bromine, but this value rises to 4.5 atoms within 4 days. This is interpreted as a rapid initial oxidation of the aldehydic group followed by a slow general oxidation (cf. Pervier and Gortner, A., 1924, ii, 71). Using a catalyst of ammonium molybdate to hasten the liberation of bromine from the bromide-bromate mixture, bromine absorption-time curves are given for various concentrations of free acid. In a solution containing 0.5-1% of acid theoretical bromine absorption occurs in about 4 min. The amount of bromate in excess is of small importance. Contrary to the results of Pervier and Gortner (A., 1923, ii, 884), the use of steam during the distillation does not lead to any increased yield of furfuraldehyde. The formation of humic substances, responsible for the lack of theoretical yield of furfuraldehyde, proceeds from the pentose and not from the furfuraldehyde.

By working under completely standardised conditions reproducible results may be obtained. The original communication should be consulted for details. T. H. MORTON.

Conversion of methylpentoses into methylfurfuraldehyde. E. VOTOČEK and F. RÁC (Coll. Czech. Chem. Comm., 1929, **1**, 516—520).—The formation of methylfurfuraldehyde by the action of mineral acids on sugars is not limited to aldehydic methylpentoses, but is also given by the keto-compounds. 2-Ketorhamnose, prepared by boiling rhamnosephenylosazone with benzaldehyde in the presence of a large excess of water, concentrating the aqueous

solution in a vacuum, and treating the resultant product with zinc and acetic acid, gives a 20% yield of methylfurfuraldehyde when distilled with 12% hydrochloric acid. 2-Ketorhamnose yields a violet and rhamnose a yellowish-brown coloration with carbazole. A. I. VOGEL.

Synthetic hexosephosphates and their phenylhydrazine derivatives. A. L. RAYMOND and P. A. LEVENE (J. Biol. Chem., 1929, 83, 619-630).-Dextrose and lævulose were phosphorylated directly by treatment with phosphoryl chloride and pyridine; diisopropylideneglucose and α - and β -diisopropylidenefructose were phosphorylated as above and the isopropylidene residues removed by graduated hydrolysis with hydrochloric acid; the resulting phosphoric esters were treated with phenylhydrazine. The ester from dextrose gave no crystalline products; the ester from diisopropylideneglucose gave an anhydrohexos-azone, m. p. 156—159°, $[\alpha]_{15}^{\infty}$ —146°, apparently identical with the compound prepared by Levene and others (this vol., 683) from α -diisopropylidenefructose through the phosphate; the ester from lævulose gave glucosazone; the ester from a-diisopropylidencfructose yielded a diphenylhydrazine salt of a phosphohydrazone, $C_{24}H_{35}O_8N_6P$, m. p. 96—98°, decomp. 123—125°, $[\alpha]_{15}^{m}$ —50.6° to —35.0° in pyridine-methyl alcohol, and the anhydrohexosazone mentioned above; the ester from β -diisopropylidenefructose gave a phenylhydrazine salt of a phosphohydrazone, $C_{18}H_{27}O_8N_4P$, which darkened at 107– 110° after sintering at 96–97°, $[\alpha]_{15}^{5}$ –15.0° to -33.6° in pyridine-methyl alcohol, and glucosazone. C. R. HARINGTON.

Transformation reactions in the carbohydrate group. II. Configuration of the furoid γ -glucose and its *iso*propylidene derivatives. K. JOSEPHSON (Ber., 1929, **62**, [B], 1913—1916).—A theoretical paper in which arguments are adduced in



favour of the structure I for furoid glucose diisopropylidene ether. The O ready migration of the acetyl group in 3-acetylglucose isopropylidene ether from position 3 to 6

and the easy formation of Fischer's anhydroglucose from derivatives of *iso*propylideneglucose are simply explained. To α - and β -glucofuranose the structures II and III are assigned.



Acetone [isopropylidene] compounds of the sugars and their derivatives. XIV. isoDiisopropylideneglucose. H. OHLE and L. VON VARGHA (Ber., 1929, 62, [B], 2425—2434; cf. A., 1928, 871). p-Toluenesulphonylglucose isopropylidene ether, m. p. 108°, is hydrolysed to the non-crystalline p-toluenesulphonylglucose, which, when treated with acetic anhydride and pyridine, gives a mixture of 6-ptoluenesulphonyl-1 : 2 : 3 : 4-tetra-acetyl- β -glucopyranose, m. p. 200°, $[\alpha]_D^{30} + 23.97^{\circ}$ in chloroform, and (?) 6-p-toluenesulphonyl-1 : 2 : 3 : 4-tetra-acetyl- α -glucopyranose (+H₂O), m. p. 129—130°, $[\alpha]_D^{30} + 105.7^{\circ}$ in chloroform. The p-toluenesulphonyl group in the isopropylidene sugar must therefore be in position 6.

The position of the p-toluenesulphonyl group in p-toluenesulphonylisoglucose diisopropylidene ether, prepared from 6-p-toluenesulphonylglucose isopropylidene ether, m. p. 108° (see above), is established as follows: (1) The dissopropylidene compound is converted in poor yield by hydrogen bromide and glacial acetic acid into a non-crystalline bromo-derivative, transformed by methyl alcohol and silver carbonate into 6-p-toluenesulphonyl-2:3:4-triacetyl-β-methylglucoside (cf. Helferich and others, A., 1927, 1174); (2) partial hydrolysis of the dissopropylidene compound by 80% acetic acid (optically controlled) affords 6-p-toluenesulphonylglucose isopropylidene ether; (3) hydrolysis of 6-p-toluenesulphonylisoglucose diisopropylidene ether by alcoholic ammonia at 100° affords a mixture of isoglucosyl-6-amine diisopropylidene ether (I) (p-toluenesulphonate, m. p. 172.5° , $[\alpha]_{D}^{20} + 30.96^{\circ}$ in water), diisoglucosyl-6-imine diisopropylidene ether, $[\alpha]_{D}^{\circ} + 41.4^{\circ}$ in chloroform [p-toluenesulphonate, m. p. 183° (decomp.), $[\alpha]_{11}^{20} + 20.1^{\circ}$ in chloroform], and glucoseen (5:6-)diisopropylidene ether (II), [a] $+33.2^{\circ}$ in chloroform; the amine is hydrolysed by



acids to the known glucosyl-6-amine, identified as the *p*-toluenesulphonate of its hydrazone. (4) Direct hydrolysis of *p*-toluenesulphonylisoglucose diisopropylidene ether by alcoholic sodium hydroxide or methoxide yields a mixture of isoglucose diisopropylidene ether and glucoseen diisopropylidene ether which cannot be separated into its components. On the other hand, isoglucose diisopropylidene ether is readily obtained by deamination of isoglucosyl-6amine diisopropylidene ether and is converted by *p*-toluenesulphonyl chloride into the initial *p*-toluenesulphonylisoglucose diisopropylidene ether. The accetate, b. p. 140°/0.4 mm., $[\alpha]_0^m + 32.8^\circ$ in chloroform,



And benzoate, b. p. 200° (bath temp.)/0.6 mm., [\$\alpha]\$\vec{n}\$ +29.5° in chloroform, of isoglucose disopropylidene ether arc non-crystalline. The methyl ether (III, R=Me), b. p. 105°/ 0.1 mm., [\$\alpha]\$\vec{n}\$ +15.3° in chloroform, is hydrolysed to glucose 6-methyl ether,

identified by its osazone. The constitution III (R=H) is thus established for *iso*glucose di*iso*propylidene ether.

isoGlucose diisopropylidene ether is transformed by methyl iodide and silver carbonate into the corresponding methyl carbonate, $C_{14}H_{22}O_8$, m. p. 111°, $[\alpha]_{2}^m$ +38·4° in chloroform. H. WREN.

Acetone [isopropylidene] compounds of sugars and their derivatives. XV. the 5:6-Anhydroglucose isopropylidene ether and the 5-methyl ether of glucofuranose. H. OHLE and L. VON VARGHA (Ber., 1929, 62, [B], 2435-2444; cf. preceding abstract).-Hydrolysis of 6-ptoluenesulphonylglucose isopropylidene ether by sodium methoxide affords 5: 6-anhydroglucose isopropylidene ether (I), m. p. 133.5° , $[\alpha]_{10}^{20} - 26.5^{\circ}$ in water, identical with the compound described by Freudenberg and others (A., 1928, 1223). It is characterised by unusual instability, being hydrolysed to dextrose by 80% acetic acid at the ordinary temperature. It is converted by sodium hydroxide into glucose isopropylidene ether, m. p. 157°, and other products derived from mono- and di-hexoses, from which d-idose isopropylidene ether is isolated in a nonhomogeneous condition. Treatment with acetic acid and pyridine transforms the crude ether into nonhomogeneous triacetyl-d-idose isopropylidene ether, b. p. $130-135^{\circ}/0.5$ mm., $[\alpha]_{D}^{30} + 58.3^{\circ}$ in chloroform, converted by successive treatment with sodium hydroxide and dilute sulphuric acid into d-idose, identified as the phenylosazone, m. p. 168°. Slightly impure trimethyl-d-idose isopropylidene ether, b. p. $92-93^{\circ}/0.007$ mm., $[\alpha]_{\rm p}$ +66.2° in methyl alcohol, is described. The production of idose isopropylidene ether (II) affords further proof of the constitution of the original material, since, under the conditions adopted, only a 5:6-anhydroglucose isopropylidene ether could undergo epimerisation to an idose derivative.



Ammonia appears to open the ethylene oxide ring of 5:6-anhydroglucose isopropylidene ether almost entirely in one direction, giving isopropylidene-glucosyl-6-amine, characterised by hydrolysis and conversion into the p-toluenesulphonate of glucosyl-6aminephenylhydrazone. Addition of sodium methoxide appears to lead exclusively to isopropylideneglucofuranose 5-methyl ether, m. p. 71–72°, $[\alpha]_{\rm b}^{20}$ -6.42° in chloroform, identified by conversion into isopropylideneglucose trimethyl ether, b. p. 138–140°/12 mm., $[\alpha]_{\rm p}$ -27.1° in methyl alcohol, and thence into glucofuranose 2:3:5:6-tetramethyl ether, b. p. $120^{\circ}/0.03 \text{ mm.}, [\alpha]_{p} - 7.28^{\circ}$ in water (cf. Irvine and Scott, J.C.S., 1913, **103**, 574). Hydrolysis of isopropylideneglucose methyl ether affords d-glucofuranose 5-methyl ether, m. p. 143-144°, [a]? +101.2° to +59.92° in water in 3 hrs. [phenylosazone, m. p. 180° (decomp.), $[\alpha]_{\rm D}$ -101.9° to -86.6° (incomplete) in pyridine]. It reduces Fehling's and ammoniacal silver solution powerfully when heated, but does not react with sulphurous acid-magenta. The possible existence of glucofuranose forms in the equilibrium mixtures derived from dextrose is suggested.

Zemplén's method of hydrolysis appears applicable only to such compounds as contain the *p*-toluenesulphonyl group very loosely united. 5:6-Di-*p*toluenesulphonylglucose *iso*propylidene ether is smoothly converted into 5-*p*-toluenesulphonyl-3:6anhydroglucose *iso*propylidene ether. 3-*p*-Toluenesulphonylglucose di*iso*propylidene ether, 6-*p*-toluenesulphonylglucose di*iso*propylidene ether, 3:5:6tri-*p*-toluenesulphonylglucose *iso*propylidene ether, and 5-*p*-toluenesulphonyl-3:6-anhydroglucose *iso*propylidene ether are unaffected. H. WREN.

New dicarbonyl sugars. B. HELFERICH and E. HIMMEN (Ber., 1929, 62, [B], 2136—2141; cf. A., 1928, 1221).—The preparation of triacetyl- β -methyld-glucoseenide is more advantageously effected from triacetyl- β -methyl-d-glucoside 6-bromohydrin than from the corresponding iodohydrin (cf. loc. cit.). β -Methyl-d-glucoseenide is hydrolysed by cold 0-1N-

СН₃ С:О ОН·С·Н Н·С·ОН ОН·С·Н ОН·С·Н СНО

(I.)

sulphuric acid to the compound (I), which, by reason of its analogy to Fischer's *d*-isorhamnose, is termed isorhamnonose. It has m. p. $125 \cdot 5 - 126^{\circ}$ (corr.), $[\alpha]_{0}^{16} - 15 \cdot 2^{\circ}$ to $-33 \cdot 6^{\circ}$ in water. It reduces Fehling's solution very strongly when heated gradually at the ordinary temperature. It immediately yields a *di*-p-nitrophenyl-

hydrazone, m. p. 120.5° (corr.; decomp.), $[\alpha]_{\rm b}^{\rm p} - 83.5°$ in pyridine. Similarly, disopropylidencgalactose ζ -iodohydrin is transformed by silver fluoride and pyridine into disopropylidene-*d*-galactoseen, m. p. 86-87° (corr.), $[\alpha]_{\rm b}^{\rm ls} - 136°$ in *s*-tetrachloroethane, $[\alpha]_{\rm b}^{\rm s} - 142.6°$ in chloroform (cf. Freudenberg and Raschig, this vol., 427), hydrolysed to the noncrystalline fuconose [*di*-p-nitrophenylhydrazone, m. p. 209-210° (corr.; decomp.), $[\alpha]_{\rm b}^{\rm s} + 59°$ in pyridine].

209—210° (corr.; decomp.), $[\alpha]_{10}^{\infty}$ +59° in pyridine]. 2:3:4-Triacetyl- β -methyl-d-glucoside 6-iodohydrin is transformed by dry technical silver fluoride in boiling methyl alcohol into a mixture of triacetyl- β methyl-d-glucoscenide and 2:3:4-triacetyl- β -methylglucoside 6-methyl ether, m. p. 107—108°. The lastnamed compound is transformed by methyl-alcoholic ammonia into β -methyl-d-glucoside 6-methyl ether, m. p. 133—135° (corr.), $[\alpha]_{12}^{\infty}$ -27.0° in water, which is not hydrolysed by emulsin. H. WREN.

Rotatory power and structure in sugar group. XX. Two isomeric crystalline compounds of *d*-mannose with calcium chloride. J. K. DALE (J. Amer. Chem. Soc., 1929, 51, 2788—2795).—When β -*d*-mannose is mixed with a concentrated aqueous solution of calcium chloride at the ordinary temperature the compound (I), C₆H₁₂O₆, CaCl₂, 4H₂O, m. p. 101—102° (corr.), crystallises. Evaporation of an alcoholic solution of I on the water-bath gives the compound (II), β -C₆H₁₂O₆, CaCl₂, 2H₂O, m. p. 159— 160° (corr.; decomp.). Conversion of II into I is effected by the addition of water to an alcoholic solution of II and subsequent evaporation at the ordinary temperature. Details are also given for the preparation of II and II from vegetable ivory. Acetylation of II with acetic anhydride and pyridine affords β -mannose penta-acetate. Mutarotation of II in water, $[\alpha]_{50}^{50}$ -7.7° after 2 min. \longrightarrow +6.73° at

 ∞ , is normal, but I shows an unusual course, $[\alpha]_{b}^{*}$ -23.68° after 0.75 min. $\longrightarrow +11.35^{\circ}$ after 23 min. $\longrightarrow +6.5^{\circ}$ at ∞ . Extrapolation of the mutarotation curve to zero time indicates an initial rotation for the mannose constituent of $[\alpha]_{D}$ about -60°, and it is presumed that the sugar residue of I is the β -form of the 1:5-ring form of mannose (cf. Hudson, A., 1926, 714). H. BURTON.

Crystalline difructose anhydride from hydrolysed inulin. R. F. JACKSON and S. M. GOERGEN (Bur. Stand. J. Res., 1929, 3, 27–38).—Although inulin consists solely of lævulose residues, hydrolysis gives only 91.8% of lævulose. The remainder contains 3% of another reducing sugar and 5.2% of an unformentable mixture of disaccharides which is hydrolysed by 0.4N-sulphuric acid at 100° to lævulose exclusively. Acetylation of the disaccharides yields a crystalline *hexa-acetate*, m. p. 137°, $[\alpha]_D^{20} + 0.54^{\circ}$ (in chloroform), from which on hydrolysis with barium hydroxide a crystalline *dilævulose anhydride*-I, $[\alpha]_D^{30}$ +27° (in water), is obtained. The acetylation mother-liquors contain one or more unisolated hexaacetates, mean $[\alpha]_D^{20} + 31^{\circ}$. C. HOLLINS.

Reaction between sugars and amino-acids. V. H. VON EULER, G. RENGMAN, and E. BRUNIUS (Svensk Kem. Tidskr., 1929, 41, 203-209; cf. this vol., 175).-Decolorisation of a methylene-blue solution by a mixture of maltose and glycine in aqueous solution attains measurable velocity at p_{π} 8, the velocity then increasing with increasing $p_{\rm fl}$. Decolorisation occurs the more slowly the longer is the incubation period, the p_{π} value also falling, whilst a corresponding fall in rotation is also observed. Maltose thus behaves in an analogous manner to dextrose. A similar relationship exists between the velocity of decolorisation of methylene-blue with a mixture of galactose and glycine in aqueous solution and the p_{π} value, but, in this case, the maximum decrease in the rotation occurs after 1.5 hrs. The specificity of enzyme action is discussed.

J. W. BAKER.

Influence of hydrogen sulphite solutions on sugars at higher temperatures. II. E. HAGG-LUND and H. URBAN (Ber., 1929, 62, [B], 2046— 2051; cf. this vol., 428).—Mannose is converted by heating with solutions of calcium hydrogen sulphite and sulphurous acid into mannonic acid; a reversion to polymeric sugars is not observed. Possibly, unstable sulphonic acids are formed as intermediate products.

Under certain conditions, lævulose becomes oxidised to $\alpha\beta\gamma$ -trihydroxy-*n*-butyric acid. The main product is apparently a fructosesulphonic acid isolated as the brucine salt, C₂₃H₂₆O₄N₂,H₂SO₃,C₆H₁₂O₆, m. p. 246– 247° (decomp.), and barium salt,

247° (decomp.), and barium salt, $(C_6H_{12}O_6,H_2SO_3)_2Ba,2H_2O$. The acid decomposes with evolution of sulphur dioxide when its aqueous solution is concentrated to a syrup. Boiling 10—15% sulphuric acid causes slow loss of sulphur dioxide. It is stable toward cold 2N-sodium hydroxide, slowly decomposed by the hot reagent. The acid and its salts slowly reduce Fehling's solution. The formation of sulphurous but not sulphuric acid as product of acid hydrolysis suggests that the sulphonic group is

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attached to a carbon atom united to a hydroxyl group. Its stability indicates that the acid is not a simple hydrogen sulphite derivative of lævulose.

H. WREN. Effect of X-rays on sucrose. M. C. REINHARD and K. L. TUCKER.—See this vol., 1248.

Alizaringlucoside and alizarinbiosides. G. ZEMPLÉN and A. MÜLLER (Ber., 1929, 62, [B], 2107– 2118).—Alizarintetra-acetylglucoside,

 $C_{14}H_6O_2(OH)\cdot O\cdot C_6H_7O_5Ac_4$, m. p. 205° after softening at 201°, is prepared by the action of silver oxide on a mixture of alizarin and acetobromoglucose in quinoline. *Alizarintetrabenzoylglucoside*, m. p. 232°, is obtained analogously. By the action of methyl-alcoholic ammonia, the tetra-acetyl and tetrabenzoyl derivatives and alizaringlucoside become transformed into the supposed diglucoside,

 $C_6H_4 < C(OH)(NH_2) > C_6H_2(O \cdot C_6H_{11}O_5)_2$, of Glaser and Kahler (A., 1927, 752). The compound does not contain acetyl or methoxyl groups. The analytical composition could not be determined exactly, but the compound is certainly a monoglucoside closely allied to alizaringlucoside; it is possibly an ammonium salt. Alizaringlucoside, m. p. 235-236°, is prepared by acid hydrolysis of the ammonia compound or by alkaline treatment of the tetra-acetyl or tetrabenzoyl glucoside.

Alizarinhepta-acetylcellobioside, m. p. 249° , is prepared from alizarin and acetobromocellobiose in presence of silver oxide and quinoline. It is transformed by acetic anhydride and pyridine into the octa-acetyl compound, m. p. 219°, and by methyl-alcoholic ammonia into the compound (?) $C_{26}H_{31}O_{14}N$, m. p. 230° after softening at 220°. Acid hydrolysis of the ammonia compound or alkaline treatment of alizarinhepta-acetylcellobioside affords alizarincellobioside, m. p. 256°. Acetobromogentiobiose and alizarin give alizarinhepta-acetylgentiobioside, m. p. 258°, which yields the octa-acetyl derivative, m. p. 232°, ammonia derivative, $C_{26}H_{31}O_{14}N$, m. p. 178—180°. Experiments with acetobromomaltose did not lead to crystalline compounds.

Ruberythric acid is certainly not identical with alizaringentiobioside. With alizarincellobioside it has a close analogy in the m. p. of the free substance and of the octa-acetyl derivative, but the identity of the compounds is not maintained. H. WREN.

Methylation of α -tetra-amylose. [SIR] J. C. IRVINE, H. PRINGSHEIM, and A. F. SKINNER (Ber., 1929, 62, [B], 2372—2378).—Repeated treatment of α -tetra-amylose with methyl sulphate and sodium hydroxide gives a product containing 36—37% of methoxyl as a maximum. Further treatment with methyl iodide and silver oxide does not cause further increase. The methylated tetra-amylose is, however, converted by the successive action of boiling thionyl chloride and sodium methoxide into a product containing 40.8% of methoxyl (maximum). Fractional extraction of a material with 37.1% or 36.1% of methoxyl with (a) boiling light petroleum, b. p. 40—60°, and (b) cold ether gave three portions which, in spite of their differing solubilities, had the same analytical composition and the same optical activity and appeared to contain tri- and di-methylglucosan residues in the ratio 1:1, 1:2, or 1:3. Hydrolysis of methylated tetra-amylose (OMe=37·1%) by boiling 1% methyl-alcoholic hydrogen chloride affords 2:3:6trimethyl- β -methylglucoside, m. p. 57° (whence 2:3:6-trimethylglucose, m. p. $110-112^{\circ}$), and a dimethylmethylglucoside, $n_{\rm D}$ 1·4738, in apparently equimolecular proportion. Hydrolysis of the dimethylmethylglucoside gives a syrupy dimethylglucose containing 7% of a monomethylglucose. It yields a lævorotatory γ -methylglucoside, but does not form a phenylosazone; attempts to condense it with acetone yield ill-defined products. Fission of methylated tetra-amylose (OMe=40·8%) gives trimethylmethylglucoside and dimethylmethylglucoside. The yields are almost exactly in the ratio 3:1.

CH-OH CH-OH	
Ó CH-OH CH-OH	
(I.) OH.O OH (II.)
└-ĊH ĊH•O	
CH ₂ -OH CH ₂ -OH	

It appears established that three of the four glucosan residues of α -tetra-amylose are symmetrical and have the constitution I or II, either of which is in harmony with the formation of 2:3:6-trimethylglucose by methylation and subsequent hydrolysis. The structure of the fourth glucosan residue which resists complete methylation is not definitely elucidated.

The formation of 2:3:6-trimethylglucose from polyamyloses indicates the possible existence in them and other polysaccharides of γ -glucose residues. In support it is found that 2:3:6-trimethyl- γ -methylglucoside and 2:3:6-trimethyl- β -methylglucoside prepared from 2:3:6-trimethylglucose are similarly hydrolysed to crystalline 2:3:6-trimethylglucose.

H. WREN.

Solubility of starch in water below the swelling temperature. M. SAMEC and N. TOMAZO (Ber., 1929, 62, [B], 2076—2078).—Contrary to the observ-ation of Hess and Smith (this vol., 914), prolonged extraction of potato starch with water at 55° removes only 0.59% as water-soluble substance; the phosphorus content and microscopic appearance of the residue is identical with that of the original material. The earlier results are possibly due to unusual amounts of free acid or to diastatic enzymes present in the material which cause enrichment of the residue in phosphorus as observed by Hess and Smith. Treatment of the residue left after extraction at 55° with water at 75-80° causes dissolution of 39.4% of the material, which includes a considerable proportion of phosphatic substances. H. WREN.

Nature of salt hydrolysis of starch considered in the light of the influence of salt on the development of bacteria. M. YASUDA (J. Biochem. Japan, 1929, 10, 259—276).—In experiments with starch and either neutral salt or peptone the hydrolysis is due exclusively to the development of bacteria, which is dependent on the salt concentration. Traces of multivalent cations have a considerable influence, and exercise a favourable effect on the transfer of oxygen to the bacteria. CHEMICAL ABSTRACTS. Inulin. VIII. H. PRINGSHEIM, J. REILLY, and P. P. DONOVAN (Ber., 1929, 62, [B], 2378—2381; cf. A., 1928, 1225).—Inulin is soluble in molten acetamide and, in concentration up to $2 \cdot 5\%$, has in it the mol. wt. required by the formula $(C_6H_{10}O_5)_2$. The carbohydrate, precipitated by alcohol from acetamide, is unchanged in elementary composition and specific rotation, but has undergone disaggregation. More prolonged action of molten acetamide transforms inulin into *inulan*, which, when freshly prepared, is freely soluble in cold water, in which it has the composition $(C_6H_{10}O_5)_2$. When preserved, it gradually becomes as insoluble in water as inulin, from which it can no longer be distinguished.

Inulin and inulan can be boiled with water in glass or quartz flasks for 5 hrs. without the reducing power attaining 1% of that of lævulose. It is inadmissible to conclude from the observation that inulin feebly reduces boiling Fehling's solution that it contains free carbonyl groups at the end of a fructose chain. Sucrose is slightly hydrolysed by water and very faintly reduces Fehling's solution without necessitating the assumption of a chain of sugar residues with terminal carbonylated groups. H. WREN.

Lignin. XI. Degradation of lignin with methylglycolic[8-methoxyethyl-alcoholic]hydrogen chloride. W. FUCHS (Ber., 1929, 62, [B], 2125-2132; cf. this vol., 1046).-Hydrochloric acid pine lignin swells rapidly in boiling 0.1N-β-methoxyethylalcoholic hydrogen chloride and, after 30 min., is mainly dissolved to a dark, viscous, difficultly filterable solution which is relatively easily filtered after boiling for a few hrs. Acetyl- and methyl-lignin, from Willstatter lignin, dissolve equally readily in the reagent in which the lignin in ordinary or methylated pine wood is almost as readily soluble. Acetylated pine wood is less easily attacked and cellulose is scarcely affected. If the solution obtained from hydrochloric acid lignin is treated with excess of water, a product is obtained (75% yield) soluble in dilute alkali hydroxide and containing 21% of methoxyl. The methylglycol derivative with diazomethane gives a product insoluble in alkali hydroxide and containing 26.5% of methoxyl. Each entering methylglycol molecule therefore corresponds with one free phenolic group, and the minimal mol. wt. of lignin is about 400. Monomethyl-lignin dissolves in β -methoxylethyl-alcoholic hydrogen chloride, giving a product containing 22.8% of methoxyl, which is soluble in alkali hydroxide. Hence, during the degradation one free hydroxyl group must be developed for every two entering methylglycol residues. This product when treated with diazomethane gives a material insoluble in alkali and containing 25.8% of methoxyl; it is very similar to the methyl ether of the methylglycol derivative of lignin. The following scheme is therefore suggested $(R'=OMe \cdot CH_2 \cdot CH_2)$,

$$\begin{array}{c} C & R(OH) \\ \| \\ C & -C_6H_4 \end{array} \xrightarrow{HC} R(OH) \\ -C(OR')_2 & HO \end{array} \xrightarrow{C_6H_3} HC & R(OMe) \\ C_6H_3 \xrightarrow{HC} C_6H_3 \xrightarrow{C_6H_3} C_{C(OR')_2} & OMe \\ C(OR')_2 & OMe \end{array}$$

Treatment of II with boiling methyl alcohol results in partial displacement of the β -methoxyethyl group. Present work, coupled with a review of the literature, suggest the mol. wt. 802 ($\pm 5\%$) as most probable for lignin.

The possibility of the rupture and reunion of components during dissolution and precipitation respectively of complex natural products is favourably discussed. The author adopts the view that large molecular compounds disintegrate into "reactals" just as a salt forms ions. A reactal is defined as a bivalent atomic group which is distinguished from the molecule by its unsaturated character and from the ion by its electrical neutrality. H. WREN.

Willstätter-lignin. B. RASSOW and P. ZICK-MANN (J. pr. Chem., 1929, [ii], 123, 189-234).-In investigations into the constitution of lignin it is essential that extraction should be effected with indifferent reagents which do not alter its structure. Attempted extraction with a large number of neutral organic solvents was found to be impossible, whilst many of the methods used by previous investigators are not free from the above objection. Owing to the resistance of lignin to hydrolysis the methods most free from objection are extraction (a) with 72%sulphuric acid, (b) with 1% hydrochloric acid under pressure, and (c) by Willstätter and Zechmeister's method (A., 1913, i, 955) with 43% hydrochloric acid at the ordinary temperature for 1 day, the last-named most nearly approaching the required conditions. Extraction of pine wood which had the composition : water 12.65; ash 0.56; pentosans 4.43; cellulose 54.7; lignin (ash-free) 30.6% by process (c) yielded a product (C, 64.2; H, 5.4%) which is acetyl-free, has 14.65% OMe ($C_{20}H_{20}O$ requires OMe 16.64%), and contains no pentosans, whilst the shortened process of Hagglund yields a product which still contains pentosans. The dark colour of the product is removed by washing with water and is due to the formation of an oxonium salt which is decomposed slowly by cold and instantly by hot water, the regenerated lignin being unaltered in composition. Most of the various colour reactions of the original wood with phenols and amines are not given by the lignin so prepared, but Klason's, Cross and Bevan's, and Maule's are typical for lignin. Lignin is unaltered by attempted reduction with active aluminium, zinc, and hydrochloric or acetic acid, and, contrary to Schwalbe's conclusion ("Die Chemie der Cellulose," 1910, 447), but in agreement with Konig's (cf. B., 1922, 9), is therefore saturated. Oxidation with permanganate gives only a small yield of oxalic acid, whilst concentrated nitric acid gives 80% of oxalic acid and 1% of picric acid. Chlorination of lignin gives no evidence concerning its structure, the products being soluble but of complex reaction, and no simple derivative could be obtained. By the action of chlorine for 15 hrs. and repeated precipitation of the product from alcoholic solution with water an intermediate product containing 32.8% Cl is obtained, whilst the final product contains 38.22% Cl. With aqua regia the final product contains 36.26% Cl, and only traces of chloroquinone are obtained. The yield of the latter never exceeds 1% and is found only when much oxidation occurs and most of the lignin is completely destroyed. Similarly, no trace of "mairogallol" or "leucogallol" obtained by Cross, Bevan, and Beadle from jute lignin (A., 1894, i, 63) could be detected. Bromination in various solvents gives a product containing 30.60% Br, an equivalent quantity of hydrogen bromide being liberated and deep-seated alteration in the structure taking place. Dry distillation of lignin in a vacuum yields a distillate (16% at 12 mm.; 11.8% in a high vacuum) in which small quantities of acetic and formic acids, formaldehyde, and methyl alcohol can be detected, and 9% of a tar containing higher phenols and in which eugenol can be detected. Fusion of lignin with potassium hydroxide under varying conditions gives a maximum yield of 3% of protocatechnic acid, but by addition of zinc dust (at 250°) to prevent oxidation, 15% of the crystalline acid can be isolated (cf. Heuser and Winsvold, A., 1923, i, 541). The various structures proposed for lignin are criticised on the basis of these results and it is concluded that lignin must contain an aromatic nucleus and a pyrone ring and contain the skeleton of 2-phenylflavone. The structure best in agreement with this is that of Klason (A., 1922, i, 324) and a scheme representing the formation of various degradation products on this basis is given. J. W. BAKER.

Action of nitrous acid on amino-compounds. III. Dimethylamine, *n*-propylamine, and glycine ethyl ester. T. W. J. TAYLOR and L. S. III. PRICE (J.C.S., 1929, 2052-2059; cf. A., 1928, 993).-The action of nitrous acid on the above aminocompounds has been investigated, a different type of product being produced in each case, namely, a nitrosoamine, an alcohol, and an aliphatic diazo-compound, respectively. In each case it is shown that the reaction velocity varies as the product [RNH₃'][NO₂'][HNO₂]. The action of nitrous acid on n-propylamine is remarkable in that the product consists of 42% of *n*- and 58% of *iso*-propyl alcohol, but the experimental work offers no explanation of the formation of these two products. In the case of glycine ethyl cster a formula for the reaction velocity has been derived which conforms with the experimental results.

J. W. PORTER. New thiocholine bromide. T. HARADA (Bull. Chem. Soc. Japan, 1929, 4, 171-176).—The action of 2-thiouracil or 4-methyl-2-thiouracil on bromocholine bromide gave thischoline bromide, slow decomp. above 220°, isoelectric point $p_{\rm H}$ 7.0°, which when oxidised with hydrobromic acid yielded bromocholine disulphide. Treatment of thiocholine bromide with silver oxide and hydrobromic acid gave a silver derivative, $C_5H_{13}NSBr_2Ag_2$, decomp. 214°. A. A. GOLDBERG.

Action of nitrosyl bromide on amino-acids. G. ZEMPLEN and Z. CSURÖS (Ber., 1929, 62, [B], 2118-2125).-The action of nitrosyl bromide on amino-acids leads smoothly to the production of bromo-acids only in the case of α -compounds. β -Aminopropionic acid can be transformed into β-bromopropionic acid, m. p. 60-61°, at about 20°, but similar change is not observed when the amino-group is more remote from the carboxyl group. If y-amino*n*-butyric acid is repeatedly treated with nitrosyl bromide at the atmospheric temperature, 68%, it can be recovered as y-benzamido-n-butyric acid, m. p. 78-79°. δ-Amino-n-valeric acid does not give δ-bromo-n-valeric acid. Similarly, ε-amino-n-hexoic

acid is not attacked (e-benzamido-n-hexoic acid, m. p. 80°). E-Benzamidoamyl iodide and ethyl sodiomalonate in alcohol yield ethyl e-benzamidoamylmalonate, hydrolysed by alkali hydroxide to E-benzamidoamylmalonic acid, m. p. 115° after softening at 112°, from which ζ-benzamido-n-heptoic acid, m. p. 80-81°, is derived. ζ-Amino-n-heptoic acid, m. p. 186°, obtained by boiling its benzoyl derivative or E-benzamidoamylmalonic acid with fuming hydrochloric acid, is unchanged by nitrosyl bromide.

H. WREN.

New crystalline form of tyrosine. J. C. ANDREWS (J. Biol. Chem., 1929, 83, 353-355).-By partial neutralisation with 4N-sodium hydroxide of a saturated solution of l-tyrosine in concentrated hydrochloric acid the amino-acid is obtained in blunt C. R. HARINGTON. prisms.

Synthesis of optically active, substituted asparagines. II. O. LUTZ (Ber., 1929, 62, [B], 1916-1921; cf. this vol., 1048).-The rotation graphs of *l*-asparagine and of the *d*-anilino-, *d*-m-toluidino-, d-p-toluidino-, and d-p-phenetidino-succinmonoamides derived from it have been determined. In any series the concentration of the organic component is maintained constant and the effect of gradual increase of acid or alkali hydroxide on the specific rotation is observed. In every case the derivative is found to belong to the series opposite to the original material. H. WREN.

Trimethyl-a-glutarobetaine. H. D. DAKIN and R. WEST (J. Biol. Chem., 1929, 83, 773-776).-Glutamic acid was treated with methyl sulphate and sodium hydroxide; the product, isolated by precipitation with phosphotungstic acid, proved to be trimethyl- α -glutarobetaine,

 $CO_2H \cdot [CH_2]_2 \cdot CH(NMe_3 \cdot OH) \cdot CO_2H$, m. p. 211—213°, $[\alpha]_D + 12 \cdot 0^\circ$ in water [chloroaurate, m. p. (anhydrous) 139—140°; chloroplatinate, m. p. 204—205°]. The compound was stable towards concentrated potassium hydroxide. C. R. HARINGTON.

Transformations of peptide-like substances. XXVII. Structure of clupeine. Autoracemisation of anhydrides of amino-acids containing arginine. M. BERGMANN, L. ZERVAS, and H. KOSTER (Ber., 1929, 62, 1901-1905).-d-Phenylalanyl-d-arginine [B],anhydride undergoes rapid racemisation in aqueous solution at 21°, the reaction being unimolecular. If the solution is treated with hydrochloric acid immediately after completion of racemisation, phenylalanylarginine anhydride hydrochloride monohydrate, m. p. about 170° and 241-243° (corr. decomp.) after resolidification, is obtained, in which both aminoacids are present in inactive form. If, however, the solution is preserved, dipeptide formation ensues as a consequence of autohydrolysis. d-Phenylalanyl-darginine is optically stable under these conditions. d-ad-Diguanido-n-valeric anhydride similarly suffers rapid autoracemisation in aqueous solution at 20°. probably owing to intermediate tautomerisation of ·CHR·CO· to ·CR:C(OH)· under the influence of the basicity of the free guanido-group. The comparatively very slow racemisation of clupeine in aqueous solution excludes the possibility of the presence in it of arginine in the form of simple anhydride. H. WREN.

Transformations of peptide-like substances. XXVIII. Syntheses of peptides containing arginine; d-tyrosyl-d-arginine and its anhydride. M. BERGMANN, L. ZERVAS, and V. DU VIGNEAUD (Ber., 1929, 62, [B], 1905—1909).—Condensation of d-arginine with the azlactone of α -acetamido-p-acetoxycinnamic acid followed by hydrogenation of the product in the presence of palladium-black affords diacetyl-d-tyrosyl-d-arginine (+CH₃·CO₂H), m. p. 196° (corr.), $[\alpha]_{11}^{21}$ —19.5° in water. Treatment with hydrochloric acid yields d-tyrosyl-d-arginine, m. p. 200—202° (corr.; decomp.) when rapidly heated, $[\alpha]_{12}^{2n}$ —105.7° in 0.2N-hydrochloric acid [salicylidene derivative, yellow needles, m. p. 192—194° (corr.) after softening, or almost colourless, hexagonal leaflets, m. p. 252—254° (corr.)]. d-Tyrosyl-d-arginine anhydride hydrochloride had m. p. about 220° (corr. decomp.) after softening at 165°, $[\alpha]_{12}^{2n}$ —40.4° in water. H. WREN.

Transformations of peptide-like substances. XXIX. Acyl migrations and hydrolytic processes with diketopiperazines. M. BERGMANN, V. DU VIGNEAUD, and L. ZERVAS (Ber., 1929, 62, [B], 1909—1913).—Glycino reacts with diacetylglycine anhydride in the presence of aqueous sodium hydroxide, yielding glycine anhydride and aceturic acid. Diacetyldiketopiperazine and d-arginine in water and chloroform afford diketopiperazine and acetyld-arginine, $[\alpha]_D^{23} +9.07^{\circ}$ in water. In presence of ethyl alcohol, diacetyldiketopiperazine undergoes alcoholysis under the catalytic influence of arginine, yielding primarily NN'-diacetylglycylglycine ethyl ester, NHAc-CH₂·CO·NAc-CH₂·CO₂Et, m. p. 74—76°, which readily loses an acetyl group under the influence of bases, giving acetylglycylglycine ethyl ester, m. p. 153° (corr.). The presence of the second acetyl group also facilitates remarkably the separation of the glycyl residues from one another. H. WREN.

Influence of structure of polypeptides and derivatives on their fission by N-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1929, 11, 45-63).derivatives (prepared by the usual methods) with N-sodium hydroxide, trypsin-kinase ($p_{\rm H}$ 7.8 and 8.4), and erepsin (none of the compounds used is hydrolysed by this enzyme) at 37° has been studied. The benzoyl, m. p. 205-207° (not sharp), p-nitrobenzoyl, m. p. 213° with darkening, and p-chlorobenzoyl, m. p. 189°, derivatives of dl-leucylglycyl-dl-leucine (I) are all hydrolysed more readily by alkali than is I; the naphthalene-2-sulphonyl, m. p. 200° with darkening, benzyl, m. p. 226° (decomp.), and methyl, m. p. 253° (decomp.), derivatives undergo fission less readily than I, but a primary acceleration is observed with the benzyl derivative. All the above compounds and chloroacetyl-dl-leucylglycyl-dl-leucine are attacked (to various extents) by trypsin-kinase at both $p_{\rm B}$ values. Glycyl-dl-leucylaniline, m. p. 115-117° after sintering at 94° (from chloroacetyl-dl-leucylaniline, m. p. 168°), dl-leucylglycyl-dl-leucylaniline (II), m. p. about 150° with darkening (from dl- α -bromoisohexoylglycyl-dl-leucylaniline, m. p. 176°), and the methyl derivative, m. p. 160-161°, of II are all hydrolysed

by alkali; di(naphthalene-2-sulphonyl)glycyl-dltyrosine is unaffected by alkali, but is hydrolysed by trypsin-kinase at $p_{\rm H}$ 8.4. Trypsin-kinase has no action on II or its methyl derivative (cf. Abderhalden and Brockmann, this vol., 180). H. BURTON.

Sulphur in proteins. IV. Effect of alkalis on cystine. R. A. GORTNER and W. B. SINCLAIR (J. Biol. Chem., 1929, 83, 681-696).-The following experiments were conducted in duplicate with *l*-cystine and inactive cystine (A., 1927, 1212), no differences being observed in the behaviour of the two forms of the amino-acid. Boiling with 1 or 5% sodium carbonate causes destruction of about 50% of the cystine in 24 hrs. in each case, although, with the 5% alkali, more sulphur is obtained as sulphide. Boiling with 6.5% barium hydroxide (hydrate) causes 50% destruction in 1 hr.; strontium and calcium hydroxides also cause extensive deamination of cystine, whilst with 20% sodium or potassium hydroxide the deamination is much less, although the sulphur is rapidly liberated; deamination of cystine in alkaline solution appears to be associated with an oxidation-reduction system requiring the integrity of the group containing sulphur. The action of lead in promoting decomposition of cystine in alkaline solution is not specific as has been claimed by Andrews (this vol., 85). The products obtained by boiling cystine for 24 hrs. with 6.5% barium hydroxide consist of an ether-soluble fraction and an alcoholsoluble fraction, both of which give positive tests for labile sulphur, and a water-soluble fraction in which the amino-nitrogen : sulphur ratio corresponds with C. R. HARINGTON. that of cystine.

Oxidation-reduction systems of biological significance. V. Composition of oxidised cobalt-cysteine complex; micro-determination of cobalt. L. MICHAELIS and S. YAMAGUCHI (J. Biol. Chem., 1929, 83, 367-373).-On addition of cysteine to a solution of cobalt sulphate, proportionate increase in colour development occurs until the ratio of 1 atom of cobalt to 3 mols. of cysteine is reached, when the colour is at maximum intensity. This confirms the previously suggested structure (this vol., 1011) of the cobalt-cysteine complex, which is formulated Co[S·CH₂·CH(NH₂)·CO₂]₃H₂. The formation of this coloured complex is made the basis of a micro-method for the colorimetric determination of cobalt. C. R. HARINGTON.

Acylation of cystine. Y. INOUE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 647-651).—Acetylation of cystine ester in pyridine solution and subsequent hydrolysis gave acetylcystine. The following were prepared: diacetyl-l-cystine, m. p. 75°; diacetyll-cystine dipropyl ester, m. p. 117-118°; diacetyll-cystine diamyl ester, m. p. 128-129°; diacetyll-cystine dibenzyl ester, m. p. 126-128°; di-p-nitrobenzoyl-l-cystine, m. p. 193-194°; and dinaphthalyll-cystine, m. p. 194-195°. The cystine esters of the lower alcohols are hygroscopic and unstable.

A. A. GOLDBERG.

Thiocyanopropionic acids. A. FREDGA (J. pr. Chem., 1929, [ii], 123, 110—128).—Treatment of a fairly concentrated solution of potassium α -bromopropionate with solid potassium thiocyanate, sub-

sequent evaporation to dryness, and extraction with alcohol affords the potassium salt (I) of a-thiocyanopropionic acid (II), m. p. $49.5-51^{\circ}$, k 3.62×10^{-3} (sodium and calcium [+2H₂O] salts). From *l*- and d-a-bromopropionic acids are obtained similarly potassium (-)- α -thiocyanopropionate, $[\alpha]_D^{35} - 58\cdot2^{\circ}$ in water [free acid (III), m. p. $51-53^{\circ}$, $[\alpha]_D^{35} - 55^{\circ}$ in alcohol], and potassium (+)- α -thiocyanopropionate, $[\alpha]_D^{35} + 58\cdot3^{\circ}$ in water [free acid (IV), m. p. $50-53^{\circ}$, $[\alpha]_{10}^{25}$ +54.2° in alcohol], respectively. When an aqueous solution of II is treated with a small amount of hydrochloric acid at the ordinary temperature a-carbamylthiopropionic acid, m. p. 125° with evolution of gas, $k 3.26 \times 10^{-4}$ (the anilide, m. p. 117°; o-toluidide, m. p. 135–137°; p-toluidide, m. p. 114– 115°; α -naphthylamide, m. p. 161–162°, and β -naphthylamide, m. p. 154–156°, are prepared by the action of the requisite arylamine hydrochloride on an aqueous solution of I, or directly from a-bromopropionic acid, potassium thiocyanate, and the amine), is obtained. Similarly, III and IV furnish (+)-a-carbamylthiopropionic acid, m. p. 117° (decomp.), $[\alpha]_{15}^{25} + 94.7^{\circ}$ in water, and (-)- α -carbamyl-thiopropionic acid, m. p. 117° (decomp.), $[\alpha]_{15}^{25} - 94^{\circ}$ in water, respectively. Hydration of III with water, hydrochloric acid, and hydrochloric acid and potassium chloride solution is followed polarimetrically; the unimolecular velocity coefficient increases with increase in the concentration of the acid, but is lowered by the addition of potassium chloride. Racemisation of III or IV occurs by the addition of potassium thiocyanate, and the velocity coefficient is a linear function of the thiocyanate-ion concentration. Prolonged action of concentrated hydrochloric acid on the above carbamyl derivatives yields 2:4-diketo-5-methyltetrahydrothiazole, m. p. 48-50° (lit. 46-47°), also formed by the action of hydrogen chloride on I in ether suspension. B-Thiocyanopropionic acid, m. p. 7.5-8.5°, k 1.32×10-4 (sodium salt), is converted by treatment with 4N-hydrochloric acid into β-carbamylthiopropionic acid.

Thiocyanoacetic acid, m. p. $35-40^{\circ}$, is obtained solid by inoculation of the oily acid with selenocyanoacetic acid. H. BURTON.

Selenocyanopropionic acid. II. α -Selenocyanobutyric acids. A. FREDGA (J. pr. Chem., 1929, [ii], 123, 129—145; cf. this vol., 426).— (-)- α -Selenocyanopropionic acid (I), m. p. 90—91°, [α]₁₀^{∞} -58·1° in alcohol (potassium salt, [α]₁₀^{∞} -67·1° in water), is obtained by the method previously described (loc. cit.) from *l*- α -bromopropionic acid. Prolonged treatment of I with 4N-hydrochloric acid affords (+)-diselenodi- α -propionic acid (II), m. p. 43—45°, [α]₁₀^{∞} +251·2° in water. When II is treated with diselenodiacetic acid, m. p. 99—100° (by the action of hydrochloric acid on selenocyanoacetic acid, k 1·79×10⁻³), the initial activity of the mixture is lowered to the extent of 19—23% after 3—5 days. Solutions of II alone do not alter in rotatory power and it is suggested that radical formation (R·Se·SerR—>2R·Se·) and subsequent recombination (R·Se·+R'.Se·->R·Se·Se·R') may occur. Diselenodi- β -propionic acid, m. p. 137°, is prepared by the action of hot hydrochloric acid on β -selenocyanopropionic acid (loc. cit.). α -Selenocyanobutyric acid, m. p. 50—51°, $k 2.7 \times 10^{-3}$ (potassium salt), and α -selenocyanoisobutyric acid, m. p. 79—80°, $k 6.1 \times 10^{-3}$ (potassium salt), are obtained by the general method and converted into diselenodi- α -butyric acid, m. p. 80—81°, and diselenodi- α -isobutyric acid, m. p. about 185° (decomp.), respectively, by treatment with hydrochloric acid. Oxidation of the above diselenides with iodine in sodium hydrogen carbonate solution proceeds quantitatively thus: ($\mathbb{R}\cdot\mathrm{Se}\cdot$)₂+ $3\mathrm{I}_2$ + $4\mathrm{H}_2\mathrm{O} \longrightarrow 2\mathbb{R}\cdot\mathrm{SeO}\cdot\mathrm{OH}$ + $6\mathrm{HI}$. The same oxidative fission also occurs when oxidation is effected with hydrogen peroxide in aqueous or acetone solution. There are thus prepared α -seleninopropionic acid, m. p. 83° (decomp.; lead and silver salts), α -seleninoisobutyric acid, m. p. 122° (decomp.), and seleninoacetic acid, m. p. 99° (decomp.).

H. BURTON.

Pseudohalogens. V. Mixed halogen, bromo-**OXYCYANOGEN.** L. BIRCKENBACH and M. LINHARD (Ber., 1929, 62, [B], 2261—2277; cf. this vol., 1265). —Oxycyanogen, (OCN)₂, does not appear to be pro-duced by the action of bromine or iodine on silver cyanate in organic liquids at low temperatures and in absence of moisture; the action of chlorine is not completely elucidated. If silver cyanate is added to a solution of bromine in ethyl chloride at -20° , silver bromide and bromo-oxycyanogen, OCN·Br, are rapidly and quantitatively produced. Conversely, bromo-oxycyanogen does not liberate bromine from silver bromide and does not react with silver evanate in presence of ethyl chloride. Bromo-oxycyanogen forms pale yellow needles, m. p. 72°. At 80-90° sudden polymerisation and partial decomposition occur. It reacts with the more readily attacked organic solvents. It is permanent in absence of light and moisture and becomes polymerised only when heated in the dark, moderately rapidly at the atmospheric temperature if exposed to sunlight. With aqueous potassium iodide, bromo-oxycyanogen reacts according to the equation $OCN \cdot Br + 2KI = I_2 +$ K-OCN+KBr, whereby a method of determining bromo-oxycyanogen is afforded. With aqucous sulphurous acid, bromo-oxycyanogen, after hydrolysis, is quantitatively and immediately reduced to cyanic acid and hydrogen bromide. The mixed halogen is hydrolysed by atmospheric moisture. If ice water is cautiously added to its solution or suspension in indifferent organic media, reaction occurs slowly in accordance with the scheme $60CN \cdot Br + 4H_2O = 3Br_2 + N_2 + 4CO_2 + 2CO(NH_2)_2$; the rate of reaction is controlled by the intermediate change $\begin{array}{l} 2\mathrm{HOCN} + \mathrm{H_2O} = \mathrm{CO}(\mathrm{NH_2})_2 + \mathrm{CO_2} \ \mathrm{or} \ \mathrm{CO}(\mathrm{NH_2})_2 + \\ 3\mathrm{Br}\cdot\mathrm{OH} = 3\mathrm{HBr} + \mathrm{CO_2} + \mathrm{N_2} + 2\mathrm{H_2O}. \quad \mathrm{In} \ \mathrm{alkaline} \\ \mathrm{solution} \ \mathrm{the} \ \mathrm{total} \ \mathrm{reaction} \ \mathrm{may} \ \mathrm{be} \ \mathrm{expressed}: \\ 3\mathrm{OCN}\cdot\mathrm{Br} + 8\mathrm{KOH} = 3\mathrm{KBr} + \mathrm{N_2} + 2\mathrm{K_2CO_3} + \mathrm{KOCN} + \end{array}$ 4H2O. Alcohol reacts violently with bromo-oxy. cyanogen. If the reaction is carried out in presence of ethyl chloride at -80°, ethyl N-bromoallophanate, m. p. 117°, separates. The product is hydrolysed by hot water to hypobromous acid and ethyl allophanate, m. p. 193°. When treated with dilute sulphurous acid, the bromine is quantitatively converted into hydrogen bromide; 1 mol. of ethyl N-bromoallophanate liberates 2 atoms of iodine from

acid potassium iodide. Determination of the mol. wt. of bromo-oxycyanogen in phosphoryl chloride gives values nearly double those required for OCN·Br. The formation of ethyl bromoallophanate by alcoholysis in ethyl chloride and determinations of mol. wt. in phosphoryl chloride show that the solutions contain dimeric bromo-oxycyanogen. The occurrence of by-products during alcoholysis and a deficit in the mol. wt. values indicate an equilibrium, 20CN·Br $(OCN \cdot Br)_2$, the constants of which depend on the solvent. This view is supported by the observation that the analogous iodo-oxycyanogen is converted by ethylene in ether into N-\$-iodoethyl-N'-phenylcarbamide, m. p. 152°, in addition to other products, thus indicating the presence of monomeric iodo-oxycyanogen. Bromo-oxycyanogen in ether or ethyl chloride slowly adds ethylene, yielding an unstable crystalline product, analysis of which establishes the presence in it of the components in the ratio 1:1. H. WREN.

Action of sodium hypochlorite on acid amides. V. I. J. RINKES.—See this vol., 1296.

Action of activated hydrogen and nitrogen on carbon monoxide. G. B. CRIPPA and M. GALLOTTI (Gazzetta, 1929, 59, 507—509).—Minute crystals of carbamide have been obtained by the interaction for several hours at 115—120° of carbon monoxide and hydrogen and nitrogen activated by the silent discharge. F. G. TRYHORN.

Preparation of dichloromethylarsine. E. V. ZAPPI and V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1929, **17**, 59-62).—See this vol., 178.

Optimum concentration of the organic halide for initiating some Grignard reactions. H. GILMAN and R. J. VANDERWAL (Bull. Soc. chim., 1929, [iv], 45, 641-644) .- The colour reaction previously described (A., 1925, ii, 1011; this vol., 303) has been used to determine the optimum concentration of the organic halide for starting Grignard reactions. With benzyl chloride and bromobenzene a concentration of 25-30% by volume gives the most rapid reaction; higher concentrations retard the reaction. Thus with 70% ethereal benzyl chloride no reaction takes place in several months. Similarly, with n-butyl bromide (in presence of iodine) and n-butyl chloride the optimum concentrations are 55% and 70%, respectively, and even in presence of iodine as catalyst the reaction at a concentration of 93-97% of butyl chloride is greatly retarded. Where a concentration of 30-40% of halide in ether cannot be obtained the use of a mixture of ether and benzene is recommended in spite of the negative catalytic effect of the latter (cf. this vol., 800).

R. BRIGHTMAN. Preparation of Grignard's reagent for the nicro-determination of hydroxyl groups

micro-determination of hydroxyl groups by Tschugaev and Zerevitinov's method. B. FLASCHENTRÄGER (Mikrochem., 1929, Pregl Fest., 87—88).—An improved method of preparation from magnesium, isoamyl ether, and methyl iodide is described. The reagent so prepared will keep good for several months in air-tight bottles.

H. F. HARWOOD. Reaction between esters and magnesium phenyl bromide. Mobility of alkyl groups in

esters. H. GILMAN and J. D. ROBINSON (Bull. Soc. chim., 1929, [iv], 45, 636-641).-Since with methyl ethylsulphonate magnesium phenyl bromide yields 21% of toluene (R·SO₂·OAlk+R'·MgX \longrightarrow R'-Alk+ R·SO₂·OMgX) and 14% of phenyl ethyl sulphone (R·SO₂·OAlk+R'·MgX \longrightarrow R·SO₂·R'+aryl·OMgX) (cf. Ferns and Lapworth, J.C.S., 1912, 101, 273; Strecker, A., 1910, i, 532), alkyl alkylsulphonates differ from alkyl arylsulphonates only in the relative extent to which the two reactions occur, arylsulphonates giving smaller amounts of sulphone (cf. A., 1928, 1124; this vol., 545). Since phenyl ethyl-sulphonate yields 74% of phenyl ethyl sulphone and 85% of phenol, it is probable that aryl esters of all sulphonic acids yield sulphones and phenols unless the presence of substituents modifies the properties of the aryl group. Methyl benzenesulphenate yields 63% of diphenyl sulphide, together with methyl alcohol, the small amount of diphenyl sulphoxide also observed (cf. A., 1926, 1239) being due to the presence of a little methyl benzenesulphinate, methyl benzenesulphinate itself affording 65% of diphenyl sulphoxide, a little methyl alcohol, but no toluene or diphenyl sulphide. In accordance with previous results obtained for the mobility of organic radicals, allyl benzoate yields 86% of triphenylcarbinol and allyl-benzene, and benzyl benzoate gives 86% of benzyl alcohol, 69.7% of phenyldibenzylcarbinol, and 6.6% of dibenzyl (cf. Gilman and Kirby, this vol., 801). Since no alkylation products are obtained in the action of magnesium phenyl bromide on alkyl esters of strong carboxylic acids the behaviour of the alkyl esters of the sulphonic acids cannot be attributed to the high dissociation constants of the sulphonic acids. Thus ethyl tribromoacetate gives bromobenzene and a little diphenyl, ethyl trinitrobenzoate 35% of phenol and 7.25% of diphenyl (cf. Gilman and McCracken, this vol., 546), and ethyl acetylenedicarboxylate 14% of diphenyl, no ethylbenzene being formed in any of these cases or with ethyl nitroacetate or triphenylacetate. R. BRIGHTMAN.

Possible interchange of radicals on heating a mixture of R'-X and R'MgX compounds. H. GILMAN and H. L. JONES (J. Amer. Chem. Soc., 1929, 51, 2480—2483).—Magnesium aryl or aralkyl halides do not react with aryl or aralkyl halides thus: R·MgX+R'·X-->R·X+R'·MgX, since decomposition of the reaction product with carbon dioxide furnishes only the acid R·CO₂H. A secondary reaction (formation of R·R') takes place to varying extents according to the reactivity of the halide (R'·X) used. Magnesium phenyl bromide and triphenylmethyl chloride afford a small amount (0.63%) of tetraphenylmethane and 47.4% of diphenyldiphenylylmethane, m. p. 111°.

1:2-Dimethylcyclopropanes. J. BAUDRENG-HIEN (Bull. Soc. chim. Belg., 1929, 38, 172-193).-See this vol., 801.

1:2-Dimethyl-3-isopropylcyclopentane. B. KASANSKI (Ber., 1929, 62, [B], 2205—2210; cf. Godchot and Taboury, A., 1913, i, 348; Zelinski and Kasanski, A., 1927, 670).—Dihydrocamphorone, b. p. $181-183^{\circ}/748.5 \text{ mm.}, d_{1}^{48} 0.8899, n^{18} 1.4412$, is transformed by ethereal magnesium methyl iodide into the

corresponding tertiary alcohol, which could not be obtained quite homogeneous, but is dehydrated by oxalic acid at 130° and then reduced in presence of nickel at 160-170° to 1:2-dimethyl-3-isopropylcyclopentane, b. p. 159—161°/757 mm., d_4^{21} 0.7883, n^{21} 1.4319. Thujamenthone, b. p. 206—208°/749 mm., d_4^{22} 0.8894, n^{22} 1.4484, is transformed into the hydrazone, converted by distillation in presence of solid potassium hydroxide and platinised earthenware into 1 : 2-dimethyl-3-isopropylcyclopentane, b. p. $159-160\cdot 5^{\circ}/757\cdot 6$ mm., d_{10}^{21} $0\cdot 7877$, n^{21} $1\cdot 4328$. The divergence of the constants of Godchot's compound is probably due to degradation of the isopropyl group owing to the relatively high temperature of the treatment with nickel. 1-Methyl-2-isopropylcyclopentane, obtained from dihydrocamphorone by the hydrazine method, has b. p. 140-142.5°/764.8 mm., $d_4^{18:5}$ 0.7750, $n^{18:5}$ 1.4257. H. WREN.

spirocycloDecane and its contact isomerisation. N. D. ZELINSKI and N. I. SCHUIKIN (Ber., 1929, 62, [B], 2180—2186).—Adipic acid, prepared in 91% yield by oxidation of cyclohexanol with permanganate in cold, very dilute alkaline solution, is converted into cyclopentanone, b. p. 130—131° (yield 76.5% in presence of barium hydroxide or 90% in presence of thorium oxide hydrate). Reduction of the ketone in aqueous-ethereal solution at $+5^{\circ}$ in a current of carbon dioxide yields mainly cyclopentanol and 2-cyclopentylcyclopentanol, b. p. 117—118°/12 mm., d_4° 0.9802, n_{10}° 1.4885; the pinacol,

 $\begin{bmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{bmatrix}_2$, m. p. 107—108°, is obtained $[CH_2, CH_2] = \frac{1}{2}$ in 3% yield. The last-named compound is converted by hot dilute sulphuric acid into 2:2-tetramethylenecyclohexanone, b. p. 98—100°/13 mm., d_4^{20} 0.9898, n_D^{20} 1.4848 (semicarbazone, m. p. 191—192°). The ketone is transformed into its hydrazone, which, when decomposed in presence of platinum and potassium hydroxide, passes into 1:1-tetramethylenecyclohexane $\begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{array} \subset \begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{array} \subset \begin{array}{c} CH_2 \cdot CH_2 \\ CH_2 \\ CH_2 \cdot CH_2 \\ CH$ (spirocyclodecane), b. p. 185—186°/745 mm., d_4^{x0} 0.8877, n_D^{x0} 1.4748. The hydrocarbon slowly decolorises dilute permanganate and with bromine yields a tetrabromide, m. p. 130-132° (decomp.). spirocycloDecane is isomerised in presence of platinised charcoal and hydrogen at 190° to a compound, $C_{10}H_{18}$, b. p. 185.5—186.5^o/750 mm., d_{10}^{∞} 0.8730, n_D^{∞} 1.4683; isomerisation occurs more The slowly in an atmosphere of carbon dioxide. product reacts slowly with permanganate. It does not become dehydrogenated in presence of palladised

Meaning of action constants in substitution reactions in the benzene nucleus. W. HUCKEL and H. HAVEKOSS (Ber., 1929, 62, [B], 2041—2043; cf. A., 1928, 987).—Examination of Holleman's data for the replacement of chlorine in chloronitro- and chlorodinitro-benzenes under the action of diethylamine and sodium methoxide shows that variations in the action constants may occur which cannot be foretold from probabilities of steric hindrance or furtherance. A theoretical basis of the relationship between constitution and action constants cannot be given. Present theories, for example that of induced

asbestos or platinised charcoal at 300°. H. WREN.

alternate polarities, do not take this into consideration and, for further progress, it is necessary to recognise the influence of action constants on velocity coefficients and to separate their part from that of activation energy. H. WREN.

Benzene and mobility of the iodoxy-group. D. VORLÄNDER (Rec. trav. chim., 1929, 48, 912-918). -Substitution in the benzene nucleus is discussed briefly (cf. A., 1919, i, 319). Oxidation of 1-iodo-2:4-dinitrobenzene with hypochlorous acid in acetic acid solution gives 1-iodoxy-2: 4-dinitrobenzene (I), explodes between 140° and 160°, according to rate of heating. The mobility of the iodoxy-group in I is great (cf. A., 1925, i, 1055). Thus, treatment of I with silver nitrate gives silver iodate and m-dinitrobenzene, sodium nitrite in the cold converts I into 1:2:4-trinitrobenzene, and the action of aqueous sodium azide yields 2: 4-dinitroazidobenzene. These results are explicable on the author's theory of H. BURTON. alternating charges.

Highly-polymerised compounds. XXI. Reduction of polystyrene. H. STAUDINGER and V. WIEDERSHEIM (Ber., 1929, 62, [B], 2406-2411; cf. this vol., 910).-Hemicolloidal polystyrenes (mean mol. wt., 1800-5000) which, according to Heuer (unpublished work), are not essentially degraded when heated in solution at 200°, are not reduced in cold solution in presence of Willstätter's platinum, platinum oxide, or nickel, but are completely hydrogenated in decahydronaphthalene at 200° in presence of Kelber's nickel to hexahydropolystyrenes, in which the absence of non-hydrogenated, aromatic nuclei is established by their inability to react with concentrated nitric acid or tetranitromethane. Reduction of a preparation of mean mol. wt. 1800 gave a product of unchanged mean mol. wt. and identical viscosity in solution. More complex products are cracked in some degree by a similar treatment, but in the main are reduced without decomposition if the process is effected rapidly in the presence of a sufficient amount of active catalyst. The smaller fragments are removed by re-precipitation, leaving mixtures of approximately the same viscosity and mean mol. wt. as the initial materials. Complex polymerisation products can therefore be subjected to chemical change without alteration of the mean mol. wt. In the solution the compound exists as molecules and not as associations and the mean mol. wt. of the products is truly determined. Mol. wts. of hydrocarbons of this order of magnitude can be accurately determined, and erroneous values are not obtained due to solvation or micelle formation. The viscosity of the solutions depends on the size of the long thread molecules, which hinder the normal movement of the liquid molecules and thus cause viscosity in the H. WREN. solutions.

Preparation of p-tolylacetylene. A. WILLEMART (Bull. Soc. chim., 1929, [iv], 45, 644—645).—p-Tolyl methyl ketone is treated with phosphorus pentachloride and the monochloro-compound,

 C_6H_4 Me·CCI:CH₂, b. p. 86—96°/12 mm. (Auwers and Keil, A., 1903, i, 620), is converted into *p*-tolylacetylene, m. p. 23°, b. p. 53—56°/11—12 mm., with 2·2 mols. of sodamide in presence of vaseline oil (cf. Meunier and Desparmet, A., 1924, i, 701; Bourguel, A., 1925, i, 770). R. BRIGHTMAN.

Homologues of diphenyl. E. BOEDTKER [with B. WIGER and R. KERLOR] (Bull. Soc. chim., 1929, [iv], 45, 645-650).-A residual specimen of Bert's pp'-dissopropyldiphenyl (A., 1923, i, 1005) on re-examination had m. p. 49°, but contained some crystals, m. p. 65-66°. p.Cumyl iodide, b. p. 236-238° with commercial copper powder yielded only Schreiner's pp'-diisopropyldiphenyl, m. p. 49° (A., 1910, i, 367). Since, however, a second experiment gave only the substance, m. p. 65-66°, either Bert's or Schreiner's product is probably *p*-isopropylphenyl-phenyldimethylmethane, $Pr^{\#}C_{6}H_{4}$ ·CPhMe₂ (cf. Weiler, A., 1896, 237, 242), and although the pp'-di-tert.butyldiphenyl obtained by Schreiner's method or from p-iodo-tert.-butylbenzene by Tschitschibabin's method (A., 1928, 404) had m. p. 122°, this product also is regarded as probably a mixture of two similar isomerides. n-Butylbenzene, b. p. 180°, d¹⁹ 0.8679, $n_{\rm b}^{7\,\circ}$ 1·4942 (yield 71% from *n*-butyl bromide, bromobenzene, and sodium), is converted by Klages and benzene, and sodium), is converted by Klages and Storp's method (A., 1902, i, 670) into p-iodo-n-bulyl-benzene, b. p. 144°/20 mm., d_4^{30} 1·4616, n_D^{30} 1·5693, yielding, with copper powder, pp'-di-n-bulyldiphenyl, m. p. 58—59°, b. p. 228—230 /14 mm., d_4^{15} 0·9499, n_D^{16} 15503. Similarly, sec.-bulylbenzene, b. p. 171·3— 172·3°, d_4^{18} 0·8612, n_1^{16} 1·4914, yields p-iodo-sec.-bulyl-benzene, b. p. 129—130°/16 mm., d_4^{14} 1·4701, n_D^{14} 1·5731, and pp'-di-sec.-bulyldiphenyl, b. p. 222—224°/20 mm., d_4^{15} 0·9530, n_D^{16} 1·5577, and tert.-amylbenzene, b. p. 139°/ 15 mm., d_4^{20} 1·4226, n_D^{20} 1·5669, and pp'-di-tert.-amyldi-phenyl, b. p. 224°/16 mm., d_4^{16} 1·5570, which after some months deposits traces of a crystalline after some months deposits traces of a crystalline substance volatilising above 200°. R. BRIGHTMAN.

Mononitro- and monoamino-derivatives of 1-methylnaphthalene. V. VESELY, F. STURSA, H. OLEJNICEK, and E. REIN (Coll. Czech. Chem. Comm., 1929, 1, 493-515) .- Nitration of 1-methylnaphthalene in acetic anhydride with excess of nitric acid $(d \ 1.52)$ below 15° yielded 4-nitro-1-methylnaphthal-ene, m. p. $68-69^{\circ}$, together with a liquid which, contrary to Lesser (A., 1914, i, 33), furnished only the 4-amino-compound (isolated as the acetyl derivative, m. p. 166-167°) on partial reduction by hydrogen and platinum-black. 2:4-Dinitro-1-methylnaphthalene was reduced by platinum-black and hydrogen or by ammonium hydrogen sulphide to 2-nitro-4-amino-1-methylnaphthalene, m. p. 131-132°, and the latter converted into 2-nitro-1-methylnaphthalene, m. p. 58-59°. Reduction of the last-named with zinc dust and acetic acid afforded 2-amino-1methylnaphthalene, m. p. 49-50° (acetyl derivative, m. p. 188-189°; benzoyl derivative, m. p. 222°), which was identical with the substance obtained from 1-methyl-2-naphthol. 3-Nitro-4-acetamido-1-methyl-naphthalene, m. p. 224-225°, obtained from 4-acetamido-1-methylnaphthalene in acetic anhydride and nitric acid (d 1.52), was converted into 3-nitro-4amino-1-methylnaphthalene, m. p. 179.5°, by warming with alcoholic hydrochloric acid, from which 3-nitro-1-methylnaphthalene (I), m. p. 81-82°, was prepared. The following compounds are described : 3-amino-1methylnaphthalene, m. p. 68° (acetyl derivative, m. p. 172-173°); 3-hydroxy-1-methylnaphthalene, m. p. 80-81°. 3:4-Diamino-1-methylnaphthalene, m. p. 91°, was produced by the reduction of 2-nitro-4methyl-a-naphthylamine with stannous chloride. Treatment of 1-methylnaphthalene in carbon tetrachloride solution at 0° with chlorosulphonic acid furnished chiefly the 4-sulphonic acid, which was converted into 1-methylnaphthalene-4-sulphonyl chloride (II), m. p. 78-30°. When II is nitrated with nitric acid (d 1.475) at -5° to 3° the 5-nitro-, m. p. $161-161\cdot5^{\circ}$, together with the 8-nitro-, m. p. $115-116^{\circ}$, -1-methylnaphthalene-4-sulphonyl chlorides are obtained, and separated by means of ether. The 5-nitro-sulphonyl chloride yielded 5-nitro-1-methylnaphthalene-4-sulphinic acid with sodium sulphite and sodium hydrogen carbonate, converted by warming with 60% sulphuric acid or 80% phosphoric acid into 5-nitro-1-methylnaphthalene, m. p. 82-83°. 5-Amino-1-methylnaphthalene, m. p. 77-78° (acetyl derivative, m. p. 194-195°; benzoyl derivative, m. p. 173-174°; 5-hydroxy-1-methylnaphthalene, m. p. 97-98°), was obtained by the hydrolysis of 5-nitro-1methylnaphthalene-4-sulphonyl chloride with alkali, reduction of the resultant sodium nitro-sulphinate with iron and dilute acetic acid, and treatment of the sodium amino-sulphonate with sodium amalgam, 5-Acetamido-1-methylnaphthalene in aceticanhydride and nitric acid $(d \ 1.525)$ at 15-20° afforded a mixture of two mononitro-compounds, separated by fractional crystallisation from ethyl acetate into 6-nitro-5-acetamido-1-methylnaphthalene (III), m. p. 245-246°, and 8-nitro-5-acetamido-1-methylnaphthalene (IV), m. p. 197-198°. Hydrolysis of III with alcoholic hydrochloric acid furnished 6-nitro.5-amino-1-methylnaphthalene, m. p. 178—179° (8-nitro-5-amino-1-methyl-naphthalene similarly prepared from IV has m. p. 163-164°), which was converted into 6-nitro-1-methylnaphthalene, m. p. 76-77° [6-amino-1-methylnaphthalene, m. p. 63-64° (acetyl derivative, m. p. 123-124°; benzoyl derivative, m. p. 155-156°)]. The orientation of 6-nitro-5-amino-1-methylnaphthalene was confirmed by reduction with stannous chloride to 5:6-diamino-1-methylnaphthalene, m. p. 151-152°, which condensed with phenanthraquinone in glacial acetic acid to give 1-methylnaphthalene-5:6-phenanthrazine, m. p. 254-256°. 8-Nitro-1-methylnaphthalene-4-sulphonic acid was prepared from the sulphonyl chloride and converted by heating with 60% sulphuric acid into 8-nitro-1-methylnaphthalene, m. p. 63-64°. 8-Amino-1-methylnaphthalene, m. p. 67-68° (acetyl derivative, m. p. 183-184°; benzoyl derivative, m. p. 195-196°), was obtained from S-amino-1-methylnaphthalene-4-sulphonic acid in the manner described above. Attempts to prepare 8-hydroxy-1-methylnaphthalene from the aminocompound were unsuccessful. Nitration of 8-acctamido-1-methylnaphthalene in acetic anhydride with nitric acid (d 1.525) and acetic anhydride afforded a mixture of mononitro-compounds, which was separated by ethyl acetate into 5-nitro-8-acetamido-1-methylnaphthalene, m. p. 193-194°, and a eutectic mixture. Partial hydrolysis of the latter with alcoholic potassium hydroxide yielded 5-nitro-1-methyl-8-naphthylamine, m. p. 162-163° (converted by elimination of the amino-group into 5-nitro-1-methylnaphthalene, m. p. 83-84°), and 7-nitro-8-acetamido-1-methylnaphthalene (V), m. p. 186-187°. 7-Nitro-1-methyl-8-naphthylamine, m. p. 150-152°, obtained from V and alcoholic hydrochloric acid, was converted into 7-nitro-1-methylnaphthalene, m. p. 98-99° (7-acetamido-1-methylnaphthalene, m. p. 158.5-160°).

amido-1-methylnaphthalene, m. p. 158.5—160°). The constitution of 8-nitro-5-amino-1-methylnaphthalene was established by reduction with stannous chloride to the 5:8-diamine, followed by oxidation of the latter in anhydrous acetic acid with ferric chloride, when 1-methyl-5:8-naphthaquinone, m. p. 121—122°, was obtained. The same quinone was produced from 5-nitro-8-amino-1-methylnaphthalene. A. I. VOGEL.

Catalytic transference of hydrogen between organic compounds. S. AKABORI and T. SUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 198-202).—See this vol., 1170.

ms-Dialkylanthracenes and "transannular tautomerism." VI. E. DE B. BARNETT and J. L. WILTSHIRE (Ber., 1929, 62, [B], 1969-1973; cf. this vol., 1171).-1:4-Dichloroanthrone, m. p. 148°, is prepared by reduction of 1:4-dichloroanthraquinone in boiling glacial acetic acid with tin and hydrochloric acid or in cold concentrated sulphuric acid with aluminium powder. 1:4-Dichloroanthryl acetate has m. p. 174°. Treatment of 1:4-dichloroanthrone with magnesium ethyl bromide or magnesium benzyl chloride affords, respectively, 1:4-dichloro-9-ethyl-anthracene, m. p. 103°, and 1:4-dichloro-9-benzyl-anthracene, m. p. 113°. Bromine in carbon disulphide transforms the last-named compound into 1:4-dichloro-10-bromo-9-benzylidene-9: 10-dihydroanthracene, m. p. 206°, from which the corresponding -10-piper-idino-, m. p. 200°, -10-methoxy-, m. p. 185°, and -10-ethoxy-, m. p. 158°, compounds are derived by means of piperidine or the requisite alcohol in presence of calcium carbonate. 1:4-Dichloro-10-bromo-9-benzylidene-9: 10-dihydroanthracene is converted by potassium acetate in acetic acid followed by boiling glacial acetic acid into 1:4-dichloro-9-a-acetoxybenzylan-thracene, m. p. 208°. 1:4-Dichloro-10-methoxy-9-benzylidene-9:10-dihydroanthracene is transformed by methyl alcohol containing a little hydrochloric acid into 1:4-dichloro- $9-\alpha$ -methoxybenzylanthracene, m. p. 118°. 1:4-Dichloro- $9-\alpha$ -ethoxybenzylanthracene, H. WREN. m. p. 135°, is prepared similarly.

Aromatic substitution from the viewpoint of electronic theory of valency. C. K. INGOLD (Rec. trav. chim., 1929, 48, 797—812).—A resume of the investigations on aromatic substitution carried out by the author and his co-workers during the last 4 years. H. BURTON.

Theories of aromatic substitution. B. FLUR-SCHEIM (Rec. trav. chim., 1929, 48, 817-820).—The electrostatic and non-electrostatic theories are discussed briefly and the former criticised.

H. BURTON.

Orienting power of substituents in the benzene nucleus. F. SWARTS (Rec. trav. chim., 1929, 48, 1025-1028).—The effect of substituents on refraction is discussed. There appears to be no relationship

between refraction and orienting power. The variation of thermal energy involved in the introduction of groups into a substituted benzene nucleus is commented on. H. BURTON.

Synthesis of aniline. M. SMIAŁOWSKI (Przemysł Chem., 1929, 13, 397-401).-Mixtures of chlorobenzene vapour and ammonia are passed through tubes heated at 250-400° and containing a catalyst consisting of 10% of nickel or cobalt intimately mixed with various carriers such as sodium or calcium carbonate, calcium oxide, pumice, lead, lead chromate. chromic oxide, and the products are analysed. Small quantities of aniline (0-1%) are found, together with ammonium carbonate, benzene, diphenyl, and carbazole, as well as traces of diphenylamine in those cases where lead is present. The presence of carbon monoxide in the reaction mixture slightly depresses the yields of aniline. The low yields of aniline obtained are due, not to inactivation of the catalyst, but probably to side reactions and to the reversal of the reaction, as mixtures of aniline and chlorobenzene vapours exhibit after passage through the tube a diminished aniline content. R. TRUSZKOWSKI.

Nitration of esters of phenylmethylcarbamic acid. P. VAN ROMBURGH (Rec. trav. chim., 1929, 48, 922—925).—A modified account of work already published (A., 1901, i, 201). Jaeger's observation (A., 1906, i, 500) that methyl 2:4:6-trinitrophenylmethylcarbamate exists in two modifications, m. p. 107° and 118°, is confirmed. Treatment of this ester with a mixture of nitric (d 1.5) and sulphuric acids gives methyl 2:4:6-trinitrophenylcarbamate.

H. BURTON.

Nitration of aromatic compounds in alcoholic solution. F. REVERDIN (Rec. trav. chim., 1929, 48, 838—842; cf. this vol., 310).—Nitration of p-methoxybenzanilide (I), p-anisylurchane (II), and p-toluenesulphonamidophenetole with nitric acid (d 1·185) in boiling alcoholic solution affords the corresponding 3-nitro-4-acylamido-derivatives; p-ethoxyacetanilide (III) undergoes hydrolysis only. With nitric acid (d 1·4) p-toluenesulphon- and 2-nitro-p-toluenesulphon-amidophenetoles yield the corresponding 3:5-dinitro-derivatives; III furnishes 3-nitro-4-acetamidophenetole under regulated conditions, whilst I and II afford mainly the mononitro-derivatives. Acyl groups other than acetyl are not hydrolysed during nitration. H. BURTON.

Phenoxyethylaniline and related compounds. D. H. PEACOCK, M. BHATTACHARYA, and B. L. RAO (J.C.S., 1929, 1926—1927).—The following compounds have been prepared by heating phenoxyethyl *p*-toluenesulphonate (Peacock and Tha, A., 1928, 1115) and the corresponding amine in the presence of rather more than the calculated amount of aqueous sodium carbonate : β -phenoxyethyl-o-toluidine, m. p. 64°; -m-toluidine, b. p. 220°/13 mm.; -p-toluidine, m. p. 52°; -ethylaniline; -diethylaniline, b. p. 212— 213°/17 mm.; -p-chloroaniline, b. p. 228°/11 mm.; - α -naphthylamine, m. p. 106°. R. K. CALLOW.

Electrochemical preparation of phenylhydrazine. R. E. McCLURE and A. Lowy.-See this vol., 1247. Stereoisomerism of diazo-compounds. W. SWIENTOSLAWSKI (Ber., 1929, 62, [B], 2034—2040; cf. A., 1920, i, 336).—A reply to Hantzsch (this vol., 805). H. WREN.

Reduction of normal diazohydrates. - A. ANGELI and Z. JOLLES (Ber., 1929, 62, [B], 2099-2100).-Benzoylphenylhydrazine is produced when a solution of benzenediazonium chloride is rendered alkaline and treated with a solution of sodium stannite containing alcohol and benzaldehyde. Support is thus afforded to the author's theory (A., 1926, 947) of the intermediate production of phenyldi-imide during the reduction of normal diazohydrates: O.NPh:NH+ $H_2=H_2O+NPh$:NH. The production of ammonia and azoimide by reduction of potassium azodicarboxylate is explained by the intermediate formation of di-imide and the formation of the compound NMe2.C6H4.N(:O):N.NH.CO.NH2 from nitrosodimethylaniline and semicarbazide by the intermediate occurrence of NH2 CO.N.NH. Di-imide also appears to be intermediately formed during the production of diazonium salts from guinones and benzenesulphonylhydrazine or azodicarboxylic acid. The oxygen atom in normal diazohydrates appears present as oxide and not as hydroxyl. H. WREN.

Constitution and reactions of diazohydrates. A. ANGELI (Atti R. Accad. Lincei, 1929, [vi], 9, 933— 940, and Ber., 1929, [B], 62, 1924—1928).—A refutation of Hantzsch's criticism (this vol., 805) of the author's views (A., 1928, 1129), in support of which Swientoslawski's thermochemical data (A., 1925, ii, 1044) are quoted. T. H. POPE.

Reactions of diazohydrates. D. BIGIAVI (Ber., 1929, 62, [B], 2101-2102).-Whereas isodiazohydrates do not react with the sodium salt of nitrohydroxylamine, the normal diazohydrates give temporary, violet-blue colorations, marked gas evolution, resinification, and production of nitrosobenzene. The change is probably due to intermediately formed nitroxyl: O:NPh:NH+N·OH \longrightarrow O:NPh+N₂+ H₂O. H. WREN.

Optically active diazo-compounds. IV. Stable alicyclic diazo-amine. C. W. BENNETT and W. A. NOVES (Rec. trav. chim., 1929, 48, 895–898). —When 2-aminofluorenonehydrazone, m. p. 209° [prepared by Gerhardt's method (A., 1920, i, 766)], is suspended in 95% alcohol in which a small amount of sodium has been dissolved and then treated with mercury acetamide, 2-amino-9-diazofluorene, m. p. 137° with evolution of nitrogen, is obtained. This is stable at the ordinary temperature, but becomes brown on long exposure to light. Resolution is not effected by d-camphorsulphonic acid. Improved methods of preparation of 2-nitrofluorene and 2-nitroand 2-amino-fluorenone are given. H. BURTON.

cis-trans-Isomerism and steric hindrance. IX. Propylcyclopentanols. G. VAVON and J. FLURER (Bull. Soc. chim., 1929, [iv], 45, 754—762).— 1-Propylcyclopentan-2-one, b. p. $67^{\circ}/8 \text{ mm.}, d_7^{-}0.9111$, n_7° 1-4470 [semicarbazone, m. p. 212—213°, yielding when hydrogenated in aqueous hydrochloric acid the hydrochloride of 1-propylcyclopentyl-2-semicarbazide (m. p. 151—152°); oxime, b. p. 109—111°/9 mm.,

hydrogen oxalate, m. p. 149-150°], with sodium and alcohol gives 70% of a mixture, b. p. 80°/10 mm., of 1-propylcyclopentan-2-ols rich in the trans-isomeride. trans-1-Propylcyclopentan-2-ol isolated through the hydrogen phthalate has b. p. 78-79°/10 mm., d^{*} 0.9018, $n_{\rm D}^9$ 1.4565 (hydrogen phthalate, m. p. 68°; hydrogen succinate, $d_{\rm M}^{16}$ 1.0686, $n_{\rm D}^{10}$ 1.4605; 3:5-dinitrobenzoate, m. p. 30-31°; phenylurethane, m. p. 61-62°). cis-1-Propylcyclopentan-2-ol, b. p. 79-80°/12 mm., do 0.9165, no 1.4600 (3:5-dinitrobenzoate, m. p. 70-71°; hydrogen phthalate, m. p. 95-96°; hydrogen succinate, m. p. 27-28°; phenylurethane, m. p. 83-84°), is obtained by hydrogenation of the ketone in presence of platinum-black in acetic acid containing hydrochloric acid and purification of the dinitro-benzoatc. A mixture richer in the *trans*-isomeride is obtained in absence of hydrochloric acid (cf. A., 1928, 1000). The cis-trans-configurations are assigned for similar reasons to those given in the case of the propyl-, isopropyl-, and cyclohexyl-cyclohexanols (A., 1927, 455, 761; 1928, 166, 516). The cis-1-propylcyclopentan-2-ol is converted into the trans-isomeride by heating its sodium derivative at 180-190° for 12 hrs. in an atmosphere of nitrogen. The cis-hydrogen phthalate is much less soluble in organic solvents than trans-isomeride. cis-2-Propylcyclopentan-1-ol the is esterified more rapidly than the trans-isomeride with acetic acid at 100°, in the absence of a catalyst, but in presence of a catalyst esterification is more rapid with the trans-isomeride at 0° and at 39°. The trans-hydrogen phthalates and succinates are hydrolysed more rapidly than the cis-isomerides, the ratio of the velocity coefficients for the trans-/cis-hydrogen phthalates in water being 4.3 at 39° and 5.5 at 0° , and in 75% alcohol, 2 at 39° and 2.5 at 68° . Similarly for the hydrogen succinates, the ratio of the velocity coefficients in 75% alcohol at 0° is 2.4 and at 39°, 2.7. Comparison of these ratios with those previously obtained for the esters of the 1-isopropylcyclopentan-2-ols (A., 1928, 100) shows that the steric effect of the propyl group in hydrolysis is less than that of the isopropyl, the propylcyclopentyl esters having greater velocity coefficients but smaller trans/cisratios than the corresponding isopropyl derivatives.

1-Propylcyclopentan-2-one is obtained by hydrogenation of 1-propylidenecyclopentan-2-one, b. p. $80^{\circ}/10$ mm., d_{9}° 0.9559, n_{D}° 1.4855 (semicarbazone, m. p. 224-225°), in ether in presence of platinum-black. The latter is obtained in 65% yield by dehydration of the ketol, b. p. 100-105°/8-9 mm., prepared from propaldehyde and cyclopentanone in presence of sodium (yield 40-45%) under 40-50 mm. in presence of 2% of oxalic acid. R. BRIGHTMAN.

Action of phenylthiocarbimide on phenols. F. MAYER and A. MOMBOUR (Ber., 1929, 62, [B], 1921— 1924; cf. Karrer and Weiss, this vol., 697).—Condensation is effected (i) with aid of aluminium chloride in carbon disulphide and (ii) by means of zinc chloride and hydrogen chloride in ether. Phenol and phenylthiocarbimide, by either method, afford p-hydroxythiobenzanilide, m. p. 164°, converted by sodium carbonate solution at 160° into hydrogen sulphide, aniline, phenol, and p-hydroxybenzanilide. Similarly, resorcinol affords 2: 4-dihydroxythiobenzanilide, m. p. 182° (Karrer and Weiss, m. p. 176°). α -Naphthol by the second method yields 4-hydroxythionaphthanilide, m. p. 207—208°, whereas by the first method it gives 1-hydroxy-2-thionaphthanilide, m. p. 183—184°. The thionaphthanilides condense with 5:7-dibromoisatin chloride, giving the compounds:

 $C_6H_2Br_2 < CO_{CO} > C:C_{10}H_5(:O) \cdot CS \cdot NHPh (C:O:CS \cdot NHPh = 2:1:4 and 1:4:3).$ H. WREN.

Acyl derivatives of o-aminophenol. V. R. E. NELSON and H. S. ROTHROCK (J. Amer. Chem. Soc., 1929, 51, 2761-2764).-Schotten-Baumann treatment of o-benzamidophenol with n-butyl chloroformate or of n-butyl o-hydroxycarbanilate with benzoyl chloride affords o-carbo-n-butoxyaminophenyl benzoate, m. p. 62.5°, hydrolysed to n-butyl o-hydroxycarbanilate. Similarly, o-carboisobutoxyaminophenyl benzoate, m. p. 85.5-85.8°, is obtained from the corresponding isobutyl derivatives as above. In both these cases acylation of o-benzamidophenol causes migration of the benzovl group from nitrogen to oxygen. o-Benzamidophenol and n-valeric anhydride afford o-benzamidophenyl n-valerate, m. p. 103.5-104.5°, whilst o-valeramidophenol, m. p. 79°, and benzoyl chloride yield o-valeramidophenyl benzoate, m. p. 73-74°. Both the diacyl derivatives are hydrolysed to o-benzamidophenol, migration of the benzoyl group from oxygen to nitrogen taking place with the benzoate. Hydrolysis of o-isovaleramidophenyl benzoate, m. p. 96-97.5° (from o-isovaleramidophenol, m. p. $100.5-102^{\circ}$), gives a small amount of the starting material in addition to o-benzamidophenol. o-Benzamidophenyl isovalerate has m. p. 113.5-117°.

Benzoylation of methyl o-hydroxycarbanilate, m. p. 122—123°, or treatment of o-benzamidophenol with methyl chloroformate affords o-benzamidophenyl methyl carbonate, m. p. 128°, hydrolysed mainly to o-benzamidophenol. In the first of these acylations migration of the carbomethoxy-group from nitrogen to oxygen occurs, but in most of the cases studied (cf. A., 1928, 168, 517) the carboalkoxy-group is able to displace the benzoyl group attached to the nitrogen atom. H. BURTON.

Electrolytic preparation of 2:4-diaminophenol. W. E. BRADT and O. W. BROWN (Amer. Electrochem. Soc., Sept., 1929. Advance copy, 14 pp.).—The effect of varying conditions on the yield and current efficiency of production of 2:4-diaminophenol by electrolytic reduction of the corresponding nitro-compound has been investigated. The best cathode material was found to be a copper gauze electrolytically coated with copper sponge. Using a catholyte of 2:4-dinitrophenol dissolved in an aqueous sodium carbonate or hydroxide solution gave poor yields, whilst in sulphuric acid solutions low solubility and volatilisation losses limited the yield. The use of a closed cell with vigorous agitation, raising the temperature, and addition of alcohol to the catholyte improved the yield. The best conditions are : catholyte consisting of 5 g. of the nitro-compound in 200 c.c. of sulphuric acid (d 1.66) and 100 c.c. of 95% alcohol vigorously stirred at 118°, with 5 amp./dm.² at the cathode. The yield and current efficiency were then 94.4%.

H. J. T. ELLINGHAM.

Action of normal sulphites on 3-chloro-βnaphthol and on 1:3-dichloro- β -naphthol. A new case of intramolecular transposition. C. MARSCHALK (Bull. Soc. chim., 1929, [iv], 45, 651-662).-When heated with dilute sodium or potassium sulphite under reflux, or in an autoclave at 120°, 3-chloro-\$-naphthol yields \$-naphthol and \$-naphthol-4-sulphonic acid, the formation of β -naphthol being greater in an autoclave. The formation of the β-naphthol-4-sulphonic acid is attributed to direct addition of the sulphite followed by elimination of sodium chloride. The absorption spectrum of 1-benzeneazo-3-naphthol-4-sulphonic acid shows bands in aqueous solution at 530 and 499, in sulphuric acid at 559 and 523. Similarly, 1:3-dichloro-β-naphthol with dilute (1.25%) potassium sulphite at 120° yields 3chloro-B-naphthol-1-sulphonic acid, hydrolysed by 45-50% sulphuric acid to 3-chloro- β -naphthol, and by 10% potassium sulphite at 170° to β -naphthol-1- and -4-sulphonic acids, and a little β -naphthol. Since 1:2aminonaphthol is converted into I-amino-β-naphthol-4-sulphonic acid by sodium sulphite solution in presence of a current of air, air should be excluded in the above operations. B-Naphthol-4-sulphonic acid is readily prepared by reduction of 1-diazo-B-naphthol-4-sulphonic acid with sodium sulphide. When treated with nitrous acid and heated with hydrochloric and acetic acids, 3-chloro-\beta-naphthol is converted successively into 3-chloro-1-nitroso-\$-naphthol and 3-chloro-2hydroxy-a-naphthaquinone, m. p. 214-215°.

R. BRIGHTMAN.

Derivatives of 2-hydroxyfluorene. II. C. Ruíz (Anal. Asoc. Quím. Argentina, 1928, 16, 225—233; cf. this vol., 1063).—It has not been found possible to methylate 1(or 3)-nitro-2-hydroxyfluorene. 3-Nitro-2-methoxyfluorene (I) (Ecker and Langecker, A., 1928, 521) is reduced to 3-amino-2-methoxyfluorene, m. p. 187°, which, when diazotised and the solution run into boiling dilute sulphuric acid, yields 3-hydroxy-2-methoxyfluorene (II), m. p. 185°. The constitution of these compounds is demonstrated by the formation of 3-nitro-2-aminofluorene when I is heated with ammonia in a sealed tube, and by the failure of II to form an indophenol, indamine, or phthalein, although it reacts with ferric chloride, nitrous acid, and diazonium salts. R. K. CALLOW.

Nitroveratroles. H. VERMEULEN (Rec. trav. chim., 1929, 48, 969-972).-The 4-nitroveratrole of Pschorr and Silberbach (A., 1904, i, 581) is a mixture (compound?) of 4 parts of the 4-nitro- (I), m. p. 96°, and 5 parts of the 4 : 5-dinitro- (II), m. p. 130-131°. derivatives, and is obtained by the action of nitric acid $(d \ 1.43)$ on I. Nitration of 4-acetamidoveratrole, m. p. 130° (lit. 136°), with nitric acid $(d \ 1.4)$ in acetic acid gives 5-nitro-4-acetamidoveratrole, prepared also by acetylating the product obtained by the partial reduction of II with stannous chloride and 2.3Nalcoholic hydrochloric acid. Nitration of I with cold nitric acid (d 1.5) gives II; at the ordinary temperature 3:4:5-trinitroveratrole (III) results, whilst 3-nitroveratrole affords III, 3: 4- and 3: 5-dinitroveratroles. 3-Acetamidoveratrole is converted by nitric acid (d 1.45) at the ordinary temperature into 5-nitro-3-acetamidoveratrole, m. p. 173°, and the 4: 5-dinitroderivative, m. p. 240° (decomp.). H. BURTON.

Aromatic allyl and propenyl compounds. III. isoSafrole dibromide. H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1929, 48, 941—943).— Bromination of crude isosafrole in carbon disulphide solution affords a product which, contrary to the results of Nagai (A., 1921, i, 857), is optically inactive. isoSafrole, purified through the pieric acid additive compound, yields a dibromide, m. p. 52—53°, d_4^{30} 1.7682, n_{10}^{20} 1.6095, which is distillable in a cathode vacuum at a temperature not above 60°.

H. BURTON.

Compounds of aldehydes with dimethyldihydroresorcinol (aldimethone compounds). G. KLEIN and H. LINSER (Mikrochem., 1929, Pregl Fest., 204-234).-The compounds formed with dimethyldihydroresorcinol (aldimethones) by the following aldehydes occurring in plant products have been prepared and studied: formaldehyde, m. p. of dimethone 187°, anhydride, m. p. 171°; acetaldehyde, m. p. 139°, anhydride, 173°; propaldehyde, m. p. 155°, anhydride, 148°; butaldehyde, m. p. 142°, anhydride, 141°; isobutaldehyde, m. p. 154°, an-hydride, 144°; isovaleraldehyde, m. p. 137°, anhydride, 168°; heptaldehyde, m. p. 135°, anhydride, 110°; acraldehyde, m. p. 135°, anhydride, 170–188°; gly-oxal, m. p. 228°, anhydride, 170°; glyoxylic acid, m. p. 239°, anhydride, 245°; aldol, m. p. 184–186°, anhydride, 126°; crotonaldehyde, m. p. 180–183°, anhydride, 120°. The anhydrides are best prepared by boiling the aldimethones with 40% sulphuric acid for 2 hrs., removing the free acid with powdered barium hydroxide, and extracting the resulting mass with light petroleum. The anhydride is obtained by evaporation of the extract. No general quantitative method for the separation of mixtures of the above compounds could be found, but in a number of cases separation can be effected by fractional sublimation or extraction with various solvents. Glyoxylic acid may be separated from the remaining aldehydes by conversion into its lead salt before forming the aldimethones. A table giving the solubilities of the above compounds in a number of solvents and illustrations of the characteristic crystalline forms of the sublimates obtained from them accompany the paper.

H. F. HARWOOD.

Action of cinnamic acid on cholesterol. A new isomeride of cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 771).—When heated with 2 mols. of cinnamic acid at 200° for $\frac{1}{2}$ hr., cholesterol is partly converted into cholesteryl cinnamate, m. p. 157—158°, but the alcoholic mother-liquors from the crystallisation of the cinnamate deposit an *isomeride* of cholesterol, m. p. 137—137.5°, [α]_p—19° (bromide, m. p. 76°; acetate, m. p. 103°; benzoate, m. p. 131— 132°), which gives the Liebermann reaction more slowly than cholesterol, and is converted into the latter by alcoholic potassium hydroxide. R. BRIGHTMAN.

Steryl phosphates. H. VON EULER, A. WOLF, and H. HELLSTRÖM (Ber., 1929, 62, [B], 2451–2456; cf. A., 1927, 1066).—Addition of cholesterol in chloroform to a solution of phosphoryl chloride in acetone yields the *dichloride* of *monocholesteryl phosphate*, $C_{27}H_{45}O_2Cl_2P$, m. p. 122° (decomp.), hydrolysed by boiling water to monocholesteryl phosphate, m. p. 193°. The chloride of dicholesteryl phosphate, $C_{54}H_{90}O_3ClP$, m. p. 171°, is obtained under certain conditions during the preparation of dicholesteryl phosphate, m. p. 204°. β -Chloroethyl-phosphoryl chloride and cholesterol in pyridine afford dicholesteryl β -chloroethyl phosphate, $C_{56}H_{96}O_4ClP$, m. p. 158°. Diergosteryl β -chloroethyl phosphate, m. p. 165—167°, is described.

The absorption curves of ergosterol and diergosteryl phosphate before and after irradiation are given; those of the irradiated materials differ much more markedly from one another than do those of the untreated materials. H. WREN.

Decomposition of cholesterylene and of cholesteryl ether by aluminium chloride. N. D. ZELINSKI and N. N. SEMIGANOVSKI (Ber., 1929, 62, [B], 2199—2202; cf. A., 1928, 731, 865).—Thermal decomposition of cholesterylene in presence of aluminium chloride, under atmospheric or 16 mm. pressure, affords optically inactive, almost nonfluorescent hydrocarbons with very small iodine values. Under like conditions (at 16 mm.), cholesterol gives dextrorotatory products of markedly unsaturated character. Cholesteryl ether gives products similar to those from cholesterylene. H. WREN.

Irradiated sterols. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 771–776).—Pure commercial cholesterol, $[\alpha]_{\rm D}$ -33.57°, and ergosterol, $[\alpha]_{\rm D}$ -117°, when recrystallised three times from 95% alcohol yield material, $[\alpha]_D = -38.28^\circ$ and -119° , respectively, which after exposure to ultra-violet light does not affect a sensitised plate, and it is concluded that activation of cholesterol and ergosterol is due to the presence of traces of isomerides which are eliminated by successive crystallisations. Since the irradiation process is unaffected by temperature and the irradiated material is free from traces of ketones which should accompany a secondary alcohol, it is improbable that the activated constituent is produced by oxidation or migration of a double linking. The transformation of ergosterol into irradiated ergosterol is a reversible process, the irradiated ergosterol rapidly losing its power of affecting a sensitised plate, even when kept in the dark, an observation which is also inconsistent with an oxidation process of activation. Cholesterol from different sources contained no lecithin or fat, and accordingly these cannot be the source of the activated material (cf. Rosenheim and Webster, A., 1927, 381, 487; Schultz, Ziegler, and Morse, A., 1927, 703). The reaction of vitamin-D or irradiated ergosterol with fuchsin (Steigmann, A., 1928, 926) could not be confirmed and was not obtained with cholesterol or ergosterol. The reducing action of vitamin-D with silver oxide is attributed to the presence of double linkings. R. BRIGHTMAN.

Destruction of cholesterol by X-rays in vitro. A. H. ROFFO and L. M. CORREA (Forschr. Röntgenstr., 1929, **39**, 882–889).—Contrary to the assertion of Schreuss and Schulze (*ibid.*, **37**, 212) that X-rays are incapable of decomposing cholesterol, it is confirmed that irradiation of 0.2% solutions in chloroform causes decomposition to the extent of **35%**. A claim for priority as to the oxidative nature of the decomposition process brought about by irradiation is made. C. W. SHOPPEE.

Effect of X-rays on cholesterol. A. BACHEM and R. P. MACFATE.—See this vol., 1249.

Heteropolar carbon compounds. VIII. Meth-oxytriphenylcarbenium salts. W. DILTHEY and W. ALFUSZ (Ber., 1929, 62, [B], 2078-2081; cf. this vol., 1067).—The perchlorates of mono- (m. p. 192°), di- (m. p. 212°), and tri- (m. p. 192-193°) methoxytriphenylcarbinol have been prepared. Titration of their solutions in anhydrous acetone with aqueous alcohol ($d \ 0.8665$) until colourless shows that hydrolysis commences and is complete more rapidly with the di- than with the tri-anisyl compound. A slowly progressive hydrolysis cannot be doubted, since the direction of change is reversed by increase of temperature or concentration or by addition of perchlorate ions and the solution develops increasing acidity. In apparently anhydrous solution the colour is more slowly but ultimately discharged by dilution. It is doubtful whether colourless carbonium ions are present in solutions which have suffered hydrolysis (alcoholysis, acetonolysis), but, until the contrary is established, salt formation and occurrence of colour must be considered to go hand in hand and the titration hydrolysis must be regarded as giving a relatively accurate picture of the increase of basicity caused by the introduction of methoxy-groups into cations of this type. H. WREN. cations of this type.

Organic molecular compounds with co-ordination centres. II. Co-ordination numbers of alkyl esters of fatty acids in choleic acids. H. RHEINBOLDT, O. KÖNIG, and R. OTTEN (Annalen, 1929, 473, 249-259).-Co-ordination compounds similar to those previously described (A., 1927, 242) are obtained from deoxycholic acid and alkyl esters of fatty acids. The co-ordination numbers of the esters (other than formates) are usually less than the values for the fatty acids of the same molecular composition. For a series of esters R·CO₂Alk, where the number of carbon atoms in Alk. is greater than in R.CO2. the co-ordination numbers of the esters are greater than the values for the acids R·CO₂H and the same as those for the alcohols Alk-OH (values assumed from acids of same carbon content). The co-ordination numbers of the octyl esters of formic to heptoic acids are all 6, whilst octoic acid has a value of 4 (loc. cit.). Octyl octoate and octyl alcohol also give the value 6. It is concluded that the heptyl group shows the value 4, and the octyl group 6. The increase in the co-ordination number from 4 to 6 is, therefore, between C7 and C8 and not C9 and C10 (cf. loc. cit.). The same result is obtained by a comparison of several pairs of esters, R·CO2Me and Me·CO2R, which show the same co-ordination numbers. The increases in the coordination numbers from 3 to 4 and 6 to 8 are between C_2 and C_3 , and C_{13} and C_{14} , respectively (cf. *loc. cit.*). The values for the acids R·CO₂H and the formates H·CO,R are identical; both carboxyl and formate groups have no influence on the co-ordination number. The esters, R.CO.R, show the next higher co-ordination number than the group R. Choleic acids are obtained from the following compounds and deoxycholic acid (the number of mols. of the latter is

given, followed by the m. p. of the choleic acid in parentheses): *n*-hexyl formate, 4 (167.5°); *n*-heptyl formate, 4 (168-169°); n-octyl formate, 6 (170.5-171°); n-dodecyl formate, b. p. 145-146°/15 mm., 6 (179°); n-tetradecyl formate, b. p. 166°/17 mm., 8 (185°); n-hexadecyl formate, b. p. 188°/17 mm., 8 (187.5°); methyl acetate, 3 (about 145° [decomp.]); *n*-propyl acetate, 4 (142—146° [decomp.]); ethyl acetate, 3 (140—145° [decomp.]); *n*-hexyl acetate, 4 (168-169°); n-heptyl acetate, 4 (169°); n-octyl acetate, 6 (172-173°); n-dodecyl acetate, 6 (180.5°); n-tetradecyl acetate, 8 (185.5-186°); n-hexadecyl acetate, 8 (189°); methyl propionate, 3 (144-148° [decomp.]); ethyl propionate, 4 (145-149° [decomp.]), n-heptyl propionate, 4 (170—171°); n-octyl propion-ate, 6 (173.5—174.5°); n-dodecyl propionate, b. p. 166-168°/20 mm., 6 (182°); n-hexadecyl propionate, b. p. 211-212°/18 mm., 8 (187°); methyl butyrate, 4 (about 148-152° [decomp.]); n-octyl butyrate, 6 (176-176.5°); n-dodecyl butyrate, b. p. 177-178°/ 19 mm., 6 (183.5°); n-hexadecyl butyrate, 8 (189°); n-butyl n-valerate, 6 (169-170°); n-octyl valerate, 6 (176-177°); n-amyl n-hexoate, 6 (173.5°); n-octyl hexoate, 6 (181-181.5°); methyl n-heptoate, 4 (169-170°); n-hexyl heptoate, b. p. 137°/19 mm., 6 (177-177.5°); n-octyl heptoate, 6 (182°); methyl octoate, 4 (169-170°); n-heptyl octoate, 6 (180.5-181°); n-octyl octoate, 6 (181-181.5°); methyl nonoate, 6 (174-175°); n-heptyl nonoate, b. p. 210° 75 mm., 6 (182.5-183°); n-octyl nonoate, b. p. 183°/ 21 mm., 8 (185°); n-nonyl decoate, b. p. 210.5-211.5°/ 20 mm., 8 (186.5—187°); methyl dodecoate, 6 (180°); ethyl dodecoate, 6 (182°); n-propyl dodecoate, b. p. 155-156°/18 mm., 6 (183.5-184°); n-butyl dodecoate, b. p. 180°/18 mm., 6 (184-184.5°); n-hexyl dodecoate, b. p. 199°/19 mm., 6 (185.5°); n-octyl dodecoate, b. p. 204-205°/17 mm., 6 (186°); methyl tetradecoate, 6 (181.5-182°); ethyl tetradecoate, 6 (183.5°); n-butyl tetradecoate, b. p. 195°/18 mm., 6 (186°); n-hexyl tetradecoate, b. p. 215°/17 mm., 6 (188°); n-tetradecyl tetradecoate, m. p. 43°, 8 (194.5-195.5°); n-hexadecyl tetradecoate, m. p. 47° , 8 (197–198°); methyl pentadecoate, 8 (184·5–185°); n-octyl alcohol, 6 (169·5–170°); n-tetradecyl alcohol, 8 (183.5-184.5°). The choleic acid, m. p. 187-188°, from n-hexadecyl acetate and apocholic acid contains 8 mols. of the latter. H. BURTON.

Optical activity of the hydrocarbons obtained by the decomposition of resin acids by aluminium chloride. N. D. ZELINSKI and N. N. SEMIGANOVSKI (Ber., 1929, 62, [B], 2202-2205).-The primary products of the decomposition of optically inactive resin acids by aluminium chloride are optically active, dextrorotatory hydrocarbons. It is probable that the optical inactivity of the acids is an accidental result of the compensation of the dextrorotatory acids with those of opposite sign. The active hydrocarbons are markedly unsaturated. The more volatile fractions of the primary product are rich in aromatic compounds. Treatment of the active fractions with aluminium chloride causes production of optically inactive hydrocarbons with very low iodine numbers. The possibility that resin acids have played a part in the formation of mineral oils is discussed. H. WREN.

1294

Chemistry of the three-carbon system. XXII. Preparation and interconversion of isomeric unsaturated nitriles. A. KANDIAH and R. P. LINSTEAD (J.C.S., 1929, 2139-2153) .- Anomalies in the chemistry of certain $\alpha \beta$ - and $\beta \gamma$ -unsaturated nitriles (Birch and Kon, ibid., 1923, 123, 2440) have led to their re-investigation. A study of the interconversion of eight pairs of nitriles by sodium ethoxide at 25° is described. The mobility is high, decreasing with increased size of the α -group, and the equilibrium is far on the side of the $\alpha\beta$ -phase, all the equilibria examined showing a predominance of ab- amounting to 90-99%. The high activity and the position of equilibrium are attributed to the powerful effect of the terminal nitrile group. A general method for the preparation of the nitriles from amides is by treatment with a solution of phosphorus pentachloride in phosphorus oxychloride.

 Δ^1 -cycloHexenylacetamide, m. p. 152°, yields Δ^1 -cyclohexenylacetonitrile, b. p. 105°/22 mm., d_4^{10} 0.9533, np 1.4843, [R_L]_p 36.30, isomeric with cyclohexylideneacetonitrile, b. p. 107—108°/22 mm., d_4^{15} 0.9483, n_D^{16} 1.4928, $[R_L]_D$ 37.1, from cyclohexylidene-acetamide, m. p. 147°. α -cycloHexylidenepropion-amide, m. p. 120°, gives α -cyclohexylidenepropio-nitrile, b. p. 102—103°/13 mm., d_4^{17} 0.9366, n_D^{17} 1.4941, $[R_L]_0$ 42.0, isomeric with α - Δ^1 -cyclohexenylpropio-nitrile, b. p. 113°/13 mm., d_4^{16} 0.9382, n_D^{16} 1.4761, $[R_L]_0$ 40.7, from α - Δ^1 -cyclohexenylpropionic acid, m. p. 38° b. p. 144°/14 mm. (anilide, m. p. 56°), by way of the amide, m. p. 90°. a-cycloHexylidenebutyronitrile, b. p. 114°/11 mm., $d_1^{1.4}$ 0.9225, $n_D^{1.4}$ 1.4887, $[R_L]_D$ 46.53, is isomeric with α - Δ^1 -cyclohexenylbutyronitrile, b. p. 112°/12 mm., d_4^{174} 0.9263, n_D^{174} 1.4794, $[R_L]_D$ 45.68, from α - Δ^1 -cyclohexenylbutyramide, m. p. 115—116°. cycloPentylideneacetonitrile, b. p. 97-98°/24 mm., $d_4^{i_{8\,4}}$ 0.9427, $n_D^{i_{8\,4}}$ 1.4805, $[R_L]_D$ 32.30, in 55% yield from cyclopentylideneacetamide, m. p. 138°, is isomeric with Δ^1 -cyclopentenylacetonitrile, b. p. 91—92°/19 mm., d_4^{184} 0.9395, n_D^{184} 1.4683, $[R_L]_D$ 31.7. β-Methyl-Δ^a-pentenonitrile has b. p. 63°/20 mm., d_4^{202} 0.8432, $n_{\rm D}^{200}$ 1.4447, $[R_L]_{\rm D}$ 30.0, and β -methyl- Δ^{β} -pentenonitrile, b. p. $60^{\circ}/19 \text{ mm.}, d_4^{205} 0.8478, n_D^{205} 1.4367, [R_L]_{D} 29.36,$ from β -methyl- Δ^{β} -pentenamide, m. p. 124–125°. 2-Methyl- $\Delta^{\text{Mor 6}}$ -cyclohexenyl-1-acetonitrile, b. p. 101°/ 14 mm., d_4^{21} 0.9384, n_D^{21} 1.47621, $[R_L]_D$ 40.4 (piperonylidene derivative, m. p. 122°), is obtained from a-cyano-1-methylcyclohexylidene-2-acetic acid, m. p. 106-107°, by distillation. 3-Methyl- Δ^1 -cyclohexenyl-1-aceto-nitrile, b. p. 113°/20 mm., d_4^{21} 0.9239, n_D^{21} 1.4732, $[R_L]_D$ 41.3 (*piperonylidene* derivative, m. p. 84°), gives an imino-compound when condensed with cyanoacetamide, hydrolysed to the ω -imide of α -cyano-3-methylcyclohexane-1: 1-diacetic acid, m. p. 225°. 4-Methyl- Δ^1 -cyclohexenyl-1-acetonitrile has b. p. 109°/16 mm., d_4^{21} 0.9232, n_D^{21} 1.4726, $[R_L]_D$ 41.0 (ω -imide of α -cyano-4-methylcyclohexane-1: 1-diacetic acid, m. p. 230°; piperonylidene derivative, m. p. 132°).

D. W. HILL.

Replacement of halogen in o-bromobenzoic acid. W. R. H. HURTLEY (J.C.S., 1929, 1870— 1873).—Salicylic acid is readily formed by boiling sodium o-bromobenzoate with sodium and copper acetates in aqueous solution. In boiling alcoholic sodium ethoxide solution in presence of copper-

bronze o-bromobenzoic acid reacts with acetylacetone to give phenylacetylacetone-o-carboxylic acid, m. p. 142°. Similarly, ethyl malonate yields ethyl o-carboxyphenylmalonate, m. p. 102°. Ethyl hydrogen homo-phthalate alone is obtained with ethyl acetoacetate or ethyl acetonedicarboxylate, and β -deoxybenzoin-o-carboxylic acid, m. p. 168° (sintering 145°) (lit. 162– 163°; 140°), with benzoylacetone. With resorcinol, either when boiled in sodium hydroxide solution and a little copper sulphate solution added, or when fused, the *lactone* of 2': 4'-dihydroxydiphenyl-2-carboxylic acid, m. p. 232°, is formed. Methylation of the lactone with methyl sulphate and alkali gives in the cold the lactone of 2'-hydroxy-4'-methoxydiphenyl-2-carboxylic acid, m. p. 141°, or, at 100°, 2':4'-di-methoxydiphenyl-2-carboxylic acid, m. p. 150°. At 160°, o-bromobenzoic acid and copper-bronze yield cuprous bromide and cuprous benzoate. In boiling water benzoic acid and 7% of diphenic acid are formed. Diphenic acid is obtained in 43% yield by heating potassium o-bromobenzoate and copperbronze at 100° and stirring in a little water. Ethyl o-bromobenzoate, p-bromobenzoic acid, and o-bromonitrobenzene do not undergo these reactions.

R. K. CALLOW. Dynamic isomerism involving mobile hydrocarbon radicals. I. The triarylbenzenylamidines. A. W. CHAPMAN (J.C.S., 1929, 2133-2138).-Dynamic isomerism as known in the cases of mobile hydrogen, anions, or valency linkings extends also to mobile hydrocarbon radicals, more drastic conditions being necessary to induce migration. N-Diphenyl-N'-p-tolylbenzamidine, NPh₂·CPh:N·C₇H₇,

and NN'-diphenyl-N-p-tolylbenzamidine, NPh:CPh·NPh·C₇H₇, are converted into an equilibrium mixture containing 60—65% of the latter by heating at 322—323° for about 4 hrs. D. W. HILL.

X-Ray investigations of optically active compounds. I. Proof of molecular asymmetry in optically active α -aminophenylacetic acid. G. L. CLARK and G. R. YOHE (J. Amer. Chem. Soc., 1929, 51, 2796—2807).—X-Ray examinations of d-, l-, and dl- α -aminophenylacetic acids have been made by the rotation and powder diffraction methods. Crystal structure analysis was possible by the rotation method, although no crystallographic or optical data were available. The d- and l-acids crystallise in the orthorhombic system, space-group C_{24}° , and the unit cell contains four molecules and has the dimensions a 15·2, b 5·05, c 9·66 Å. No molecular symmetry is possible. Whilst the crystal form of the dl-acid differs from that of the d- and l-acids, it is not possible to distinguish between d- and l-forms by X-ray diffraction methods.

l- α -Aminophenylacetic acid, sublimes at 245—248° (lit. 227—310°), $[\alpha]_{00}^{20}$ —149° in 0·14*N*-hydrochloric acid, and *d*- α -aminophenylacetic acid, m. p. 242—244°, $[\alpha]_{00}^{20}$ +147° in 0·105*N*-hydrochloric acid, are obtained by resolution of the *dl*-acid with *d*-camphorsulphonic acid. H. BURTON.

2-Bromo-3-hydroxybenzoic acid. P. H. BEIJER (Rec. trav. chim., 1929, 48, 1010-1011).---Nitration of *m*-acetamidobenzoic acid by Kaiser's method (A., 1886, 149), separation of the 2-nitro-derivative through its barium salt, and subsequent boiling with potassium hydroxide solution affords 2-nitro-3-hydroxybenzoic acid, reduced by alkaline sodium sulphide to the corresponding 2-amino-derivative. This is converted by the usual method into 2-bromo-3-hydroxybenzoic acid, m. p. 160—161°. H. BURTON.

Derivatives of 6-amino-3-hydroxybenzoic acid. E. PUXEDDU and G. SANNA (Gazzetta, 1929, 59, 489-495).—The methyl ester, m. p. 158° (hydrochloride, m. p: 223°), and ethyl ester, m. p. 140° (hydrochloride, m. p. 214°), of 6-amino-3-hydroxybenzoic acid (cf. this vol., 555) have been prepared. Condensation of the acid with chloroacetyl chloride yields 6-chloroacetamido-3-hydroxybenzoic acid $(+0.5H_2O)$, m. p. 222°. This could not be esterified directly, but the methyl ester, m. p. 187°, was obtained from the aminoester, and yielded, when treated with dimethylamine, methyl 6-dimethylaminoacetamido-3-hydroxybenzoate, m. p. 149°. The preparation of the carbamido-derivative and the ureide from 6-amino-3-hydroxybenzoic acid described by Froelicher and Cohen (J.C.S., 1921, 119, 1425) is confirmed. The acid condenses with R. K. CALLOW. ethyl acetoacetate.

Elimination of carbon dioxide from organic compounds. VII. Pyrogenic degradation of cyclic hydroxy-acids. Salicylic, protocatechuic, gallic, o-hydroxycinnamic, 3:4-dihydroxycinnamic, and cyclogallipharic acids and their derivatives alone and in presence of phloroglucinol, aniline, and pyridine. H. KUNZ-KRAUSE and P. MANICKE (Arch. Pharm., 1929, 267, 555-571; cf. A., 1920, i, 312).-Salicylic acid does not decompose smoothly into phenol and carbon dioxide when heated at 250°. After 1 hr. only 17.56% of carbon dioxide is evolved; phenyl salicylate and a small amount of phenol are also obtained. Increased evolution of carbon dioxide occurs when the heating is carried out in presence of phloroglucinol at 250° pyridine at 180°, or aniline at 175-180°; in the last case 1 mol. of carbon dioxide is eliminated from 1 mol. of the acid after 135 min. heating. With acetylsalicylic acid at 250° only a small amount of carbon dioxide is evolved; acetic anhydride, salicylosalicylic and trisalicylosalicylic acids are formed also. Protocatechuic acid evolves 1 mol. of carbon dioxide in presence of phloroglucinol at 218-225°, but the residue has properties corresponding with a tannoid (cf. loc. cit.); in presence of aniline or pyridine evolution of carbon dioxide occurs at 180° or 150°, respectively. Decomposition of gallic acid (cf. loc. cit.) takes place at 170° in presence of aniline, and at 110-120° in presence of pyridine. It is necessary to raise the temperature for evolution of 1 mol. of carbon dioxide. o-Hydroxy- and 3:4-dihydroxy-cinnamic acids de-compose readily at about 200° into carbon dioxide and the corresponding styrene; in presence of aniline or pyridine a lower temperature is required. cyclo-Gallipharic acid (Kunz-Krause and Manicke, A., 1911, i, 130) is decomposed by heating with aniline at 160° into carbon dioxide and cyclogallipharol. Coumarin, umbelliferone, and daphnetin do not climinate carbon dioxide at 220-250°. H. BURTON.

Phthalide derivatives. F. MAYER, W. SCHAFER, and J. ROSENBACH (Arch. Pharm., 1929, 267, 571584).—Magnesium ethyl bromide converts α -naphthaldehyde-8-carboxylic acid into the lactone, m. p. 68°, of 1-a-hydroxypropylnaphthalene-8-carboxylic acid. Bromination of 2-methyl- α -naphthoyl chloride (I) at 155-160°, subsequent conversion of the product formed into ethyl 2-bromomethyl-a-naphthoate, and elimination of ethyl bromide from this by heating gives the lactone, m. p. 152-153°, of 2-hydroxymethyl- α -naphthoic acid. Chlorination of I at 150-170° under the influence of arc-lamp irradiation and hydrolysis of the product formed with water and calcium carbonate affords β -naphthaldehyde-1-carboxylic acid, m. p. 176° (oxime, m. p. 215°, not sharp). 1-Bromo-2-methyl-5:6:7:8-tetrahydronaphthalene, b. p. 140-155°/11-12 mm., is converted by the usual Grignard method into 2-methyl-5:6:7:8-tetrahydronaphthalene-1-carboxylic acid, m. p. 172—173° (chloride, b. p. 170—175°/26 mm.; ethyl ester, b. p. 194—196°/21 mm.), oxidised by nitric acid to mellophanic acid. Treatment of the sodium hydrogen sulphite compound of 2-methoxy-a-naphthaldehyde with aqueous potassium cyanide gives the corresponding cyanohydrin, m. p. 112°, reduced and hydrolysed by boiling hydriodic (d 1.99) and acetic acids to 2-hydroxynaphthylacetic acid, m. p. 147° (lactone, m. p. 103-104°). Magnesium methyl iodide reacts with the anhydride of naphthalene-2: 3-dicarboxylic acid, yielding the lactone, m. p. 127°, of $2-\alpha$ -hydroxyisopropylnaphthalene-3-carboxylic acid.

Oximinoaceto-5:6:7:8-tetrahydro-a-(II), m. p. 179°, and $-\beta$ -naphthylamides (III), m. p. 168[°], are prepared by Sandmeyer's method (A., 1919, i, 318). When II is heated with slightly diluted sulphuric acid (cf. (loc. cit.) conversion into the corresponding isatin, m. p. 230°, occurs. The mixture of 4- and 6-methyl-isatin, m. p. 187° (lit. 169°), obtained similarly from oximinoaceto-*m*-toluidide (cf. A., 1925, i, 1315) is converted by treatment with sodium hydroxide and hydrogen peroxide into a mixture of 2-amino-p-toluic and 6-amino-o-toluic acids, m. p. 118° (lit. 125°). The mixture of isatins formed from III yields by treatment 2-amino-5:6:7:8-tetrahydrosimilar naphthalene-1., m. p. 137° (3 parts), and -3-carboxylic acids, m. p. 179° (1 part) (melhyl ester, m. p. 69°), separable by partial esterification. Electrolytic reduction of a series of aminobenzoic acids (obtained by oxidation of the requisite isatin), using lead electrodes and 20% sulphuric acid, gives usually good yields of the corresponding aminobenzyl alcohols. The following are described : 2-amino-3-methyl-, m. p. 71°; 2ing are described : 2-amino-3-methyl., m. p. 71°; 2-amino-5-methyl., b. p. 145—150°/13 mm., m. p. 123°; 2-amino-6-methyl., m. p. 85°; 2-amino-4-methyl., m. p. 141°; 2-amino-3: 5-dimethyl., m. p. 73°, and 2-amino-3: 6-dimethyl-benzyl alcohols, m. p. 106°. 2-Amino-1-hydroxymethyl., m. p. 87°, and 2-amino-3-hydroxy-methyl-5: 6: 7: 8-tetrahydronaphthalenes, m. p. 158°, are obtained similarly; 1-amino-5: 6: 7: 8-tetra-hydroxybalanes, academic functional func hydronaphthalene-2-carboxylic acid furnishes a compound, m. p. 215°, and a small amount of a substance, m. p. 108°. 2-Amino-3-hydroxymethylnaphthalene (diacetyl derivative, m. p. 149°) has m. p. 183°. The amino-alcohols are converted by the usual method into the cyanobenzyl alcohols, which on hydrolysis with sodium hydroxide solution afford the corresponding phthalides. The following are described : o-cyanobenzyl alcohol, b. p. 170-175°/30 mm., hydrolysed to phthalide; 2-cyano-5-methylbenzyl alcohol, m. p. 110-112°, yielding 4-methyl-1: 2-phthalide, m. p. 118° (cf. Perkin and Stone, A., 1926, 64); 2-cyano-3: 5dimethylbenzyl alcohol, m. p. 85°, hydrolysed to 4: 6dimethyl-1: 2-phthalide, m. p. 100°, and 2-cyano-3hydroxymethylnaphthalene, m. p. 130° (corresponding phthalide, m. p. 206°). H. BURTON.

Action of sodium hypochlorite on amides. V. 1. J. RINKES (Rec. trav. chim., 1929, 48, 960-964). —Treatment of benzoylformamide with sodium hypochlorite at -5° gives benzoic acid; in presence of methyl alcohol at -10° methyl benzoate results, and treatment of the residue with hydrazine acetate and then with acetic acid affords hydrazodicarbonamide. Δ° -Pentenoamide is converted in methylalcoholic solution at -5° into methyl Δ° -butenylcarbamate, m. p. 25—26°, hydrolysed by 15% sulphuric acid to *n*-butaldehyde. o-Nitrophenylpropiolamide, m. p. 159° (from the chloride and ammonia in benzeno solution), is converted by aqueous sodium hypochlorite into the N-chloro-derivative, m. p. 127.5° (cf. A., 1921, i, 27). When maleamide is beated with zinc chloride a small amount of malcimide is obtained. Treatment of methyl styrylcarbamate (A., 1927, 652) with ozonised air in ethyl acetate solution, and decomposition of the oily ozonide by boiling with water and calcium carbonate affords benzaldehyde and N-carbomethoxyformamide, b. p. 94°/10 mm., m. p. 91°. H. BUBTON.

Compounds of bivalent carbon. III. Acetals of dicarbonic oxide and their decomposition into carbonic oxide acetals. H. SCHEIBLER and E. BAUMANN (Ber., 1929, 62, [B], 2057-2065; cf. A., 1926, 711) .- The solid reaction product from ethyl diphenoxyacetate and sodium ethoxide, suspended in light petroleum, is decomposed by addition of cold water or by the successive action of phosphoryl chloride, hydrogen chloride, and excess of sodium ethoxide into diphenoxyacetic acid and aa-diethoxyββ-diphenoxyethylene, b. p. 140-145°/0.8 mm. The constitution of the last-named compound is deduced from its transformation by aqueous-alcoholic hydrochloric acid into ethyl diphenoxyacetate and thence into diphenoxyacetic acid. Attempts to prepare diphenoxyketen from diphenoxyacetyl chloride, b. p. 148-150°/0.7 mm., were unsuccessful, since it appears to yield ketenium bases with pyridine and trimethylamine, whereas diphenoxybromoacetyl bromide does not react with zinc. Diphenoxyacetyl chloride is converted by bromine in chloroform into dibromophenoxybromoacetyl bromide, m. p. 63°. Ethyl di-p-tolyloxyacetate, b. p. 186-187°/6 mm., is prepared from dichloroacetic acid and p-cresol followed by esterification of the product. Ethyl di-p-tolyloxymalonate, b. p. 203-205°/0.8 mm., m. p. 62-63°, derived from ethyl dibromomalonate and sodium p-tolyloxide, is hydrolysed to di-p-tolyloxymalonic acid, m. p. 160° (decomp.), converted by thionyl chloride into carbon dioxide and di-p-tolyloxyacetyl chloride. Ethyl di- α -naphthoxyacetate has m. p. 73°. Diphenyldithiol-acetic acid, m. p. 104°, may be prepared from dichloroacetic acid and thiophenol. H. WREN.

Syntheses in the hydroaromatic series. V. Δ^4 -Tetrahydro-o-phthalic acid. O. DIELS and

K. ALDER (Ber., 1929, 62, [B], 2087–2090; cf. this vol., 1297).—Mainly a reply to Farmer and Warren (this vol., 812). The hypothesis that the product of the condensation of maleic anhydride and butadiene is $cis-\Delta^4$ -tetrahydro-o-phthalic anhydride is confirmed by oxidation of the compound to butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acid, m. p. 188–189° [dianhydride, m. p. 246–248° (decomp.)]. H. WREN.

Asymmetric oxidation. Y. SHIBATA and R. TSUCHIDA (Bull. Chem. Soc. Japan, 1929, 4, 142-149).--- A solution of *l*-amminochlorodiethylenediaminecobaltic bromide was added to a solution of τ -3: 4-dihydroxyphenylalanine containing a buffer solution of phosphate; the whole was then placed in a thermostat at 20°, and observations were made of the rotatory power of samples removed from time to time. The curve produced by plotting the angle of rotation against the time of reaction, although displaying marked irregularities for the first few hours, shows from its general type that the complex cobaltic bromide oxidises the l-component of racemic 3: 4-dihydroxyphenylalanine more readily than the d-component, and that a lævorotatory quinonic (?) compound is intermediately produced. The latter is then transformed into an inactive compound, the solution becoming less lævorotatory and finally dextrorotatory owing to the remaining d-dihydroxyphenylalanine. The possible mechanism of the reaction is discussed. B. W. ANDEBSON.

Chlorides of tetrachlorophthalic acid. A. KIR-PAL and H. KUNZE (Ber., 1929, 62, [B], 2102-2106).as-Tetrachlorophthalyl chloride, m. p. 137° (or +C₆H₆, m. p. about 118-120°, according to rate of heating), is prepared by the action of phosphorus pentachloride on tetrachlorophthalic acid under pressure at 220°. Distillation of the asymmetric chloride followed by immediate cooling of the distillate and extraction of it with cold light petroleum permits the isolation of s-tetrachlorophthalyl chloride, m. p. 48°, which passes slowly when solid, more rapidly when dissolved, and almost immediately in the presence of animal charcoal into the as-variety. The last-named substance is converted by protracted heating at its b. p. (more rapidly in presence of chlorine) into pentachlorobenzoyl chloride, m. p. 87°, slowly transformed by methyl alcohol into methyl pentachlorobenzoale, m. p. 97°. Treatment of as-tetrachlorophthalyl chloride with absolute ethyl alcohol at the ordinary temperature affords ethyl &-tetrachlorophthalate, m. p. 126°; protracted exposure of the ψ -ester to the reaction mixture results in its isomerisation to ethyl tetrachlorophthalate, m. p. 60.5°, under the influence of the liberated hydrogen chloride. s-Tetrachlorophthalvl chloride dissolves very readily in ethyl alcohol and the ψ -ester soon separates from the solution; possibly, the ψ -chloride of the hydrogen ester is intermediately formed. Thionyl chloride transforms ethyl hydrogen tetrachlorophthalate into

the compound $C_6Cl_4 < CO^{CO}(OEt) > 0$, m. p. 54°.

H. WREN.

Isomeric $\alpha\beta$ -diphenylglutaric acids. I. Optically inactive acids. II. Optically active acids. S. AVERY and W. D. MACLAY (J. Amer. Chem. Soc.,

1929, 51, 2833-2839).-I. When (trans)-a3-diphenyllight for the set of the methyle ster, m. p. 143°, m. p. 143°, m. p. 226-228°, is heated with acetyl chloride at 140° the *anhydride* (II), m. p. 126·5°, of (*cis*)-*α*β-diphenylglutaric acid (III), m. p. 208-210° (corr.) (cf. Meerwein and Dott, A., 1919, i, 21), is produced. Hydrolysis of the methyl ester, m. p. 143°, for a standard methyle ster methy of I with alcoholic potassium hydroxide also affords III in addition to I. The amide prepared from II is identical with the monoamide obtained from y-cyanoβy-diphenylbutyric acid (A., 1928, 1243) and is converted by boiling with alcoholic hydrochloric acid into the *imide*, m. p. 225–229°, of III. The same imide is obtained by treatment of methyl γ -cyano- $\beta\gamma$ -diphenylbutyrate with concentrated alcoholic potassium hydroxide, subsequent evaporation, acidification with acetic and hydrochloric acids, and re-evaporation. The anilic acid from II and aniline has m. p. 201-202°. The transformation III \longrightarrow I occurs with hydrochloric acid at 200°. Hydrolysis of the esters of III with hydrochloric acid above 180° gives mainly I, whilst alkaline hydrolysis gives a mixture of I and III. Hydrolysis of the above cyano-compound with acid below 150° gives the amide and III; above 150° I and III are formed and the amount of I increases with increase of temperature.

II. Resolution of trans- $\alpha\beta$ -diphenylglutaric acid is effected by brucine yielding d-, m. p. 224–226°, $[\alpha]_{0}^{m}$ +58.7° in acetone, and 1- $\alpha\beta$ -diphenylglutaric acids, $[\alpha]_{0}^{m}$ -58° in acetone, to which are assigned $(+\alpha-\beta)$ and $(-\alpha+\beta)$ configurations, respectively. Similarly, III gives d- $(+\alpha+\beta)$, $[\alpha]_{0}^{m}$ +140.6° in acetone, and 1- $(-\alpha-\beta)$ -diphenylglutaric acids, m. p. 202°, $[\alpha]_{0}^{m}$ -140° in acetone. H. BURTON.

Syntheses in the hydroaromatic series. IV. Addition of maleic anhydride to arylated dienes, trienes, and fulvenes. O. DIELS and K. ALDER [with P. PRIES] (Ber., 1929, 62, [B], 2081-2087; cf. this vol., 819).-3: 6-Diphenyl-cis- Δ^4 -tetrahydrophthalic anhydride, m. p. 207°, is prepared by melting transtrans- α S-diphenylbutadiene with maleic anhydride. The constitution of the compound follows from the transformation of the calcium salt of the corresponding acid into p-diphenylbenzene by distillation with a mixture of calcium oxide and zinc dust. α -Phenylbutadiene and maleic anhydride give 3-phenyl- Δ^4 -cis-tetrahydrophthalic anhydride, m. p. 120°, degraded to diphenyl. In these cases the addition takes place in the 1: 4-position. On grounds of analogy, the product from α -phenyl- δ -methylbutadiene is regarded as 3-phenyl-6-methyl Δ^4 -cis-tetrahydro-ophthalic anhydride, m. p. 158-159°. Maleic anhydride yields the compounds C₂₂H₁₈O₃, m. p. 194°, with α ^ζ-diphenylfulvene, C₁₂H₁₂O₃, m. p. 137°, with 6: 6-diphenylfulvene, and C₁₈H₁₄O₃, m. p. 137°, with 6: 6-dimethylfulvene; the mode of addition has not been established definitely. H. WREN.

Studies in "strainless" rings. I. β -Substituted stereoisomeric decalins. K. A. N. RAO (J.C.S., 1929, 1954—1969).—A number of substituted decalins of the type $C_9H_{16}>C<_Y^X$, where X and Y are (a) identical, (b) different, (c) replaced by a symmetrical ring, (d) replaced by an unsymmetrical ring, have been

prepared and their stereoisomeric relationships studied. When X and Y are identical or replaced by a symmetrical ring only one isomeride corresponding with each decalin is formed. When X and Y are different, four isomerides are possible and replacement of X and Y by an unsymmetrical ring does not diminish the number of isomerides. These results are in harmony with Mohr's theory (A., 1919, ii, 229; 1922, i, 441). cis- and trans- β -Decalones (cis-, m. p. 105°, b. p. 119°/16 mm., d_1^{3**} 1·00298, n_D^{3**} 1·49366; semicarbazone, m. p. 185–186°; trans-, b. p. 117°/16 mm., d_1^{292} 0.97624, $n_D^{2r^2}$ 1.48337; semicarbazone, m. p. 193°) condensed with ethyl cyanoacetate and alcoholic ammonia give the *cis*- and *trans*-decahydronaph-thalene-2: 2-dicyanoacetimides [*cis*-, m. p. 242-243° (decomp.); *trans*-, m. p. 280° (decomp.)], which are converted into the dicarbamylimides (cis-, m. p. 260-261°; trans-, m. p. 234-235°). These on hydrolysis yield the cis- and trans-decalin-2: 2-diacetic acids yield the cis- and trans-decalin-2: 2-diacetic actus [cis-, m. p. 167°; ethyl ester, b. p. 213°/21 mm., $d_4^{18'8}$ 1·04874, $n_5^{18'3}$ 1·47918 (*imide*, m. p. 205°; anhydride, m. p. 91°); trans-, m. p. 175° (methyl ester, b. p. 192°/12 mm.; ethyl ester, b. p. 209°/16 mm., $d_4^{10'3}$ 1·04115, $n_5^{16'8}$ 1·47702; *imide*, m. p. 201°; anhydride, m. p. 37°, b. p. 240°/20 mm.)]. Each of the anhydrides gives a pair of arilic acids on keeping with aniline gives a pair of anilic acids on keeping with aniline (cis-, stable form, m. p. 167°, unstable, m. p. 200°; trans-, stable form, m. p. 159—161°, unstable, m. p. 165-166°). Each pair yields the same anil (cis-, m. p. 210°; trans-, m. p. 205°).

 $\Delta^{2:3(1:2)}$ -trans-Decahydronaphthalene-2-acetonitrile (octahydronaphthylacetonitrile), b. p. 164°/26 mm., was prepared by distillation of the acid obtained on hydrolysing ethyl trans-decahydro- β -naphthylidenecyanoacetate. The latter on treatment with alcoholic potassium cyanide gives the dicyano-ester,

C₉H₁₆>C(CN)·CH(CN)·CO₂Et, b. p. 200°/18 mm., $d_4^{30^{\circ}}$ 1·04947, $n_D^{30^{\circ}}$ 1·47594. Hydrolysis of this yields two 2-carboxy-trans-decahydronaphthalene-2-acetic acids [(A) m. p. 197°; anilic acid, m. p. 193°; anil, m. p. 166—167°; di-p-toluidide, m. p. 171°; anhydride, m. p. 94°; (B) m. p. 175°; anilic acid, m. p. 198°; anhydride, m. p. 98° (cf. Hūckel and Wiebke, A., 1927, 150)]. α-trans-Decahydronaphthylidene-2-propionitrile, b. p. 170—172°/18 mm., $d_4^{19^{\circ}}$ 0·9802, $n_D^{19^{\circ}}$ 1·51245, is prepared by hydrolysis of ethyl α-cyano- $\alpha - \Delta^{2:3(1:2)}$ -trans-decahydronaphthalene-2-propionate, b. p. 192°/17 mm., $d_4^{18^{\circ}}$ 1·03663, $n_D^{18^{\circ}}$ 1·49098, obtained by methylating ethyl trans-decahydro-β-naphthylidenecyanoacetate. Partial hydrolysis of ethyl α: 2dicyano-trans-decahydronaphthalene-2-acetate gives two 2-carboxy - trans - decahydronaphthalene - 2 - acetimides, m. p. 210° and 145°. The latter yields a trans-amic acid, C₁₀H₁₆(CO₂H)·CH₂·CO·NH₂, m. p. 217°, when hydrolysed. D. W. HILL.

Condensation of pinonic acid with aldehydes. O. FERNANDEZ and G. DE MIRASIERRA (Rec. trav. chim., 1929, 48, 852-854).—Pinonic acid condenses with salicylaldehyde in presence of alcohol and sulphuric acid, yielding, probably, 2:2-dimethyl-3-β-carbethoxycyclobutyl o-hydroxystyryl ketone, m. p. 159-161° with softening; the analogous 4-hydroxy-3-methoxystyryl derivative, m. p. 240° with softening, is prepared in presence of aqueous sulphuric acid. Aldehydes other than phenolic aldehydes do not condense with pinonic acid. H. BURTON.

Stereochemistry of diphenyl compounds. III. Resolution of 2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid. W. M. STANLEY and R. ADAMS (Rec. trav. chim., 1929, 48, 1035—1040).— Oxidation of 2:3 hydroxynaphthoic acid with ferric chloride in boiling aqueous solution, or more conveniently in alkaline solution, yields 2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid, m. p. 331— 333° (decomp.; all m. p. are corr.) (ethyl ester, m. p. 230—232°). Resolution of this is effected with brucine; the 1-acid (I) has m. p. 326—329° (decomp.), $[\alpha]_{1}^{\infty} - 171.9^{\circ}$ in pyridine (brucine salt, m. p. 244—246° after softening at 235—237°, $[\alpha]_{1}^{n} - 84.9^{\circ}$ in pyridine; ethyl ester, m. p. 218—220°, $[\alpha]_{2}^{m} - 134^{\circ}$ in pyridine; and the d-acid, m. p. 326—329° (decomp.), $[\alpha]_{2}^{m} + 171^{\circ}$ in pyridine. Racemisation of I is not effected by heating with acetic or hydrochloric acid; slight racemisation occurs with boiling potassium hydroxide solution. The isomerism of substituted *p*-phenyldiphenyls is discussed briefly. H. BURTON.

Syntheses by means of radiant energy. III. Acenaphthene and benzaldehyde. R. DE FAZI (Atti R. Accad. Lincei, 1929, [vi], 9, 1004—1006).— The products formed when a benzene solution of benzaldehyde and acenaphthene was exposed in a sealed tube to sunlight for 2 years were: Ciamician and Silber's tetrameride (A., 1909, i, 306) and Mascarelli's trimeride (A., 1906, i, 962; 1910, i, 389) of benzaldehyde, stilbene, *iso*stilbene, a resin, and 7-benzoylacenaphthene, m. p. 195—198°.

T. H. POPE.

Action of guanidine hydrogen carbonate on the sodium hydrogen sulphite additive products of benzylideneanilines. J. B. EKELEY and M. C. SWISHER (Rec. trav. chim., 1929, 48, 1052-1054).--When benzylideneaniline is dissolved in aqueous sodium hydrogen sulphite and the solution evaporated, sodium anilinophenylmethanesulphonate (I),

sodium anilinophenylmethanesulphonate (I), NHPh·CHPh·SO₃Na, separates. This salt begins to decompose when removed from the mother-liquors. Treatment of I with guanidine hydrogen carbonate in aqueous solution gives the a-anilinobenzyl ester, m. p. 143°, of guanidine hydrogen sulphite. This is decomposed by boiling with dilute acid to sulphur dioxide, benzylideneaniline, and guanidine, and with dilute alkali to benzaldehyde, aniline, and guanidine. The same ester is obtained by treating the benzaldehydesodium hydrogen sulphite additive compound with aniline and guanidine hydrogen carbonate in aqueous solution, or by treating a mixture of the aldehyde, amine, and guanidine carbonate with sulphur dioxide in aqueous medium. A similar reaction occurs when I is treated with aminoguanidine hydrogen carbonate or carbamide hydrochloride. The following esters of guanidine hydrogen sulphite are described : a-anilinoguandine hydrogen subinte are described : α -antiino-4-methylbenzyl, m. p. 172°; α -anilino-o-nitro-3:4-methylenedioxybenzyl, m. p. 205°; α -anilino-3:4-methylenedioxybenzyl, m. p. 163°; α -p-toluidinobenzyl, anhydrous and $+H_2O$, m. p. 148°; α -p-toluidino-3:4-methylenedioxybenzyl, m. p. 169°; α -p-toluidino-4-methylbenzyl, m. p. 176°; $\alpha\alpha'$ -p-phenylenediaminodibenzyl, m. p. 155°. o-Nitrobenzylideneaniline does not yield a compound analogous to I. H. BURTON.

Colour and constitution from the viewpoint of recent electronic theory. H. H. HODGSON (J. Soc. Dyers Col., 1929, 45, 259—263).—An electronic interpretation of the Reimer-Tiemann reaction as applied to phenol, o- and m-cresol, o- and m-chloro-, m-bromo-, and m-iodo-phenol is given. The results obtained in a study of the absorption maxima of the p-nitrophenylhydrazones of a series of substituted benzaldehydes are in accord with the electronic theory. The theory is applied to the influence of chlorine alone and in conjunction with the sulphonic acid group on the colours of substituted benzeneazophenols. A. I. VOGEL.

Polarimetric study of intramolecular rearrangement in inactive substances. VII. T.S. PATTERSON and G. THOMSON (J.C.S. 1929, 1895-1900).-In continuation of previous work (A., 1911, i, 648), the rate of change of a number of o_{-} , m_{-} , and p-substituted benzsynaldoximes into the anti-forms has been compared by observing the change of rotation induced in solutions of ethyl tartrate. The influence of the position and nature of substituent groups is shown by the following values of 1000k: benzsynaldoxime, 2.52; o-NO₂, 0.35; m-NO₂, 1.27; p-NO₂, 1.35; m-Cl, 1.32; p-Cl, 1.82; o-Br, 0.73; m-Br, 1.55; p-Br, 2.33; m-I, 1.27; p-I, 2.88; p-CH₃ 1.58. The following figures are recorded for methyl ethers: 0.23;β-O-methyl-m-nitrobenzsynaldoxime, B-0methyl-p-nitrobenzsynaldoxime, 0.18. N-Methyl-mnitrobenzaldoxime solution shows no change of rotation, and the change of rotation is too small for measurement of the rate of transformation of β into *a*-acetylbenzaldoxime. R. K. CALLOW.

Catalytic hydrogenation under reduced pressure. III. Reduction of nitriles in a vacuum. R. ESCOURROU (Bull. Soc. chim., 1929, [iv], 45, 735—744; cf. A., 1928, 1353; this vol., 173). —When hydrogenated at 190°/240 mm. phenylacetonitrile affords mainly phenylacetaldimine, b. p. 213— 214°/750 mm., $n_{\rm b}$ 1.5402 (hydrochloride, m. p. 180° with sublimation), together with a little ethylbenzene and β -phenylethylamine; at 200°/220 mm. the aldimine is obtained alone. It is fairly stable in absence of air and moisture. In moist air it polymerises to the trimeric hydrate, (CH₂Ph·CH:NH,H₂O)₃, m. p. 83—85° (sublimes); in dry air a compound of hydrobenzamide type is slowly formed. It is hydrolysed to ammonia and phenylacetaldehyde with boiling 5% potassium hydroxide, but not with water alone (cf. Mignonac, A., 1920, i, 442). Benzonitrile is converted in presence of nickel at 175°/10—11 mm. into benzaldimine, $n_{\rm b}^{2}$ 1.5725, d¹³ 1.009 (hydrochloride, m. p. 203 —204°; cf. Busch, A., 1896, i, 677), which rapidly polymerises to hydrobenzamide on exposure to the air, and more slowly in a closed vessel; at 140°/50 mm., benzylamine and a fraction, b. p. 300—305°, with an ammoniacal odour are also formed.

R. BRIGHTMAN.

Isolation of the intermediate Grignard additive compound, CHPh:CH·CHMe·OMgBr. I. E. MUSKAT and H. LUDEMAN (Ber., 1929, 62, [B], 2284— 2286).—The isolation of the compound CHPh:CH·CHMe·OMgBr (also $+1Et_2O$) by the action of magnesium methyl bromide on cinnamaldehyde in ether is described. It is hydrolysed to styrylmethylcarbinol. The ether-free compound appears less active than the corresponding etherate, thus suggesting that the function of ether is to activate Grignard reagents, possibly by formation of oxonium salts. H. WREN.

Isomerism of phthalaldehydic esters. A. K. KIRPAL and K. ZIEGER (Ber., 1929, 62, [B], 2106— 2107).—The chloride of phthalaldehydic acid, m. p. 61°, is converted by methyl alcohol in the presence of potassium hydroxide exclusively into the ψ -ester. If the chloride is exposed to the action of methyl alcohol during 9 days, the normal ester results. Methyl ψ -phthalaldehydate is slowly transformed by alcoholic hydrogen chloride into the normal ester. ψ -Esters of phthalaldehydic acid therefore resemble o-ketonic esters in their behaviour towards alcoholic hydrogen chloride. H. WREN.

Synthesis of syringin. H. PAULY and L. STRASSBERGER (Ber., 1929, 62, [B], 2277-2284).-Addition of potassium carbonate to a solution of pyrogallol dimethyl ether in anhydrous chloral leads to the production of 3: 5-dimethylpyrogallyltrichloromethylcarbinol, m. p. 162°, converted into 4-hydroxy-3:5-dimethoxybenzaldehyde, m. p. 113°, in 75% yield; the potassium and sodium salts, semicarbazone, m. p. 188°, and benzidide, m. p. 260°, are described. The sodium derivative is converted by chloromethyl ether into 3:5-dimethoxy-4-methoxymethoxybenzaldehyde, b. p. 157-158°/2 mm., m. p. 54° (semicarbazone, m. p. 141.5°), which condenses with acetaldehyde in alkaline solution to 3:5-dimethoxy-4methoxymethoxycinnamaldehyde, m. p. 102°, b. p. about 190°/2 mm. (partial resinification) [semicarb-azone, m. p. 202°]. The last-named compound is hydrolysed by boiling 50% acetic acid containing a little sulphuric acid to 4-hydroxy-3:5-dimethoxycinnamaldehyde, m. p. 108° (potassium salt; semi-carbazone, m. p. 211° to a red liquid; benzidide). Acetobromoglucose and the potassium compound afford 3:5-dimethoxy-4-tetra-acetylglucosyloxycinnam- $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_2(OMe)_2 \cdot CH \cdot CH \cdot CHO$, aldehyde, m. p. 182°. Fermentative reduction of the aldehyde followed by treatment of the product with ammonia yields 3 : 5-dimethoxy-4-glucosyloxycinnamyl alcohol, m. p. 192°, $[\alpha]_D^{m} - 17.25^{\circ}$ in water for the anhydrous material, identical with natural syringin. Hydrolysis of syringin with 5% hydrochloric acid affords noncrystalline, polymeric syringenin, m. p. about 160°. Fission with emulsin permits the isolation of the monomeric variety, m. p. 105-107°. H. WREN.

cis-trans-Isomerism and steric hindrance. X. 1:3-Dipropylcyclopentan-2-one and 1:3dipropylcyclopentan-2-ols. G. VAVON and J. FLURER (Bull. Soc. chim., 1929, [iv], 45, 763-767). -1:3-Dipropylidenecyclopentan-2-one, b. p. 122-125°/12 mm., obtained from the secondary product, b. p. 135-150°, in the condensation of propaldehyde and cyclopentanone (cf. this vol., 1290), by dehydration with oxalic acid, when hydrogenated in ether in presence of platinum-black is converted into

cis-1: 3-dipropylcyclopentan-2-one, b. p. 96-97°/8 mm., d₀¹² 0.892, n_D¹² 1.4495 (semicarbazone, m. p. 158-159°, yielding on hydrogenation 1:3-dipropylcyclopentanyl-2-semicarbazide, m. p. 78-80°; oxime, b. p. 139-142°/10 mm.). The rate of reaction of cyclopentanone with hydroxylamine is about 10 times as great as that of 1-propylcyclopentan-2-one, and 440 times as great as that of cis-1 : 3-dipropylcyclopentan-2-one. When reduced with sodium and alcohol, cis-1: 3-dipropylcyclopentan-2-one yields a mixture of 1:3-dipropyl-cis-cis-cyclopentan-2-ols, rich in the trans-isomeride, from which the trans-1: 3-dipropylcis-cis-cyclopentan-2-ol, b. p. 108-109°/11 mm., di 0.8930, n¹¹_D 1.4578 (hydrogen phthalate, m. p. 58.5-59.5°; 3:5-dinitrobenzoate, m. p. 45-46°; phenylurethane, m. p. 46-47°), is obtained through its dinitrobenzoate. Hydrogenation in acetic acid in presence of platinum-black affords a mixture rich in the cis-isomeride, from which cis-1: 3-dipropyl-ciscis-cyclopentan-2-ol, m. p. 33-33.5°, b. p. 106°/8 mm. (hydrogen phthalate, m. p. 117-119°; 3:5-dinitrobenzoate, m. p. 40.5-41.5°; phenylurelhane, m. p. 118-119°), is isolated through its hydrogen phthalate. The sodium derivative of the cis-pentanol is converted into the trans-isomeride when heated at 180-190° in an atmosphere of nitrogen. In 75% alcohol the trans-hydrogen phthalate is hydrolysed 7.4 times as rapidly as the cis-isomeride at 68°, and 8 times as fast at 39°. Comparison of these results with those obtained on the hydrogen phthalates of the 1-propylcyclopentan-2-ols indicates that the steric effect of introducing the cis-propyl group into cis-1-propylcyclopentan-2-ol is to reduce the velocity coefficient 20 times, whilst the introduction of the trans-propyl group into the trans-isomeride decreases the velocity coefficient of hydrolysis only 5 times.

R. BRIGHTMAN.

Halogen derivatives of acetophenone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 532– 537).—Quantitative yields of ω -chloro- ω -bromoacetophenone, m. p. 37–37.5°, are obtained by the bromination of ω -chloroacetophenone, but not by the chlorination of the corresponding bromo-derivative. The following substances are prepared : $\omega\omega$ -chlorobromo-3-nitro- and ω -4-dichloro- ω -bromoacetophenone, m. p. 43–44° and 83–83.5°, respectively, $\omega\omega$ -dichloro-3-nitro-acetophenone, m. p. 57–58°, and ω -iodo-3-nitroacetophenone, m. p. 92–93°. R. TRUSZKOWSKI.

ω-Halogen derivatives of acetonaphthone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1929, 9, 538–545).—The following substances have been prepared: ω-chloro-α- and -β-acetonaphthones, m. p. 34—36° and 62—63°, respectively, the corresponding iodo-derivatives, m. p. 46·5—48° and 91—91·5°; ω-bromo-β-acetonaphthone, m. p. 82·5—83·5°, and ωω-dichloro-β-acetonaphthone, m. p. 83—84°.

R. TRUSZKOWSKI.

Halogen substitution products of 4-aminobenzophenone. W. A. WATERS (J.C.S., 1929, 2106—2111).—Halogenation of 4-amino- and 4-acetamido-benzophenone is in accordance with accepted views on substitution. The structure of 3:5-dichloro-4-aminobenzophenone (Chattaway, *ibid.*, 1904, 85, 340) is confirmed by conversion into 3:5-dichloro-

benzophenone, m. p. 65°. The a-oxime, m. p. 137°, of the latter yields 3:5-dichlorobenzanilide, m. p. 148°, whilst the β -oxime, m. p. 118°, gives a mixture of the dichlorobenzanilide and benz-3: 5-dichloroanilide, m. p. 148.5°. 3-Bromo-4-acetamidobenzophenone, m. p. 106° (corr.), gives 3-bromo-4-aminobenzophenone, m. p. 158° (benzoyl derivative, m. p. 124°), on hydrolysis and 3 : 5-dibromo-4-acctamidobenzophenone, m. p. 214°. 3:5-Dibromo-4-aminobenzophenone, m. p. 148° (diacetyl derivative, m. p. 137°), gives 3:5-dibromo-benzophenone, m. p. 75°, on deamination. 3-Iodo-4-aminobenzophenone, m. p. 177° (benzoyl derivative, m. p. 162°), from 4-aminobenzophenone and iodine monochloride in acetic acid, yields 3:5-di-iodo-4-aminobenzophenone, m. p. 153° (diacetyl derivative, m. p. 187°), at water-bath temperature with the same reagent. The structure of 3: 5-di-iodobenzophenone, m. p. 91°, is established by synthesis from 3:5-dinitrobenzophenone, m. p. 131°, by way of 3-nitro-5-aminobenzophenone, needles, m. p. 130°, or plates, m. p. 146° (diacetyl derivative, m. p. 191° after sintering at 115-125°), 5-iodo-3-nitrobenzophenone, m. p. 118°, and 5-iodo-3-aminobenzophenone (not isolated). 3-Bromo-5-iodo-4-aminobenzophenone, m. p. 148° (diacetyl derivative, m. p. 161°), is obtained either by iodinating 3-bromo-4-aminobenzophenone or by brominating 3-iodo-4-aminobenzophenone. Nitration of 4-acetamidobenzophenone is not effected.

D. W. HILL.

Organic compounds of sulphur. XIV. Relationship between the dissociation tendency of thioacetals and compounds of the ethane series; investigation of hexaphenylethane. A. SCHONBERG and O. SCHUTZ [with M. AREND, U. OST-WALD, and F. KAPLAN] (Ber., 1929, 62, [B], 2322-2337; cf. A., 1927, 667) .- A comparison is effected between the thermal stabilities of dibenzyldithioldiphenylmethane and a series of thioacetals by placing small amounts of the substances in precisely similar capillary tubes, which are evacuated, sealed, and placed for the same length of time in a bath of such temperature that both specimens are melted. Dissociation is evidenced by the formation of blue thiobenzophenone derivatives. Marked dependence of relative thermostability of thioacetals on temperature has not been observed. In addition to thiobenzophenone, the production of benzylmercaptan is always observed; other products (sulphur, hydrogen sul-phide, stilbene, diphenyl disulphide) are formed according to the nature of the benzyl mercaptol and the temperature, but it is uncertain whether these are primary or secondary compounds. When dibenzyldithioldiphenylmethane is adopted as standard, the following compounds exhibit greater heat stability (smaller tendency to dissociate) : H₂C(SR)₂, CHPh(SR)₂, Me₂C(SR)₂, (CH₂Ph)₂C(SR)₂,

 $C_{6}H_{4} > C(SR)_{2}$, $(SR)_{2}CPh \cdot Bz$ $(R=CH_{2}Ph)$. Similar thermal stability is exhibited by the compounds $(SR)_2CPh C_6H_4 \cdot Cl (o)$ and $(SR)_2C(C_6H_4Cl p)$, whereas smaller thermal stability is shown by the substances $(SR)_2C(C_6H_4 \cdot OMe \ o)_2, (SR)_2CPh \cdot C_{10}H_7 \ \alpha, (SR)_2CPh \cdot C_6H_4 \cdot OMe \ p)_2, (SR)_2CPh \cdot C_{10}H_7 \ \alpha, (SR)_2CPh \cdot C_6H_4 \cdot OO_2 \ p),$

 $(SR)_2C[C_6H_3Me(OEt)]_2, (SR)_2CPh \cdot C_{10}H_7\beta,$

 $(SR)_2C(C_6H_4 \cdot Ph \ p)_2, O < C_6H_4 > C(SR)_2,$ $S < C_6H_4 > C(SR)_2.$ The thioacetals,

p-OMe·C₆H₄·C(SR)₂·CO·C₆H₄·OMe p, p-NMe₂·C₆H₄·C(SR)₂·CO·C₆H₄·NMe₂ p and I are less stable towards heat than dibenzyldithiolbenzoylphenylmethane. Re-(I.) placement of the phenyl groups by H, Me, CH_2Ph , or $o-C_6H_4C_6H_4$ restricts dissociation, which is facilit-CO-C(SR)2 ated by the radicals o-OMe·C₆H₄', α -C₁₀H₇', p-NO₂·C₆H₄', $O < C_{6}^{C_{6}H_{4}}$, p-OMe·C₆H₄', β -C₁₀H₇', p-Ph·C₆H₄', $S < C_{6}^{C_{6}H_{4}}$. Comparison of the dissociation tendency of benzylthioacetals with that of the corresponding members of the ethane series [for example, $H_2C(SCH_2Ph)_2$ with $(H_3C)_2$ and $Ph_2C(SCH_2Ph)_2$ with $(CPh_3)_2$] permits the deduction of the following rule. If a symmetrical replacement of two or four or six phenyl groups of hexaphenylethane by uni- or bi-valent residues leads to a compound with greater (smaller) tendency towards dissociation, the analogous replacement (replacement of one or both phenyl groups) effected in dibenzylthiol-

diphenylmethane gives similarly a compound of greater (less) dissociation tendency. The thermal dissociation of benzylthioacetals is directly parallel with the solvatic dissociation of certain ethane derivatives and with the thermal dissociation of polymeric thicketones and thicaldehydes and must be attributed to the same causes. The following compounds do not appear to have been described previously: dibenzyldithioldi-o-methoxyphenylmethane, m. p. 106-107°; dibenzyldithiolphenyl- α -naphthylmethane, m. p. 136°; dibenzyldithiolphenyl- β -naphthylmethane, m. p.

98°; dibenzyldithiolphenyl-p-chlorophenylmethane, m. p. 106-107°; dibenzyldithioldi-p-chlorophenyl-methane, m. p. (indef.) 90-95°; dibenzyldithiol-phenyl-p-nitrophenylmethane, m. p. 101-105°; di-benzyldithioldi-2-ethoxy-m-tolylmethane, m. p. 92-93°; thioxanthone benzyl mercaptal, m. p. about 83°; dibenzyldithiolphenyl-p-diphenylylmethane, m. p. 108°; dibenzyldithioldi-p-diphenylylmethane, m. p. 115-116°; dibenzyldithiol-p-dimethylaminobenzoyl-p-dimethylaminophenylmethane, m. p. about 166° (de-H. WREN. comp.).

Heteropolar compounds of carbon. IX. Action of the nitro-group on the halochromism of chalkones. W. DILTHEY, L. NEUHAUS, and W. SCHOMMER (J. pr. Chem., 1929, [ii], **123**, 235-240).-By condensation of the appropriate substituted acetophenone with the substituted benzaldehyde the following chalkones are prepared; 4'-nitro-, m. p. 149-150°; 4'-nitro-4-methoxy-, m. p. 176-177°; 3'-nitro-, m. p. 131°; 3'-nitro-4-methoxy-, m. p. 171-172°; 2'-nitro-, m. p. 128-129°; 2'-nitro-4-methoxy-, m. p. 100°, and 2-nitro-, m. p. 125° (the last being best obtained with sodium methoxide as the con-densing agent) and the effects of the substituent densing agent), and the effects of the substituent groups on the halochromism in concentrated sulphuric acid are compared. Contrary to its hypsochromic effect in the aldehyde component of the chalkone,

substitution of a nitro-group in the ketonic component has a bathochromic effect, the magnitude of which decreases in the order p > m > o. The 4 and 4' positions in the molecule are not optically equivalent. Thus a methoxy-group has a stronger bathochromic effect in the 4 (aldehyde) than in the 4' (ketone) position. Hence a bathochromic effect is produced by a positive substituent in the aldehyde and a negative substituent in the ketone component. It is suggested that this effect is due to the presence of a dipole in the chalkone molecule oriented with its positive end in the ketone component and that substituent groups which increase this dipole deepen the colour, and vice versa. J. W. BAKER.

Tautomerisation of chalkonesemicarbazones by light. H. STOBBE and K. BREMER (J. pr. Chem., 1929, [ii], 123, 241-256). -Both the α- and γ-chalkonesemicarbazones (Heilbron and Wilson, J.C.S., 1912, 101, 1482) are stable in the dark, but exposed to ultraviolet light they become yellow, the change occurring readily even in diffuse daylight in the case of the γ-compound. Both yellow forms give colourless solutions in alcohol or chloroform, from which by concentration in the dark the colourless form crystallises out, whilst concentration in light yields the yellow forms. The colourless forms give yellow solutions in alcoholic sodium alkoxide solution, in sodium hydroxide, or in piperidine, from which the colourless form is obtained on acidification. These colour changes are explained by the existence of tautomeric forms of the types R:N·NH·CO·NH₂ (I), R:N·NH·C(OH):NH (II), and R:N·N:C(OH)·NH₂ (III) (R=CHPh:CH·CPh:). The yellow colour in sodium alkoxide solution is due not, as Heilbron and Wilson (loc. cit.) suggest, to stereoisomerism, but to salt formation with types II or III, whilst the yellow forms obtained by exposure to light are equilibrium mixtures of type I with type II or III. The absorption spectra of the α - and y-semicarbazones in alcoholic and alcoholic sodium ethoxide solutions have been plotted. For a 10 mm. length in 0.01N-alcoholic solution the limit of absorption for the α - and γ -forms occurs at $1/\lambda$ 2650 and 2800, respectively (bands at 3000-4100 and 3300, respectively), whilst in alcoholic sodium ethoxide solution it is at $1/\lambda$ 2350 and 2525, respectively, salt formation causing a similar shift towards the red in each case. 4-Methylchalkone also gives two semicarbazones, a (stable to light), m. p. 193°, and γ (unstable to light), m. p. 185–187°, which are separated by fractional crystallisation from alcohol, the α being the less soluble; their absorption spectra in alcohol and alcoholic sodium ethoxide are similar to those of the chalkonesemicarbazones. 4-Methoxychalkone also gives a y-semicarbazone, m. p. 190° (Stobbe and Hensel, A., 1926, 1248), and an a-semicarbazone, m. p. 168° (stable to light), the latter being formed in hot alcoholic solution. The following substituted chalkones yield only one semicarbazone, 4-methyl-, γ , m. p. 172—174°; 4 : 4'-dimethyl-, γ , m. p. 186—187°; 4-methoxy-4'-methyl-, α , m. p. 184—186°; 4 : 4'-dimethoxy-, α , m. p. 177—178°; and 3 : 4-dioxymethyl-ene-, α , m. p. 203—205°. The γ -forms are less stable to light and become coloured in diffuse daylight, whilst both a- and y-forms become coloured on exposure to

ultra-violet light for 15 min. Comparison of the above derivatives with the *semicarbazone*, m. p. 135—137°, of 4'-methyldihydrochalkone (*p*-tolyl β -phenylethyl ketone) and other saturated aromatic and aliphatic ketones and with various arylideneacetones shows that only the derivatives of unsaturated ketones become coloured on exposure to ultra-violet light, give coloured solutions in sodium ethoxide, or colours with ferric chloride, the change, therefore, being due to tautomerism consequent on the presence of conjugated double linkings, and the colour in the last two cases due to salt formation with the enol forms.

J. W. BAKER. Oxidation of benzoins to diketones with iodine. B. B. CORSON and R. W. MCALLISTER (J. Amer. Chem. Soc., 1929, 51, 2822–2825).—Oxidation of benzoin, furoin, anisoin, and piperoin with iodine in presence of methyl-alcoholic sodium methoxide solution and in absence of oxygen affords good yields of benzil, furil, anisil, and piperil, respectively. A mechanism involving the intermediate formation of sodium stilbenedioxide is suggested. The method is not applicable to the preparation of aliphatic 1:2-diketones.

The reddish-purple coloration produced by treating benzoin with sodium methoxide solution is intensified by the addition of benzil; the diketone itself gives no coloration. The test is also given by furoin and benzofuroin, but not by anisoin or piperoin.

H. BURTON.

Auto-oxidation of benzoin in alkaline solution. A. WEISSBERGER, H. MAINZ, and E. STRASSER (Ber., 1929, 42, [B], 1942-1952).-The purplish-red colour produced by addition of aqueous potassium hydroxide to alcoholic solutions of benzoin (cf. Hantzsch and Glover, A., 1907, i, 538) is not observed in the complete absence of air; the colour is discharged when the solutions are shaken with air. The sensitive, coloured compound is also produced when alkaline alcoholic solutions of benzoin are treated with nitrobenzene, *p*-benzoquinone, or benzil. Alkaline alcoholic solutions of benzil when warmed for a short time develop a violet colour which is discharged when the cold solution is shaken with air. If the solution is boiled for about 5 min., the coloration becomes purplish-red and decolorisation does not occur when the cold solution is shaken with air. Quantitative examination shows that I mol. of oxygen is required for the auto-oxidation of 1 mol. of benzoin and that the primary products are 1 mol. of benzil and 1 mol. of hydrogen peroxide or alkali peroxide. The lastnamed compound oxidises benzil to benzoic acid, whereas it scarcely attacks benzoin. The rate of absorption of oxygen by alkaline alcoholic solutions of benzoin is measured in an apparatus in which such thorough contact occurs between gas and liquid that the latter remains saturated with oxygen. Under these conditions the reaction proceeds at rates which depend on the alkalinity of the solutions, temperature, and solvent, but are independent of the concentration of the acyloin and of illumination. If the solutions become impoverished with respect to oxygen the stilbenediolate formed by isomerisation gradually accumulates and the violet compound in equilibrium with it and benzil is produced. The auto-oxidation

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of benzoin appears to proceed in accordance with the schemes : $OH \cdot CHPh \cdot COPh + KOH \Longrightarrow$ OK · CHPh · COPh + H₂O and OK · CHPh · COPh + O₂ \longrightarrow Ph · CO · COPh + KHO₂. H. WREN.

Reducing effect of binary system, $MgX_2 + Mg$, on organic compounds in anhydrous solvents. M. GOMBERG (Rec. trav. chim., 1929, 48, 847—851).— The mechanism of the reaction with aromatic ketones, 1:2-diketones, acids, acyl peroxides, and aldehydes is discussed (cf. A., 1927, 245, 1190; 1928, 1373).

H. BURTON.

Action of hydrazine hydrochloride on aromatic ketones. N. SCHAPIRO [with BRACHMANN] (Ber., 1929, 62, [B], 2133-2136).-The action of hydrazine hydrate on ketones in absence of solvent or presence of alcohol leads to the production of hydrazones. The presence of strong mineral acids is excluded, since hydrolysis of the products is thereby induced. This is not the case with formic and acetic acids, in the presence of which ketazines are produced; these compounds are also produced smoothly and almost quantitatively when hydrazine hydrochloride in alcohol is used. Benzilketazine, m. p. 201–202°, and *isatinketazine*, $C_{16}H_{10}O_2N_4$, decomp. about 300°, are described. Benzoin and hydrazine hydrochloride afford benzilketazine and amarone, m. p. 245°. Furoin and furil give brown, amorphous compounds which do not appear to be ketazines or hydrazones. Contrary to expectations, anisil gives anisilhydrazone, m. p. 163-164°. H. WREN.

Some reactions of mm'-dinitrobenzil. A. A. BOON and H. B. NISBET (J.C.S., 1929, 1901—1902). mm'-Dinitrobenzil condenses with o-phenylene- and o-tolylene-diamines to yield, respectively, 2:3-di-mnitrophenylquinoxaline, m. p. 208°, and the 5-methyl derivative, m. p. 208—210°. With benzidine in alcohol an additive compound, m. p. 163·5°, is formed, which may be utilised to separate mm'-dinitrobenzil from the product of nitration of benzil. An additive compound, m. p. 164°, is formed with o-toluidine. mm'-Dinitrobenzil condenses with 1 mol. only of acetophenone to yield dehydroacetophenone-mm'-dinitrobenzil (β-benzoyl-α-m-nitrobenzoyl-m-nitrostyrene), m. p. 158°. mm'-Dinitrobenzil yields no crystalline condensation product with acetone.

R. K. CALLOW.

Nuclear condensation of phenols and phenol ethers with nitriles yielding phenol and phenol ether ketimines and ketones. III. Synthesis of cotogenin, protocotoin, isoprotocotoin, and methylprotocotoin (oxyleucotin). J. HOUBEN and W. FISCHER (J. pr. Chem., 1929, [ii], 123, 89— 109; cf. Späth and Bretschneider, A., 1928, 1136).— Condensation of phloroglucinol trimethyl ether (I) with acetonitrile in presence of ethereal hydrogen chloride and zinc chloride yields the hydrochloride of 2:4:6-trimethoxyacetophenoneimine, m. p. 95—96°, hydrolysed by boiling with water to 2:4:6-trimethoxyacetophenone, m. p. 100—103°. Similar condensation of resorcinol and 3:4-methylenedioxybenzonitrile (II) and subsequent hydrolysis affords a 21% yield of 2:4-dihydroxy-3':4'-methylenedioxybenzonhenone, m. p. 215—216°; with ferric chloride as the condensing agent and prolonged treatment with

hydrogen chloride the yield of intermediate ketimine is improved. Phloroglucinol dimethyl ether and II give (ferric chloride method) a mixture of 46% of the ketimine hydrochloride (III) of 4-hydroxy-2:6dimethoxy-3': 4'-methylenedioxybenzophenone [iso-protocotoin], m. p. 165-166° (hydrochloride), and 11% of the ketimine hydrochloride (IV) of 2-hydroxy-4:6-dimethoxy-3':4'-methylenedioxybenzophenone [protocotoin], m. p. 141-142°. Isolation of IV is effected by prolonged treatment of the ethereal and aqueous mother-liquors from III with stannous chloride and hydrochloric acid. When the above condensation is carried out with zinc chloride the main product is III. Ferric or zinc chloride condensation of I and II gives the hydrochloride of the ketimine, m. p. 117-118°, of 2:4:6-trimethoxy-3':4'-methylenedioxybenzophenone [methylprotocotoin], m. p. 132-133°. 3:4-Diacetoxybenzonitrile and I yield (zinc chloride method) after hydrolysis with aqueous methyl-alcoholic sodium hydroxide about 16% of 3:4-dihydroxy-2':4':6'-trimethoxybenzophenone (V) [cotogenin], m. p. 222.5° (corr.; decomp.). Hydrolysis of the initial reaction mixture with sodium hydroxide solution in presence of light petroleum and subsequent removal of zinc as sulphide affords the ketimine, m. p. 265° (decomp.; hydrochloride; sulphate), of V. Colour reactions of the above benzophenones with various reagents are given.

When a mixture of ferric chloride and ether is saturated with hydrogen chloride the compound FeCl₃,HCl,2Et₂O is formed. H. BURTON.

Solubility of benzoquinhydrone in aqueous alcohol. A. E. BRODSKY and M. I. ALFEROV (Ber., 1929, 62, [B], 2132-2133).—The solubility of benzoquinhydrone in water and aqueous alcohol ($25\cdot55$, $49\cdot81$, and $71\cdot31$ wt.-%) is $0\cdot0158$, $0\cdot0330$, $0\cdot0684$, and $0\cdot1158$ mol. per litre. H. WREN.

Derivatives of naphthaquinones. R. LANTZ and A. WAHL (Bull. Soc. chim., 1929, [iv], 45, 744-754).-Mainly a recapitulation of earlier work (A., 1925, i, 820, 910, 1159; 1926, 617; B., 1924, 902; 1925, 200; 1927, 39). When agitated with air and aniline in presence of copper hydroxide, 1-amino-B-naphthol yields the cupric derivative of 2-hydroxy-a-naphthaquinone-1-imine-4-anil, and phenyldinaphthoxazine, the latter probably resulting from condensation of the imine with the aminonaphthol. Nitroso-B-naphthol with aniline in presence of copper powder and in methyl alcohol gives the same products, but in the absence of copper the oxazine is not formed and 2-hydroxy- α -naphthaquinone-1-imine-4-anil, orange, m. p. 231-234° (decomp.), is obtained alone in both cases. With sodium hydrogen sulphite at 0° in alkaline solution the latter yields a colourless hydrogen sulphite, from which alkalis regenerate the imine, but acids afford anilino-\beta-naphthaquinone. Zinc and dilute acid reduce the sulphite to 1-amino-4-anilinoβ-naphthol. 2-Hydroxy-α-naphthaquinone-1-imine-4-p-methylanil, m. p. 213-214° (decomp.), 2-hydroxyz-naphthaquinone-1-imine-4-o-methylanil, m. p. 229-230° (decomp.), and 2-hydroxy-a-naphthaquinone-1imine-4-p-aminoanil, decomp. 250°, are obtained by agitating 1-amino-B-naphthol-4-sulphonic acid in sodium hydrogen carbonate solution with air and the amine. Reduction with hyposulphite or with hydrogen sulphide or stannous chloride in alcohol converts the imine-anils into 1-amino-4-arylamino- β naphthols. 1-Amino-4-anilino- β -naphthol, oxidised to the imine in aqueous solution (cf. Goldstein and Radovanovitch, A., 1926, 1134), in non-aqueous media yields an oxazine condensation product. The oxazine colours of Dahl (G.P. 82,097) are probably similarly formed by condensation of an intermediate imine with the aminonaphtholsulphonic acid followed by cyclisation accompanied by hydrolysis of an iminogroup. R. BRIGHTMAN.

Condensation of acenaphthenequinone with phenols. I. MATEI (Ber., 1929, 62, [B], 2095-2098).-Addition of concentrated sulphuric acid to a solution of acenaphthenequinone in phenol yields 7:7-di-p-hydroxyphenyl-8-ketoacenaphthene, m. p. 257-258° (diacetate, m. p. 141°). With quinol in presence of glacial acetic and concentrated sulphuric acids acenaphthenequinone affords anhydro-7:7-di-2': 5'-dihydroxyphenyl-8-keto-acenaphthene, m. p. 281° (diacetate, m. p. 125° after softening at 110°). Resorcinol and pyrocatechol give corresponding di-2': 4'and 5': 4'-dihydroxyphenylacenaphthenones, m. p. 266-268° (decomp.) (cf. Zsuffa, A., 1910, i, 861), and m. p. 250-270° after incipient decomp. above 200° (tetra-acetate, m. p. 97-98°). H. WREN.

Syntheses in the hydroaromatic series. VI. Partly hydrogenated naphtha- and anthraquinones with hydrogen in the γ - or δ -position. O. DIELS, K. ALDER, and G. STEIN [with P. PRIES and H. WINCKLER] (Ber., 1929, **62**, [B], 2337—2372; cf. A., 1928, 1018).—Addition of hydrocarbons with conjugated double linkings to quinones yields partly hydrogenated naphthand anthra-quinones of the type I, which are actually diketones. It is proposed to consider them as quinone derivatives on account of their

close relationships to these compounds. The unusual hydrogenation of the "twin" carbon atoms induces the authors to denote these positions by γ in the naphthalene and δ in the anthracene series.

α-Naphthaquinone is converted by butadiene at 100° into Δ^2 -tetrahydroanthraquinone (I), m. p. 105— 106° (dioxime, decomp. 250° when rapidly heated). The very pronounced tendency of the 8-hydrogen atoms to migrate to the carbonyl group causes the compound to be converted by boiling acetic anhydride into 9:10-diacetoxy-1:4-dihydroanthracene, m. p. 263-262° [corresponding dibromide, m. p. 233-234° (decomp.)], hydrolysed by alcoholic potassium hydroxide to the potassium derivative of 9:10-dihydroxy-1:4-dihydroanthracene, also obtained by dissolving Δ^2 -tetrahydroanthraquinone in alcoholic potassium hydroxide. Exposure of the enolate solutions to air leads to the formation of anthraquinone. Treatment of an alcoholic solution of Δ^2 -tetrahydroanthraquinone with colloidal palladium in the absence of air causes migration of the δ-hydrogen atoms to the carbonyl group, with formation of 9: 10-dihydroxy-1: 4-dihydroanthracene, converted by crystallisation in presence of air into 1 : 4-dihydroanthraquinone, m. p. 208-210° (decomp.) when very rapidly heated. Reduction of Δ^2 -tetrahydroanthraquinone in presence of colloidal palladium yields 1:2:3:4-tetrahydroanthraquinone, m. p. 158°. Isoprene and a-naphthaquinone afford isoprene-a-naphthaquinone, C15H14O2, m. p. 81°; the corresponding diacetate, C19H18O4, m. p. 191°, is converted by successive treatment with alcoholic potassium hydroxide and air into 2-methylanthraquinone, m. p. 175°. Day-Dimethylbutadiene and α -naphthaquinone yield 1: 3-dimethyl- Δ^2 -tetrahydroanthraquinone, m. p. 81°, from which the corresponding diacetate, m. p. 174°, and 1: 3-dimethylanthraquinone, m. p. 162°, are successively derived. 1:1:3-Trimethyl-A2-tetrahydroanthraquinone, m. p. 119° (from aay-trimethylbutadiene), and its oxidation in alkaline solution by air to 1:1:3-trimethyl-1:4-dihydroanthraquinone, m. p. 162° (decomp.), are described.

 $\Delta^{1:3}$ -cycloHexadiene and α -naphthaquinone afford 1:4-endoethylene- Δ^2 -tetrahydroanthraquinone (II), m. p.



135°, converted into the diacetate, $C_{20}H_{18}O_4$, m. p. 185°, which is successively hydrolysed and oxidised by air to 1:4-endoethylene-1:4-dihydro-

anthraquinone, decomposed at 180–190° into ethylene and anthraquinone. *p*-Benzoquinone and cyclohexadiene at 100° yield 1:4-5:8-diendoethylene- $\Delta^{2:6}$ -octahydroanthraquinone (III), m. p. 196–197°, oxidised



by air in alcoholic alkaline solution to 1:4-5:8diendoethylene-1: 4:5:8-tetrahydroanthraquinone, which decomposes at about 180° into ethylene and anthraquinone. α -Phellandrene and α -naphthaquinone yield 1:4-endoisopropylethylene-2-methyl- Δ^2 -tetrahydroanthraquinone, m. p. 88°, transformed by oxidation into 1:4-endoisopropylethylene-2-methyl-1:4-dihydroanthraquinone, decomposed by heat into 2-methylanthraquinone and isopropylethylene. α -Naphthaquinone is converted by α -phenylbutadiene into 1-phenylanthraquinone, m. p. 177—178°.

 γ -Hydrogenated naphthaquinones are very readily prepared by the addition of 1 mol. of diene hydrocarbon to 1 mol. of *p*-benzoquinone. Thus with butadiene in benzene at the atmospheric temperature *p*-benzoquinone yields $\Delta^{2:6}$ -tetrahydronaphthaquinone (IV), m. p. 58°, which on exposure to sunlight becomes transformed into a (?) polymeride, m. p. 252°. It is converted by acetic anhydride into 5:8-diacetoxy-



1:4-dihydronaphthalene, m. p. 134-135°, hydrolysed by alcoholic potassium hydroxide to 5:8-dihydroxy-1:4-dihydronaphthalene, m. p. 211-212°. The lastnamed compound is also obtained from tetrahydro-

naphthaquinone by the action of warm, glacial acetic acid containing a trace of hydrogen bromide. The acetate is catalytically hydrogenated in the presence of alcohol and colloidal palladium to 5:8-diacetoxy-1:2:3:4-tetrahydronaphthalene, m. p. 186–187°, hydrolysed to 5:8-dihydroxy-1:2:3:4-tetrahydro-naphthalene, m. p. 185° (also obtained by catalytic reduction of 5: 8-dihydroxy-1: 4-dihydronaphthalene), which is identified by oxidation with ferric chloride to 1:2:3:4-tetrahydro- α -naphthaquinone, m. p. 57°. 5:8-Dihydroxy-1:4-dihydronaphthalene is similarly oxidised by ferric chloride to 1: 4-dihydroa-naphthaquinone, m. p. 109°. p-Benzoquinone and $\Delta^{1:3}$.cyclohexadiene in benzene afford 1:4-endoethylcne-Δ^{2:6}-tetrahydro-α-naphthaquinone (V), m. p. 98° (corresponding diacetate, $C_{16}H_{16}O_4$ m. p. 164°), isomerised by hydrogen bromide in glacial acetic acid to 5:8-dihydroxy-1:4-endoethylene-1:4-dihydro-naphthalene, m. p. 178°, from which 1:4-endoethylene-1:4-dihydro-a-naphthaquinone, m. p. 98-99°, is obtained by oxidation with ferric chloride. The quinone is characteristically decomposed by heat into ethylene and a-naphthaquinone. With a-phellandrene, pbenzoquinone gives 2-methyl-1: 4-endoisopropylethylene-A2:0-tetrahydro-a-naphthaquinone, m. p. 119°

Bisdienequinones are obtained readily by the addition of 2 mols. of the diene to 1 mol. of p-benzoquinone. Thus isoprene and p-benzoquinone in alcohol at 100° afford a mixture of 2 : 6-dimethyl- Δ^2 ⁶-octahydroanthraquinone, m. p. 170—171° (oxime, decomp. about 290° when rapidly heated), and 2 : 7-dimethyl- Δ^2 ⁶-octahydroanthraquinone, m. p. 145—146° (dioxime, decomp. 290—295° when rapidly heated). Successive treatments of the respective quinones with alcoholic potassium hydroxide and air yields 2 : 6-dimethylanthraquinone, m. p. 237—238°, and 2 : 7-dimethylanthraquinone, m. p. 169°. The quinones are isomerised by boiling acetic anhydride, when heated at about 200°, or when treated with alkali hydroxide in alcohol to compounds, m. p. 243° and 242°, respectively, which can be similarly dehydrogenated to 2 : 6- or 2 : 7-dimethylanthraquinone. Von Euler and Josephson (A., 1920, i, 489) appear to have obtained a mixture of these two compounds by their more drastic treatment of isoprene with p-benzoquinone. 1 : 4-endoMethylene- Δ^2 : ^{5 : 7}- tetrahydroanthraquin-

1:4-endoMethylene- $\Delta^{2:5:7}$ -tetrahydroanthraquinone does not yield a diacetate when treated with acetic anhydride, but, in consequence of its instability, is transformed into cyclopentadiene, α -naphthaquinol diacetate, and 1:4-endomethylene-1:4-dihydroanthraquinone, m. p. 156°. The last-named compound is reduced by hydrogen in presence of colloidal palladium to 1:4-endomethylene-1:2:3:4-tetrahydroanthraquinone, m. p. 138°. Hydrogenation of 1:4-endomethylene- $\Delta^{2:5:7}$ -tetrahydroanthraquinone wields 1:4-endomethylene- $\Delta^{5:7}$ -hexahydroanthraquinone, m. p. 117°, which is acetylated to 9:10-diacetoxy-1:4endomethylene-1:2:3:4-tetrahydroanthracene, m. p. 185°; when warmed with alcoholic potassium hydroxide and treated with air these compounds pass into 1:4-endomethylene-1:2:3:4-tetrahydroanthraquinone.

Acetylation of 1:4-endomethylene- Δ^2 -hexahydronaphthaquinone (cf. Albrecht, Å., 1906, i, 674) is similarly complicated by decomposition of the compound with formation of cyclopentadiene; the main products are 9: 10-diacetoxy-1: 4-5: 8-diendomethylene-1:4:7:8-tetrahydroanthracene, colourless crystals, m. p. 250°, quinol diacetate, m. p. 124-125°, and 1: 4-5: 8-diendomethylene-1: 4: 5: 8-tetrahydro. anthraquinone, red crystals, m. p. 252° (decomp.). The colourless acetyl compound is hydrolysed to 9:10dihydroxy-1: 4-5: S-diendomethylene-1: 4:5: S-tetrahydroanthracene, m. p. 298° after darkening at 280°, which is oxidised by chromic acid in acetic acid to the red quinone, m. p. 252° (decomp.). 1:4-5:8-Diendomethylenedidecahydroanthraquinone is dehydro. genated by cautious treatment with bromine in chloroform to 9: 10-dihydroxy-1: 4-5: 8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 289° (diacetate, m. p. 226°), which is oxidised by chromic acid in glacial acetic acid to 1:4-5:8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthraquinone, m. p. 252°. Catalytic reduction of 1:4-5:8-diendomethylene-1:4:5:S-tetrahydroanthraquinone vields 9: 10-dihydroxy-1: 4-5: 8-diendomethylene-1:2:3:4:5:6:7:8-octahydroanthracene, m. p. 289° (diacetate, m. p. 226°). 1:4-endo Methylene-1: 4-dihydro-a-naphthaquinone, m. p. 70°, is obtained by isomerisation of 1:4-endomethylene- $\Delta^{2/6}$ -tetrahydro-a-naphthaquinone by hydrogen bromide in glacial acetic acid and subsequent oxidation of the product with ferric chloride. H. WREN.

Benzanthrone. A. LÜTTRINGHAUS and H. NERESHEIMER [with H. WOLFF and H. EMMER] (Annalen, 1929, 473, 259–289).—Treatment of Bz-1bromobenzanthrone with copper powder at 280– 300° affords Bz-1: Bz-1'-dibenz-



anthronyl (I). m. p. 412-414°, which when treated with very concentrated methyl-alcoholic potassium hydroxide at 115-120° yields dibenzanthrone (cf. Scholl and Seer, A., 1913, i, 56), formed

by atmospheric oxidation of the intermediate dihydro-derivative. When benzanthrone (II) is treated with alcoholic potassium hydroxide at 100-105°, 2:2'-dibenzanthronyl (III), m. p. 320-321°, is obtained together with small amounts of 2-hydroxybenzanthrone (IV) (Perkin and Spencer, J.C.S., 1922, 121, 474), and a phenolic substance (removed by treatment of the crude product with anhydrous sodium carbonate and methyl p-toluenesulphonate in presence of trichlorobenzene at 195°). Treatment of II in presence of finely-divided potassium hydroxide and benzene with isopropyl alcohol at $30-35^{\circ}$ in a current of nitrogen also affords III; it is produced similarly with methyl and ethyl alcohols at 85° and $70-75^{\circ}$, respectively. Sodium anilide in aniline solution (prepared by treating aniline containing small amounts of nickel oxide and copperbronze with sodium at $170-180^{\circ}$ in a current of nitrogen) at $40-45^{\circ}$ converts II into III: at the same time a small amount of 2-anilinobenzanthrone, m. p. 215° , is formed. This last-named substance is converted by 50% potassium hydroxide solution at 250° into IV. The formation of 2:2'-dibenzanthronyl from benzanthrone is presumed to occur through a primary enolisation of the keto-group with the pro-

duction of a quinonoid system resulting in free valency at position 2, whereby doubling of the molecule occurs, the resulting dihydro-derivative being oxidised by air. 6:6'-Dimethyl-, m. p. 357-358°, and 6: 6'-dichloro-2: 2'-dibenzanthronyls (V), m. p. 407-408°, are obtained by similar treatment of the corresponding benzanthrones with alcoholic potassium hydroxide. Fusion of III with potassium hydr-oxide and sodium acetate at 240-250° also yields dibenzanthrone (6:6'-dimethyl derivative obtained similarly); ring closure is also effected by heating with 80% sulphuric acid containing a small amount of mercuric sulphate at about 200°, but the product is contaminated with, probably, sulphonic acids. 6:6'-Dichlorodibenzanthrone is obtained by the acid treatment of V. 2-Aminobenzanthrone is converted by the Sandmeyer reaction into 2-chlorobenzanthrone (VI), m. p. 204-205°. Treatment of an equimolecular mixture of II and VI with sodium anilide at 5° in a current of nitrogen yields about 50% of the theor-etical amount of III together with 2-anilinobenzanthrone. 6-Methyl- (VII), m. p. 329-330°, and 6-chloro-2: 2'-dibenzanthronyl (VIII), m. p. 313-314°, are obtained similarly from VI and 6-methyl- and 6-chloro-benzanthrone, respectively. Treatment of a solution of 2:6-dichloroanthraquinone in slightly diluted sulphuric acid with a mixture of glycerol and copper-bronze at 130-135° affords 2: 6-dichlorobenz-anthrone, m. p. 234°, which when treated with II and potassium anilide yields VIII. Potassium hydroxide fusion of VII gives 6-methyldibenzanthrone.

When benzanthrone is treated with an alcoholic potassium hydroxide melt at temperatures between 120° and 220° a mixture of dibenzanthrone and isodibenzanthrone (cf. Scholl and Seer, loc. cit.) results. The maximum amount of the iso-derivative (about 33%) is formed at $170-175^{\circ}$; at 220° only dibenzanthrone is obtained. With isopropyl alcohol and potassium hydroxide the corresponding figures for the iso-derivative are 37% and 140°. The isomerides are readily separated owing to the insolubility of the sodium salt of the dihydroisodibenzanthrone in 4% sodium hydroxide solution. The production of the iso-derivative occurs presumably through the intermediate 2: Bz-1'-dibenzanthronyl (formed by addition of a benzanthrone molecule at the Bz-1-position to position 2 of an enolised benzanthrone molecule), which was not detected. 2: Bz-1'-Dibenzanthronyl (IX), m. p. 331-332°, is obtained in about 50% yield when an equimolecular mixture of II and Bz-1chlorobenzanthrone (X) is treated with sodium anilide at -5° in a current of nitrogen. Conversion of IX into isodibenzanthrone is effected by treatment with alcoholic potassium hydroxide at 130° and subsequent heating of the aqueous solution in presence of air, or with sodium anilide at 125° in a current of nitrogen. Nitration of benzanthrone in nitrobenzene suspension with 87% nitric acid first at the ordinary temperature and then at 40-50° affords Bz-1-nitro-benzanthrone, m. p. 244-245° (isolated by washing the nitration product with much alcohol), reduced by 15% sodium sulphide solution to Bz-1-aminobenzanthrone, m. p. 239-240°. Diazotisation of this with nitrosylsulphuric acid, subsequent treatment of the diazonium sulphate with hydrofluoboric acid, and

decomposition of the diazonium fluoborate at 150° yields Bz-1-fluorobenzanthrone (XI), m. p. 194—195°. An equimolecular mixture of II and XI is converted by treatment with sodium anilide into IX. 6-Methyl-(XII), m. p. 371—372°, and 6-chloro-2: Bz-1-dibenzanthronyl (XIII), m. p. 375—376, are prepared similarly from X and the corresponding benzanthrone. Alcoholic potassium hydroxide treatment of XII and XIII affords 6-methyl- and 6-chloro-isodibenzanthrone.

When XI is treated with sodium anilide at -5° to 2° in a current of nitrogen and then acidified, 36% of the theoretical amount of Bz-1-fluoro-2: Bz-1'-dibenzanthronyl, m. p. $350-352^{\circ}$, is produced, presumably by addition of the halogen in one molecule to the activated 2-position of the second molecule, and subsequent elimination of sodium fluoride. This fluoro-derivative is converted by alcoholic potassium hydroxide at 110-125° into *iso*dibenzanthrone.

H. BURTON.

Saponins, sapogenins, and related substances. I. Trimethylnaphthalene from gypsogenin. L. RUZICKA and A. G. VAN VEEN (Rec. trav. chim., 1929, 48, 1018-1024).-Crude Gypsophila saponin is hydrolysed by dilute aqueous-alcoholic sulphuric acid to gypsogenin (I) (the sapogenin of van der Haar, A., 1927, 341). Thermal decomposition of I at 290° in an atmosphere of carbon dioxide gives no recognisable product, whilst the methyl ester of I (cf. Karrer and others, A., 1924, i, 1091) is decomposed at 400-500°, yielding an ether-like product, b. p. 125-135°/12 mm., d_4^{14} 0.969, n_5^{1} 1.513. Dehydrogenation of this with selenium at 300–320° affords a product, b. p. 125– $140^{\circ}/12$ mm., which yields a picrate, m. p. 127-128°, identical with the trimethylnaphthalene picrate obtained from amyrin (this vol., 932). The same trimethylnaphthalene fraction is formed by similar dehydrogenation of I at 330-360°; a further small fraction, b. p. $140^{\circ}/0.3$ mm., gives an unidentified picrate, m. p. 138°. Oxidation of the crude trimethylnaphthalene with potassium ferricyanide affords the acid (methyl ester, m. p. 152-153°) previously described (this vol., 932).

Cholatrienecarboxylic acid (Wieland and Weil, A., 1912, i, 830) is dehydrogenated by selenium at 330°, yielding mainly a product, b. p. 210-230°/high vac.; only traces of picrates were isolated from the material of lower b. p. H. BURTON.

Saponins, sapogenins, and related substances. Relation between sapogenins, higher II. terpene compounds, and sterols. L. RUZICKA and A. G. VAN VEEN (Z. physiol. Chem., 1929, 184, 69-82; cf. preceding abstract) .- The sapogenins, æscigenin, caryocarsapogenin, cyclamiretin, guaiac-sapogenin, glycyrrhetic acid, hederagenin, mimusops-sapogenin, quillaiasapogenin, sarsasapogenin, ursolic acid, sugar-beet sapogenin, and the triterpenes betulin and lupeol were dehydrogenated by means of selenium and the products fractionated. From the middle fractions of all except sarsasapogenin and lupeol a picrate, m. p. 127⁶, was obtained. The hydrocarbon was regenerated and the styphnate formed; this was identical with the styphnate of trimethylnaphthalene, for which the name sapotalin is proposed. The lower fraction of sarsasapogenin

yielded methylheptenone. Amyrin, lupeol, and betulin, unlike cholesterol, give no precipitate with digitonin. J. H. BIRKINSHAW.

Interpretation of the colorimetric hydrogenation curve of carotinoids. L. ZECHMEISTER and V. VRABELY (Ber., 1929, 62, [B], 2232-2235; cf. A., 1928, 524, 1252).—The graph connecting the intensity of colour (as percentage of original intensity) with the mols. of hydrogen absorbed during the catalytic treatment in glacial acetic acid of methylbixin (which undoubtedly contains nine double linkings in uninterrupted conjugation) is a straight line which becomes inflected shortly before the point representing the absorption of 8 mols. The curve exactly corresponds with the analogous carotin curve to the point 9H_o. The result does not contradict the hypothesis that the double linkings of carotin and xanthophyll fall into two groups, but the division is more probably into 9+2 than into 8+3, as previously assumed.

Bixin may be determined colorimetrically by comparison with 0.2% potassium dichromate.

H. WREN.

Cyclamin. E. BURES and J. BERGAUER (Časopis Českoslov. Lek., 1928, 8, 208—211; Chem. Zentr., 1929, i, 2655).—Extraction of the tubers of wild Cyclamen Europæum with 89% alcohol yields cyclamin, m. p. 254° (decomp.) after purification, which reacts with alkali to form a substance of lactonic nature. Cyclamin is strongly hæmolytic. A. A. ELDRIDGE.

Principal constituent of olive gum (resin). Olivil and derivatives. B. L. VANZETTI (Gazzetta, 1929, 59, 373—378).—A republication of work already abstracted (cf. Koerner and Vanzetti, A., 1903, i, 430; 1912, i, 352). R. K. Callow.

Constitution of active principle of Embelia Ribes. I. R. KAUL, A. C. RAY, and S. DUTT (J. Indian Chem. Soc., 1929, 6, 577-586).-Extraction of the dry berries of Embelia Ribes (Vidanga or Baberang) with benzene affords an aliphatic oil and embelin (I), $C_{18}H_{28}O_4$, m. p. 142° [previously named embelic acid (Warden, A., 1889, 408; Heffter and Feuerstein, A., 1900, i, 498)]. Embelin contains two reactive hydroxyl groups and two keto-groups, since it furnishes the following derivatives : lead and silver salts; diacetate, m. p. 54°; dibenzoate (II), m. p. 97-98° [cf. Heffter and Feuerstein, loc. cit. ; dioxime, m. p. 139°; disemicarbazone, m. p. 221° (decomp.)]; dicarbethoxy-derivative, m. p. 266° (decomp.); dimethyl ether; dioxime (III), m. p. 278°; tetra-oxime, m. p. 175° (indicating ketonisation of the hydroxyl groups present); bisphenylhydrazone, m. p. 189—190° (decomp.); disemicarbazone, m. p. 236° (decomp.); dihydrazone, m. p. 204-205°. When I is boiled with aniline dianilinoembelin (IV), m. p. 167-168° (cf. loc. cit.) [dioxime, m. p. 162° (decomp.), obtained also from III and aniline; disemicarbazone, m. p. 145° (decomp.)], results. Di-o-toluidino-, m. p. 144-145°: di(methylamino)-, m. p. 216°, and di(ethylamino)-embelin, m. p. 212°, are also described. These aminoderivatives are hydrolysed by hydrochloric acid to I. Secondary amines and I do not react. Dianilinodibenzoylembelin, m. p. 176°, is prepared by benzoylation of IV or from aniline and II. Treatment of I with moist zine dust in boiling acetic anhydride affords the tetra-acetyl derivative, m. p. 124°, of dihydroembelin [previously named dihydroembelic acid (loc. cit.)]. Bromination of I in carbon tetrachloride solution gives a tetrabromo-derivative, m. p. 132°, whilst oxidation with nitric acid (d 1·51) yields isododecoic acid. Oxidation with potassium permanganate affords oxalic and isododecoic acids and not formic and dodecoic acids as stated by Heffter and Feuerstein (loc. cit.). H. BURTON.

Paleuphorbons from resin of Euphorbia palustris, L. J. A. MÜLLER (J. pr. Chem., 1929, [ii], 123, 148-159).-Extraction of the dry, acidfree resin with 96% alcohol and subsequent purification of the solid extracted by crystallisation from acetone affords 10 fractions (designated paleuphorbon 1 to 10). These have varying m. p. and analytical compositions. Paleuphorbon 1 (composition $C_{38}H_{62}O_4$ sinters at 75°, becomes opaque at 83°, and melts at 96° (all m. p. are corr.) with frothing, $[\alpha]_{\mu}^{\mu}$ $+37.23^{\circ}$ in benzene, when heated at 140° eliminates water, yielding a brittle lac, m. p. 72-73°, [a]¹⁰ $+40.83^{\circ}$ in benzene. Addition of bromine occurs to paleuphorbon 1 in chloroform solution, but similar treatment of the lac causes substitution. Acetylation of paleuphorbon 10 (composition $C_{39}H_{62}O_2$), which sinters at 105° and melts with frothing at 115°, with acetic anhydride gives a very small amount of a *diacetate*, m. p. 129°. The various fractions are partly precipitated by digitonin in alcohol solution. The nonprecipitable parts of the ten fractions fall into two classes, (a) sinter above 70° and m. p. above 80°. (b) m. p. about 70°. The recovered euphorbons from the digitonin complexes (by heating with benzene) afford three groups, (A) sinter at 70°, m. p. 75°, (B) sinter and melt between 76° and 98°, and (C) sinter and melt above 100°. H. BURTON.

"Cadechol" and "camphochol." H. RHEIN-BOLDT, O. KÖNIG, and E. FLUME (Z. physiol. Chem., 1929, 184, 219—224).—M.-p. curves show that deoxycholic and apocholic acids form 1:1 molecular compounds with camphor. By crystallising or fusing the components together 2:1 compounds are obtained. J. H. BIRKINSHAW.

Xanthophyll. II. L. ZECHMEISTER and P. Tuzson (Ber., 1929, 62, [B], 2226-2232; cf. this vol., 1252).-Xanthophyll is rapidly and economically obtained from stinging nettles by extraction with aqueous alcohol, followed by a modification of the method of Willstätter and Mieg (A., 1907, i, 865); chlorophyll and carotin are neglected. Catalytic hydrogenation of the product leads to disappearance of the colour after absorption of 8 mols. of the gas, and the intermediate product has the composition of a hexadecahydroxanthophyll. The perhydro-compound is, however, dextrorotatory, whereas the earlier compound (loc. cit.) was lævorotatory. From the present material the acetone method yields xanthophylls, the perhydro-derivatives of which are less markedly but decidedly dextrorotatory. Perhydroxanthophyll appears optically stable when heated at 80° for several hrs. and then preserved for a year. Analytically pure specimens of xanthophyll obtained from the same plant material by the acetone and alcohol methods had respectively $[\alpha]_{c} + 137^{\circ}$ and

+192° in chloroform, whereas a second set of specimens from material gathered by the authors had $[\alpha]_{\rm D}$ +162.5° and +139°. The "alcohol" preparations are not altered by exposure to acetone, and the "acetone" products are unchanged by alcohol. Xanthophyll from the green leaf appears to be composed of similar but oppositely active components.

Carotin and xanthophyll appear to absorb 8 mols. of bromine in chloroform solution, the former substance reacting slightly the more slowly. The substances are distinguished qualitatively from one another by the transitory formation in the case of xanthophyll of a temporary, olive-green colour which becomes brown and could not be obtained with carotin. H. WREN.

Isoprene and caoutchouc. XVI. Constitution of caoutchouc. H. STAUDINGER and H. F. BONDY (Ber., 1929, 62, [B], 2411-2416).-The cyclo-products derived from caoutchouc and gutta-percha are unsaturated compounds which absorb bromine and iodine chloride without thereby allowing an exact determination of the number of double linkings in the molecule. On exposure to air they undergo autooxidation, absorbing 1 atom of oxygen for 3-8 isoprene residues in about 2 years. The mean mol. wt., viscosity of the solutions, and the temperatures at which the products soften and liquefy do not thereby undergo marked alteration. The products with greater mean mol. wt. liquefy at higher temperatures than those with smaller mol. wt., since the inter-molecular forces are greater. The slight changes in the structure of the chains due to auto-oxidation do not appreciably affect the physical properties. It is therefore considered that the determinations of mol. wt. of the cyclocaoutchoucs afford true values not obscured by association and that the differences in the viscosities of the solutions depend on differences in mol. wt., and not on degree of association. Since the cyclo-products are hemicolloidal in character, the eucolloidal caoutchouc and gutta-percha must have a much higher mol. wt., considerably above 10,000, as previously deduced.

The conclusions of Meyer and Mark (A., 1928, 1252) are adversely criticised. H. WREN.

Constitution of stannic acid. P. PFEIFFER and O. ANGERN (Z. anorg. Chem., 1929, 183, 189—192). —*Cineole trichlorotrihydroxystannate*,

 $[SnCl_3(OH)_3][H \cdot C_{10}H_{18}O]_2$, has been prepared by treatment with cincole of a solution of the crystalline compound, $SnCl_3OH, H_2O, Et_2O$, obtained from an aqueous solution of stannic chloride by addition of ether. The substance is also produced by warming cincole with stannic chloride pentahydrate until a clear liquid is obtained, and cooling the mixture. The corresponding *tribromo*-compound,

 $[SnBr₃(OH)₃][H \cdot C₁₀H₁₈O]₂, has been prepared by an analogous method. H. F. GILLBE.$

Piperitone. IX. Oxidation reactions of piperitone. J. READ, A. J. WATTERS, G. J. ROBERT-SON, and R. S. HUGHESDON (J.C.S., 1929, 2068-2076).—Hydrogenation of piperitone in the presence of colloidal palladium at 25° gave thymol in yields of 3-25%, accompanied by isomenthone. Vaporised piperitone mixed with hydrogen and passed over palladised asbestos at 350° gave small quantities of thymol; similar treatment, using a platinised asbestos catalyst, yielded 22% of thymol, whilst with a nickel-pumice catalyst at 355° the product contained 10% of thymol. The hydrogenation of piperitone is a reversible process and the conditions favouring the dehydrogenative phase have been partly elucidated. The mechanism of the dehydrogenation is discussed; the hydrogenation of piperitone is considered to be an essential preliminary to its dehydrogenation and Δ^2 -enol-menthone to be the probable precursor of thymol in the processes investigated.

Piperitone is stable towards alkaline potassium ferricyanide and other mild oxidants, and was practically unaffected when vaporised and passed over nickel oxide at 360° in admixture with air. Similar procedures using 5% platinised asbestos at 340° gave 10% yields of thymol.

Piperitone does not yield stable dihalogenides, but the halogenated ketone undergoes spontaneous evolution (accelerated by heat) of hydrogen bromide with the formation of thymol, bromomenthone, and tarry material. The decomposition of the halogenated product was also accomplished by heating with quinoline, calcium carbonate, etc. The yields of thymol were greatest when bromine was used and least with iodine.

Emulsification of piperitone with bromine water led to a mixture of piperitone dibromide and bromohydrin. dl-*Piperitone chlorohydrin*, m. p. 101-102°, was isolated by long shaking of a solution of piperitone in acetone containing acetic acid with an aqueous solution of chlorocarbamide; it was unaffected by chromic anhydride in acetic acid solution, and sodium amalgam or zinc dust reconverted it into piperitone. Treatment with sodium methoxide led to an impure *methoxyl* derivative, $n_{\rm P}^{\rm m}$ 1·4748, whilst heating with excess of moist silver oxide gave a *substance*, $n_{\rm P}^{\rm m}$ 1·4640, possibly 2-hydroxy- Δ^6 -menthen-3-one.

R. J. W. LE FEVRE.

Piperitone. X. Synthesis of certain menthadienes, menthenes, and menthanols. J. READ and A. J. WATTERS (J.C.S., 1929, 2165-2172).-Piperitone reacts readily with the appropriate Grignard reagents to form directly 3-substituted homologues of α -terpinene; intermediate Δ^1 -menthenols cannot be isolated. The following $\Delta^{1:3}$ -menthadienes are described : 3-methyl-, b. p. 184-186°/737 mm., d_4^{25} 0.8585, n_p^{25} 1.4845; 3-ethyl-, b. p. 83-85°/15 mm., $199-202^{\circ}/737 \text{ mm.}, d_{4}^{25} 0.8631, n_{D}^{25} 1.4854; 3-n-propyl-,$ b. p. $104-106^{\circ}/14$ mm., d_{4}^{25} 0.8872, n_{13}^{23} 1.4865; 3phenyl-, b. p. 145-148°/15 mm., d4 0.9552, np 1.5525. The first three hydrocarbons were slightly dextrorotatory when prepared from *dl*-piperitone owing to interaction between the Grignard reagents and the lævorotatory impurity present in the Eucalyptus piperitone used.

In contrast to the above results, both *l*-menthone and *d*-isomenthone react with Grignard reagents to give 3-substituted menthan-3-ols; the following are recorded: 3-methyl-, b. p. 101-102°/17 mm., $[\alpha]_{16}^{16}$ -6.47°, d_{45}^{25} 0.8964, n_{25}^{25} 1.4605; 3-ethyl-, b. p. 112-113°/16 mm., 217-219°/759 mm., $[\alpha]_{16}^{36}$ +1.54°, d_{45}^{25} 0.8992, n_{25}^{25} 1.4650; 3-n-propyl-, b. p. 123-125°/16 mm., $[\alpha]_{17}^{3}$ -0.68°, d_{45}^{25} 0.8957, n_{25}^{25} 1.4664; 3-phenyl-, b. p. 170—172°/18 mm., $[\alpha]_{\rm P}^{15}$ -22.87°, d_4^{25} 0.9872, $n_{\rm P}^{25}$ 1.5265; 3-methyl-isomenthan-3-ol, b. p. 105—106°/20 mm.; 3-ethyl-, b. p. 105—106°/10 mm., and 3-phenyl-, b. p. 150—152°/9 mm. Each of the foregoing menthanols undergoes dehydration by heating with anhydrous oxalic acid or sodium hydrogen sulphate to the corresponding known substituted menthone. The products from piperitone are individuals, but those from the menthones are probably mixtures of stereoisomerides. None of the ketones reacts with magnesium isopropyl iodide (steric hind-rance ?).

l-Piperitone and *d*-isomenthone gave gummy compounds when treated with specially prepared magnesium bromide under ether; *l*-menthone gave a crystalline compound, $2C_{10}H_{18}O,MgBr_2$. Recovery of the ketones from these by addition of water gave a partly "inverted" *d*-isomenthone and a completely racemised piperitone, suggesting that the complexes should have some such enol formula as $CR' O \cdots (MgBr_2) \cdots O CR'$. Piperitone reacts with H H Piperitone reacts with alcoholic potassium cyanide to yield a stable dicyclic anhydramide, $C_{11}H_{17}ON$, b. p. $151-153^{\circ}/13$ mm., d_4^{33} $0.9720, n_D^{23}$ 1.4680. R. J. W. LE FEVRE.

Camphenes acylated in the ω -position. P. LIPP and M. QUAEDVLIEG (Ber., 1929, 62, [B], 2311-2322; cf. A., 1927, 883).-ω-Acetylcamphene, b. p. 112.6—114° (corr.)/14 mm., $d_4^{n+0.98178}$, $[\alpha]_{11}^{20}$ -43.66°, is prepared: (i) yield 10.7% by the action of acetonitrile on the product of the action of magnesium and bromocamphene in ether (intermediate ketimine hydrochloride, decomp. 171-173°), (ii) yield 2.3% from camphene, acetyl chloride (preferably bromide), and magnesium bromide in ether, and (iii) yield 5.2% from camphene, acetyl chloride, and tin tetrachloride in ether. The semicarbazone, m. p. 199.5-200.5° (corr. : decomp.), and oxime, m. p. (indef.) 95-105°, are described. As an ag-unsaturated ketone it exhibits halochromism when treated with concentrated mineral acids. It is reduced by hydrogen in presence of spongy platinum to acetylisocamphane, b. p. 117°/ 11 mm. [semicarbazone, m. p. 203° (decomp.)]. It is oxidised by permanganate to acetic acid and camphenilone. With magnesium methyl iodide it yields ill-defined products, whereas it is converted by magnesium phenyl bromide through the non-isolable carbinol into the hydrocarbon, C₈H₁₄}C:CH·CPh:CH₂, b, p. 126-127°/0.19 mm., readily auto-oxidised with elimination of the methylene group as formaldehyde. ' "Grignarded " ω-bromocamphene and isovaleronitrile afford w-isovalerylcamphene, b. p. 131-132°/9 mm., d¹²² 0.9437 [semicarbazone, m. p. 186-187° (decomp.)]. The action of benzonitrile on "Grignarded " w-bromocamphene is remarkable for the stability of the intermediate ketimine, b. p. 132-133°/0.4 mm. (hydrochloride, decomp. 213.5-214.5°; chloroplatinate). ω -Benzoylcamphene has b. p. 137–138.5°/0.7 mm., d_1^{108} 1.0568. It is oxidised by permanganate to benzoic acid and camphenilone. Hydrogen bromide in glacial acetic acid is added with quantitative production of ω -benzoylbornyl bromide, m. p. 73°, smoothly transformed into w-benzoylborneol. The carbonyl group of ω -benzoylcamphene does not react

with the customary ketonic reagents. The action of magnesium methyl iodide gives the hydrocarbon described above from ω -acetylcamphene and magnesium phenyl bromide. With the last-named reagent ω -benzoylcamphene appears to yield mainly the compound (I), b. p. 176—177°/0·5 mm., m. p. 83—84°, which is shown to contain one ethylenic linking. Oxidation of the hydrocarbon with permanganate is complex and yields only benzoic acid; this is true also for ozonisation.

$$\begin{array}{cccc} CH_2-CH-CMe_2 & CH_2-CH-CH_2 \\ CH_2 & CH_2 & CHe_2 \\ (I.) & CH-CH-C & CH-CH & (II.) \\ & CPh_2 \cdot CH & C \cdot CH \cdot CPh_2 \end{array}$$

The action of magnesium phenyl bromide on phenylcamphylidenedihydrofuran (loc. cit.) gives $\alpha\alpha$ diphenyl- β -tricyclenylethylene (II), b. p. 183—186°/0·5 mm., m. p. 70—71°, which absorbs markedly more than 1 mol. of hydrogen and is converted by ozone into benzophenone and tricyclenic acid. The oxygen bridge of furan appears less stable than usually considered towards Grignard reagents. The formulation of the furan derivative is thus confirmed, but it is not completely homogeneous; when oxidised it yields small amounts of camphenilone, due to the presence of ω -benzoylcamphene. H. WREN.

Constitution of Manasse's β -hydroxycamphor and a new method of preparing epicamphor. III. J. BREDT and M. BREDT-SAVELSBERG [with E. BUND] (Ber., 1929, **62**, [B], 2214—2216).— β -Hydroxycamphor in aqueous solution is reduced by sodium amalgam to epicamphor, m. p. 182° (semicarbazone, m. p. 230°), which yields bromoepicamphor, m. p. 133°, [α]²⁴_D —68° in ethyl alcohol. Manasse's β -hydroxycamphor is therefore 2-hydroxy-3-ketocamphane. H. WREN.

New crystalline compounds from essential oils. H. WIENHAUS and H. SCHOLZ (Ber. Schimmel, 1929, 267-282).-I. Bulnesol, a compound occurring with guaiol in guaiacum wood oil. When guaiacum wood oil is triturated with acctone and the filtered solution is cooled in a freezing mixture, an unsaturated, dicyclic, tertiary sesquiterpene alcohol bulnesol, $C_{15}H_{26}O$ (I), m. p. 69–70°, b. p. 136–138°/4 mm., d^{70} 0.9389, n^{70}_{70} 1.48915, isomeric but not identical with guaiol, separates. The potassium derivative is converted by phthalic anhydride in xylene and subsequent acidification into a liquid hydrogen phthalate (amorphous silver, m. p. indefinite, 103-109°, and potassium salts, amorphous phenylurethane, and α -naphthylurethane, oily chromate). Bulnesol is not reduced by hydrogen and platinum in methyl alcohol, but in acetic acid solution it is converted into the saturated dihydrobulnesol, m. p. 75-76° (liquid chromate). Oxidation with aqueous · potassium permanganate in benzene solution at 0° converts I into a ketoglycol, C₁₅H₂₄O(OH)₂, m. p. 173°, but no crystalline acid could be obtained. Oxidation with 45% hydrogen peroxide in acetic acid at 25° yields a liquid substance, C₁₂H₂₂O₃, the trihydric alcohol similar to that obtained by the oxidation of guaiol not being obtained. When I is heated with 85% formic acid the corresponding unsaturated hydrocarbon, bulnesene (II), $C_{15}H_{24}$, b. p. 113.5— 115°/6 mm., d^{20} 0.9149, n_D^{20} 1.50467, α_D -14.4° (? in 1 dm. tube), which is probably a mixture of isomerides, is obtained. A similar mixture is obtained by heating I with zinc at 250°. Catalytic reduction of II with platinum-black in acetic acid yields a saturated hydrocarbon, $C_{15}H_{28}$, b. p. 107—109°/5 mm., d^{20} 0.8910, n_D^{20} 1.47994, α_D -12.7°.

II. Cryptomeradol, a sesquiterpene alcohol from Japanese cedarwood oil. By removal of primary and secondary alcohols from this oil (from Cryptomeria japonica, Don.) by heating with phthalic anhydride in benzene first at 80° and again at 130° and fractionation of the unesterified portion is obtained an unsaturated, tertiary sesquiterpene alcohol, cryptomeradol, $C_{15}H_{26}O$ (III), m. p. 79–80°, b. p. 141– 142°/4 mm., d^{60} 0.9515, n_{D}^{60} 1.49317, α_{D} +24.2° (methyl ether, b. p. 133.5-134.5°/5 mm., d²⁰ 0.9503, n_{11}^{20} 1.49601, α_{D} +34.1°; amorphous hydrogen phthalate, phenylurethane, and α -naphthylurethane; liquid chromate). This is reduced by hydrogen and platinum-black in acetic acid at 20°/751 mm. to the saturated dihydro-derivative, m. p. 81-82° (liquid chromate), the methyl ether being similarly reduced to dihydrocryptomeradyl methyl ether, b. p. 124.5- $125.5^{\circ}/5$ mm., d^{20} 0.9365, $n_{\rm D}^{20}$ 1.48626, $\alpha_{\rm D}$ +11.3°. Oxidation of III with potassium permanganate at 0° yields a substance, m. p. 107— 108° , probably the trihydric alcohol $C_{15}H_{25}(OH)_3$, but no crystalline acid could be isolated.

III. Germacrol, a crystalline compound from Bulgarian geranium oil. The solid fraction of Bulgarian geranium oil (described erroneously as tricosane, C23H48, by Rovesti; Notiz. chim.-ind., 1927, 2, 438) has the composition $C_{16}H_{24}O$ and is given the name germacrol (IV), m. p. 54-55°, d⁶⁷ 0.9549, n_{10}^{50} 1.51610, optically inactive. By reduction with platinum-black and hydrogen in acetic acid, 6 atoms of hydrogen are absorbed and fractionation of the product yields two fractions, b. p. 120-123°/3.5 mm., d^{20} 0.9156, $n_{\rm D}^{20}$ 1.47662, and b. p. 123–126°/3.5 mm., d^{20} 0.9188, n_D^{20} 1.47838, both having the composition C₁₆H₃₀O. Germacrol probably contains only two double linkings and an oxide ring which is converted into a tertiary alcohol group in the hexahydro-compound. In agreement with this, IV yields no colour with chromic oxide in carbon tetrachloride, whilst the hexahydro-derivative becomes reddish-yellow, and with sodium in anhydrous ether gives a substance resembling an alkoxide. J. W. BAKER.

l-Difenchyl ether and *l*-difenchene. O. ZEIT-SCHEL (Ber. Schimmel, 1929, 317-324).—*l*-Fenchyl alcohol is converted by 10% of sulphuric acid at 100° into l-difenchyl ether, b. p. 151-152°/4 mm., d_4^{30} 0.946, n_D^{30} 1.48439, $[\alpha]_D$ -74.00°, which is unattacked by heating with sodium, but is oxidised by hot nitric acid (d 1.355) to fenchone. The ether is not obtained by heating fenchyl alcohol in benzene solution with fused zinc chloride, the product of this reaction being l-difenchene, b. p. 158°/4 mm., 321-325°/751 mm., d^{15} 0.9488, n_D^{30} 1.50762, $[\alpha]_D$ -5.15°. J. W. BAKER.

Furan compounds derived from sugars. IV. Compounds from hydroxymethylfurfuraldehyde and acid amides and glycine anhydride. J. KARASHIMA (Z. physiol. Chem., 1929, 184, 268– 271).— ω -Hydroxymethylfurfuraldehyde and carbamide react in aqueous solution at 100° in an atmosphere of carbon dioxide, forming a small amount of a *compound*, $C_8H_{12}O_4N_4$, m. p. 164°. With ethyl carbamate and acetamide in presence of a CH-CH trace of hydrochloric

 $\begin{array}{c} \text{CH-CH} \\ \text{HO-CH}_2 \cdot \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{CH}(\text{NHR})_2 \\ \text{(I.)} \end{array} \begin{array}{c} \text{three on hydroculule} \\ \text{acid, the compounds (I, R = \cdot \text{CO}_2\text{Et and Ac, respectively), m. p. 173^\circ} \end{array}$

and 206°, respectively, result in yields of 31.8% and 18.7%; benzamide yields the substance $C_{20}H_{18}O_4N_2$, m. p. 180°.

 ω -Acetoxymethylfurfuraldehyde condenses with glycine anhydride in presence of acetic anhydride and sodium acetate at 120—130°, affording 2:5-diketo-3:6-di- ω -acetoxymethylfurfurylidenepiperazine, m. p. 220° (decomp.). H. BURTON.

Preparation and properties of new furan compounds. H. WIENHAUS and H. LEONHARDI (Ber. (König and Hey, A., 1926, 175) is reduced with hydrogen at 80°/20 atm. in alcoholic solution with a nickel catalyst to 2-furfurylacetaldehyde, b. p. 59-61°/4 mm., d²⁰ 1.074, n²⁰ 1.47818 (semicarbazone, m. p. 82-83°; dimethylacetal, b. p. 77°/4 mm., d.º 1.026, $n_{\rm p}^{20}$ 1.45502), together with a fraction, b. p. 61-76°/ 4 mm., which is probably the corresponding alcohol. Similar reduction of α -2-furyl- $\Delta^{\alpha\gamma}$ -hexadien-z-one (Röhmer, A., 1898, i, 300) at 100° gives y-furfurylbutyl methyl ketone, b. p. 93-95°/2 mm., d²⁰ 0.995, n²⁰ 1.47023 (semicarbazone, m. p. 121-122°). Furfuraldehyde condenses with methyl isobutyl ketone in the presence of 2% alcoholic potassium hydroxide to give β -2-furyl- α -isopropylvinyl methyl ketone (or ? β-2-furylvinyl isobutyl ketone), b. p. 115-116°/3 mm., d²⁰ 1.011, n²⁰₁ 1.55282 (semicarbazone, m. p. 175-176°). Reduction of furfurylidenemesityl oxide at 140- $150^{\circ}/24$ atm. yields β -2-tetrahydrofurylethyl isobutyl ketone, b. p. 103–106°/3 mm., d^{20} 0.939, $n_{\rm D}^{20}$ 1.44982. Furfuraldehyde condenses with butyl acetate in the presence of sodium to give, in poor yield, butyl β-2-furylacrylate, b. p. 117-118°/3 mm., d²⁰ 1.045, $n_{\rm p}^{20}$ 1.53361. The corresponding isoamyl ester, b. p. 136—139°/5 mm., d^{20} 1.025, n_D^{20} 1.52438, is similarly J. W. BAKER. prepared.

Hoesch syntheses of phenolic ketones. III. Condensation of phenylcyanopyruvic esters with polyhydric phenols. W. BORSCHE and J. NIEMANN (Ber., 1929, 62, [B], 2043-2045).-Ethyl phenylcyanopyruvate reacts with resorcinol in glacial acetic acid in presence of zinc chloride and hydrogen chloride, yielding ethyl 7-hydroxy-3-phenylcoumarin-4-carboxylate (+H₂O), m. p. 190-191°, hydrolysed to 7-hydroxy-3-phenylcoumarin-4-carboxylic (+H₂O), m. p. 300-301°. Ethyl 7-methoxy-3-phenylcoumarin-4-carboxylate, m. p. 123-124° (from the hydroxy-ester and diazomethane) yields successively 7-methoxy-3-phenylcoumarin-4-carboxylic acid, m. p. 288°, and 7-methoxy-3-phenylcoumarin, m. p. 124°. Under similar conditions, orcinol and ethyl phenylcyanopyruvate afford ethyl 7(?)-hydroxy-3-phenyl-5(?)methylcoumarin-4-carboxylate, m. p. 231°, whereas phloroglucinol yields ethyl 5:7-dihydroxy-3-phenylcoumarin-4-carboxylate, decomp. 298°. Ethyl acetoacetate and resorcinol give 7-hydroxy-4-methylcoumarin. H. WREN.

Phthalein-metal compounds. E. BURES, J. BERGAUER, and A. KRACIK (Casopis Českoslov. Lek., 1928, 8, 180–183; Chem. Zentr., 1929, i, 2532).— Mercury fluorescein [potassium, m. p. 85° (decomp.), sodium, lithium, and barium salts), mercury dibromofluorescein (corresponding salts), and mercury phenolphthalein (corresponding salts) are described.

A. A. ELDRIDGE.

Aldehydofluorescein and dyes derived from it. R. N. SEN and K. N. BANERJEA (J. Indian Chem. Soc., 1929, 6, 505-516).—The Reimer-Tiemann reaction with fluorescein (oxime, not melted at 260°)



affords aldehydoftuorescein (I), not melted at 260° (45° /_o yield; *phenylhydrazone*, semicarbazone, and dioxime, all m. p. above 260°), which dyes wool and silk with a deep orange shade. Alkaline solutions of I are red with a

subdued green fluorescence. Condensation of I with aminoazobenzene, p-toluidine, p-nitroaniline, benzidine, o-, m-, and p-phenylenediamines, and rosaniline affords the corresponding azomethines, all of which have m. p. above 260°. These dye wool and silk with shades varying from yellow to brown. Con-densation of I with dimethylaniline gives pp'-tetramethyldiaminodiphenylfluoresceinylmethane, m. p. 70-72°, oxidised by lead peroxide to a blue dye. The corresponding diphenylfluoresceinylmethane derivative, not melted at 260°, from o-cresotic acid and I is oxidised by nitrosvl sulphate at 50-60° to a red dyc. This gives a deep brown shade to wool and silk. The pyronine dyes from *m*-dimethylaminophenol and resorcinol and I give wool and silk bluish-violet and orange-red shades, respectively. Fluorescein and *m*-dimethylaminophenol afford a *due*, softens at 245° (dyes bluish-pink), whilst the pentabromo-derivative of the pyronine from resorcinol and I dyes with a deep red shade. H. BURTON.

Condensation of esters with resorcinol. dimethylaniline, and *m*-diethylaminophenol. R. N. SEN and A. MUKHERJI (J. Indian Chem. Soc., 1929, 6, 557-563).-When ethyl benzoate (1 mol.) is heated with resorcinol (2 mols.) and zinc chloride at 180° in a current of hydrogen chloride (cf. A., 1925, i, 554) an improved yield of resorcinolbenzein (Sen and Sinha, A., 1924, i, 288) (potassium salt; bromoderivative, decomp. 200°) is obtained. The following are prepared similarly, using the appropriate ester : resorcinol-o-nitrobenzein, not melted at 290°; -o-aminobenzein; -p-aminobenzein, decomp. 290° (dibromoderivative); -naphthalein, not melted at 290° (tetrabromo-derivative, decomp. 260°); -stearein (I), and -ole-ein (II), softens at 140° (hexabromo-derivative, C₃₀H₃₆O₃Br₆). These compounds dye wool and silk with shades varying from yellow to red (bromoderivatives), and alkaline solutions are deep red, showing usually a green fluorescence when diluted. The difference in solubility of I and II in benzene is utilised in their separation from the reaction mixture obtained from olive oil and resorcinol. Dyes similar to the above are formed analogously from resorcinol and castor and coconut oils. When ethyl benzoate (1 mol.) and resorcinol (1 mol.) are heated at 140° in presence of zinc chloride, 2:4-dihydroxybenzophenone results; pyrogallol yields similarly 2:4:6-trihydroxybenzophenone. The former ketone reacts with 1 mol. of resorcinol at 180°, giving resorcinolbenzein.

Dimethylaniline condenses with ethyl benzoate and salicylate in presence of phosphoryl and zinc chlorides, yielding malachite-green and o-hydroxymalachitegreen (bluish-green; the colours given in parentheses are the shades on wool, silk, and tannined cotton), respectively. *m*-Diethylaminophenol and ethyl benzoate, anthranilate, and stearate in presence of zinc chloride condense to benzorhodamine, softens at 210° (bluish-red), anthranilorhodamine, and stearorhodamine (pink), respectively. H. BURTON.

Behaviour of anthocyanins at varying hydrogen-ion concentrations. B. H. BUXTON and F. V. DARBISHIRE (J. Genetics, 1929, 21, 71-80).—Anthocyanins are differentiated as of the blue or red group according to the reaction of coloured flowers in media of varying hydrogen-ion concentrations. The effect of yellow flavones on the colours is considered.

CHEMICAL ABSTRACTS. Cyclic sulphides. IV. J. VON BRAUN and K. WEISSBACH (Ber., 1929, 62, [B], 2416-2425; cf. A., 1925, i, 1445).—Addition of a solution of benzylthiolacetyl chloride in chloroform to aluminium chloride covered with carbon disulphide affords benzyl chloride and 4-ketoisothiochroman, $C_6H_4 < CH_2 \cdot S$ m. p. 64° (cf. Lesser and Mehrländer, A., 1923, i, 827); the semicarbazone, m. p. 236°, and condensation product with isatin, $C_{17}H_{11}O_2NS$, m. p. 255—260° (decomp.) after darkening at 220°, are described. Reduction of the ketone by Clemmensen's method leads to 1-methylthiophthalan, $C_6H_4 < CH_2 \cdot S$ m. p. 115—116°/16 mm. (methiodide, m. p. 137°; mercurichloride compound, m. p. 121°), which is prepared synthetically from α -methyl-o-xylylene bromide and potassium monosulphide. With potassium disulphide, the bromide yields the substance $S \cdot CHMe \cdot C_6H_4$.

Phenyl a-methylbenzyl sulphide, b. p. 167—170°/15 mm., is prepared by the action of amalgamated zinc and hydrochloric acid on phenacyl phenyl sulphide or on a mixture of acetophenone and thiophenol; the corresponding sulphone has m. p. 114°. The isomeric phenyl β -phenylethyl sulphide, b. p. 188°/16 mm. (sulphone, m. p. 58°), is derived from β -phenylethyl bromide and the sodium compound of thiophenol.

4-Ketoisothiochroman is reduced by sodium amalgam to 4-hydroxyisothiochroman, b. p. $138-140^{\circ}/0.1$ mm., converted by phosphorus trichloride into 4-chloroisothiochroman, b. p. $117^{\circ}/0.4$ mm. Either chloro- or hydroxy-compound is transformed by zinc and hydrochloric acid into isothiochroman in poor yield. If the hydroxy-compound is heated above 200° or, preferably, distilled with potassium hydrogen sulphate in a vacuum, isothiochromen, $C_6H_4 < CH_2 \cdot S_{CH=CH}$, b. p. 124°/13 mm., is obtained; it is distinguished from isothiochroman by the readiness with which it

becomes polymerised. Reduction of ketoisothiochromanoxime with sodium and alcohol causes rupture of the heterocyclic ring with formation of α -o-tolylethylamine, b. p. 89-91°/ 14 mm. (hydrochloride, m. p. 173°; picrate, m. p. 206°; quaternary methiodide, m. p. 176°, degraded to o-methylstyrene), and a base $SH \cdot CH_2 \cdot C_6H_4 \cdot CHMe \cdot NH_2$ or C6H4Me.CH(NH2).CH2.SH, b. p. 144-146° (picrate, m. p. 168°; unstable hydrochloride). If, however, the oxime is reduced by sodium amalgam, the product is 4-aminoisothiochroman, b. p. 153-155°/14 mm. (hydrochloride, m. p. 229°; picrate, m. p. 219°). When cautiously treated with methyl iodide, the amine gives the quaternary iodide, C12H18NSI, m. p. 162°, converted by treatment with silver oxide and distillation into isothiochromen and 4-dimethylaminoisothiochroman, b. p. 154-155°/13 mm. (very hygroscopic hydrochloride; picrate, m. p. 113°).

β-Phenylethylthiolacetic acid, m. p. 61°, b. p. 185°/ 4 mm., prepared from chloroacetic acid, sodium hydroxide, and β-phenylethyl mercaptan, is converted into the corresponding chloride, b. p. 175—176°/15 mm., which is transformed by aluminium chloride into β-phenylethyl chloride and 1-keto-6:7-benzohexamethylene sulphide, $C_6H_4 < CH_2 + CH_2 > S$, b. p. 181—

183°/15 mm. (oxime, m. p. 151–152°; semicarbazone, m. p. 244°). Similarly, γ -phenylpropylthiolacetic acid, b. p. 187–188°/0.6 mm., yields the corresponding chloride, b. p. 193–195°/13 mm., converted by aluminium chloride into γ -phenylpropyl chloride and ketobenzoheptamethylene sulphide, C. H. $< CH_2$ CH₂ CH₂ CH₂

b. p. 160°/0.4 mm.

Phenacyl bromide is transformed by dimethylamine in benzene into *phenacyldimethylamine*, b. p. 126—128°/18 mm. (*picrate*, m. p. 150°). The base is converted by zinc in hydrochloric acid solution into dimethylamine, ethylbenzene, and (?) α -chloroethylbenzene. H. WREN.

Sulphur-containing hydroxyquinones [thionaphthens]. I. G. FARBENIND. A.-G.—See B., 1929, 807.

Condensation products and vat dyes of the benzanthrone series. I. G. FARBENIND. A.-G.— See B., 1929, 808.

Preparation of 2-phenylpyrroline. P. LIPP and H. SEELES (Ber., 1929, 62, [B], 2456—2458).— γ -Chlorobutyronitrile is converted by magnesium phenyl bromide in ether into 2-phenylpyrroline, m. p. 45°, b. p. 118°/11 mm. (hydrochloride, m. p. 206— 207°), converted by phthalic anhydride into γ -phthalimidopropiophenone. H. WBEN.

Existence of the *p*-indole ring. H. SOBOTKA (Ber., 1929, **62**, [B], 2191—2194; cf. von Braun, A., 1912, i, 497; Ferber, this vol., 308).—Unsuccessful attempts to obtain the hypothetical *p*-dihydroindole are described. Treatment of β -phenylethyl bromide with nitric acid (d 1.52) at -70° affords β -p-nitrophenylethyl bromide, m. p. 68° ; the by-products contain β -m-nitrophenylethyl bromide in considerable amount. β -p-Nitrophenylethyl chloride, m. p. 48° , is similarly prepared in satisfactory yield. Reduction of the nitro-compounds in alcoholic solution in presence of platinum oxide leads smoothly to p- β bromoethylaniline hydrobromide, m. p. 219° (decomp.) [corresponding hydrochloride, m. p. 214—216° (decomp.)], and p- β -chloroethylaniline hydrochloride, m. p. 210—211° (decomp.). p- β -Bromoethylbenzanilide has m. p. 137°. p- β -Bromoethylaniline, when heated in ether at a temperature not exceeding 65° , appears to yield the base, CH₂Br·CH₂·C₆H₄·NH·[CH₂]₂·C₆H₄·NH₂, and products of high mol. wt. H. WREN.

4-Phenyldihydro-2-picolone. W. GOHDES (J. pr. Chem., 1929, [ii], 123, 169-188).-The main product of the hydrolysis of ethyl 4-phenyldihydro-2picolone-3: 5-dicarboxylate (ethyl 6-keto-4-phenyl-2-methyltetrahydropyridine-3: 5-dicarboxylate) (I) (Knoevenagel and Brunswig, A., 1902, i, 640) with boiling 8% sodium hydroxide is ethyl 6-keto-4-phenyl-2-methyltetrahydropyridine-3-carboxylate (II), m. p. 156° (also obtained by heating I with sodium acetate and acetic anhydride). Contrary to Knoevenagel and Brunswig (loc. cit.), only a very small yield (29%) of the corresponding free acid (III), $+H_2O$ and an-hydrous, m. p. 199–202° (decomp.), could be obtained. In agreement with the resistance of II to hydrolysis, the free acid could not be esterified. Attempted hydrolysis of II converts it into y-acetoβ-phenylbutyric acid. Great difficulty was found in decarboxylating III by heating at 190°. From the product, having an indefinite m. p. 130-270°, only a small quantity of a substance, m. p. indefinite 265° (decomp.), could be isolated. This is erroneously described by Knoevenagel and Brunswig as 4-phenyldihydro-2-picolone, but a mol. wt. determination shows that it consists of a double molecule formed by union of two dihydropyridine nuclei during decarboxylation. By dry distillation of III, however, 4-phenyldihydro-2-picolone, m. p. 141°, is actually obtained and is identical with the specimen obtained by the method of Vorlander and Knoetzsch (A., 1897, i, 285) and described by them as the amide anhydride of y-acetyl-β-phenylbutyric acid (lit. m. p. 137°). This product has the correct (mono) mol. wt., and the specimens obtained by either method are converted by distillation with zinc in a current of hydrogen into 4-phenyl-2-methylpyridine [Bülow and Issler, A., 1903, i, 718; picrate, m. p. 210-213° (decomp.) (lit. 203°); perchlorate, m. p. 142-143°; chloroplatinate, m. p. 211-213° (decomp.); chloroaurate, m. p. 161-163°]. J. W. BAKER.

Stereoisomerism in substituted 1:2:3:4tetrahydroquinolines. I. S. G. P. PLANT and R. J. ROSSER (J.C.S., 1929, 1861—1870).—2:3-Dimethylquinoline, prepared by a modification of Pfitzinger's method (A., 1898, i, 207), yields on reduction the cis- and trans-forms of 2:3-dimethyl-1:2:3:4-tetrahydroquinoline, (A), m. p. 38—39° (benzoyl derivative, m. p. 92°; hydrochloride, m. p. 240—243°, picrate, m. p. 178°), and (B), liquid (benzoyl derivative, m. p. 96—97°; hydrochloride, m. p. 169— 170°). The 2:3-dimethyl-1:2:3:4-tetrahydroquinoline described by Ferratini (cf. A., 1893, i, 602) is a mixture of the two forms, whilst the compound described by von Braun, Gmelin, and Schultheiss (A., 1923, i, 836) is the *B* modification, although somewhat impure. A method of separating the products is described and the relative amounts of the two forms present in the reduction product have been determined in four cases, using different reducing agents.

Reduction of 2:3-dimethyl-4-keto-1: 4-dihydroquinoline, m. p. $319-320^{\circ}$ (hydrochloride, m. p. $248-249^{\circ}$), with sodium amalgam yields first 2:3-dimethylquinoline, and with excess of the reducing agent the two tetrahydro-compounds. The reduction of tetrahydroacridone (cf. A., 1925, i, 63) probably proceeds by similar stages.

2:3-Diphenylquinoline (cf. Pfitzinger, loc. cit.) with certain reducing agents also yields a mixture of stereoisomerides, 2:3-diphenyl-1:2:3:4-tetrahydroquinoline (A), m. p. 130—131°, insoluble in aqueous hydrochloric acid, but yielding with dry hydrogen chloride in ether a hydrochloride, m. p. 198—199°; (nitrosoamine, m. p. 150°; acetyl derivative, m. p. 145°), and (B), m. p. 92° (hydrochloride, m. p. 239— 242°; nitrosoamine, m. p. 138°). The effect of various reducing agents on the relative proportions of the two stereoisomerides formed has also been studied in this case.

It is not known in either case which of the stereoisomerides has the *cis*- and which the *trans*-configuration (cf. A., 1928, 527). The bearing of the results on previous work on stereoisomerism in polycyclic structures is discussed. R. CHILD.

Derivatives of tetrahydrocarbazole. VIII. Formation and reactions of nitric acid addition products. S. G. P. PLANT and K. H. RUTHERFORD (J.C.S., 1929, 1970—1975; cf. A., 1926, 1151; 1928, 1259).—The 9-o-, -m-, and -p-toluoyl- and -chlorobenzoyl-tetrahydrocarbazoles all give with nitric acid in glacial acetic acid solution 5-nitro-substitution products; the 9-p-toluoyl and 9-p-chlorobenzoyl compounds give also, like 9-benzoyltetrahydrocarbazole (J.C.S., 1923, 123, 676), products formed by addition of OH and NO₂ at the double linking.

9-o-Toluoyltetrahydrocarbazole, b. p. 260-270°/22 mm. (from tetrahydrocarbazole by successive treatment with magnesium ethyl bromide and o-toluoyl chloride), on nitration yields the 5-nitro-compound, m. p. 154°; 9-m-toluoyltetrahydrocarbazole, b. p. 260-290°/12 mm., gives the 5-nitro-derivative, m. p. 148°, and the 9-p-toluoyl compound, b. p. 250-280°/12 mm., m. p. 126°, gives a 5-nitro-derivative, m. p. 136°, and the additive product, 11-nitro-9-p-toluoyl-10hydroxyhexahydrocarbazole, m. p. 149° (decomp.). 9-o-Chlorobenzoyl-, b. p. 260-270°/20 mm., m. p. 117° (5-nitro-derivative, m. p. 195°), 9-m-chlorobenzoyl, b. p. 250-280°/15 mm., m. p. 93° (5-nitroderivative, m. p. 155°), and 9-p-chlorobenzoyl, b. p. about 285°/18 mm., m. p. 106° (5-nitro-compound, m. p. 148°, and 11-nitro-9-p-chlorobenzoyl-10-hydroxyhexahydrocarbazole, m. p. 153°), derivatives of tetrahydrocarbazole are described. All of the 5-nitrosubstitution products mentioned give on hydrolysis the corresponding acid and 5-nitrotetrahydrocarbazole. Benzoylation of 6-nitrotetrahydrocarbazole (J.C.S., 1921, **119**, 1825) leads to the 9-benzoyl derivative, m. p. 180°, and of 7-nitrotetrahydrocarbazole (from cyclohexanone-m-nitrophenylhydrazone) to the 9-benzoyl compound, m. p. 138°. Nitrie acid has no effect on 5-, 6-, or 7-nitro-9-benzoyltetrahydrocarbazoles, nor on 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole. The last-named compound is converted by boiling alcohol into 9-benzoyl-10:11-dihydroxyhexahydrocarbazole, m. p. 142°, which with boiling aqueous-alcoholic potassium hydroxide gives 11-hydroxytetrahydrocarbazolenine, m. p. 79° (cf. loc. cit.). The mcchanism of the conversion of 11-nitro-9benzoyl-10-hydroxyhexahydrocarbazole into δ -obenzamidobenzoylvaleric acid by means of alkalis is discussed.

9-Cinnamoyltetrahydrocarbazole, m. p. 117°, gives on nitration a mixture of the 5-nitro-compound, m. p. 177°, and 9-cinnamoyl-10: 11-dihydroxyhexahydrocarbazole, m. p. 204°. R. CHILD.

Stereoisomerism in polycyclic systems. VI. B. K. BLOUNT, W. H. PERKIN, jun., and S. G. P. PLANT (J.C.S., 1929, 1975—1987).—A mixture of ethyl cyclopentanone-2-carboxylate and aniline, when kept for a fortnight in a vacuum over calcium chloride, gave ethyl 1-anilino- $\Delta^{1:2}$ -cyclopentene-2-carboxylate, which at 260° readily passed into 12-keto-2:3:5:12tetrahydro- β -quinindene, m. p. 327° (after previous blackening); this compound by reduction with sodium amalgam followed by benzoylation of the crude bases gave a mixture of two stereoisomeric 5-benzoyl-2:3:4:5:12:13-hexahydro- β -quinindenes, A, m. p. 173°, and B, m. p. 158—159°.

When boiled together ethyl cyclopentanone-2-carboxylate and aniline yielded cyclopentanone-2-carboxyanilide, m. p. 104°, which with hot sulphuric acid formed 5-keto-2:3:5:6-tetrahydro- α -quinindene, m. p. 256°. Reduction as above led to the 5-keto-2:3:4:5:6:13-hexahydro- α -quinindenes, A, m. p. 210-211°, and B, m. p. 135.5°, whilst similar treatment but with sodium and boiling alcohol in addition gave, after benzoylation, only one of the two possible modifications of 6-benzoyl-2:3:4:5:6:13-hexahydro- α -quinindene, m. p. 94.5-95°, from which, by hydrolysis with alcoholic potassium hydroxide, 2:3:4:5:6:13-hexahydro- α -quinindene, m. p. 42.5° (6-phenylcarbamyl derivative, m. p. 99°), was obtained.

Ethyl cyclohexanone-2-carboxylate and aniline, under the conditions employed for the cyclopentanone analogue, formed ethyl 1-anilino- $\Delta^{1:2}$ -cyclohexene-2-carboxylate, m. p. 58.5°, converted by heating into tetrahydroacridone; when boiled together, however, cyclohexanone-2-carboxyanilide, m. p. 105-105.5°, was produced. By the action of hot sulphuric acid on the last compound 9-keto-5:6:7:8:9:10-hexahydrophenanthridine, m. p. 267-268°, was obtained.

An alcoholic solution of aniline and 2-hydroxymethylenecyclopentanone precipitated slowly 2-phenyliminomethylcyclopentanone, from which hot sulphuric acid etc. produced ammonium 2-phenyliminomethylcyclopentanone-4'-sulphonate and thus the free acid.

A mixture of anthranilic acid and α -hydrindone heated to 210° afforded 14-keto-7: 14-dihydrobenzo-
β-quinindene, m. p. above 360°; cyclopentanone and aniline condensed to form small yields of a substance, $C_{17}H_{19}O_2N$, m. p. 272°.

The colour reactions of most of the above and other compounds in 65% sulphuric acid at 0° with one drop of concentrated aqueous potassium dichromate have been determined; those giving a crimson colour contain the N-acyltetrahydroquinoline structure, whilst those giving a blue colour contain the N-acyldihydroindole structure. Strychnine falls in the latter group and should therefore contain an N-acyldihydroindole skeleton, e.g., as in the latest formula of Fawcett, Perkin, and Robinson.

The nomenclature of the parent substances has been modified slightly in this paper : α - and β -quinindenes are now, respectively,





2-Ethylpyrrole. (FRL.) M. E. A. DE JONG (Rec. trav. chim., 1929, **48**, 1029—1030).—The various methods of preparation quoted in the literature are examined. Thermal decomposition of N-ethylpyrrole at 650° and careful fractionation of the product formed appears to be a suitable method of preparation. H. BURTON.

Formation of aminopyridine by the action of ammonia on pyridine in presence of catalysts. J. P. WIBAUT and L. M. F. VAN DE LANDE (Rec. trav. chim., 1929, 48, 1005—1009).—Small amounts of 2-aminopyridine are formed when a mixture of pyridine vapour and ammonia is passed over iron-and nickel-asbestos catalysts at 300—500°. In absence of catalyst at 550° or with baked clay at 600° traces of 2:2'-dipyridyl result. The reaction is endothermic : $C_5H_5N+NH_3 \longrightarrow NH_2 \cdot C_5H_4N+H_2$ —4·4 kg.-cal. The heat of reaction between benzene and ammonia is calculated to be -8.0 kg.-cal. (cf. Briner, Ferrero, and Luserna, A., 1924, i, 503).

H. BURTON.

Action of benzoyl peroxide on pyridine. J. OVERHOFF and G. TILMAN (Rec. trav. chim., 1929, 48, 993—996).—Interaction between pyridine and benzoyl peroxide at 100° occurs mainly, $(CO_2Ph)_2+$ $C_5H_5N \longrightarrow Ph \cdot CO_2H + CO_2 + Ph \cdot C_5H_4N$ (cf. Gelissen and Hermans, A., 1925, i, 379); 46% of a mixture of 2- and 4-phenylpyridines is isolated. Small amounts of benzene, 4-pyridyldiphenyl, m. p. 175°, and p-phenylbenzoic acid are also isolated.

H. BURTON.

Derivatives of quinoline [atophan]. R. WOLF-FENSTEIN.—See B., 1929, 835.

Pyrimidines. CVIII. Synthesis of nitrogensubstituted uracils of known constitution. T. B. JOHNSON (Rec. trav. chim., 1929, 48, 872—874).— Preliminary details of a method of synthesising 3(N)-alkyluracils are given. Treatment of benzylidenemethylamine with malonic acid in warm alcohol affords about equal amounts of cinnamic acid and α -methylamino- β -phenylpropionic acid, m. p. 168— 169°. The last-named acid is converted by potassium cyanate into the corresponding carbamide, which when treated with hydrochloric acid yields 4-phenyl-3-methyl-4: 5-dihydrouracil, m. p. 158—159.5°. Bromination of this affords the 5-bromo-derivative, which when treated with pyridine or dilute alkali loses hydrogen bromide, forming 4-phenyl-3-methyluracil. H. BURTON.

Indigotin group. VIII. Complex reaction products from indigotin and benzoyl chloride. T. POSNER, W. ZIMMERMANN, and S. KAUTZ (Ber., 1929, 62, [B], 2150—2166; cf. A., 1926, 1155, 1156). —Höchst-yellow U, $C_{22}H_{12}O_2N_2$, m. p. 284°, is prepared from Höchst-yellow R or Dessoulavi's compound (cf. Diss., Neufchâtel, 1909) by prolonged action of warm, concentrated sulphuric acid. It is oxidised by boiling nitric acid (d 1.4) through a compound, $C_{18}H_9O_4N_3$, m. p. above 360°, to a substance, $C_{14}H_6O_6N_2$, m. p. 284—285° after softening at 280— 281°, and phthalic and picric acids. It is therefore probably a derivative of anthraquinone. Successive treatment of the dye in aqueous pyridine with sodium hydroxide and hyposulphite followed by methyl sulphate gives a dimethyl derivative of the leucocompound, $C_{35}H_{18}O_2N_2$, m. p. 210°. Benzoylation cannot be effected in the aqueous vat, but if the latter is extracted with acetone and the extract treated with benzoyl chloride and pyridine a dihydroproduct, $C_{23}H_{14}O_2N_2$, m. p. 276—279° after softening, is obtained from which benzoic acid cannot be derived by the action of alkali. Use of acetic anhydride in place of benzoyl chloride leads to the compound $C_{25}H_{16}O_3N_2$, m. p. 270° after softening. Prolonged treatment of Höchst-yellow U with boiling alcoholic sodium ethoxide leads, with fission of the ring, to a monohydrate, $C_{23}H_{14}O_3N_2$, m. p. 283—284° after becoming yellow at 210—220°, characterised as its monomethyl derivative, $C_{24}H_{16}O_3N_2$, m. p. 166°; when heated, the hydrate regenerates the dye.

Höchst-yellow R, $C_{30}H_{18}O_4N_2$, m. p. 350°, is oxidised by boiling concentrated nitric acid to picric and benzoic acids: the formation of phthalic acid was not observed. Treatment of the leuco-product with benzoyl chloride gives a monobenzoyl compound, $C_{37}H_{24}O_5N_2$, m. p. 223°. Treatment with alcoholic sodium ethoxide affords a yellow acid, $C_{14}H_{11}O_3N$, m. p. 178°, of unknown constitution and benzoic acid; in another experiment, azobenzene, the above acid, benzoic acid, and a colourless, unrecognised acid, m. p. 225–227° (ammonium salt), were obtained. Treatment of indigotin with boiling benzoyl chloride in presence of zinc chloride affords Höchst-yellow R, whereas a mixture of R and U is obtained if benzoyl chloride is replaced by benzoic anhydride at 150– 160°.

Treatment of indigotin with benzoyl chloride and copper powder in xylene yields a small amount of Höchst-yellow R and a "xylene substance,"

Höchst-yellow R and a "xylene substance," $C_{37}H_{22}O_5N_2$, m. p. 243—244°, hydrolysed by sulphuric acid to benzoic acid and Höchst-yellow R, oxidised by nitric acid to picric and benzoic acids, and yielding with sodium ethoxide the same compounds as yellow R, including azobenzene. The "xylene substance" is obtained from Höchst-yellow R by the action of benzoyl chloride and copper powder in boiling xylene and similarly from diacetylindigotin. The Dessoulavi compound is derived from Höchst-yellow R by prolonged treatment with boiling acetic anhydride and acetyl chloride and from dibenzoylindigotin and benzoyl chloride. With methyl-alcoholic ammonia it gives a *derivative*, $C_{30}H_{20}O_2N_4$, m. p. 247°. Höchstyellow U with acetic anhydride and zinc dust affords the *dihydroleuco-monoacetate*, $C_{25}H_{18}O_3N_2$, softening at 230°. Ciba-yellow and sodium methoxide yield a *product*, $C_{23}H_{16}O_4N_2$, m. p. 273°. The relationships of the substances are indicated as follows :



The following compounds are incidentally described: benzoyl-2-indole-2'-thionaphthenindigotin, m. p. 281°: dibenzoyl-2-indole-2'-thionaphthenleucoindigotin, C₃₀H₁₈O₄NS, m. p. 234°; tribenzoyl-2-indole-2'-thionaphthenleucoindigotin, m. p. 222°, and the corresponding triacetyl compound, m. p. 210-215°. H. WREN.

Phthalazines. I. J. S. AGGARWAL, N. L. DAR-BARI, and J. N. RAY (J.C.S., 1929, 1941—1945).— Arylbenzoylhydrazones, CHAr:N·NHBz, are converted into phthalazines by dehydration with phosphoric oxide, phosphorus oxychloride, or (best) amylalcoholic hydrogen chloride. The reduction products (C:N \longrightarrow CH·NH) of the arylbenzoylhydrazones do not undergo intramolecular dehydration. The phthalazines are hydrolysable to o-aldehydoketones. The following substances are described: veratraldehydebenzoylhydrazone, m. p. 176°; 6:7-dimethoxy-1-phenylphthalazine, m. p. 193—194°; s-benzoyl-3:4-dimethoxybenzylhydrazone, m. p. 167° (by reduction of the above hydrazone by sodium amalgam in alcohol; anisaldehydebenzoylhydrazone, m. p. 147°; 7-methoxy-1-phenylphthalazine, m. p. 167° (picrate, m. p. 208°); s-benzoyl-4-methoxybenzylhydrazone, m. p. 170°; 6:7-methylenedioxy-1-phenylphthalazine, m. p. 200°; s-benzoyl-3:4-methylenedioxybenzylhydrazine, m. p. 130°; 1-phenylphthalazine, m. p. 174—175°, from benzaldehydebenzoylhydrazine (Curtius, A., 1891, 56); s-benzoylbenzylhydrazine, m. p. 115°; m-nitrobenzaldehydebenzoylhydrazone, m. p. 190°; 6(or 8)nitro-1-phenylphthalazine, m. p. 165°; o-methoxybenzaldehydebenzoylhydrazone, m. p. 179°; 5-methoxyl-phenylphthalazine, m. p. 135°; s-benzoyl-o-methoxybenzoylhydrazine, m. p. 80°.

Aqueous copper sulphate and alcoholic benzoylhydrazine give an almost quantitative precipitate of a copper salt. R. CHILD.

Synthesis of pyocyanine and certain homologues. F. WREDE and E. STRACK (Ber., 1929, 62, [B], 2051—2057).—Pyrogallol methyl ether is converted by treatment with lead dioxide in dry benzene followed by addition of o-phenylenediamine in glacial acetic acid and benzene into 1-methoxyphenazine, m. p. 169°, converted by fuming hydrobromic acid into 1-hydroxyphenazine, from which pyocyanine is derived by treatment with methyl sulphate at 100°; the constitution of the dye has not been completely established. Treatment of 1-hydroxyphenazine with ethyl sulphate at 140° affords 10 : 10'-diethylnorpyocyanine, m. p. 173°, which closely resembles pyocyanine, but is more stable to air in presence of alkali; the chloroplatinate, m. p. 225—228°, chloroaurate, m. p. 177°, perchlorate, m. p. 277° after softening at 265°, and picrate are described. 10:10'-Din-propylnorpyocyanine, C₃₀H₂₈O₂N₄, m. p. 168°, its chloroplatinate, m. p. 272°, and picrate, incipient decomp. 180°, have been prepared.

2:3-Dinitroanisole, m. p. 118°, prepared from m-nitroanisole and nitric acid (d 1·48) at 0°, is reduced by stannous chloride and hydrochloric acid to 2:3diaminoanisole hydrochloride, m. p. 250°. 3-Amino-2-methylaminoanisole hydrochloride, m. p. 250° (decomp.), could not be condensed to a phenazine derivative. 2:3-Diaminoanisole hydrochloride and 3:5diamino-o-benzoquinone afford 1:3-diamino-8(5)methoxyphenazine, isolated as the perchlorate, m. p. 171-173°. De-amination of the compound yields 1-methoxyphenazine. H. WREN.

Bases containing two isoquinoline rings. R. CHILD and F. L. PYMAN (J.C.S., 1929, 2010—2021).— A number of compounds containing two isoquinoline nuclei united through the 1 : 1'-positions by chains of methylene groups have been synthesised for comparison with emetine. The following amides were obtained by heating mixtures of the appropriate ethyl ester and amine: oxalo-, malono-, succino-, glutaro-, adipo-, pimelo-, subero-, azelao-, sebaco-, nonane-1: 9-dicarboxy-, and decane-1: 10-dicarboxydi-β-phenylethylamides with m. p. 186° (lit. 180°, 186°), 129—130°, 200°, 159—160°, 184°, 147—148°, 166, 151°, 159°, 151—152°, and 157°, respectively; oxalo-, succino-, glutaro-, adipo-, pimelo-, subero-, azelao-, sebaco-, nonane-1: 9-dicarboxy-, and decane-1: 10-dicarboxy-di-β-veratrylethylamides. with m. p. 173—174°, 174—175°, 131°, 169°, 143—144°, 161°, 148—149°, 156°, 152—153°, and 155—156°, respectively; adipodi β -piperonylethylamide had m. p. 208°. From ethyl succinate N- β -phenylethylsuccinimide, m. p. 133–134°, and N- β -veratrylethylsuccinimide, m. p. 129°, were also formed.

Ring closure was effected with adipo-, pimelo-, and sebaco-di- β -veratrylethylamides (failures attended attempts with the corresponding β -phenylethylamides) by boiling with phosphorus oxychloride in toluene solution. Thus were prepared, in order, α 8-bis-(6 : 7-dimethoxy-3 : 4-dihydroisoquinolyl-1)-butane, m. p. 172—173° [hydrochloride, m. p. 263—264° (decomp.); hydriodide, m. p. 260—261° (decomp.); hydrogen sulphate, m. p. 255—260° (decomp.); succinate, m. p. 202—203° (decomp.); dimethiodide, m. p. of monohydrate, 240—241° (decomp.)], reduction of which by tin and hydrochloric acid gave α 8-bis-(6 : 7-dimethoxytetrahydroisoquinolyl-1)-butane, m. p. 127° [hydrochloride, m. p. 268—270° (decomp.); lactate, m. p. 212—213° (decomp.)]. The above dimethiodide by digestion with silver chloride followed by reduction with tin and hydrochloric acid gave eventually α 8-bis-(6 : 7-dimethoxy-2-methyltetrahydroisoquinolyl-1)-butane, m. p. 108—109° (hydrochloride, m. p. 244—245°).

 $x_{\rm E}$ -Bis-(6:7-dimethoxy-3:4-dihydroisoquinolyl-1)pentane, m. p. 57—58° [hydrochloride, m. p. 235—236° (eff.); hydriodide, m. p. 220—222° (decomp.); hydrogen tartrate, m. p. 189—190° (eff.); dimethiodide, m. p. 236—237° (decomp.)]; $x_{\rm E}$ -bis-(6:7-dimethoxytetrahydroisoquinolyl-1)-pentane hydrochloride, m. p. 225—227°; x_0 -bis-(6:7-dimethoxy-3:4-dihydroisoquinolyl-1)-octane, m. p. 116° [hydrochloride monohydrate, m. p. 172° (eff.), anhydrous, m. p. 208—210° (decomp.); hydriodide, m. p. 208—209° (eff.); succinate, m. p. 187°]; and $x_{\rm E}$ -bis-(6:7-methylenedioxy-3:4-dihydroisoquinolyl-1)-butane, m. p. 210—211° [hydrochloride dihydrate, m. p. 270° (decomp.); hydriodide, m. p. 277—280° (decomp.); dimethiodide, m. p. 285—287° (decomp.)], were prepared analogously to the above butane derivatives. Qualitative tests showed that azelao-, subero-, nonane-1:9-dicarboxy-, and decane-1:10-dicarboxy-di-β-veratrylethylamides also underwent isoquinoline condensation under the action of phosphorus oxychloride.

Similar treatment of succinodi- β -veratrylethylamide resulted in extensive decomposition, whilst glutarodi- β -veratrylethylamide gave small yields of a base, $C_{25}H_{30}O_4N_2$, isolated as hydriodide, m. p. 239—240° (corresponding hydrochloride, m. p. 199—200°), along with traces of a second hydriodide, $C_{25}H_{32}O_5N_2$,HI, m. p. 203—204°. (All m. p. given above are corr.)

Of the seven compounds examined for amœbicidal properties none prevented the growth of Entamæba histolytica in cultures at a dilution of 1 in 5000, whilst emetine was effective in a dilution of 1 in 500,000. Similarly, they had neither antimalarial nor trypanocidal activities. Methyl and ethyl β -3 : 4-dimethoxyphenylpropionates, m. p. 38—39°, b. p. 194°/30 mm., 174—175°/12 mm., and m. p. 13°, b. p. 193°/20 mm., d_{155}^{155} 1·1123, respectively, are described incidentally in an improved preparation of β -veratrylethylamine. R. J. W. LE FEVRE.

Diphthalimidonaphthalenes and benzoylenenaphthiminazoles. G. B. CRIPPA and P. GALIM-BERTI (Gazzetta, 1929, 59, 510-519).—The reaction

which takes place when 1:2-naphthylenediamine is heated with phthalic anhydride has been reinvestigated. From the product obtained at 170° , 1:2-diphthalimidonaphthalene, m. p. 280° , is extracted by chloroform. The residue contains 1:2(1':2')-benzoylene- β -naphthiminazole (I), m. p. 299-300°, accompanied by 1': 2'-naphthiminazole-2-benzoic acid. At $270-280^{\circ}$ the chief product is 1:2(1':2')-benzoylene- α -naphthiminazole (II), m. p. 208° (cf. Bistrzycki and



Risi, A., 1926, 67). 1:2-Diphthalimidonaphthalene is converted by boiling potassium hydroxide solution into 1:2-naphthylenediphthalamic acid,

 $C_{10}H_6[NH \cdot CO \cdot C_6H_4 \cdot CO_2H]_2$, which is dehydrated to the phthalimido-compound when heated. The constitutions of the isomerides I and II have been confirmed by synthesis. I-Nitro-B-naphthylamine yields 1-nitro-2-phthalimidonaphthalene, m. p. 203°, which is reduced by iron and acetic acid to a mixture of 1-amino-2-phthalimidonaphthalene (not isolated, but yielding I when boiled in acetic acid) and I. Similarly, 2-nitro-1-phthalimidonaphthalene, m. p. 211°, is converted into II. The following compounds are also described: 1:4-diphthalimidonaphthalene, m. p. above 320° (from 1 : 4-naphthylenediamine and phthalic anhydride); 1:4-naphthylenediphthalamic acid; 1-nitro-4-phthalimidonaphthalene, m. p. 223°; 1-nitronaphthalene-4-phthalamic acid; 1-amino-4phthalimidonaphthalene (yielding 1:4-diphthalimidonaphthalene with phthalic anhydride); 1:5-diphthalimidonaphthalene, m. p. 253°; 1:5-naphthylenediphthalamic acid. R. K. CALLOW.

α- and β-Isatol. G. HELLEB and A. SILLER (J. pr. Chem., 1929, [ii], **123**, 257–261).—Acetylation of α-isatol with acetic anhydride and sulphuric acid gives an acetyl derivative (I), $C_{26}H_{17}O_7N_3$, m. p. 245–246° (decomp.) after sintering and darkening above 235°, thus demonstrating the termolecular nature of the parent substance (cf. Hantzsch, A., 1925, i, 700). Oxidation of α-isatol with chromic oxide and acetic acid affords a 85.4% yield of anhydroisatin-o-aminobenzanilide (II), formed also in small amount by similar oxidation of I. When β-isatol is heated with acetic acid (cf. A., 1925, i, 1166) there is obtained isatoid (III), $C_{16}H_{10}O_{12}$, m. p. 210–211° (cf. Hantzsch, *loc. cti.*), whilst chromic acid oxidation gives a 50% yield of II. When an alkaline solution of III is kept, II is formed (cf. A., 1920, i, 765). H. BURTON.

Di-2-($\alpha\beta$ -naphth-1:2:3-triazolyl)stilbene. G. CHARRIER (Gazzetta, 1929, 59, 479–489).—Bromination of 2-*p*-tolyl- $\alpha\beta$ -naphth-1:2:3-triazole in hot nitrobenzene yields the ω -dibromo-compound, m. p. 230–231°. Treatment of the latter under various conditions gives none of the expected anthracene derivative. When heated with copper powder in nitrobenzene it yields 4':4''-di-(2-naphthtriazolyl)-



slilbene (I) (decomp. without melting). The latter is oxidised by chromic acid in acetic acid and acetic anhydride to 2 - phenylnaphthtriazoleo-quinone-p'-carboxylic -2 acid (decomp. without

melting), which yields with phenylhydrazine the a-hydroxy-\beta-benzeneazo-derivative, m. p. 283-284°. Controlled oxidation of I with the same reagent yields a bis-o-quinone (decomp. without melting) (a-hydroxyβ-benzeneazo-derivative), the double linking being unattacked. A series of similar limited oxidations has been carried out with other compounds. Thus 2-o-tolylnaphthtriazole, m. p. 96–97°, yields 2-o-tolylnaphthtriazole-o-quinone, m. p. 213° (α -hydroxy- β -benzeneazo-derivative, m. p. 137–148°; phenazine derivative, m. p. 209–210°), or, with excess of chromic acid, the p'-carboxylic acid. Similarly, the m-tolyl compound, m. p. 123-124°, gives the o-quin. one, m. p. 210° (α-hydroxy-β-benzeneazo-derivative, m. p. 190°; phenazine derivative, m. p. 251-252°), or, by oxidation with hydrogen peroxide, 2-m-tolyl-4-o-carboxyphenyl-1:2:3-triazole-5-carboxylic acid (II: R=m-Me), m. p. 240°. The p-tolyl compound,

$$\mathbf{R} \cdot \mathbf{C}_{6} \mathbf{H}_{4} \cdot \mathbf{N} < \mathbf{N} - \mathbf{C} \cdot \mathbf{C}_{6} \mathbf{H}_{4} \cdot \mathbf{CO}_{2} \mathbf{H}(o) \\ \mathbf{N} - \mathbf{C} \cdot \mathbf{CO}_{2} \mathbf{H}$$
(II.)

m. p. 148-149°, yields the o-quinone. m. p. 216-217° (α-hydroxy-β-benzeneazo-derivative, m. p. 184-185°; phenazine derivative, m. p. 258°), which with alkaline permanganate or hydrogen peroxide in acetic acid yields 2-p-carboxyphenyl-4-o-carboxyphenyl-1:2:3triazole-5-carboxylic acid (II; $R = p - CO_2H$), m. p. 288°. The last acid is also obtained directly from 2-p-tolylnaphthtriazole and from the ω -dibromocompound. 2-p-BromophenyInaphthtriazole, m. p. 202°, yields the o-quinone, m. p. 195–196° (α -hydroxy-β-benzeneazo-derivative, m. p. 235°; phenazine deriv-ative, m. p. 306°). ω -Dibromo-2-p-tolylnaphthtriazole yields the o-quinone (decomp. without melting) (α-hydroxy-β-benzeneazo-derivative, m. p. 196°; phen-azine derivative, m. p. 282°). R. K. CALLOW. azine derivative, m. p. 282°).

Dimethyldipropylalloxantin and its reduction potential. E. BIILMANN and T. TER BRAAK (Rec. trav. chim., 1929, 48, 919-921).-Treatment of theobromine with aqueous potassium hydroxide and propyl iodide or of the silver theobromine with this iodide gives propyltheobromine, m. p. 137°. Oxidation of the latter with potassium chlorate and hydrochloric acid at 50° and subsequent reduction of the alloxan produced with hydrogen sulphide affords dimethyldipropylalloxantin. Determination of the reduction potential of this by the method previously described (A., 1923, ii, 605) gives values of 0.3643 and 0.3616 volt at 18° and 25°, respectively. The value for tetramethylalloxantin is modified to 0.3660 volt at 18° (cf. loc. cit.). H. BURTON.

Synthesis of mesoporphyrins. H. FISCHER and A. KIRRMANN (Compt. rend., 1929, 189, 467-469).-Three more of the isomeric mesoporphyrins, I, IV. and XIV (cf. Ber., 1927, 60, 2645) have been synthesised by fusion of the appropriate pair of bromodipyrrylmethenes with succinic acid, and the following derivatives prepared : mesoporphyrin I [methyl, m. p. 170°

(191° on remelting), and ethyl, m. p. 167°, esters; copper, m. p. 217°, iron, m. p. about 265°, salts]; mesoporphyrin IV (methyl ester, m. p. 238°; copper, m. p. 267°, and iron, m. p. 270°, salts); mesoporphyrin XIV (methyl ester, m. p. 210°; copper, m. p. 215°, and iron, m. p. 261°, salts). They are also differentiated from natural mesoporphyrin (IX) by the solubilities of their sodium salts, that of natural mesoporphyrin being precipitated when the concentration of sodium hydroxide exceeds 0.1N, whilst the new isomerides remain soluble in 2% sodium hydroxide, the sodium salts crystallising slowly from a 3% solution.

J. W. BAKER. Dioximes. LIV. G. PONZIO and M. TORRES (Gazzetta, 1929, 59, 461-478).—The "isooxazole transformation" (cf. Angeli, A., 1893, i, 261; Wieland and Semper, A., 1908, i, 108), which takes place when actually certain "arylmethylglyoxime peroxides' arylmethylfuroxans (I); cf. Ponzio, A., 1928, 888] are heated with alcoholic potassium hydroxide, is now shown to yield 4-imino-5-hydroxy-3-aryl-4:5-dihydroisooxazoles (II), not the 4-oximino-compounds, and the following mechanism is suggested :

$\frac{\text{MeC} - \text{CAr}}{\text{O'N} \text{O'N}} \xrightarrow{+ \Pi \text{ O}}$	$\mathbf{OH}\textbf{\cdot}\mathbf{CH}_{2}\textbf{\cdot}\mathbf{C}(\textbf{:}\mathbf{NH})\textbf{\cdot}\mathbf{CAr}\textbf{:}\mathbf{NO}_{2}\mathbf{H}$
(I.) (I.)	-H,O NH:C CAr (II.)

4-Imino-5-hydroxy-3-p-anisyl-4: 5-dihydroisooxazole (III), m. p. 182° (decomp.) (cf. Wieland and Semper, loc. cit.), is conveniently prepared by the addition of p-anisylmethylfuroxan to a hot alcoholic solution of sodium ethoxide, and separates on acidification. The action of phenylhydrazine in acetic acid yields a substance, $C_{23}H_{18}ON_4$, m. p. 129°. The hydroxyl group in III reacts with the formation of a benzoyl derivative, m. p. 147°, a methyl ether, m. p. 108°, and a phenylurethane, m. p. 166° (decomp.). Ethyl nitrite yields the 4-nitrosimino-derivative, m. p. 83-84° (decomp.) [silver and sodium (+2H20) salts]. By boiling with an aqueous solution of hydrazine, III is isomerised to 4-amino-5-hydroxy-3-p-anisylisooxazole, m. p. 122-123° (decomp.) (IV), which is reconverted into the imino-compound by sodium hydroxide solution. It yields p-methoxybenzonitrile with hot dilute sulphuric acid, and is converted by phenylcarbimide into the phenylurethane of the imino-compound. The anisylidene derivative has m. p. 159-160° (decomp.). 4-Amino-5-chloro-3-p-anisylisooxazole, m. p. 81-82° [hydro-chloride, m. p. 159-160° (decomp.)], is obtained from III or IV and concentrated hydrochloric acid, or, best, by treatment of IV with hydrogen chloride in ether. The following derivatives are described : benzylidene, m. p. 128-129°; anisylidene, m. p. 68°; acetyl, m. p. 155-156°; benzoyl, m. p. 165-166°. Reduction of III with zinc dust in sodium hydroxide solution yields 4-amino-3-p-anisyl-4: 5-dihydroisooxazole, m. p. 80° [hydrochloride, m. p. 198° (decomp.); derivatives : acetyl, m. p. 133-134°: benzoyl, m. p. 148°; anisylidene, m. p. 109-110°].

The following analogous compounds are also described : 4-imino-5-hydroxy-3-phenyl-4:5-dihydroisooxazole, m. p. 179—180° (decomp.) [methyl ether, m. p. 90° (decomp.); acetyl derivative, m. p. 104°

(decomp.); benzoyl derivative, m. p. 152° (decomp.); phenylurethane, m. p. 153-154° (decomp); substance, m. p. 119°, formed by the action of phenylhydrazine]; 4-amino - 5 - hydroxy - 3 - phenylisooxazole, m. p. 105° (decomp.); 5-chloro-4-amino-3-phenylisooxazole, m. p. 73° [hydrochloride, m p 142° (decomp); derivatives : benzylidene, m. p. 62-63°; acetyl, m. p. 127-128°; benzoyl, m. p. 172°]; 4-imino-5-hydroxy-3-p-bromophenyl-4: 5-dihydroisooxazole, m. p. 184-185° (decomp.); 4-amino-5-hydroxy-3-p-bromophenylisooxazole, m. p. 112-113° (decomp.); 5-chloro-4-amino-3-p-bromophenylisooxazole, m. p. 98-99°; 4-imino-5-hydroxy-3-p-methoxybromophenyl-4:5-dihydroisooxazole, m. p. 198° (decomp.); 4-amino-5-hydroxy-3-p-methoxybromophenylisooxazole, m. p. 143° (decomp.); 5-chloro-4-amino-3-p-methoxybromophenylisooxazole, m. p. 128° (decomp.).

Phenylethylglyoxime, m. p. 215-216° (decomp.), is converted by the action of sodium hypochlorite into an oily peroxide which does not react with sodium ethoxide, and is, therefore, probably a true peroxide (cf. A., 1928, 888), although the furoxan structure in which the reactive methyl group is not in the nucleus is not excluded. R. K. CALLOW.

Ketophenmorpholine synthesis from 5-aminoeugenol. E. PUXEDDU and G. SANNA (Gazzetta, 1929, 59, 519-524).-5-Aminoeugenol reacts with chloroacetyl chloride to give 5-chloroacetamidoeugenol. m. p. 89° (dibromide, m. p. 125°); this is converted by heating with alcoholic potassium hydroxide into 8-methoxy-3-keto-6-allyl-2: 3-dihydro-1: 4-benzoxazine, m. p. 194°, which yields two substances, m. p. 125° and 175°, when treated with bromine.

R. K. CALLOW.

Formation of heterocyclic compounds from ethyl carbethoxythiocarbamate. P. C. GUHA and S. R. A. SALETORE (J. Indian Chem. Soc., 1929, 6, 565-575).-Ethyl carbethoxythiocarbamate (I), m. p. 46° (cf. Delitsch, A., 1875, 358) (methyl derivative, m. p. 32-33°, obtained from methyl iodide and the potassium derivative of I; benzyl derivative, m. p. 45-46°), reacts with ethylenediamine, forming the compound C₂H₄-NH C·OEt (II), m. p. 218°, and small amounts of the substances

 $\begin{array}{l} [\mathrm{CO}_2\mathrm{Et}\text{-}\mathrm{N}\text{:}\mathrm{C}(\mathrm{OEt})\text{\cdot}\mathrm{NH}\text{\cdot}\mathrm{CH}_2\text{\cdot}]_2 \text{ and } \\ \mathrm{CO}_2\mathrm{Et}\text{-}\mathrm{N}\text{:}\mathrm{C}(\mathrm{OEt})\text{\cdot}\mathrm{NH}\text{\cdot}\mathrm{CH}_2\text{\cdot}\mathrm{CH}_2\text{\cdot}\mathrm{NH}\text{\cdot}\mathrm{C}(\mathrm{SH})\text{:}\mathrm{N}\text{\cdot}\mathrm{CO}_2\mathrm{Et}, \\ \mathrm{m.} \ \mathrm{p.} \ 101\text{---}102^\circ \text{ and } 123^\circ, \ \mathrm{respectively}. \end{array}$ o-phenylenediamine the compound (II, C2H4 replaced by C₆H₄), m. p. about 330°, results. Hydrazine hydrate and I afford 5-ethoxy-3-keto-2: 3-dihydro-1:2:4-triazole, m. p. 170-172° (2-phenyl derivative, m. p. 150-151°, obtained similarly from phenyl-hydrazine), hydrolysed by hydrochloric acid to urazole. 4-Phenyl- and 4-p-tolyl-thiosemicarbazides $\dot{\mathbf{N}} \mathbf{R} \cdot \mathbf{N} \mathbf{H}$ $\mathbf{C} \cdot \mathbf{O} \mathbf{E} \mathbf{t}$ (R= furnish compounds the

NHPh·CS· and NH·C₆H.Me·CS·, respectively), m. p. 246-248° and 186-187°, respectively. 2-Di-p-tolylguanidino - 5 - ethoxy - 3 - keto-2 : 3-dihydro-1 : 2 : 4-triazole, m. p. 229-230°, is formed from I and aminodi-p-tolylguanidine and is hydrolysed by hydrochloric acid to a substance, m. p. 256-257° (decomp.). Carbamide and thiocarbamide yield 4:6-diketo-, 4 8

m. p. 171-173°, and 2-ethoxy-6-keto-4-thicketo-3:4:5:6-tetrahydro-1:3:5-triazine, m. p. 150° after shrinking at 110°, respectively. Aniline, o- and ptoluidines, α - and β -naphthylamines, and benzidine react with I, giving s-diphenyl-, s-di-o- and di-ptolyl-, s-di-a- and di-B-naphthyl-carbamides, and carbonylbenzidine, respectively. H. BURTON.

Benzidine rearrangement in heterocyclic series. III. B. C. DAS-GUPTA and P. K. BOSE (J. Indian Chem. Soc., 1929, 6, 495-504).—Phenacyl bromide and 1-m-nitrophenylthiosemicarbazide, m. p. 187° (from *m*-nitroaniline, potassium thiocyanate, and alcoholic hydrogen chloride), react in alcohol, forming 2 - m - nitrophenylhydrazino - 4 - phenylthiazole, m. p. 192-193° (acetyl derivative, m. p. 186°), which when boiled with dilute hydrochloric acid undergoes a benzidine rearrangement (cf. A., 1928, 188; this vol., 79) into 2.amino-4-phenyl-5-o-nitro-p-aminophenylthiazole, m. p. 253° (picrate, m. p. 213°; dihydrochloride, decomp. 230°; diacetyl derivativo, decomp. above 295°). Similarly, 2-m-nitrophenylhydrazino-4-p-tolylthiazole, m. p. 189° (acetyl derivative, m. p. 178°), yields 2-amino-4-p-tolyl-5-o-nitrop-aminophenylthiazole, m. p. 163° (decomp.) [di-acetyl derivative, m. p. 253° (decomp.)], and 2-mnitrophenylhydrazino-4-methylthiazole, m. p. 138° (decomp.) (acetyl derivative, m. p. 155°), affords 2-amino-5-o-nitro-p-aminophenyl-4-methylthiazole, decomp. 110° (diacetyl derivative, decomp. 180°). Similar rearrangements are undergone by 2-a-naphthylhydrazino-4-phenyl-, m. p. 174° (acetyl derivative, m. p. 160-161°), 2-α-naphthylhydrazino-4-p-tolyl-, m. p. 180° (acetyl derivative, m. p. 161°), and 2-α-naphthylhydrazino-4-methyl-thiazoles, m. p. 188° (decomp.; acetyl derivative, m. p. 149-150°), giving 2-amino-4-phenyl-5-4'-amino-a-naphthyl-, m. p. 236° (decomp.) [picrate, m. p. 193°; dihydrochloride, m. p. 245° (decomp.); diacetyl derivative, m. p. 248°], 2-amino-4-p-tolyl-5-4'-amino-a-naphthyl-, m. p. 280° (diacetyl derivative, m. p. 208°), and 2-amino-5-4'-amino- α -naphthyl-4-methyl-thiazoles, decomp. 110° (diacetyl

derivative, decomp. 260°), respectively. Phenacyl bromide and 1-o-nitrophenylthiosemicarbazide, m. p. 201°, react in alcohol, forming the compound (I) $CR \cdot N \gg C \cdot NH \cdot N \cdot C_6 H_4 \cdot NO \cdot OH$ (o) (R=Ph), decomp. 190° (acetyl derivative, m. p. 175°), soluble in alkali hydroxide solution, giving a deep violet coloration. Formation of I occurs presumably by rearrangement of the intermediate 2-o-nitrophenylhydrazino-4-phenylthiazole. The substance (I, R= p-Me·C₆H₄·), m. p. 185° (decomp.) (acetyl derivative, m. p. 206°), and the compound (I, R=Me), decomp. 165° (acetyl derivative, m. p. 167°), are prepared similarly from w-bromo-p-methylacetophenone and chloroacetone, respectively. The analogous com-pounds [I, :NO·OH (o)=:NO·OH (p); R=Ph, p-Me C_6H_4 , and Me, respectively] from 1-p-nitro-phenylthiosemicarbazide, m. p. 203°, and ω -bromoacetophenone, w-bromo-p-methylacetophenone, and chloroacetone have m. p. 189° (decomp.) (acetyl derivative, m. p. 185°), 178° (acetyl derivative, m. p. 182°), and decomp. 145° (acetyl derivative, m. p. 178°), H. BURTON. respectively.

The lupin alkaloids. II. G. R. CLEMO and R. RAPER (J.C.S., 1929, 1927—1940; cf. A., 1928, 1030; Schöpf and others, *ibid.*, 1144; Karrer and others, this vol., 200).—Lupinus luteus is a better source than L. pilosus of l-lupinine, $C_{10}H_{19}ON$, m. p. 70— 71°. Lupinine methiodide, m. p. 305—306°, on fusion in a vacuum with potassium hydroxide and treatment of the resulting base (b. p. 108—110°/10 mm.) with methyl iodide yields α -methyl-lupinine methiodide, m. p. 224—225°. The usual Hofmann inethod leads to a mixture of bases yielding a mixture of methiodides, m. p. 190—205°; treatment of the mixture of methyl-lupinines so obtained with phosphorus pentachloride gives a mixture of chloromethyllupinines (b. p. 90—92°/1 mm.), the mixed methiodides of which are separated into α -chloromethyllupinine methiodide, $C_{11}H_{20}NCI,MeI$, m. p. 215—216°, and β -chloromethyl-lupinine methiodide, m. p. 182°; these both yield bases, $C_{12}H_{22}NCI$, b. p. 100°/1 mm., when subjected to Hofmann degradation. These do not yield crystalline picrates or methiodides; it is therefore uncertain whether one or more chlorodimethyl-lupinines are present in these products.

methyl-lupinines are present in these products. Chlorolupinine methiodide, $C_{10}H_{18}N$,MeI, m. p. 204°, by treatment with silver oxide followed by vacuum distillation yields ψ -anhydrolupinine, $C_{10}H_{17}N$, b. p. $63^{\circ}/0.5$ mm., $[\alpha]_{\rm D} -35\cdot3^{\circ}$ in acetone [picrate, m. p. 154° ; chloroplatinate, m. p. 210° (decomp.)]. This base gives two stereoisomeric methiodides, α -, m. p. 172° , and β -, m. p. 263°; treatment of the former with silver chloride and distillation of the resulting methochloride regenerates ψ -anhydrolupinine, whilst treatment with silver oxide by the Hofmann method leads to a base, b. p. $60^{\circ}/1$ mm., yielding with methyl iodide ψ -anhydromethyl-lupinine methiodide,

 $C_{11}H_{19}N,MeI, m. p. 186-187^{\circ}$. The same product is similarly obtainable from the mixture of α - and β - ψ -anhydrolupinine methiodides.

 ψ -Anhydrodihydrolupinine, C₁₀H₁₉N, b. p. 58—59°, [α]₀ +21.7° in acetone (*picrate*, m. p. 176—177°; α -methiodide, m. p. 310—312°; a second methiodide could not be isolated pure), is obtained by reduction of ψ -anhydrolupinine with hydrogen and palladium.

Treatment of chlorolupinine methiodide with silver oxide at 100° and subsequent degradation furnishes anhydromethyl-lupinine, $\dot{C}_{11}H_{19}N$, b. p. 63°/1 mm., which is not quite homogeneous, although one anhydromethyl-lupinine (α) preponderates (*picrate*, m. p. 162—163°; *chloroplatinate*, decomp. 210°; methiodide, m. p. 191-192°); the base undergoes a complex change when heated with 15% hydrochloric acid, among the products being an isomeric base (methiodide, C11H19N,MeI, m. p. 219°). Anhydromethyl-lupinine methiodide on Hofmann degradation gives a high-boiling (? polymeric) base. Anhydromethyl-lupinine is reduced with hydrogen and palladium to a mixture of anhydrodihydromethyl-lupinines, C₁₁H₂₁N, b. p. 60°/1 mm.; this mixture gives mainly a-, m. p. 195-196°, and β-, m. p. 145-146°, -methiodides, and also traces of γ -methiodide, m. p. 199–200°, presumably derived from β -anhydromethyllupinine in the starting material; a-anhydrodihydromethyl-lupinine picrate has m. p. 145-146°, 3-picrate, m. p. 132°. Anhydrolupinine, under reduction conditions similar to the above, yields a mixture of lupinanes, $C_{10}H_{21}N$, *i.e.*, absorbs four atoms of hydrogen. The foregoing results on the degradation of chlorolupinine methiodide are discussed in the light of Karrer's formula for lupinine (this vol., 201), ψ -anhydrolupinine on this basis appearing to contain C:C·C·O

an eight-membered ring fused to piperidine, O CCC·C·N·C

N-Piperidyl-lupinine, $C_{15}H_{28}N_2$, strongly alkaline, b. p. 128—130°/1 mm. (from chlorolupinine and piperidine in the presence of sodium acetate and copper powder), differs from sparteine and deoxylupanine in forming a *dimethiodide*, m. p. 324° (decomp.), and in not containing an easily oxidisable •CH₂• group.

When distilled with potassium hydroxide in a vacuum, sparteine methiodide (α - or α' -) yields a *methylsparteine*, C₁₆H₂₈N, b. p. 135—136°/1 mm., not identical with the known isomerides (Moureu and Valeur, A., 1908, i, 44; Schöpf, *loc. cit.*) [*methiodide*, m. p. 247° (decomp.)]. Oxysparteine (cf. Schöpf, *loc. cit.*) has b. p.

Oxysparteine (cf. Schöpf, loc. cit.) has b. p. 204°/9 mm., m. p. 86—87°, $[\alpha]_{\rm D}$ —10·4° in alcohol [picrate, m. p. 185° (Schöpf, 183°); methiodide, m. p. 231° (Ahrens, A., 1893, i, 232, 191—193°), methiosulphate, m. p. 179°]. Hofmann degradation of oxysparteine methiodide leads to α-methyloxysparteine, C₁₆H₂₆ON₂, m. p. 85—87° (picrate, m. p. 248°; methosulphate, m. p. 268°); treatment of oxysparteine methosulphate with sodium amalgam gives the same base. Fusion of oxysparteine methiodide with potassium hydroxide produces β-methyloxysparteine, b. p. 210—215°/1 mm., m. p. 86°, $[\alpha]_{\rm D}$ +55·8° (picrate, m. p. 237°; methiodide, C₁₆H₂₆ON₂, MeI,2H₂O, m. p. 247°); fusion of the α-base with potassium hydroxide gives the β-isomeride.

Hofmann degradation of β -methyloxysparteine methiodide leads partly to the original material and partly to a dimethyloxysparteine, $C_{17}H_{28}ON_2$ (methiodide, m. p. 194°); the latter methiodide is almost entirely converted by the Hofmann method into the original base, and does not lose trimethylamine.

The action of cyanogen bromide on α -methyloxysparteine gives an additive *product*,

 $\hat{C}_{16}H_{26}ON_2$, 2CNBr, decomp. 244°, and a compound, $C_{16}H_{23}ON_3$, m. p. 202°, in which a methyl group is replaced by cyanogen.

The new results on sparteine are discussed in the light of Karrer's suggested formulæ. R. CHILD.

Identification of atropine with Wagner's reagent. C. C. FULTON (J. Assoc. Off. Agric. Chem., 1929, 12, 312-317).-In the identification of atropine by means of iodine and potassium iodide, four types of crystal can be distinguished at very high magnification, viz., I, reddish-brown rods, II, yellow plates, III, bicoloured yellow and red crystals, and IV, orange-red hexagonal elongated plates. All types are very small, but increase in size in the order given and also change from one to the other in this order as the proportion of atropine or of potassium iodide is increased, but all require an excess of iodine to atropine. If iodine is not in excess, red and yellow prisms are formed as described by Putt (A., 1913, ii, 259). For the formation of the various types of crystal a reagent containing 1 g. of potassium iodide in 100 c.c. of water and the following amounts of potassium iodide is recommended: I, 2.75 g.; II, 8 g.; III, 35 g.; and IV, 50 g. The reagent containing the lowest concentration of potassium iodide is the most sensitive and it will definitely identify atropine at a concentration of 1:200,000.

H. J. DOWDEN.

Microchemical reactions of sparteine. M. WAGENAAR (Pharm. Weekblad, 1929, 66, 809-812). —The most sensitive reactions are those with cadmium and zinc iodides, and gold chloride, which will detect 0.5-1 mg. at a dilution of 1 in 1000.

S. I. LEVY. Identity of pectinin with carnegin. E. SPĀTH and F. KUFFNER (Ber., 1929, 62, [B], 2242—2243).— Comparison of the hydrochlorides, pierates, and trinitro-m-tolyloxides of carnegin and pectinin from *Cereus pecten abbriginum*, Engelm., establishes the identity of the alkaloids. Pectinin is therefore 6:7-dimethoxy-1:2-dimethyl-1:2:3:4-tetrahydro *iso*quinoline. It is optically inactive. The replacement of the name pectinin by carnegin is advocated. U Wary

H. WREN.

Angostura alkaloids. IV. 4-Methoxy-2-namylquinoline, a basic component of angostura bark. E. SPATH and J. PIKL (Ber., 1929, 62, [B], 2244-2251).-The total bases of the angostura bark are separated into phenolic and non-phenolic compounds and the latter into stronger and weaker bases. The bulk of the casparin and galipin is separated (as hydrochlorides) from the more strongly basic fraction and the residual bases are distilled with steam. The distillate yields 4-methoxy-2-n-amylquinoline, b. 110-115°/0.001 mm. [chloroplatinate, m. p. 220° (decomp.); picrate, m. p. 132° after softening]. Treatment of the base with methyl iodide followed by distillation in a vacuum yields the methoxyl-free substance, $C_{15}H_{19}ON$, m. p. 101°. Hydrolysis of the base with fuming hydrochloric acid at 185–190° affords 4-hydroxy-2-n-amylquinoline, m. p. 144°, converted by diazomethane into the natural alkaloid. Oxidation of the compound, m. p. 101°, gives hexoic acid. The phenolic base is transformed by phosphorus pentachloride and phosphoryl chloride into 4-chloro-2-n-amylquinoline, converted by hydrogen in presence of palladised charcoal into 2-n-amylquinoline, b. p. 150-155°/11 mm. (chloroplatinate; picrate, m. p. 124-126°). 2-n-Amylquinoline is prepared synthetically by condensation of 2-methylquinoline with *n*-butaldchyde to the unsaturated base, $\hat{C}_{14}H_{15}N$, b. p. 167—168°/13 mm. (*picrate*, m. p. 140.5—141.5°), and hydrogenation of the latter compound in presence of palladised charcoal. 4-Hydroxy-2-n-amylquinoline is synthesised by condensation of *ethyl hexoylacetate*, b. p. 118—121°/13 mm., with aniline and heating of the product, NPh:C(C_5H_{11})·CH₂·CO₂Et, at 250— 255°, and is methylated to the alkaloid. Oxidation of the synthetic phenolic base with potassium permanganate affords N-hexoylanthranilic acid, m. p. 93.5°, identical with the product derived from n-hexoyl chloride and anthranilic acid in ether.

H. WREN.

Chloroiodoquinine. F. X. ERBEN (Ber., 1929, 62, [B], 2393-2394).—The action of iodine chloride on quinine salts in dilute aqueous solution affords

chloroiodoquinine, $C_{20}H_{24}O_2N_2CII$, m. p. about 155° after darkening at about 100°, in which addition appears to have occurred by saturation of the double linking in the vinyl group. Hydroquinine hydrochloride, when treated with chlorine in aqueous solution in the presence of iodine, gives *iodohydroquinine*, $C_{20}H_{25}O_2N_2I$. H. WREN.

Constitution of oxyacanthine. E. SPATH and J. PIKL (Ber., 1929, 62, [B], 2251-2260; cf. Spath and Kolbe, A., 1926, 82; Gadamer and von Bruchhausen, ibid., 627) .- The formation of a simple dicarboxylic acid during the cautious oxidation of oxyacanthine could not be established. Fusion of the alkaloid with alkali hydroxide gives p-hydroxybenzoic acid, which cannot be present originally as the p-hydroxy- or p-methoxy-benzyl residue, since anisic acid is not obtained by the oxidation of oxyacanthine or its methyl ether. Oxyacanthine is conveniently converted by diazomethane into its methyl ether, from which the dimethiodide (loc. cit.) is prepared. The salt is transformed into the corresponding ammonium base, which, when boiled with potassium hydroxide, gives an optically inactive base, C40H46O2N2, m. p. 152-153° after slight softening. Oxidation of the base with potassium permanganate affords 2-methoxydiphenyl ether 3: 4'-dicarboxylic acid, m. p. 313-314° (vac.) (methyl ester, m. p. 97-98°, also synthesised from methyl p-bromobenzoate and the potassium derivative of methyl isovanillate).

The ready degradation by the methods of Hofmann and Emde establishes the presence of two tetrahydroisoquinoline nuclei in oxyacanthine. These processes and determination of methylimino-groups prove both nitrogen atoms to be monocyclically combined and to be united with a methyl group. Further, oxyacanthine must be so constituted that the first stage of the Hofmann degradation causes the production of a base without an asymmetric carbon atom. The benzene nuclei of the two isoquinoline residues carry the four residual oxygen atoms of the alkaloid. In oxyacanthine methyl ether, three of the four oxygen atoms of the isoquinoline complexes are present as methoxyl, whilst for the fourth an ether-like union between the two benzene nuclei remains. The following constitutions are therefore deduced for oxyacanthine (R=H) and its methyl ether (R=Me).



The position of the hydroxyl group in oxyacanthine is elucidated as follows. The alkaloid is transformed into its *ethyl ether* and thence into the corresponding *dimethiodide*, $C_{41}H_{50}O_6N_2I_2$. The salt, after successive treatment with silver oxide and potassium hydroxide, gives the base, $C_{41}H_{48}O_6N_2$, m. p. 131— 132°, oxidised to 2-ethoxydiphenyl ether 3 : 4'-dicarboxylic acid, m. p. 288·5—289·5° (methyl ester).

The following compounds have been prepared for

purposes of comparison: methyl isovanillate, m. p. 66-67°; 2-methoxydiphenyl methyl ether 4:4'-dicarboxylate, m. p. 71-72° (corresponding acid, m. p. 256-257°); 2:2'-dimethoxydiphenyl methyl ether 3:3'-dicarboxylate, m. p. 135-136° [corresponding acid, m. p. 294-296° (vac.)]; 3-bromoanisic acid, m. p. 214°. H. WREN.

Potentiometric determination of morphine with an iodomercuric reagent. L. MARICQ (Bull. Soc. chim. Belg., 1929, 38, 265—275).—Morphine may be determined satisfactorily as follows. To 10 c.c. of a 0.1% solution of the alkaloid are added 10 c.c. of a reagent prepared by adding a slight excess of mercuric iodide to 4.150 g. of potassium iodide in 100 c.c. of water, and about 0.5 g. of mercuric iodide. The mixture is shaken, heated on a water-bath for 30 min., cooled, diluted to 50 c.c., and filtered. The filtrate is titrated electrometrically after adding nitric acid and diluting. C. W. GIBBY.

Strychnos alkaloids. L. Transformations of the base, $C_{17}H_{20}O_3N_2Br_2$, from cacothelin. H. LEUCHS (Ber., 1929, 62, [B], 1929—1935).—The compound $C_{17}H_{20}O_3N_2Br_2$ is strongly alkaline and cannot be alkylated with diazomethane or methyl alcohol and hydrogen chloride. The methiodide, m. p. 245° (decomp.) after becoming discoloured, nitrate, hydriodide, m. p. 235—240° (decomp.), and hydrochloride are described. The sulphate, acetate, and sulphite appear freely soluble. It does not react with hydroxylamine or semicarbazide. With bromine in hydrobromic acid it affords the compound

 $C_{17}H_{18}O_3N_2Br_4$, HBr. It is converted by methylalcoholic ammonia at 100° into the compound $C_{17}H_{21}O_3N_2Br$, isolated as the hydrobromide. With aqueous ammonia the substances $C_{17}H_{22}O_4N_3$, HBr and $C_{17}H_{20}O_5N_2$, HBr are obtained. The compound $C_{19}H_{24}O_7N_2$, HBr is prepared from it by means of barium hydroxide. Treatment of the hydrobromide with silver carbonate or sodium hydroxide gives the free base, $C_{17}H_{22}O_5N_2$ (methiodide, decomp. about 220° after softening at 210°; acetyl derivative, m. p. 118° after softening at 95°), which does not appear to contain the carboxyl or carbonyl group. The bromide of the compound $C_{17}H_{22}O_5N_2$ is oxidised by bromine in hydrobromic acid to the substance $C_{17}H_{22}O_7N_5$, HBr, is derived. Yellow mercuric oxide converts the compound $C_{17}H_{22}O_7N_2$ into the substance $C_{17}H_{22}O_8N_2$, which yields a nitrate, a bromide, and an iodide.

H. WREN.

Strychnos alkaloids. LI. Degradation of derivatives of brucine and strychnine to the same product. H. LEUCHS and F. KRÖHNKE (Ber., 1929, 62, [B], 2176—2180).—Strychnine is converted by nitric acid (d 1·41) at 0—20° into mononitrostrychnine, m. p. 240° after softening (nitrate; perchlorate; picrate), converted by boiling 5% nitric acid into dinitrostrychnine nitrate. Dinitrostrychnine hydrate is transformed by methyl-alcoholic hydrogen chloride into the methyl ether [hydrochloride, C₂₂H₂₄O₇N₄.HCl, softening at 215—230° (decomp.)]. Nitrostrychnine nitrate and dinitrostrychnine hydrate nitrate are reduced by stannous chloride and hydrochlorio acid to aminostrychnine, m. p. 275—278° (vac.), and

diaminostrychnine, m. p. not below 300°, respectively. Oxidation of either amine by chromic acid in aqueous sulphuric acid affords the acid, $C_{17}H_{22}O_6N_2$, $[\alpha]_{b}^{\infty}$ + 45.5° in water, identical in all respects with the acid obtained from brucine. Brucine is therefore the *o*-dimethoxy-derivative of strychnine.

Nitrostrychnine in acetone is oxidised by permanganate to nitrostrychninonic acid, m. p. 256-266° (decomp.) after softening according to the rate of heating. H. WREN.

Strychnos alkaloids. LII. Reduction and oxidation of the C_{17} alkaloids from brucine. H. LEUCHS and A. HOFFMANN (Ber., 1929, 62, [B], 2303—2311).—The mother-liquors from the oxidation of cacothelin are rendered ammoniacal and extracted with chloroform and the base, $C_{17}H_{20}O_3N_2Br$, is separated as the hydrobromide or sulphurous acid compound. It contains an alcoholic hydroxyl group, since it readily yields a monoacetyl derivative analysed as the *acetate*, $C_{19}H_{22}O_4N_2Br_2, C_2H_4O_2$, which softens and becomes discoloured at about 210°, and the hydrobromide. The sulphurous acid compound is transformed by methyl-alcoholic ammonia into the base $C_{17}H_{21}O_3N_2Br$, m. p. 232—234° (decomp.) (hydrobromide). Reduction of the base.

is transformed by incurry rate on one atministration to the base $C_{17}H_{21}O_3N_2Br$, m. p. 232—234° (decomp.) (hydrobromide). Reduction of the base, $C_{17}H_{20}O_3N_2Br_2$, with sodium amalgam yields two isomeric bases, $C_{17}H_{20}O_3N_2Br_2$, with sodium amalgam yields two discoloured at 270° or m. p. 220° after softening at 120°, and m. p. 290° (decomp.) after becoming discoloured at 270° or m. p. 300° (vac., decomp.), respectively. Under non-reproducible conditions a hydriodide, $C_{17}H_{20}O_3N_2.2HI$, has been isolated. Oxidation of the base $C_{17}H_{22}O_3N_2$, m. p. 220°, with chromic acid affords the compound, $C_{17}H_{22}O_4N_2$, isolated as the hydrobromide, m. p. 220° (decomp.) after softening at 93°. The preparation of the base $C_{17}H_{20}O_3N_2Br_2$ with barium hydroxide and its mono-and di-acetyl derivatives is described. Oxidation of the alkaloids $C_{17}H_{20}O_3N_2Br_2$ in water or acetone and $C_{17}H_{22}O_5N_2$ in water with permanganate gives no recognisable products. With chromic acid the lastnamed base gives a substance, $C_{17}H_{20}O_3N_2$, which is further oxidised to an acid, $C_{17}H_{20}O_6N_2$, which is further oxidised to an acid, $C_{17}H_{20}O_6N_2$, which is vol., 707), who assign the composition $C_{17}H_{22}O_6N_2$

Bromination of several phenylarsinic acids. A. LEULIER and Y. DREYFUSS [J. Pharm. Chim., 1929, [viii], 10, 258-263).—In part an account of work already published (this vol., 945). Bromination of 3-nitro-4-hydroxyphenylarsinic acid with 48% hydrobromic acid and hydrogen peroxide gives an 84% yield of the monobromo-derivative, decomp. 280°. A 70% yield of a monohalogeno-derivative is similarly obtained from 3-nitro-4-aminophenylarsinic acid; no definite product could be obtained with stovarsol, whilst oxanilarsinic acid (lethal dose for a guinea-pig 0-05 g. per kg.) is increased by increasing bromine substitution (lethal dose 0-01 g. per kg. for the monobromo-, <0-01 g. per kg. for the dibromo-derivative). J. W. BAKER.

Synthesis of 4:4'-dithiolarsenobenzene. S. KRISHNA and R. KRISHNA (J. Indian Chem. Soc.,

1929, 6, 665-672).—Treatment of an alkaline solution of potassium ethyl xanthate with diazotised *p*-aminophenylarsinic acid at $55-60^{\circ}$ and hydrolysis of the intermediate *p*-xanthyldiazobenzenearsinic acid (*potassium* salt) with hydrochloric acid affords 4:4'-dithiolarsenobenzene (I), decomp. above 280° (disodium and potassium salts; dihydrochloride; disulphate). Acetylation of I with acetyl chloride gives the diacetyl derivative (+AcCl), whilst I and thionyl chloride yield a product hydrolysed by water to the substance.

 $SO_2H\cdot S\cdot C_6H_4\cdot As(\dots SO_2H):As(\dots CI)\cdot C_6H_4\cdot S\cdot SO_2H$ (trisodium salt). Additive compounds of I and the following substances are described (the numbers in parentheses are the number of mols. of the substance per 1 mol. of I); ethyl chloroformate (1), pieric acid (2), perchloric acid (2), methyl iodide (2); with methyl sulphate 4:4'-dimethyl dithiolarsenobenzene, $+2Me_2SO_4$, results. Oxidation of I with chlorine in alcoholic suspension gives probably p-sulphophenyl-arsinic acid (II), whilst with 30% nitric acid II and diphenyl disulphide-4:4'-diarsinic acid are formed. Oxidation with alkaline hydrogen peroxide affords p-thiolphenylarsinic acid, decomp. above 250°.

The Béchamp reaction with potassium benzenesulphonate gives an impure sulphophenylarsinic acid (unstable chloride decomposing into benzenesulphonyl chloride and arsenic acid). H. BURTON.

Derivatives of phenarsazine. O. SEIDE and J. GOPSKI (Ber., 1929, 62, [B], 2186-2191).-10-Chloro-5: 10-dihydrophenarsazine is converted by magnesium methyl iodide into 10-methyl-5: 10-dihydrophenarsazine, m. p. 107-108°; 10-ethyl-5: 10-dihydrophenarsazine, m. p. 71-72°, 10-phenyl-5:10-dihydro-phenarsazine, m. p. 148-149°, and 10-a-naphthyl-5: 10-dihydrophenarsazine, m. p. 154-155°, are prepared similarly by use of magnesium and the requisite alkyl or aryl bromide. Chlorine in carbon tetrachloride converts 10-methyl-5: 10-dihydrophenarsazine into a perchloride, decomposed when heated with formation of 10-chloro-5: 10-dihydrophenarsazine, also obtained similarly from 10-phenyl-5: 10dihydrophenarsazine. When heated in a current of hydrogen chloride at 100-150°, 10-methyl-5: 10-dihydrophenarsazine is decomposed into methyldichloroarsine and diphenylamine; reaction apparently proceeds without production of intermediate compounds, since the same products result when the compound is heated with an equimolecular amount of hydrogen chloride in chloroform at 100°. 10-Phenyl-5: 10-dihydrophenarsazine similarly yields diphenylamine and phenyldichloroarsine. 10-Chloro-5: 10dihydrophenarsazine is converted by hydrogen chloride into arsenic trichloride and diphenylamine.

H. WREN.

Thiazoles. XV. Benzthiazole arsenicals of arsphenamine (salvarsan) type. M. T. BOGERT and F. G. HESS (Rec. trav. chim., 1929, 48, 904— 911).—2-o-Hydroxyphenylbenzthiazole, m. p. 131·7— 132·2° (cf. A., 1926, 531), reacts with arsenic acid at 150—160°, forming 2-o-hydroxyphenylbenzthiazole-5'arsinic acid (I), m. p. about 315·5° (decomp.; all m. p. except this are corr.), obtained also by the Bart reaction on 2-5'-amino-2'-hydroxyphenylbenzthiazole

(II), m. p. 190-190.5° (diacetyl derivative, m. p. 268-268.5°). Treatment of zinc o-aminophenylmercaptide with 5-nitrosalicylaldehyde in boiling acetic acid and decomposition of the product formed with hydrogen sulphide affords 2-5'-nitro-2'-hydroxyphenylbenzthiazole, m. p. 219.1-219.6°, reduced by sodium hyposulphite in sodium hydroxide solution to II. Coupling of benzenediazonium chloride with 2-ohydroxyphenylbenzthiazole and reduction of the resulting dye with sodium hyposulphite also gives II. Nitration of I with nitric (d 1.42) and sulphuric acids affords the corresponding 3'(?)-nitro-derivative, m. p. 297.7-298.7°, reduced by stannous chloride and hydrochloric acid in acetic acid solution to 5(?):5'(?)diamino-4: 4'-dihydroxy-3: 3'-di-(2-benzthiazolyl)arsenobenzene dihydrochloride. Alkaline sodium hyposulphite reduction of I gives 4:4'-dihydroxy-3:3'di-(2-benzthiazolyl)arsenobenzene, m. p. 240.8-241.3°. 2-op-Dihydroxyphenylbenzthiazole, m. p. 201-201.5° (diacetate, m. p. 196.1-196.6°), reacts with arsenic acid at 160-170°, yielding the corresponding 5'(?)-arsinic acid, m. p. about 279.9° (decomp.), reduced by stannous chloride and hydrochloric and acetic acids to impure 4:6:4':6'-tetrahydroxy-3:3'-di-(2-benzthiazolyl)arsenobenzene. 2-3': 4'-Dihydroxyphenylbenzthiazole (diacetate, m. p. 155.9-156.4°) has m. p. 222.3-222.8°, and is obtained from zine o-aminophenylmercaptide and protocatechualdehyde.

H. BURTON.

Halogenomercuriphenols. J. F. CAIUS and J. H. WADIA (J. Indian Chem. Soc., 1929, 6, 613— 616).—Treatment of an alkaline solution of 2:4-diacetoxydimercuriphenol with a saturated solution of the appropriate sodium halide and subsequent acidification with acetic acid affords 2:4-difluoro-, m. p. 197.5—198°; 2:4-dichloro-, decomp. 278°; 2:4-dibromo-, colours at 230°, and 2:4-di-iodo-dimercuriphenol, decomp. 142°. The mixture of o- and pacetoxymercuriphenols obtained during the mercuration of phenol is treated with the sodium halide and the mixture of halogenomercuriphenols extracted with boiling water to give the o-compound and with alcohol to yield the p-derivative. The following are described: o-fluoro-, m. p. 192.5°; o-chloro-, m. p. 146—146.5°; o-bromo-, m. p. 121.5—122°; o-iodo-, m. p. 106.5°; p-fluoro-, m. p. 204°; p-chloro-, m. p. 216°; p-bromo-, colours at 185° without melting, and p-iodomercuriphenol, becomes yellow at 180° without melting. H. BURTON.

Mercurated terephthalic acid. F. C. WHIT-MORE and L. L. ISENHOUR (J. Amer. Chem. Soc., 1929, 51, 2785-2787).-When ethyl terephthalate is heated with mercuric acetate and a small amount of acetic acid at 117°, or when terephthalic acid is boiled with a mixture of mercuric and sodium acetates and aqueous acetic acid, anhydro-2-hydroxymercuriterephthalic acid (I) is obtained. Treatment of I with phosphorus pentachloride in chloroform suspension affords the corresponding chloride, converted by the usual methods into n-butyl 2-chloromercuriterephthalate (II), m. p. 82-85°, 2-chloromercuriterephthalamide, and 2-chloromercuriterephthalanilide, not melted at 300°. n-Butyl 2-chloromercuribenzoate is obtained similarly to II and is hydrolysed more readily than II by boiling 90% alcohol. 2-Bromoterephthalic acid is obtained when I is treated with a solution of H. BURTON. bromine in sodium bromide.

Mercuration of aurin and attempts to mercurate other triphenylmethane dyes. F. C. WHIT-MORE and G. J. LEUCK (J. Amer. Chem. Soc., 1929, 51, 2782-2784).-Treatment of aurin with mercuric acetate in a boiling mixture of ethyl acetate and acetic acid affords acetoxymercuriaurin (I). With alcohol and a small amount of acetic acid as solvent di(acetoxymercuri)aurin results, whilst in alcohol tri-(aceloxymercuri)aurin (II) is formed. When I is boiled with alcohol, II and aurin are obtained, and prolonged treatment of I or II with sodium chloride and boiling alcohol gives tri(chloromercuri)aurin. Pararosaniline is mercurated readily to a tri(acetoxymercuri)-derivative. A small amount of a dimercurated product is obtained from the base of malachite-green, but crystal-violet, N-phenylmethyl-violet, and malachite-green are not mercurated. H. BURTON.

Aromatic tin compounds of higher mol. wt. E. KRAUSE and K. WEINBERG (Ber., 1929, **62**, [B], 2235–2241).—4-Bromodiphenyl ether, b. p. 165.5°/16 mm., m. p. 18°, d_4^{191} (vac.) 1.4225, n_p^{191} 1.60877, prepared from p-dibromobenzene, phenol, potassium hydroxide, and copper-bronze, is converted by the successive action of magnesium and tin tetrachloride into tin tetra-p-phenoxyphenyl, m. p. 171°. p-Chlorobromobenzene is converted analogously into tin tetrap-chlorophenyl, m. p. 199° (also $+2C_6H_6$), which, when brominated in presence of pyridine at -15° , affords tin tri-p-chlorophenyl bromide, m. p. 96-97° after softening at 94°. Treatment of an ethercal solution of the bromide with aqueous potassium hydroxide yields tin tri-p-chlorophenyl hydroxide, from which tin tri-p-chlorophenyl chloride, m. p. 110-111° after softening at 107°, and tin tri-p-chlorophenyl iodide, m. p. 93-95° after softening at 91°, are derived. Tin tri-p-chlorophenyl fluoride is best obtained from the bromide in ether-alcohol and aqueous-alcoholic potassium fluoride. The tetra-p-chlorophenyl compound and bromine in carbon tetrachloride yield tin di-pchlorophenyl dibromide, m. p. 73° after slight softening, decomp. about 300°. Hexa-p-chlorophenyldistannane, m. p. 139°, is obtained from tin tri-p-chlorophenyl bromide and sodium in boiling xylene. Tin tri- α -naphthyl chloride, m. p. 204–205°, and tin tri-p-anisyl fluoride, decomp. 239°, are obtained in attempts to prepare the corresponding tetra-compounds. The following mixed tin aryls are derived from tin triphenyl halides and the requisite magnesium aryl halide; tin triphenyl p-phenoxyphenyl, m. p. 161-162° after slight softening; tin triphenyl p-chlorophenyl, m. p. 139°; tin triphenyl p-bromophenyl, m. p. 224°. H. WREN.

Crystalline tripeptide from living cells. (SIR) F. G. HOPKINS (Nature, 1929, 124, 445).- A crystalline tripeptide containing glycine, glutamic acid, and cysteine has been isolated from extracts of yeast and red blood corpuscles, the separation being based on the insolubility of the cuprous salt in N-sulphuric acid. Hence glutathione, as previously described by the author, is not an individual substance.

A. A. ELDRIDGE.

Detection of pyrrole- and pyridine-ring systems in proteins. N. TROENSEGAARD and H. G. MYGIND (Z. physiol. Chem., 1929, 184, 147-156).-By acetylation of gliadin, hydrogenation of the product with sodium and amyl alcohol, and cold hydrolysis followed by fractionation of the bases, piperidine hydrochloride was isolated. None could be obtained from globin, serum-albumin, and serumglobulin. Casein gave isoamylamine.

J. H. BIRKINSHAW.

Clupein. I. K. FELIX and K. DIRR (Z. physiol. Chem., 1929, 184, 111-131) .-- Clupein was esterified by methyl alcohol and hydrochloric acid and the product was divided into four fractions by their differing solubility in methyl-alcoholic hydrogen chloride. These four protamine esters differ in composition, optical activity, methoxyl content, and in mol. wt. The clupeins possess esterifiable carboxyl groups, but no free amino-groups. A crystalline substance with characteristic properties was isolated, browning at 220° and decomposing sharply at 242°. J. H. BIRKINSHAW.

Thymonucleic acid. P. A. LEVENE and E. S. LONDON (J. Biol. Chem., 1929, 83, 793-802).-Hydrolysis of thymonucleic acid with intestinal juice yields guanine nucleoside, $[\alpha]_{p}^{25} - 36.0^{\circ}$ in N-sodium hydroxide; hypoxanthine nucleoside, no m. p., shrinking at 200°, $[\alpha]_{D}^{2}$ -21.0° in dilute sodium hydroxide; thymine nucleoside, m. p. 185°, $[\alpha]_D^{23} + 32.5^\circ$ in Nsodium hydroxide; cytidine nucleoside, no m. p., shrinking at 190°, $[\alpha]_{p}^{23} + 40^{\circ}$ in water. The hypoxanthine nucleoside is presumably derived from adenine nucleoside; all the above nucleosides yield, when hydrolysed, the appropriate base and a deoxypentose (cf. this vol., 590). The formula of thymo-nucleic acid thus becomes $C_{39}H_{51}O_{25}N_{15}P_4$. C. R. HARINGTON.

Substituted proteins. Nitration and iodin-ation of globin. H. BAUER and E. STRAUSS (Biochem. Z., 1929, 211, 163-190).-The amount of iodine attached to carbon in iodinated derivatives of ovalbumin, serum-albumin, and serum-globin is stoicheiometrically related to their tyrosine contents. The tyrosine takes up two atoms of iodine, not by adsorption. Globin takes up, in addition, two more atoms of iodine which are situated in the histidine portion of the molecule. Nitroglobin, which contains one nitro-group in the tyrosine portion and one in the tryptophan portion of the molecule, can be reduced to aminoglobin. When nitroglobin is iodinated one atom of iodine enters the tyrosine portion and two atoms enter the histidine portion. Part of the iodine of iodoglobin and of iodonitroglobin is eliminated by cold sulphurous acid. This part is probably attached to an imino-group. It is deduced from their iodine contents that globin and nitroglobin after iodination in hydrogen carbonate solution contain two iminogroups capable of taking up iodine, whilst nitroglobin after iodination in ammoniacal solution contains three such groups. These groups are the points attacked by pepsin-hydrochloric acid. The changes in solubility in dilute acid that the substituted proteins undergo and the extent to which they are attacked (if at all) by pepsin-hydrochloric acid are

described and compared with the changes the proteins themselves undergo on heating. W. MCCARTNEY.

Micro-determination of carbon in solid substances by oxidation with chromic and sulphuric A. BOIVIN (Compt. rend. Soc. Biol., 1929, acids. 100, 502-504; Chem. Zentr., 1929, i, 2560).-Oxidation of the carbon monoxide formed in Nicloux's method is completed by means of a glowing platinum wire, oxygen originating from the heated mixture.

Micro-determination of carbon in precipitates. A. BOIVIN (Compt. rend. Soc. Biol., 1929, 100, 505-507; Chem. Zentr., 1929, i, 2560-2561).-The material is collected on an asbestos plug in a constricted glass tube; the relevant portion is cut off and the determination is completed by Nicloux's method. A. A. ELDRIDGE.

Elementary organic analysis by Pregl's microchemical method. F. HERNLER (Mikrochem., 1929, Pregl Fest., 140-153).-An account of the author's experience with Pregl's methods; a new form of apparatus for maintaining the lead peroxide employed at a constant temperature during the analysis is described. H. F. HARWOOD.

Adaptation of Pregl's micro-combustion to a semi-micro-combustion method for determination of carbon and hydrogen. W. M. LAUER and F. J. DOBROVOLNY (Mikrochem., 1929, Pregl Fest., 243-252).- A method based on those of Pregl and Wise for the determination of carbon and hydrogen in organic substances; 20 mg. of material suffice for the analysis, and the weighings may be carried out on an ordinary balance sensitive to 0.05 mg. It is claimed that the technique is more easily acquired than that of the usual macro-combustion method.

H. F. HARWOOD.

Adaptation of Pregl's micro-combustion to a semi-micro-combustion method for determination of nitrogen. W. M. LAUER and C. J. SUNDE (Mikrochem., 1929, Pregl Fest., 235-242).-A method for the determination of nitrogen in organic compounds which is based on Pregl's microchemical method but does not necessitate the use of a microbalance has been devised; 20 mg. of material suffice for the analysis, and the weighings can be carried out on an ordinary balance sensitive to 0.05 mg. H. F. HARWOOD.

Simultaneous determination of nitrogen and mercury in the microchemical analysis of organic mercury compounds. F. HERNLER (Mikrochem., 1929, Pregl Fest., 154-164).-The front portion of the combustion tube used projects 80-120 mm. beyond the furnace, and during the determination of the nitrogen this part is kept well cooled by being wrapped with wet cloths. When the nitrogen determination is complete, the nitrometer is disconnected, and the combustion tube connected with a weighed glass tube packed with gold wire, into which the mercury is driven by gentle heating. The results are quite satisfactory, but the method requires very careful work. H. F. HARWOOD

Microanalytical determination of sulphur in organic compounds by a volumetric method. A. FRIEDRICH (Mikrochem., 1929, Pregl Fest., 91102).-A combustion of the substance is made by Dennstedt's method, using 4-7 mg. of the compound, the evolved gases being passed through dilute hydrogen peroxide. The resulting solution is evaporated on a water-bath and titrated with N/45-sodium hydroxide. A quantity of N/45-sulphuric acid equivalent to the alkali used is then added, the solution is evaporated to dryness, and the hydrogen sulphate present is determined by a second titration, this corresponding with the sulphuric acid formed by the combustion. The method yields satisfactory results for substances which contain either nitrogen or halogen in the molecule in addition to sulphur, but has so far not been tested for compounds containing all three of H. F. HARWOOD. these elements.

Micro-determination of selenium and tellurium in organic compounds. H. D. K. DREW and C. R. PORTER (J.C.S., 1929, 2091-2095).-Accurate methods for the quantitative precipitation and filtration of 3-5 mg. of selenium or tellurium are described. The processes are modifications of the larger-scale gravimetric methods. Halogens can be determined accurately in the presence of tellurium.

J. G. A. GRIFFITHS.

Micro-analytical determination of iodine in organic substances. T. LEIPERT (Mikrochem., 1929, Pregl Fest., 266—271).—The following procedure is recommended; 5 mg. of the material are burnt in oxygen according to Pregl's method, and the iodine is absorbed in concentrated sodium hydroxide. The solution is exactly neutralised with 2N-sulphuric acid, 3 drops excess of acid are added, and the whole is diluted to 60 c.c.; 2 c.c. of bromine are added, and the excess is expelled by maintaining the solution at the b. p. for 7 min. by a vigorous current of steam. After cooling, 1 g. of potassium iodide is added, and the liberated iodine titrated with 0.01N-thiosulphate.

H. F. HARWOOD.

Microchemical determination of iodine [in organic substances]. G. LUNDE, K. CLOSS, and J. BÖE (Mikrochem., 1929, Pregl Fest., 272-292).-The iodine in the material is converted into alkali iodide by treatment with potassium hydroxide and carbonate, ignition being repeated until all organic matter has been destroyed; the addition of a little nitrate is advisable in certain cases. The cold mass is extracted with 96% alcohol, the extract evaporated, and the iodine in the residue determined either colorimetrically or volumetrically. Special precautions must be taken if the original material contains much lime, otherwise the whole of the iodine cannot be extracted by alcohol. In order to determine the iodine present in various forms of combination in an organic substance, the material is extracted with water, and the "lipoid iodine" removed from the acidified solution by extraction with ether. "Albuminoid iodine" can be precipitated by the addition of alcohol or acetone, and the "inorganic iodine " determined by liberation with nitrous acid and extraction with ether, or by precipitation with palladous chloride. H. F. HARWOOD.

Rapid volumetric determination of formic and acetic acids in presence of each other. P. FUCHS (Z. anal. Chem., 1929, 78, 125-127).—The solution containing the acids is exactly neutralised

with N-sodium hydroxide, and boiled to expel any acetaldehyde. Solid sodium acetate and an excess of a saturated solution of mercuric chloride are added, and the liquid is kept just below the b. p. for 15 min., when the following reaction occurs: HCO,Na+ 2HgCl₂=NaCl+Hg₂Cl₂+HCl+CO₂. The cooled solution is filtered and the free acid in the filtrate titrated with N-sodium hydroxide. H. F. HARWOOD.

Colorimetric determination of methylglyoxal, dihydroxyacetone, and glyceraldehyde. E. BAER (Arbeitsphysiol., 1928, 1, 130-135; Chem. Zentr., 1929, i, 2087).-Mendel and Goldscheider's method for the determination of lactic acid has been extended to that of the above substances. Proteins and carbohydrates are removed with phosphotungstic acid and calcium hydroxide and copper sulphate, the residual solution then being treated with concentrated sulphuric acid and alcoholic veratraldehyde. The determination of methylglyoxal, dihydroxyacetone, or glyceraldehyde is made colorimetrically, standard and test solutions being compared with a dilute alcoholic solution of carbol-fuchsin containing a drop of orange G solution. The accuracy is 4 mg.-%, 0.02 mg. being determinable. A. A. ELDRIDGE.

Determination of arylamides of aromatic sulphonic acids. K. HELLER and Z. FLEISCHHANS (J. pr. Chem., 1929, [ii], 123, 146-147).-The sulphonarylamide is dissolved in an excess of 0.1Nsodium hydroxide [whereby salt formation occurs, $R \cdot SO_{\circ}NHR' + NaOH \rightarrow R \cdot SO(:NR)(ONa) + H_2O]$ and titrated with 0.1N-hydrochloric acid until a faint turbidity appears. The method is accurate to the extent of about 1%. Pyrazolones can also be titrated with sodium hydroxide as above. H. BURTON.

Determination of basic amino-acids in small amounts of protein. H. O. CALVERY (J. Biol, Chem., 1929, 83, 631-648).-The method of Vickery and Leavenworth (A., 1928, 511) has been modified for application to 5 g. of protein, and the modified method applied to caseinogen and edestin. In the latter case the results agree well with those already obtained by the above-mentioned authors. The determinations by actual isolation were satisfactorily checked in the case of histidine by nitrogen determinations and by the methods of Hanke and Koessler (A., 1920, ii, 784) and of Plimmer and Phillips (A., 1924, ii, 576), the technique of the latter method being discussed in detail; in the case of arginine, determinations of the total nitrogen of the arginine fraction were useless, but the method of Van Slyke (A., 1912, ii, 1008) gave results in good agreement with those of isolation. For quantitative precipitacid concentration must be 3-5%. C. R. HARINGTON. ation of histidine by mercuric sulphate, the sulphuric

Determination of tyrosine and of tryptophan by the method of Tillmans, Hirsch, and Stoppel. H. BAUER and E. STRAUSS (Biochem. Z., 1929, 211, 191-198).-The method (cf. A., 1928, 1278) cannot be used in the case of food-proteins which are insoluble in hot dilute nitric acid or undergo alteration if heated with the acid. If proteins are kept in contact with nitric acid (d 1.42) for 18 hrs. at the ordinary temperature and allowance is made for the fact that the tyrosine present may be either mono- or di-nitrated, satisfactory results are obtained. In the case of certain proteins the results must be checked by those obtained by other methods. The modified method cannot be used for iodinated or nitrated globins.

W. MCCARTNEY.

Biochemistry.

Micro-respiration apparatus for simultaneous determination of oxygen and carbon dioxide. J. FRHR. VON LEDEBUR (Mikrochem., 1929, Pregl Fest., 253-265).-An apparatus permitting the simultaneous determination of oxygen and carbon dioxide is described, the former gas being determined by volume and the latter by absorption in 0.012Nbarium hydroxide and measurement of the change in electrical conductivity of this solution. The accuracy attainable in the case of both gases is 0.5 c.mm. if the temperature be kept constant to 0.05°. The complete absorption of the carbon dioxide requires up to 40 min. even if the apparatus be shaken, hence readings should not be taken more frequently than every H. F. HARWOOD. half-hour.

Role of hæmoglobin in the blood. A. B. HASTINGS (Coll. Symp. Mon., 1928, 6, 139-154) .--A discussion. CHEMICAL ABSTRACTS.

Relation between hæmoglobin content and oxygen supply of the organism. F. MAINZER (Pfluger's Archiv, 1928, 220, 234-242; Chem. Zentr., 1929, i, 1958).

Blood-cell metabolism. IV. Effect of methylene-blue on metabolism of leucocytes. E. S. G. BARRON. V. Metabolism of leucocytes. E. S. G. BARRON and G. A. HARROP, jun. (J. Biol. Chem., 1929, 84, 83-87, 89-100).-IV. Methyleneblue causes increase in the oxygen consumption of leucocytes and increased oxidation of dextrose during glycolysis (decreased formation of lactic acid); the effects are less marked than those previously observed with mammalian erythrocytes (this vol., 460).

Aduptation of Presl's micro-commetin

V. For the successful observation of the metabolism of the white cells it is necessary to centrifuge for a short time only, to work in low concentration and for short periods, and to avoid cooling and the use of anticoagulants which interfere with respiration. Glycolysis produced by polynuclear lymphocytes is about five times as great as that produced by leucocytes; in their fermentative reactions the leucocytes resemble normal cells and the polynuclear lymphocytes cancer cells. C. R. HARINGTON.

Development of foetal blood in the cow. I. Volume, dry matter, and corpuscular hæmoglobin content of cow's blood. II. Fœtal blood.

D. VON DESEÖ (Pflüger's Archiv, 1928, 221, 321– 326, 327–335; Chem. Zentr., 1929, i, 1956).—Cow's blood contains 197 g. of water per 100 g. of dry substance (86 wt.-% hæmoglobin); during the development of the fœtus the dry matter in the blood rose from 26 to 29 wt.-%. A. A. ELDRIDGE.

Rate of settling of red blood-corpuscles and surface tension. A. PINES and M. JOFFE (Biochem. Z., 1929, 211, 420-425).—There is no relation between the settling rate and the surface tension at the plasma/air boundary. J. H. BIRKINSHAW.

Tryptoporphyrin. G. MONASTERIO (Biochem. Z., 1929, 212, 71-79; cf. A., 1928, 82).—The small amount of iron which remains in tryptoporphyrin prepared by the method of Fränkel and Prinz cannot be removed by any of the processes known to succeed in the case of hæmatin. By some of these processes the chief constituent of tryptoporphyrin is attacked and small amounts of a compound having an iron content similar to that of hæmin but without its spectroscopic properties can be isolated. It is concluded that the iron in hæmoglobin and in hæmatin is present in two forms, in one of which the iron is loosely bound, whilst in the other it resists the effects of the processes mentioned.

W. MCCARTNEY. Determination of fibrinogen by centrifuging. K. SAMSON (Med. Klin., 1928, 4 pp.; Chem. Zentr., 1929, i, 2339).—The fibrinogen is precipitated at 55° in a graduated tube, cooled, and the height of the column of precipitate is read after centrifuging for a definite time. The tubes are graduated by parallel nitrogen determinations. A. A. ELDRIDGE.

Sulphur content of fibrins from various mammals. Z. Aszódi (Biochem. Z., 1929, 212, 158—161).—The sulphur content of fibrin from men, pigs, cattle, horses, and dogs has been determined and compared with that of the globulin from the same animals. Values which varied considerably from species to species and from individual to individual were obtained. In the dog there was usually less, in the horse usually more, sulphur in the fibrin than in the globulin. W. MCCARTNEY.

Sulphur content of various serum-globulins. Z. Aszódi (Biochem. Z., 1929, 212, 102-114; cf. this vol., 206).—The sulphur contents of serum-globulin from men, pigs, cattle, horses, and dogs have been determined. Great individual variations in these contents are found within the same species. Serumglobulin from dogs usually contains more than 1·30% S, but values as high as this are only occasionally found in the other animals. There is uo connexion between either the sex or the purity of the breed of a dog and the sulphur content of its serum-globulin. W. MCCARTNEY.

Behaviour of Congo-red to serum-colloids. Determination of blood by the Congo-red method of Griesbach. L. HEILMEYER (Biochem. Z., 1929, 212, 430—442).—The absorption spectrum of Congored in serum solutions is essentially different from that in aqueous solutions due to union with serum-colloids. This forms a source of error in Griesbach's method (Deut. med. Woch., 1921) for determination of blood.

The error is quantitatively ascertained and is dependent on the absolute concentration of the serum-Congo-red solution. P. W. CLUTTERBUCK,

Determination of proteins in blood-serum. F. SCHNEIDER (Biochem. Z., 1929, 211, 207-212).-The refractometric method of Robertson, the Kjeldahl method, and the gravimetric method for the determination of proteins in blood-serum have been compared. Serum from 51 subjects, some in a mild, others in a chronic, pathological condition, was used. The results of the Kjeldahl and gravimetric methods agreed satisfactorily. Those of the refractometric method were less accurate. Where great accuracy is not required, the refractometric method, which is rapid, may be used. If the limits of error must not exceed ± 0.3 g.-%, one of the other methods should be employed. W. MCCARTNEY.

Amylase of horse-serum and the variation of its activity as a function of successive bleedings. B. ROUSSEU, Z. GRUZEWSKA, and G. ROUSSEL (Compt. rend., 1929, 189, 501-503).—Sterile serum from the animal was incubated with a sterilised 1.4%starch solution for 24 hrs. at $p_{\rm H}$ 7.4—7.6. After deproteinisation the sugar was determined by Bertrand's method. Since dextrose was the only sugar obtained at the end of 48 hrs., maltase must be present in the sera. The experimental results indicate a periodicity in the activity of the amylase as a function of the bleedings as well as an individual variation in the amylase activity of different sera. C. C. N. VASS.

Changes in activity of blood-catalase. A. KULTJUGIN and G. SAVOSTJANOV (Biochem. Z., 1929, 211, 131-143).-The activity of catalase from erythrocytes of the cat in blood solutions decreases when the solutions are kept, at a rate which is much greater during the first $2\frac{1}{2}$ hrs. than in the second and varies according to the animal from which the blood is taken. Rise of temperature also causes reduction of the activity, which is completely lost at 60°. The presence of chlorides or nitrates greatly reduces the activity, but sulphates have little effect. Blood-serum from various animals, blood- and eggalbumin increase the activity as their concentrations increase (up to 1%); soluble starch, gelatin, and dextrin are without influence, although all these colloids retard the loss of activity which occurs in their absence on preserving the solutions. This protecting effect of the colloids (except starch and gelatin) persists when the temperature is raised except in the case of the higher concentrations of the colloids. The influence of chlorides and nitrates is greatly reduced and sometimes suppressed altogether if blood-serum from various animals, blood-albumin, or egg-albumin is present. Starch and gelatin do not affect the influence of these electrolytes.

W. MCCARTNEY.

Action of the bile and bile acids on serumlipases in the organism. A. BACULO and E. IANTRIA (Riv. Pat. Sper., 1928, 3, 52—59; Chem. Zentr., 1929, i, 2064).—The lipolytic activity of dogserum is uninfluenced by addition of dog's or ox bile, but the inhibitive action of quinine is no longer observed. Sodium taurocholate appears to be more active than the glycocholate. A. A. ELDRIDGE. Fate of acetylcholine in the blood. G. VIALE and J. M. SONCINI (Pflüger's Archiv, 1929, 221, 594— 598; Chem. Zentr., 1929, i, 2199).—The esterase, supposed by Galehr and Plattner to hydrolyse acetylcholine, is not present in the blood. It is not proved that the vagus substance is identical with acetylcholine. A. A. ELDRIDGE.

Chemical modifications of blood following intravenous injection of urea. B. V. FUENTES, J. DUOMARCO, and A. MUNILLA (Rev. asoc. med. Argentina, 1928, 41, 885—909).—Intravenous injection of urea (1.5—5.0 g. per kg.) into dogs causes an increase in the ratio urea-: total-nitrogen (normally 0.5) to 0.9, the total blood-nitrogen exceeding 100 mg. No modification of the blood-uric acid, creatine, or creatinine, or of the calcium, sodium chloride, and inorganic phosphorus metabolism was observed.

CHEMICAL ABSTRACTS.

Micro-determination of creatinine and creatine in blood. E. Koplowitz (Biochem. Z., 1929, 211, 475—486).—The methods, depending on the colour reaction of creatinine with alkaline sodium pierate solution, permit of the determination of creatinine and creatine in blood-plasma and total blood in 20 c.c. of blood. No difference in creatinine and creatine content was found between arterial and venous blood. J. H. BIRKINSHAW.

Determination of uric acid in blood. II. J. D. B. H. VAN ASSENRAAD (Pharm. Tijdschr. Ned.-Indie, 1929, 6, 65—69; Chem. Zentr., 1929, i, 1974).— The uric acid is oxidised to allantoin with potassium ferricyanide in the cold; dextrose is not attacked under these conditions. A mixture of serum (3 c.c.), water (3 c.c.), and 1.65% uranyl acetate solution (3 c.c.) is centrifuged, and 3 c.c. of the clear liquid is treated with 2.5 c.c. of a solution containing 0.329 g. of potassium ferricyanide and 6 g. of sodium carbonate per litre; after at least 5 min. 2 drops of concentrated sulphuric acid are added, the solution is diluted to 20 c.c., and the colour is compared with that of standard solutions of uric acid which have been similarly treated. A. A. ELDRIDGE.

Determination of cholesterol [in blood]. E. HERZFELD (Schweiz. med. Woch., 1928, 58, 103– 110; Chem. Zentr., 1929, i, 2089–2090).—Serum is treated dropwise with absolute alcohol, boiled, and filtered, the residue being washed first with alcoholic chloroform, and then with chloroform alone. The residue on evaporation of the filtrate is dissolved in warm chloroform. Aliquot portions diluted to varying degrees are tested by Liebermann's reaction. In disease of the liver and in diabetes the blood-cholesterol is high (300–800 mg.-%).

A. A. ELDRIDGE.

Determination of blood-cholesterol. G. FET-TICH (Klin. Woch., 1929, 8, 362—363; Chem. Zentr., 1929, i, 2089).—The serum-cholesterol is hydrolysed by Aczel's method, extracted with chloroform, and the extract is subjected to Liebermann and Burchard's reaction, the green colour being compared in an Autenrieth colorimeter. A. A. ELDRIDGE.

Physico-chemical state of lecithin and cholesteryl esters in blood-serum and -plasma. M. A. MACHEBGUF (Bull. Soc. chim., 1929, fiv], 45, 662—666).—The phosphoaminolipin-protein previously described (this vol., 206, 838) is very resistant to fractionation and is regarded as a compound of lecithin and cholesteryl esters with plasma-proteins. The lipins isolated by treating its solutions with boiling alcohol to coagulate the proteins and then extracting with ether are insoluble in water even in presence of ammonia or serum-albumin, and yield unstable milky aqueous suspensions from which ether extracts the lipins. R. BRIGHTMAN.

Inorganic constituents of the blood of pupæ of butterflies (Sphynx pinastri, Pieris brassicæ) and changes in the content of these constituents during the pupal stage. L. BRECHER (Biochem. Z., 1929, 211, 40-64).-In addition to a minute quantity of sodium, the blood of the pupze of S. pinastri contains the following average amounts of inorganic material per 100 c.c. : potassium, 137.8 mg., calcium, 33 mg., magnesium, 56 mg., chlorine, 59 5 mg., phosphorus, 66 mg. (total phosphorus 207 mg.). As regards the potassium, calcium, magnesium, and inorganic phosphorus contents of the blood there is no difference between male and female pupe. The blood contains an excess of 0.050 g.-equiv. per litre of bases which are presumably combined with organic acids. During the period in which P. brassicæ is passing through the caterpillar and pupal stages there is an increase in the potassium content, a decrease in the calcium and chlorine contents, and a large decrease in the magnesium content of its blood. The total phosphorus content of the blood first falls, then rises greatly during the same period. W. MCCARTNEY.

Serum-calcium in the negro. C. L. HARRELL (Amer. Rev. Tuberculosis, 1929, 19, 350-352).—The average normal value was 10.93 mg. per 100 c.c. (0.43 mg. higher than for white individuals); in suspected tuberculosis the value was 9.8 mg.

CHEMICAL ABSTRACTS.

Micro-determination of calcium in serum and plasma. B. GROAK (Biochem. Z., 1929, 212, 47—52).—The calcium in 0·1 c.c. of serum or plasma is precipitated by ammonium oxalate and the excess of permanganate left after the oxalic acid liberated by sulphuric acid has been oxidised is determined by addition of potassium iodide and titration with thiosulphate. The accuracy of the method (error $\pm 2.5\%$) is greater than that of the Kramer–Tisdall process. W. MCCARTNEY.

Composition of bone. VII. Equilibration of serum solutions with calcium hydrogen phosphate. M. J. SHEAR, M. WASHBURN, and B. KRAMER. VIII. Conductivity titrations of calcium ions. M. J. SHEAR, B. KRAMER, and L. RESNIKOFF (J. Biol. Chem., 1929, 83, 697—720, 721—735).—VII. On shaking either distilled water or artificial serum with calcium hydrogen phosphate, equilibrium is attained after 1 hr. The ionic solubility product [Ca]"×[HPO₄]" is $(3\cdot 2\pm 0\cdot 1) \times 10^{-6}$ at the ordinary temperature and $(3\cdot 4\pm 0\cdot 1) \times 10^{-6}$ at 38° for artificial serum. Sera in which the product Ca×P (expressed in mg. per 100 c.c.) is less than 50 (*i.e.*, all rachitic sera) are under-saturated with respect to calcium hydrogen phosphate. The results are discussed in their possible relation to the process of calcification. VIII. Normal conductivity titration curves were obtained on adding solutions of sodium chloride, sodium acetate, and sodium lactate to one of calcium chloride; abnormal curves were obtained with sodium citrate and calcium chloride, which affords additional evidence for the supposed formation of a slightly ionised soluble calcium citrate complex.

C. R. HARINGTON.

Simple apparatus for the determination of the alkali reserve of the blood. M. SCHLESINGER (Biochem. Z., 1929, 212, 115—126).—The apparatus consists of a U-shaped tube one arm of which forms the reaction vessel whilst the other (longer) arm, which is a capillary tube, is graduated. By its use the volume of carbon dioxide in 100 c.c. of blood is directly obtained and with the help of the tables given the alkali reserve can be calculated. One c.c. of plasma is used. W. MCCARTNEY.

Determination of $p_{\rm H}$ and carbon dioxide in single small sample of blood-serum. A. T. SHOHL (J. Biol. Chem., 1929, 83, 759-763).—A special apparatus is described which permits the determination of the $p_{\rm H}$ of 0·1-0·2 c.c. of blood-serum or plasma by the method of Hastings and Sendroy (A., 1924, ii, 869) and the subsequent use of the same sample for determination of carbon dioxide by the manometric method of Van Slyke and Neill (A., 1924, ii, 872). C. R. HARINGTON.

Measurement of $p_{\rm H}$ in flowing liquids. K. GOLLWITZER-MEIER and W. STEINHAUSEN (Pflüger's Archiv, 1928, 220, 551—557; Chem. Zentr., 1929, i, 2337).—Measurements on circulating blood are described. A. A. ELDRIDGE.

Micro-determination of $p_{\rm H}$ of blood and other biological fluids. A. J. SALLE (J. Biol. Chem., 1929, 83, 765—772).—By means of a special apparatus which enables minimal contact to be obtained between the solution and a platinum electrode previously saturated with hydrogen, equilibrium is reached so rapidly as to obviate the difficulties due to the evolution of carbon dioxide and the liberation of oxygen from oxyhæmoglobin. It thus becomes possible to make rapid electrometric determinations of the $p_{\rm H}$ of small amounts of blood, the results obtained agreeing well with those of colorimetric determinations. C. R. HARINGTON.

Acid-base equilibrium of the blood. I. Normal variation in $p_{\rm H}$ and carbon dioxide content of blood-serum. I. P. EARLE and G. E. CULLEN. II. Changes in acid-base equilibrium during the day. G. E. CULLEN and I. P. EARLE (J. Biol. Chem., 1929, 83, 539-544, 545-559).—I. In normal individuals the $p_{\rm H}$ of the blood-serum lies usually between 7.4 and 7.5, not between 7.3 and 7.4 as previously stated (A., 1922, ii, 672).

II. There is a general tendency for an increase of 0.01-0.07 in the p_{II} of normal human blood-serum from early morning to late evening. Fluctuations due to digestion are irregular, and moderate exercise has little effect. C. R. HARINGTON.

Determination of carbon in filtrates of precipitated blood. J. ROCHE (Compt. rend. Soc. Biol., 1929, 100, 278—280; Chem. Zentr., 1929, i, 1844).— The filtrate after treatment of the blood with phosphotungstic acid is evaporated with sodium sulphate at the ordinary temperature over sulphuric acid, the residue being transferred to Nicloux's apparatus for the determination. The results are accurate to 1-2%. A. A. ELDRIDGE.

Content of reducing substances in the blood of some invertebrates. B. KISCH (Biochem. Z., 1929, 211, 292—294).—Only traces of reducing substances were found in the blood of *Aplysia*, but 0.01— 0.02 mg. per 100 c.c. was present in the blood of *Sipunculus*, *Carcinus*, and *Eriphia*.

J. H. BIRKINSHAW.

Blood-sugar of Selachii. B. KISCH (Biochem. Z., 1929, 211, 276—291).—Reducing substances in the blood of Scyllium and Torpedo amount to 20—40 mg. per 100 c.c. The amount is independent of the fulness of the stomach and intestines. Extirpation of the liver leads to a lowering of the blood-sugar to 5—10 mg. per 100 c.c. after several days. Asphyxia causes hyperglycæmia, noticeable at 15° only after 1 hr., but earlier at higher temperatures. Water rich in oxygen causes a still further increase in the bloodsugar, which returns to normal only after several days. The increase in sugar is derived from the liver, since it does not arise when the sugar is removed. Adrenaline causes marked asphyxia in Scyllium.

J. H. BIRKINSHAW.

Mitogenetic radiation of blood. A. POTOZKY and I. ZOGLINE (Biochem. Z., 1929, 211, 352-361; cf. Gurwitsch and Gurwitsch, A., 1928, 914).—The mitogenetic sources of radiation of mammalian blood (in contrast to frog's blood) are of two kinds, namely, glycolysis and oxidation of polypeptides. The failure of the mitogenetic radiation of blood taken during fasting is due to an inhibition of these two enzymic processes. J. H. BIRKINSHAW.

Blood coagulation. XX. Inhibition of blood coagulation by heparin. XXI. Blood coagulation and the fluorine content of the blood. B. STUBER and K. LANG (Biochem. Z., 1929, 212, 16-21, 96-101).—XX. By checking glycolysis heparin retards the coagulation of blood, very greatly *in vitro*, less so *in vivo*. Intravenously injected it has no effect on the sodium, calcium, chlorine, or albumin content of the blood.

XXI. In Kiel the blood of residents contains fluorine and it coagulates more slowly than the blood of residents of Freiburg-im-Breisgau, which contains none. Kiel drinking water contains six times as much fluorine as does Freiburg drinking water, and fluorine is found in Kiel milk but not in Freiburg milk. Since, also, the blood of hæmophilics and of animals such as geese (of which the blood coagulates very slowly) has a high fluorine content, it is concluded that increase in the time of coagulation is due to the presence of fluorine. W. MCCARTNEY.

Effect of alkali on oleate and taurocholate hæmolysis. K. C. SEN, A. C. ROY, and N. N. MITRA (J. Indian Chem. Soc., 1929, 6, 489—494).— The hæmolysis of sheep's erythrocytes by mixtures of potassium oleate and sodium hydroxide varies considerably with experimental conditions. When the oleate concentration is comparatively small the hæmolytic action of the oleate-alkali mixture may exceed that of the pure cleate. With medium concentrations of oleate the action of the mixture is invariably lower than that of the pure oleate, whilst with high concentrations of oleate the reverse action takes place. The time-dilution curves often show abnormalities. The time interval after which the alkali is added to the oleate-corpuscle mixture is important; the results obtained are similar to those using normal serum (this vol., 951). It is suggested that the acceleration of hæmolysis by normal serum is due to its alkali content. A retardation or acceleration of taurocholate hæmolysis is observed, using small amounts of sodium hydroxide, depending on whether the alkali is added to the corpuscles before or after the hæmolyser. H. BURTON.

Cold-hæmagglutinin. N. YU (Acta Med. Keijo, 1928, 11, 23—34).—Cold-agglutinin is the hæmagglutinin which reacts strongly at 0° but is not active at 37°. Rabbit serum contains the auto-cold-hæmagglutinin, but horse serum contains little. The substance is not injured by heating for 30 min. at 60° , is slightly affected at 65° , and is destroyed at 70° . CHEMICAL ABSTRACTS.

Content of complement compounds in dialysed guinea-pig serum. Content of complement compounds in the fractions obtained by precipitation with ammonium sulphate. Content of complement compounds in guinea-pig serum fractionated by passing carbon dioxide through it. Action of alcohol on the complement of guinea-pig serum. H. TOKUNAGA (Acta Schol. Mcd. Univ. Imp. Kyoto, 1928, **11**, 273-286, 287-296, 297-312, 313-317). CHEMICAL ABSTRACTS.

Separation of cystine from histidine. Basic amino-acids of human hair. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1929, 83, 523-534).-Cystine is more or less completely precipitated by the metallic precipitants (particularly silver) customarily employed for the isolation of histidine and must therefore be expected to occur as an impurity in preparations of the latter. Cystine, however, whether partly racemised or not, forms an insoluble copper compound, and can be conveniently separated from histidine by boiling the solution with cupric hydroxide. Human hair was hydrolysed with hydrochloric acid, the greater part of the cystine was removed by direct crystallisation, and the basic amino-acids were then determined by the author's method, utilising the above-mentioned copper compound to remove the rest of the cystine; there was then found histidine 0.5%, arginine 8.0%, and lysine 2.5%; the cystine amounted to 16.5%.

C. R. HARINGTON. Composition of flesh of the Italian buffalo. C. COLELLA and M. NAPOLI (Arch. Sci. biol., 1928, 13, 235-240; Chem. Zentr., 1929, i, 2197).—The following values are recorded: water 75.96, dry residue 24.04, ash 1.15, total nitrogen 3.49, fatty acids 1.11, total phosphorus 0.186%. A. A. ELDRIDGE.

Occurrence of anserine and carnosine in reptiles and birds. F. A. HOPPE-SEYLER, W. LINNEWEH, and F. LINNEWEH (Z. physiol. Chem., 1929, 184, 276-280).—Varying amounts of anserine

(this vol., 944) have been isolated by the method previously described (*loc. cit.*) from the muscletissue of the hen, turkey, pigeon, crow, and crocodile. Carnosine is probably not present in the muscle of the goose and the above birds, but it has been isolated from the boa constrictor (anserine not present) and the crocodile. Anserine nitrate has m. p. 220-222° (cf. *loc. cit.*). H. BURTON.

Generative glands. I. The substance $C_6H_{13}O_5N_6Me_3$ in testes. S. FRANKEL and G. MONASTERIO (Biochem. Z., 1929, 212, 61-65).-Fresh tissue from testes is boiled with water containing acetic acid, and the extract is concentrated in a vacuum and mixed with warm alcohol. After precipitation of gelatinous material the solution is again evaporated in a vacuum until crystallisation begins. The substance thus obtained has the formula $C_6H_{13}O_5N_6Me_3$, the methyl groups being attached to nitrogen. Recrystallised from water, in which it is easily soluble, it has m. p. 279°, and $[\alpha]_1^m + 173 \cdot 91°$. It is a neutral substance sparingly soluble in alcohol. It does not reduce ammoniacal silver solutions and it fails to react with bromine or with many other commonly used reagents. Fermentations by yeast are not accelerated by the substance. W. MCCARTNEY.

Composition of bone skeletal substance. R. KLEMENT (Z. physiol. Chem., 1929, 184, 132—142).— The inorganic portion of bone consists principally of basic calcium phosphate, $3Ca(PO_4)_2, Ca(OH)_2$, with smaller amounts of calcium carbonate and alkali hydrogen carbonate. J. H. BIRKINSHAW.

Cholesterol content of mucous membrane of human large intestine. M. BÜRGER and H. D. OETER (Z. physiol. Chem., 1929, 184, 257-260; cf. this vol., 839).—The cholesterol content of the mucous membrane is approximately 1.8% and is about three times as great as the amount in the total intestinal wall (cf. *loc. cit.*). Sterol esters are not detectable. H. BURTON.

Determination of cholesterol in gall-stones. M. AIAZZI-MANCINI (Biochem. Terap. sperim., 1929, 16, 9—13; Chem. Zentr., 1929, i, 1974).—The cholesterol is extracted with ether and purified, or is acetylated, and the acid liberated by hydrolysis is titrated. A. A. ELDRIDGE.

Unsaponifiable substance. II. Unsaponifiable substance, cholesterol, and fatty acid in incubated eggs. E. IGARASHI (Sei-i-kwai Med. J., 1929, 48, No. 1, 19—32).—Fertilised eggs of a particular hen contain large quantities of unsaponifiable matter and more cholesterol than unfertilised eggs, in which the two quantities are nearly equal. The amino-acid contents are similar.

CHEMICAL ABSTRACTS.

Arachidonic acid in lipins of thyroid, adrenal, and spleen. J. B. BROWN (J. Biol. Chem., 1929, 83, 777-782).—The fatty acids obtained by hydrolysis of the lipins from thyroid, adrenal, and spleen were converted into their methyl esters and the latter were brominated. The amount of arachidonic acid, calculated from the weight of ether-insoluble bromide, was 0.4, 5.5, and 4.0% of the total fatty acids, respectively. Arachidonic acid is the only highly unsaturated acid to occur in the lipins of the abovementioned organs. C. R. HARINGTON.

A new highly unsaturated fatty acid in the lipins of the brain. J. B. BROWN (J. Biol. Chem., 1929, 83, 783—791).—Lipin from ox brain was hydrolysed and the fatty acid fraction esterified with methyl alcohol; 10% of the original material was recovered as cholesterol, and 24% as methyl esters which could be distilled from 185° to 280°. Determination of the ether-insoluble bromides indicated 11.5-18.4% of highly unsaturated acids. Reduction of the ether-insoluble bromides yielded a mixture of methyl arachidonate and (possibly) methyl tetracosapentenoate. C. R. HARINGTON.

Cerebroside [content of brain]. P. KIMMEL-STIEL (Biochem. Z., 1929, 212, 359—362).—During the first 2 hrs. after removal of brain from an animal, decomposition of cerebroside occurs with liberation of reducing substances, and this must be taken into account in determining the cerebroside content in terms of the galactose liberated on hydrolysis.

P. W. CLUTTERBUCK. Influence of formalin fixation on lipins of central nervous system. A. WEIL (J. Biol. Chem., 1929, 83, 601-609).—Preservation of central nervous tissue in a 4% aqueous solution of formaldehyde results in a progressive hydrolysis of the phosphatides, the phosphoric acid passing into the fixing fluid; the cerebrosides are scarcely affected, so that formalinfixed central nervous tissue contains an abnormally high proportion of the latter compounds; this fact accounts for certain histological phenomena hitherto unexplained. C, R. HARINGTON.

Effect of formalin fixation of organs on the extractability of the lipins. P. KIMMELSTIEL (Z. physiol. Chem., 1929, 184, 143—146; cf. Mladenovic and Lieb, this vol., 591).—In alcohol-ether extracts of organs fixed with formalin, low values for phosphatides but normal values for cholesterol and cerebrosides are obtained. J. H. BIRKINSHAW.

Protein-sulphuric acid ester in the liver. S. FRÄNKEL and G. MONASTERIO (Biochem. Z., 1929, 211, 264–269).—In an investigation of the substances in ox liver of value in pernicious anæmia a peptidesulphuric acid ester was isolated. It contains the tyrosine group and a carbohydrate group, but no tryptophan, phenylalanine, or cystine.

J. H. BIRKINSHAW. Protein-sulphuric acid ester from the anterior lobe of the pituitary. S. FRANKEL and G. MONA-STERIO (Biochem. Z., 1929, 211, 259—263).—A substance resembling a globulin isolated from the anterior lobe of the pituitary was found to be the sulphuric acid ester of a protein. It contains tyrosine and phenylalanine groups, but no tryptophan or cystine. It promotes the clotting of blood.

J. H. BIRKINSHAW.

Mol. wt. of myoprotein, determined by Du Noüy's surface-tension method. L. DE CARO (Atti R. Accad. Lincei, 1929, [vi], 9, 1025-1029).--Before reaching the corresponding dynamic value, the surface tension of very faintly alkaline aqueous solutions of the myoprotein of the dog exhibits three characteristic minima at the dilutions 1:37,000, 1:55,000, and 1:80,000. If these correspond with the formation of unimolecular layers of different orientations, the dimensions of the molecular parallelepiped are $225\cdot6$, $151\cdot7$, and $104\cdot3$ Å., respectively, the volume of the molecule is $3,569,513 \times 10^{-24}$ c.c., its mass $2,644,084 \times 10^{-24}$ g., and the mol. wt. 16×10^5 ; for the anhydrous myoprotein this value for the mol. wt. is probably much too high. The proportion of myoprotein in muscle is sufficient to cover approximately the whole surface of the myofibrils with a unimolecular layer. T. H. POPE.

Occurrence of preformed methylguanidine in muscle tissue. S. A. KOMAROV (Biochem. Z., 1929, 211, 326-351).—Since in the isolation of methylguanidine by the silver-baryta and the mercuric acetate methods the possibility of oxidation of creatine to methylguanidine is not excluded, the presence of the base in muscle was shown by isolation as the pure picrate by way of the picrolonate from the phosphotungstate fraction of ox-muscle extract. The best yield of the base was 0.06 g. per kg. of fresh muscle. This represents only a portion of that actually present. J. H. BIRKINSHAW.

Occurrence of muscle-adenylic acid and hexosemonophosphoric acid (lactacidogen) in the heart. K. POHLE (Z. physiol. Chem., 1929, 184, 261—264).—Muscle-adenylic acid (Embden and Schmidt, this vol., 591) has been isolated in 0.02%yield from the muscle-tissue of ox heart by the method of Embden and Zimmermann (A., 1927, 749). The hexosemonophosphoric acid present has a smaller rotatory power ($[\alpha]_{25}^{25}$ +19.77°) than that isolated from rabbit muscle (Embden and Zimmermann, *loc. cit.*). H. BURTON.

Distribution of argininephosphoric acid in the musculature of invertebrates. O. MEYERHOF (Arch. Sci. biol., 1928, 12, 536-548; Chem. Zentr., 1929, i, 2203).—The argininephosphoric acid, which is present in the musculature of various invertebrates, is decomposed by muscular activity; its distribution in the invertebrates examined is recorded.

A. A. ELDRIDGE.

Sodium, potassium, calcium, and magnesium in muscle fluid and its ultra-filtrate. G. QUAGLIARIELLO (Atti R. Accad. Lincei, 1929, [vi], 9, 1029—1030).—None of the sodium, about one third of the potassium, and about two fifths of the calcium and magnesium of the muscle fluid of the dog are present in a form incapable of ultra-filtration. T. H. POPE.

Lipolytic action of saliva. B. KOLDAJEV and PIKUL (Biochem. Z., 1929, **212**, 53—60).—Saliva from fistulæ in the parotid and submaxillary glands of dogs has a distinct lipolytic effect on tri- and mono-butyrin and on olive oil, that from the parotid gland having a more powerful effect than that from the submaxillary. The lipolytic action is independent of the kind of food consumed and of the amount of amylolytic enzyme in the saliva, is most vigorous at $p_{\rm H}$ 7.6—7.8, and is destroyed when the saliva is boiled. Saliva from fistulæ of the parotid glands of dogs to which dilute hydrochloric acid has been administered does not hydrolyse fats. W. MCCARTNEY.

Theories of hydrochloric acid formation in the stomach. F. HOLLANDER (J. Amer. Inst. Homeopathy, 1929, 22, 311-321) .- The gastric juice of an accessory stomach (Pavlov pouch) in dogs had $p_{\rm H} 0.90 \pm 0.01$ (0.55% HCl); identical values for free hydrochloric acid and total acidity were obtained. Neutral chlorides were absent. Hydrolysis of sodium chloride occurred when similar isotonic solutions were separated by the skin of a recently killed frog. The results are discussed from the physiological point of view. CHEMICAL ABSTRACTS.

Composition of "histamine-gastric juice." L. GRIMBERT and P. FLEURY (Compt. rend. Soc. Biol., 1929, 100, 312-314; Chem. Zentr., 1929, i, 2203).—After administration of histamine the gastric juice contains an abnormal amount of protein, the average nitrogen content being 14.4%.

A. A. ELDRIDGE.

Determination of fat-splitting [activity] in duodenal juice. A. SCHMIDT-OTT and K. H. STAUDER (Deut. Arch. klin. Med., 1929, 163, 156-160; Chem. Zentr., 1929, i, 2453-2454).-The lipase value of fasting duodenal juice is practically constant (by Willstatter's method, 0.64 unit); in non-pathological cases the value is greater during the digestive process than during fasting. Bile has an activating effect. In pathological conditions the results are A. A. ELDRIDGE. variable.

Determination of urinary sugar with fermentation tubes. H. MELCHER (Apoth.-Ztg., 1929, 44, 305; Chem. Zentr., 1929, i, 1974).—The mercury (5 g.) and yeast (0.3 g.) used with Lohnstein's tube are accurately weighed, urine containing more than 1% of sugar is diluted with normal urine, and fermentation is allowed to proceed for 9-10 hrs. at 37° (cf. Will, Apoth.-Ztg., 1929, 44, 56).

A. A. ELDRIDGE. Urine adialysate. H. PRIBRAM (Biochem. Z., 1929, 211, 412-419).—Intravenous injection of the non-dialysable portion of human urine into rabbits produced miosis and a state of sleep. J. H. BIRKINSHAW.

Nitrification of urine treated with clay and the loss of free nitrogen which it undergoes. W. GRODZINSKA (Bull. Acad. Polonaise, 1928, B, 251-299).-Urine which has been treated with clay, either by being filtered several times through it or by keeping in contact with it, allows the growth of nitrifying bacteria, with consequent nitrification of part of the nitrogen it contains, at higher concentrations than does untreated urine, which at 10% concentration exhibits an antiseptic action. The degree of nitrification depends on the concentration of the urine. Cow's urine whether treated with clay or not readily gives up part of its nitrogen, this process being independent of nitrification. W. O. KERMACK.

Influence of feeding on certain acids in the fæces of infants. I. Comparison of effects of human and modified cow's milk on the excretion of volatile acids. J. R. GERSTLEY, C. C. WANG, R. E. BOYDEN, and A. A. WOOD (Amer. J. Dis. Children, 1928, 35, 580-589).—The total titratable acidity and volatile acid content of the fæces remain

constant during feeding with human milk, but wide variations follow the ingestion of cow's milk mixtures. CHEMICAL ABSTRACTS.

Amino-acid content of the blood in health and disease. E. G. SCHMIDT (Arch. Int. Med., 1929, 44, 351-361).-The amino-acid content of the blood determined by Folin's colorimetric method employing sodium 3-naphthaquinone-4-sulphonate does not alter significantly from the normal in patients suffering from a considerable variety of diseases, including renal diseases, with the exception of leucæmia and acute vellow atrophy, in which cases it is considerably increased. It is also concluded from the literature that a rise in amino-acid content also takes place in polycythæmia vera, and in poisoning from hydrazine sulphate, "synthalin," chloroform, and phosphorus. W. O. KERMACK.

Cancer and blood-lactic acid. E. HAINTZ (Klin. Woch., 1929, 8, 546; Chem. Zentr., 1929, i, 2555).-In a case of cancer of the lower lip (male) the blood-lactic acid value was 17.5 mg. per 100 c.c., the normal value being 19 mg. per 100 c.c.

A. A. ELDRIDGE.

Lactic acid formation in tissue culture. F. DEMUTH and R. MEIER (Biochem. Z., 1929, 212, 399-418).-Hen fibroblasts (of cartilage and heart) and rat fibroblasts form considerably less lactic acid in proportion to their increase in growth than rat sarcoma and mouse carcinoma. In hen fibroblasts the quotient lactic acid (mg.)/size of culture (mm.²) is dependent on the velocity of growth and on the duration of the experiment. The more quickly a culture attains a given size, the smaller is the quotient. With equal velocity of growth the quotient increases with the duration of the experiment. With slowly growing fibroblasts and with rat sarcoma and mouse carcinoma the quantity of lactic acid is dependent on the size of the culture. P. W. CLUTTERBUCK.

Mitogenetic behaviour of blood from carcinomatous animals. L. GURWITSCH and S. SALKIND (Biochem. Z., 1929, 211, 362-372).-The blood of carcinomatous mice and men is found to lack mitogenetic power. In the case of mice this phenomenon belongs to the early symptoms of carcinoma. The enzymic processes on which the mitogenetic radiation depends are inhibited in J. H. BIRKINSHAW. carcinomatous blood.

Colloidal lead in cancer treatment. R. K. NEWMAN (J. Cancer Res. Comm. Univ. Sydney, 1929, 1, 106-113) .- A review. Blair Bell's method of preparing solutions of colloidal lead in the presence of gelatin and calcium chloride is considered the most satisfactory, and Wyard's failure to obtain results is attributed to the fact that his preparation was not truly colloidal. The effectiveness of a colloidal lead preparation appears to lie in its ability to initiate tumour regression. The only other preparation which has been successfully used is the colloidal lead orthophosphate of Ullman. P. G. MARSHALL.

Halibut tumour oil. E. D. KAMM (Rept. Lancs. Sea-Fish. Lab., 1928, 125-127) .- The oil separated from a lipoma found in the body-cavity of a halibut (Hippoglossus vulgaris) was mobile and of a pale yellow colour. It had n_{11}^{20} 1.4750, iodine value 171.5, saponification equivalent 312.3, unsaponifiable material 0.4%, in which was a slight trace of sterol(s) precipitable by digitonin, but no squalene. An approximate analysis of the fatty acids (methyl ester fractionation) gave: saturated acids, C_{14} 0.13%, C_{16} 9.81%, C_{18} 5.2%; unsaturated acids, C_{16} , C_{18} , C_{20} , C_{22} (with respective average unsaturations of -2H, -2.5H, -3.2H, -10H), 5.09, 42.09, 25.93, and 10.71%, respectively. No trace of vitamin-A was found, and negative results were obtained with antimony and arsenic chloride colour tests. Small absorption bands were shown at λ_{max} 2705 and 2775 Å. and an inflexion at λ 2806 Å., indicating probably the presence of a small amount of ergosterol. E. LEWKOWITSCH.

Gymnema sylvestre in diabetes mellitus. R. N. CHOPRA, J. P. BOSE, and N. R. CHATTERJEE (Indian J. Med. Res., 1928, 16, 115—124).—Gymnemic acid, or an extract of the leaves of *G. sylvestre* (which contain a substance which hydrolyses sucrose, and an oxidase-like substance which acts on dextrose), when administered subcutaneously to rabbits, does not affect the blood-sugar. CHEMICAL ABSTRACTS.

Effect of uncooked starches on the bloodsugar of normal and of diabetic subjects. II. S. M. ROSENTHAL and E. E. ZIEGLER (Arch. Int. Med., 1929, 44, 344-350).—Uncooked starch may be administered in considerable quantities (50-75 g.) to normal or diabetic persons without appreciably increasing the blood-sugar. In the majority of cases, normal and diabetics, a slight fall in bloodsugar occurs within 1 hr. after administration of the starch. W. O. KERMACK.

Failure of a diabetic patient to utilise dried artichoke powder. L. E. WESTCOTT and E. C. WISE (Arch. Int. Med., 1929, 44, 362-367).—The carbohydrate tolerance of the patient was not increased by the administration of dried powdered artichoke; it appears therefore that this powder has no advantage over starch as a diabetic food.

W. O. KERMACK.

Effect of liver on the blood-sugar. H. BLOTNER and W. P. MURPHY (J. Amer. Med. Assoc., 1929, 92, 1332—1336).—Liver fractions effective in the treatment of pernicious anæmia do not affect the bloodsugar, whilst ineffective fractions behave similarly. Liver treatment in diabetes lowers the blood-sugar. CHEMICAL ABSTRACTS.

Pathological fat metabolism. II. Conditions in which colloidal silver restrains phosphorus fatty degeneration. C. CIACCO and G. TRIMARCHI (Boll. Soc. Ital. Biol. sper., 1928, 3, 106–108; Chem. Zentr., 1929, i, 2202).

Respiratory metabolism in infancy and childhood. VIII. Respiratory exchange in marasmus: basal metabolism. S. Z. LEVINE, J. R. WILSON, and G. GOTTSCHALL (Amer. J. Dis. Children, 1928, 35, 615-629). CHEMICAL ABSTRACTS.

Millon reaction of urine in mental diseases. H. LIEB and E. SCHADENDORFF (Z. physiol. Chem., 1929, 184, 108—110; cf. Scheiner, this vol., 465).— The crystalline substance from the urine of patients suffering from mental diseases isolated according to Schemer's method is sodium acetate. The Millon reaction is due to impurity. J. H. BIRKINSHAW.

Cerebrospinal fluid in myxcedema. W. O. THOMPSON, P. K. THOMPSON, E. SLIVEUS, and M. E. DAILEY (Arch. Int. Mcd., 1929, 44, 368—373).—In myxcedema the protein content of cerebrospinal fluid is high and is reduced after administration of thyroid. The ratio of chloride in the fluid to that in plasma is decreased by administration of thyroid to myxcedematous patients. W. O. KERMACK.

Effect of prolonged ultra-violet irradiation in experimental rickets. P. SCHULTZER (Biochem. Z., 1929, 211, 445—453).—Young rats fed on a rachitic diet for 23 weeks did not develop rickets when irradiated with ultra-violet light, although there was some osteoporosis. The treated rats grew better than the control animals.

J. H. BIRRINSHAW.

Calcium and magnesium metabolism in rickets. W. SCHULER (Monatsschr. Kinderheilk., 1928, 36, 25—41; Chem. Zentr., 1929, i, 2074).— In a 14 months old child recovering from rickets the average calcium retention was 0.523 g. CaO and the magnesium retention 0.229 g. MgO.

A. A. ELDRIDGE.

Effect of parenterally administered organic and inorganic phosphates in rickets. W. HEYMANN (Z. Kinderheilk., 1928, 45, 232—241; Chem. Zentr., 1929, i, 2074).—Of the phosphorus administered parenterally as sodium glycerophosphate, 50% is excreted as inorganic phosphate in the urine of normal infants, whereas up to 100% may be so excreted by rachitic infants. In neither case is disodium hydrogen phosphate retained. A. A. ELDRIDGE.

Disturbance of phosphate metabolism in rickets. II. Excretion of endogenous phosphate. III. Blood-phosphate curves of rachitic and non-rachitic infants after parenteral administration of organic and inorganic phosphate. W. HEYMANN (Z. Kinderheilk., 1928, 46, 575-583, 584-587; Chem. Zentr., 1929, i, 2074).—The inorganic phosphate content of body fluids is diminished in rickets, whilst the excretion of endogenous phosphorus in the urine is twice as great as normally. Increased hydrolysis of organic phosphates occurs in rickets. The blood-phosphate curve is abnormally flat in rickets; organic phosphate and disodium hydrogen phosphate gave similar results.

A. A. ELDRIDGE.

Proteins in blood-serum and in pathological serous fluids. C. ACHARD and A. ARCAND (Compt. rend., 1929, 189, 510—512).—Blood-serum contains more albumin, globulin, and myxoprotein than does the plasma of pathological serous fluids. It is concluded that the proteins of serous fluids are derived chiefly, although not exclusively, from the bloodserum. A. A. GOLDBERG.

Analysis of a preputial stone. G. SOIKA (Arch. Pharm., 1929, 267, 465-467).—The stone, which weighed 10.47 g., consisted of a hard core and a softer shell. The chief constituents were calcium and magnesium urates and calcium, magnesium, and magnesium ammonium phosphates. S. COFFEY.

Calcium content of muscular tissue during parathyroid tetany. H. H. DIXON, H. A. DAVEN-PORT, and S. W. RAWSON (J. Biol. Chem., 1929, 83, 737-739).-No difference was observed between the calcium content of the striated muscle of normal and of parathyroidectomised dogs. C. R. HABINGTON.

Muscle-phosphorus. III. Distribution of acid-soluble phosphorus compounds during parathyroid tetany. H. A. DAVENPORT, H. H. DIXON, and S. W. RAWSON (J. Biol. Chem., 1929, 83, 741-746).-No change was observed in the content or distribution of acid-soluble phosphorus in the striated muscle of dogs as the result of parathyroidectomy. C. R. HARINGTON.

Correlation of calcium metabolism, para-thyroid function, and chronic pulmonary tuberculosis. II. P. ELLMAN (Tubercle, 1929, 10, 257-266).-In pulmonary tuberculosis the serumcalcium varies within normal limits. Calcium retention is promoted by the administration of calcium or parathyroid extract over long periods.

CHEMICAL ABSTRACTS.

Course and duration of experimental uræmia and salt content of the brain cortex. E. KERPEL-FRONIUS and F. LEÖVEY (Arch. exp. Path. Pharm., 1929, 144, 372-380; cf. this vol., 345).-In experimental uræmia of rabbits brought about by ligation of the ureters, the sodium chloride in the grey substance of the brain is increased by 16.8% and in the white substance by 12.7%. The corresponding figures for residual nitrogen are 142% and 93%, respectively. Ingestion of sodium chloride or of carbamide accelerates death, but does not otherwise essentially alter the findings. W. O. KERMACK.

Colloidal gold for use in Lange's reaction. Use of electrodialysed water in preparation of gold sols. R. WERNICKE and F. MODERN (Anal. Asoc. Quim. Argentina, 1928, 16, 247-256).-In order to prepare gold sols for use in Lange's reaction (with cerebrospinal fluid), distilled water electrodialysed through parchment paper is employed with good results. Collodion membranes cannot be used. If dextrose is used as the reducing agent and the boiling of the alkaline solution is prolonged before addition of the gold salt, the sol obtained is less sensitive in Lange's reaction, but more sensitive to the addition of salts. R. K. CALLOW.

Ratio of urea-nitrogen to non-protein-nitrogen in the blood in normal pregnancy. W. DENIS, E. L. KING, and F. BRIGGS (Amer. J. Obstet. Gyn., 1929, 17, 386-391).-In normal pregnancy there is usually a slight decrease in the non-protein-nitrogen (a) and a large decrease in the urea-nitrogen (b) of the blood. During pregnancy the ratio b:a diminishes, whilst after parturition it increases.

CHEMICAL ABSTRACTS.

Effect of age on the rate of dying of skeletal muscles. C. F. FAILEY and G. VAN WAGENEN (Z. physiol. Chem., 1929, 184, 209-218).-The rate at which the power of synthesising hexosediphosphoric acid is lost by the muscle of the rat and calf on keeping depends on the animal's age, being greater the younger is the animal. The rate falls more quickly at 18° than at 0°. J. H. BIRKINSHAW.

Combination of carbon dioxide with muscle: its heat of neutralisation and its dissociation curve. G. STELLA (J. Physiol., 1929, 58, 49-66) .--The neutralisation of 1 mol. of carbonic acid in resting or fatigued muscle gives rise to 9400 g.-cal., 75% of which must be due to neutralisation of muscleprotein and 25% to inorganic buffers. The carbon dioxide dissociation curves of frog's muscle indicate that the interior of muscle is more acid than blood at the same pressure of carbon dioxide. Between $p_{\rm H}$ 7 and 8, the hydrogen-ion concentration of muscle is proportional to pressure of carbon dioxide.

E. BOYLAND.

Is there a definite relationship between lactic acid- and ammonia-formation in muscle contraction ? M. LEHNARTZ (Z. physiol. Chem., 1929, 184, 183-195).-The ammonia formed by isotonic, auxotonic, or isometric stimulation of frog's gastroenemius depends on the interval between successive stimuli. For 100 stimuli at 4 sec. intervals no ammonia is formed; the amount is considerable with 1 sec. intervals. The lactic acid/ammonia ratio varies from 9-22 with 1 sec. intervals to infinity at the J. H. BIRKINSHAW. longer intervals.

Elimination of lactic acid in athletics. I. SNAPPER and A. GRÜNBAUM (Deut. med. Woch., 1929, 55, 181; Chem. Zentr., 1929, i, 1710).-In athletics lactic acid (1-2 g.) is almost always eliminated. In short exercise it is excreted in the urine, whilst in long-continued exercise it is eliminated chiefly through the skin. During rest the sweat has a high lactic acid (0.25-0.3%) and a low chlorine (up to 0.16%) concentration; during work the corresponding values are 0.1% and 0.27-3.5%. A. A. ELDRIDGE.

Excretion of acids in the urine during work. III. Excretion of phosphorus during work of varying intensity. M. S. RESNITSCHENKO and N. P. KOSMIN (Biochem. Z., 1929, 212, 87-95).-Short periods of vigorous muscular activity cause the inorganic phosphorus content and the acidity of human urine to increase. Exceptions to this rule may occur, and the volume of the urine, the nature of the activity, the experimental conditions, and the state of combination of the phosphorus must be taken into account when the metabolic changes are W. MCCARTNEY. being considered.

Physico-chemical phenomena during regeneration. III. Buffering [effects] in the tissues of regenerating limbs of axolotl. N. OKUNEFF (Biochem. Z., 1929, 212, 1-15) .- In the regenerating limbs of axolotl the buffering power of the tissues as compared with that of normal tissues increases during the first three weeks, and during this period, in addition to the normal maximum of buffering power (p_{Π} between 6 and 7), a second maximum $(p_{\rm H} \text{ between 5 and 6})$ is encountered. The acidosis of the first two days of the regeneration period is accompanied by increase of buffering power; there follows, in the period between the two waves of acidosis (third and fourth days), a slow increase of buffering power, and this reaches its maximum at the time of the second wave of acidosis (fifth to eighth day). Normal values are attained at the BIOCHEMISTRY.

end of the third week after amputation, *i.e.*, one week before the return of normal reaction. The increase in buffering power in the initial stages of regeneration may be due either to local accumulation of decomposition products of proteins or of cartilage or to increase in the adsorptive powers of the tissues. W. MCCARTNEY.

Source of lactic acid in the central nervous system. H. JUNGMANN and P. KIMMELSTIEL (Biochem. Z., 1929, 212, 347-358).-The changes of lactic acid, inorganic phosphorus, cerebroside, and glycogen contents of freshly-removed brain are investigated after keeping for 1 min. and 1 hr., respectively. A few seconds after removal the lactic acid content of brain increases very rapidly and the glycogen content decreases and then remains constant. When the lactic acid and glycogen values have attained their maximal and minimal values the cerebroside content decreases slowly. The inorganic phosphorus increases considerably. The lactic acid of brain arises most probably from glycogen and not from ccrebroside-galactose, since the breakdown of the latter is too slow to account for the rapid formation of lactic acid. P. W. CLUTTERBUCK.

Carbohydrate exchange and degradation of the dextrose molecule. E. SCHNEIDER and E. WIDMANN (Klin! Woch., 1929, 8, 536-541; Chem. Zentr., 1929, i, 2204).—After intravenous injection of dextrose into dogs the blood-sugar rises to a smaller extent than is anticipated; the lactic acid remains constant. Injection of dihydroxyacetone affects neither the blood-sugar nor the lactic acid, presumably being converted immediately into carbon dioxide and water. Lactic acid is first converted into the alkali salt and then transformed into glycogen, which is stored by the liver; repeated injection of small quantities of lactic acid gradually raises the bloodsugar, the storing capacity of the liver for glycogen being overstepped. Intravenous injection of a small quantity of methylglyoxal does not affect the bloodsugar or lactic acid; repeated doses gradually raise the blood-sugar and lactic acid and diminish the alkali reserve. A. A. ELDRIDGE.

Physiological efficiency of lactose, lactic acid, and sucrose, and the influence of these substances on resorption of nutrients by ruminants. W. VOLTZ and H. JANTZON (Z. Tierzücht., 1929, 11, 13 pp.; Chem. Zentr., 1929, i, 2440).—The physiological efficiency for ruminants was 77.7, 62.0, and 62.5%, respectively, of the energy content.

A. A. ELDRIDGE.

Resorption of pentoses in nutrition, and the assimilation of pentoses. A. ROCHE (Compt. rend. Soc. Biol., 1929, 99, 1973—1976; Chem. Zentr., 1929, i, 1709).—In experiments with animals, xylose and arabinose passed into the blood, but pentose was not detected in the blood after administration of xylan or araban. A. A. ELDRIDGE.

Furan compounds derived from sugars. III. Fate of acetoxymethylfurfurylideneacetic acid in animal organism. J. KARASHIMA (Z. physiol. Chem., 1929, 184, 265—267; cf. A., 1927, 1107).— Administration of sodium ω -acetoxymethylfurfurylideneacetate (this vol., 450) to the dog leads to the excretion in the urine of 16.9-29.6% of 5-carboxy-2-furfurylideneacetic acid +H₂O, decomp. 235°, m. p. (anhydrous) 277°; with the rabbit or hen 11.2-32.1% of hydroxymethylfurfurylideneacetic acid (loc. cit.) is excreted. H. BURTON.

Metamorphosis of insects. J. HALLER (Acta Biol. Exp., Warsaw, 1928, 2, 225-315).-The percentage compositions of Deilephila euphorbia larva, pupæ, and imagos are respectively as follows : water 79, 75, 68.25; fats 3.5, 3.83, 6.10; nitrogen 1.54, 2.21, 3.34; protein 9.375, 13.30, 19.7; chitin 0.676, 1.30, 3.13; ash 0.90, 1.175, 1.90, and non-nitrogenous extractives 6.55, 5.435, 0.92. The total energy used up during metamorphosis is a fairly constant quantity per unit body-weight of different insects and amounts per unit body-weight of different insects and since the state in this case to 1833 g.-cal., of which 32.5% is supplied by fat and 67.5% by other substances. During the stage of pupation, 44.8% of the energy requirements are supplied by fat, 13% by protein, and 42.2% by carbohydrates, whilst in the pupa stage only 21.6%is given by fat, 41.3% by proteins, and 37.1% by carbohydrates. The average percentage composition of the mature butterflies on death from inanition is : water 55.7, fat 4.5, nitrogen 4.96, protein 28.1, chitin 7.5, ash 3.08, and non-nitrogenous extractives 1.04. During the period of inanition, 964 g.-cal. are used, of which 499 are supplied by fat, 435 by protein, and 26 by carbohydrates. R. TRUSZKOWSKI.

Chemical composition of the hæmolymph of Deilephila euphorbiæ larvæ. A. MOKŁOWSKA (Acta Biol. Exp., Warsaw, 1929, 3, 241-253).-The following values in mg. per 100 c.c. are found for the hæmolymph $(d \ 1.031)$ of the larva of *D. euphorbia*: total nitrogen 1180, protein-nitrogen 825, non-proteinnitrogen 355, amino-acid-nitrogen 170, uric acid 14, dextrose (?) 127, calcium 41.25, magnesium 43.5, iron 5.8, ionic chlorine 48.6, phosphate-phosphorus 12.05. The amino-acid content is practically independent of conditions of nutrition. In the pupal stage, the protein-nitrogen content remains constant, whilst the uric acid content falls almost to zero, pointing to a sharp decrease in protein metabolism. The protein content of the hæmolymph of fully grown larvæ falls to one half after 4-5 days of inanition, whilst amino-acid, uric acid, and non-protein-nitrogen contents remain constant. These differences between artificial and physiological inanition are confirmed by refractometric measurements, very similar readings being obtained in artificial inanition and during moults (46 and 37) and in fed larvæ and pupæ (61.5 R. TRUSZKOWSKI. and 65).

Normal standard of the gastric functions in Egyptians. A. BEY, M. GAAFAR, and H. ERFAN (J. Egyptian Med. Assoc., 1929, 12, 80-88).—In experiments on 100 normal individuals (19-26 years), using the fractional test-meal devised by Rehfuss, the volume of resting gastric juice varied between 3 and 200 c.c. (average 59 c.c.). The average free acidity was equivalent to about 12 c.c. of 0.1Nsodium hydroxide, whilst the average for total acidity was 30 c.c. No case of achlorhydria was observed. Hypertonic stomachs have a normal acidity, whilst hypotonic stomachs have an acidity which is either normal or increased. P. G. MARSHALL.

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Production of ammonia from amino-acids in surviving organs. A. BORNSTEIN and H. F. ROESE (Biochem. Z., 1929, 212, 127—136).—When surviving livers, lungs, or limbs from fasting dogs are perfused with blood from fasting dogs the ammonia content of the blood either does not change or falls slightly. If glycine is added to the blood the ammonia content increases, very greatly in the liver (up to 100 times normal), slightly in the lungs, and not at all in the limbs. Alanine, asparagine, and aspartic acid act like glycine, but leucine has no effect, at any rate in the liver. W. MCCARTNEY.

Decomposition of proteins and amino-acids of food as measured by the ammonia [content] of the blood. A. BORNSTEIN (Biochem. Z., 1929, 212, 137—148; cf. preceding abstract).—Intravenous administration of glycine, alanine, or asparagine to fasting dogs is followed, in a few minutes, by considerable increase in the ammonia content of their blood. The urea content of the blood also increases, but after a longer period. Oral administration of the amino-acids leads to the same results, but after much longer periods (about 1 hr.). Similarly, feeding with raw fat-free meat causes increase in the ammonia and urea contents of the blood after 4—5 hrs.

W. MCCARTNEY.

Exclusive meat diet. Effect on carbohydrate tolerance. Effect on blood constituents. E. TOLSTOI (J. Biol. Chem., 1929, 83, 747-752, 753-758).—After 1 year on an exclusive meat diet the carbohydrate tolerance was diminished, but returned to normal after 2-4 weeks' resumption of a normal diet. No significant changes in the composition of the blood were observed except for an increase in the fats and cholesterol; these abnormalities also rapidly disappeared on return to normal food.

C. R. HARINGTON. Variation of glutathione in isolated organs. I. S. VISCO and S. CASTAGNA (Boll. Soc. Ital. Biol. sperim., 1928, 3, 282—283; Chem. Zentr., 1929, i, 2203).—In the isolated liver the glutathione content is diminished during the first 12 hrs.; this is followed by an increase over the original value and a final diminution. A. A. ELDRIDGE.

Crystalline tripeptide from living cells. M. DIXOU and N. U. MELDRUM (Nature, 1929, 124, 512).—Unlike impure glutathione, pure glutathione does not catalyse the oxidation of the proteins of thermostable muscle preparations. The crystalline reduced form is auto-oxidisable owing to the presence of traces of catalytic metals, but is rendered stable towards oxygen by treatment with kaolin owing to removal of the metals by adsorption.

A. A. ELDRIDGE.

Rôle of the liver in the metabolism of purine substances. PAROULEK (Acta Med. Scand., 1928, 68, 79—95; Chem. Zentr., 1929, i, 1836).—When minced liver is kept at a constant temperature for several hours the uric acid content increases. If uric acid is added, a considerable part of it disappears. Autolysis of minced liver leads to an increase in ammonia, non-protein-nitrogen, and hydrogen-ion concentration. A. A. ELDRIDGE.

Changes in the amount of carotinoids in hen's eggs during incubation. H. VON EULER and H. HELLSTRÖM (Biochem. Z., 1929, 211, 252-258). —The colours (measured in a tintometer) produced when antimony trichloride acts on chloroform solutions of xanthophyll and of lutein are very similar. Spectroscopic examination shows that the amount of lutein in the yolks of incubating eggs changes only slightly between the sixth and the twelfth days, and up to the twelfth day there is little or no consumption of lutein. Lutein exhibits specific growth-promoting properties. W. MCCARTNEY.

Metabolism of the hexone bases and the origin of the purine nucleus in the development of hen's eggs. G. Russo (Arch. Sci. biol., 1927, 10, 128-137; Chem. Zentr., 1929, i, 2200).—During the embryonic development of the hen there is a marked diminution of arginine and histidine. Since only a fraction of this serves for the production of guanidine and creatine, the remainder is regarded as the precursor of pyrimidine and purine, both of which increase during the process. A. A. ELDRIDGE.

Embryonic metabolism. IV. Basic aminoacids of the hen's egg during development. H. O. CALVERY (J. Biol. Chem., 1929, 83, 649-656). —The arginine content of the hen's egg remains constant throughout the whole period of development. Determinations of histidine and lysine gave inconsistent results, but there is a general tendency for both these bases to diminish in amount during development. Arginine therefore is not a precursor of purines, whilst histidine may be.

C. R. HARINGTON.

Embryochemical investigations with the injection method. I. Uric acid formation in the hen's embryo. M. TOMITA and M. TAKAHASHI (Z. physiol. Chem., 1929, 184, 272—275).—Injection of solutions of carbamide, lactic or tartronic acid into eggs and incubation for 14—19 days causes an increase in the amount of uric acid in the allantoic liquid and embryo. A mixture of carbamide and tartronic acid gives under parallel conditions a greatly increased amount of uric acid. The changes involved are probably : lactic acid <u>oxidation</u> tartronic acid <u>carbamide</u> dialuric acid <u>carbamide</u> uric acid (cf. Wiener, Hofmeister's Beiträge, 1902, 2, 42). H. BURTON.

"Internal cycle" of iodide in man. F. BERGER (Klin. Woch., 1929, 8, 118—119; Chem. Zentr., 1929, i, 2075).—In 1.5 hrs. after the injection of alkali iodide 90.6 mg. of iodine were excreted by the kidneys, and 32.6 mg. through the gastric glands. The quotient 100I'/Cl' is for the blood 1.36, stomach 7.83, and urine 9.65—48.6. A. A. ELDRIDGE.

Behaviour of iodine in body fluids after ingestion of alkali iodides and iodoproteins. G. BARKAN and W. LEISTNER (Klin. Woch., 1929, 8, 117—118; Chem. Zentr., 1929, i, 2075).—After administration of alkali iodide intravenously or perorally, "organic" iodine was not found in the blood or urine. Feeding of rabbits and dogs with iodised protein is followed by the appearance of some "organic" iodine in the blood and particularly in the urine. A. A. ELDRIDGE.

Radium content of some foodstuffs. E. BURKSER, M. SCHAPIRO, and K. BRONSTEIN (Biochem. Z., 1929, 211, 323-325) .-- The radium content of various animal and vegetable foodstuffs, determined by the emanometer, was in all cases of the order 10-150%. J. H. BIRKINSHAW.

Boundary surface energy and activity in a protoplasm model. V. EFIMOV and P. REHBINDER (Biochem. Z., 1929, 211, 154-162).-Using Nirenstein's mixture (Pfluger's Archiv, 1920, 179, 233) and the apparatus of Rehbinder (J. Biol. Med. exp., Moscow, 1927, 4, 939) the boundary surface tensions of aqueous solutions of dyes (neutral-red, toluidineblue, crystal-violet, formyl-violet, trypan-blue, fuchsin-S) have been measured. The boundary surface activities of these dyes at the interface Nirenstein's mixture-aqueous solution run parallel to their coefficients of distribution in the two phases, *i.e.*, to their staining powers. The limit of adsorption is reached at low concentrations and corresponds with complete saturation of the interface with oriented molecules of the dye. The results of parallel experiments showed that many dyes which exhibit great boundary surface activity at the interface aqueous solution-oil are almost or quite inactive at the surface aqueous solution-air. The biological consequences W. MCCARTNEY. of this are emphasised.

Swelling of [cod] fish skins in solutions of inorganic and organic acids. J. C. KERNOT and J. KNAGGS (with Appendix by M. KAYE) (Proc. Roy. Soc., 1929, B, 105, 280-297).-Measurements have been made of the degree of swelling undergone by cod skins (in the fresh or dried condition or after treatment with sodium hydroxide solution and sulphur dioxide solution), when immersed in dilute solutions of hydrochloric acid, sodium hydroxide, or organic acids. In solutions of hydrochloric acid or sodium hydroxide dry or treated skins swell more than wet, whatever the concentration of the acid or alkali, but dry skins swell more than treated skins between $p_{\rm H}$ 3.5 and 8.0. With dry skins the percentage swelling is practically constant in the range $p_{\rm ff}$ 1-11.0. With all skins, below $p_{\rm B}$ 4.0 and above $p_{\rm H}$ 11.0, considerable quantities of nitrogen go into solution. With fatty acids (acetic, propionic, and butyric) the swelling of wet and treated fish skins increases with the mol. wt. of the acids, the swelling of the treated being three to four times as great as that of the wet skins at the same $p_{\rm H}$. In the case of dry skins, the swelling is greater with acetic acid and least with butyric acid. The following acids have also been employed : mono-, di-, and tri-chloroacetic, lactic, pyruvic, oxalic, tartaric, citric, and salicylic. It has not been possible to explain completely the complicated results observed. Cod skin differs histologically from mammalian skin in that the fibres are not interwoven, but are arranged in layers, the fibres of one layer being at right angles to those of the next and being held together by an occasional fibre. The structure is irreversibly altered by drying and by treatment with alkali followed by sulphur dioxide. Cod skin contains very small amounts of elastic fibre tissue and no fatty material. W. O. KERMACK.

Biometry of calcium, inorganic phosphorus, cholesterol, and lipoid phosphorus in the blood of rabbits. III. Influence of various types of light environment. A. R. HARNES (J. Exp. Med., 1929, 49, 859-882).-After an accommodation period following exposure to light, the effects may be grouped in the order : ultra-violet light, Cooper-Hewitt lamp light or daylight, total darkness.

CHEMICAL ABSTRACTS.

Changes in the ion content of organs [of animals] exposed to irradiation and to the climate of high altitudes. A. LOEWY and L. PINCUSSEN (Biochem. Z., 1929, 212, 22-34).-Rats, some of which were kept under normal conditions, some exposed to ultra-violet irradiation, and some living in air kept at a pressure of 0.5 atm. were allowed to grow under otherwise identical conditions in Berlin and in Davos. Determinations of the potassium, calcium, and magnesium contents of their livers, lungs, hearts, kidneys, and hind-leg bones showed that irradiation, and still more reduced atmospheric pressure, cause absolute increase in the calcium contents and absolute decrease in the potassium contents of these parts of the body. The favourable effects, in disease, of irradiation and of the climate of high altitudes may be related to these changes.

W. MCCARTNEY.

Stimulation of metabolism by alcohol. L. D. SEAGER, D. J. VERDA, and W. E. BURGE (Science, 1929, 69, 383-384).-Direct determinations with goldfish show that ethyl alcohol stimulates sugar metabolism to nearly the same extent as do fat and protein. L. S. THEOBALD.

Adrenaline content of blood during narcosis. H. SCHLOSSMANN and H. MÜGGE (Arch. exp. Path. Pharm., 1929, 144, 133-141).-The increase of adrenaline in the peripheral arterial blood which occurs during anæsthesia (chloroform, ether, or acetylene) is due to liberation of adrenaline by the adrenals, not by direct action of the anæsthetic, but as the result of the lowering of the blood-pressure.

W. O. KERMACK.

Detection of veronal in urine. A. KÜHN (Deut. Z. ges. gerichtl. Med., 1929, 13, 115-123; Chem. Zentr., 1929, i, 2562-2563).-The urine (100 c.c.) is acidified with sulphuric acid and treated with potassium permanganate solution until the precipitate no longer redissolves. After 5-10 min. the precipitate is removed with hydrogen peroxide, and the liquid is then evaporated in a vacuum to 20-30 c.c. After repeated (mechanical) extraction with ether the united ethereal extracts are evaporated and the veronal is purified with animal charcoal followed by sublimation. The yield is 85-95%. A. A. ELDRIDGE.

Oxidation of dextrose in phloridzin glycosuria. W. M. BOOTHBY, C. M. WILHEMJ, and H. E. C. WILSON (J. Biol. Chem., 1929, 83, 657-679).-Complete phloridzinisation raises the basal metabolic rate of dogs as much as 90% above the normal level; administration of dextrose to dogs in this condition causes a decrease in the heat production and an increase in the respiratory quotient corresponding with oxidation of 18-25% of the ingested sugar. Since the dextrose accounted for by oxidation and excretion was not in excess of that administered, no evidence was obtained of the conversion of fat into C. R. HARINGTON. sugar.

Effect of small doses of phloridzin on the excretion of nitrogen. P. THOMAS, M. MALEVA-NAIA, and R. IMAS (Compt. rend. Soc. Biol., 1929, 100, 375-377; Chem. Zentr., 1929, i, 2202).-In addition to excretion of sugar, phloridzin causes an increase in the total nitrogen, particularly ureanitrogen, dependent on the dose. There is also increased elimination of creatinine. Protein degradation is of greater importance than glycosuria in phloridzin poisoning. A. A. ELDRIDCE.

Ammonium chloride acidosis. H. DENNIG, D. B. DILL, and I. H. TALBOTT (Arch. exp. Path. Pharm., 1929, 144, 297-310).-When ammonium chloride is administered to a normal person marked acidosis is present during the first 5-7 days, and an excess of sodium and potassium is excreted in the urine, most of the acid being neutralised by these bases. By the second week the production of ammonia by the body has increased so that the hydrogen-ion concentration of the blood is again normal and the excessive secretion of sodium and potassium ceases. It therefore appears that during acidosis the production of ammonia increases only slowly and reaches its maximum in 5-7 days. In the same way when the administration of ammonium chloride is stopped after 2 weeks, the excess production of ammonia by the body does not cease at once, but drops only gradually, so that alkalosis is produced, which gradually disappears.

W. O. KERMACK.

Action of caffeine on membranes and proteins. H. BRUHL (Biochem. Z., 1929, 212, 291-317).-Filtration experiments using collodion membranes on which protein had been deposited showed a reversible increase of permeability in presence of caffeine and also on displacement of the $p_{\rm H}$ to the isoelectric point of the protein, the former being due to changes of the degree of dispersion of the protein covering the pore walls and the latter to changes of the degree of swelling. Caffeine increases the degree of dispersion of such colloids and increases the solubility of amino-acids, probably on account of the formation of complex compounds having a greater solubility, the complex formation being demonstrable by compensation dialysis in the case of proteins and by f.-p. determinations in the case of amino-acids. The diuretic effect of caffeine is explained in terms of the results of these filtration experiments. P. W. CLUTTERBUCK.

Alteration of the basal metabolism on imbibing chicory and chicory-coffee beverages. S. SCHIMMEL, M. DYE, and C. S. ROBINSON (Z. Unters. Lebensm., 1929, 57, 576-584),-Addition of chicory to coffee does not hinder extraction of caffeine and caffetannic acid from the latter. Ingestion of 200 c.c. of water at 50-60° has no effect on the basal metabolism; 200 c.c. of coffee infusion prepared from 20 g. of coffee containing 0.25 g. of caffeine raised the basal metabolism about 6%. Addition of 10% of chicory did not alter this effect, and an infusion of 10 g. of chicory in 200 c.c. of water had no effect by itself. W. J. BOYD.

Action of pilocarpine on the blood-sugar. J. SZEP (Arch. exp. Path. Pharm., 1929, 144, 277-282).-The blood-sugar of a rabbit (2-3 kg.) falls after the subcutaneous administration of 1 mg. of pilocarpine, whilst if larger doses are administered a rise in blood-sugar precedes a fall. When 1.5 mg. of pilocarpine is administered through a stomach tube a rise in blood-sugar takes place, but when fed without a tube the blood-sugar falls. The rise is the result of irritation by the tube. W. O. KERMACK.

Metabolism of heart-muscle. I. Heartglycogen. M. HAENDEL and A. MUNILLA (Biochem. Z., 1929, 212, 35-46).-The glycogen contents of the heart-muscle, skeletal muscle, and liver and the sugar content of the blood of dogs receiving intraperitoneal injections of dextrose to which digitalis, ouabain, caffeine, camphor, calcium chloride, potassium chloride, adrenaline, insulin, or thyroxine had been added have been determined. Digitalis caused considerable reduction in heart-glycogen, but not in muscle- or liver-glycogen. Ouabain, in large doses, caused mobilisation of glycogen generally, in small ones, reduction in heart- and liver-glycogen. Large doses of camphor reduced all the glycogen values, but small doses had no effect on the heart-glycogen. The action of caffeine was similar to that of camphor, but the former acted more powerfully on muscle-glycogen. Potassium chloride had no effect on heart-glycogen but reduced muscle- and liver-glycogen. Calcium chloride greatly reduced heart-glycogen and, in large doses, muscle- and liver-glycogen also. Adrenaline had a general mobilising effect on the glycogen. The heart-glycogen was not affected by insulin. Thyroxine had little effect on the glycogen content of the heart, but it reduced the muscle- and liver-glycogen. Ouabain, camphor, and calcium chloride caused hyperglycæmia. Potassium chloride caused hypoglycæmia. W. MCCARTNEY.

Action of antimony compounds on the adrenals. R. N. CHOPRA, J. C. GUPTA, and S. G. CHOUDHURY (Indian J. Med. Res., 1928, 16, 441-446).-With rabbits intravenous injection of organic antimony compounds causes an increase in the adrenaline content of the adrenals. CHEMICAL ABSTRACTS.

Cobalt and blood. KLARA WALTNER and KARL WALTNER (Klin. Woch., 1929, 8, 313; Chem. Zentr., 1929, i, 2069) .- A toxicological study of the effect on the blood of rats of ingestion or injection of cobalt A. A. ELDRIDGE. salts.

Preparation of colloidal lead. D. GANASSINI (Arch. Ist. Biochim. Ital., 1929, 1, 3-12).-Colloidal lead stabilised by means of sodium thiosulphate exhibits perfect colloidal properties and very gradual maturation. It undergoes partial sulphuration, which becomes very slow in presence of gelatin, affects less than one fourth of the metal in a month, and is not complete after 6 months. The preparation is more stable than any other yet described. The traces of lead sulphide formed on ageing are not toxic and do not diminish the biological activity. T. H. POPE.

Colloidal lead in toxicological tests. G. LORENZINI (Arch. Ist. Biochim. Ital., 1929, 1, 13— 26).—Ganassini's colloidal lead (preceding abstract) is harmless in therapeutic doses, rabbits tolerating doses sixtyfold those given to human beings. Even in the colloidal state, lead hydroxide is toxic in very small doses, and exerts an intense hæmolytic effect and an irritant action on the kidneys. Without addition of sodium thiosulphate, colloidal lead is appreciably toxic, especially towards the elements of the blood. T. H. POPE.

Pharmacological action of stabilised colloidal lead. I. SIMON (Arch. Ist. Biochim. Ital., 1929, 1, 47-68).—In contact with the tissues of the organism, colloidal lead passes into the granular metallic state. This occurs in subcutaneous, peritoneal, and pulmonary tissues, in the anterior chamber of the eye, and, when the preparation is injected intravenously, in all the internal organs with the exception of the central nervous system. With intravenous injection, the fixation of the colloidal lead may be facilitated by retarding local circulation. Sabbatani's results (A., 1914, i, 356, 357) are confirmed. T. H. POPE.

Therapy of mercury poisoning. E. HESSE (Arch. exp. Path. Pharm., 1929, 144, 327-330; cf. A., 1927, 73; also Haskell and Forbes, this vol., 470).—In confirmation of previous results, the power of strontium thioacetate to counteract the effects of the administration of mercuric chloride to mice, rabbits, rats, guinea-pigs, and cats has been demonstrated. W. O. KERMACK.

Pathological fat formation. II. The problem of lecithin. G. ROSENFELD (Biochem. Z., 1929, 211, 270—275).—Hens suffering from phosphorus poisoning, when fasting, receiving dextrose alone, or dextrose and caseinogen, all showed about the same percentage of lecithin in the total extract of the liver as did unpoisoned fasting controls.

J. H. BIRKINSHAW. Malt-amylase. VII. Adsorption of amylase from malt extracts by kaolin and elution [of the amylase therefrom]. T. SABALITSCHKA and R. WEIDLICH (Biochem. Z., 1929, 211, 229—238; cf. this vol., 721).—The amylase in aqueous malt extracts, the dry substance of which contains 96% of maltose, is completely adsorbed by kaolin at $p_{\rm H}$ 4·2 (19·5 g. of malt require 2·5 g. of kaolin). The adsorbed amylase is removed by elution with sodium phosphate solution at $p_{\rm H}$ 7·6 and remains active. Aqueous solution of carbon dioxide at $p_{\rm H}$ 5·9 does not remove the adsorbed amylase. As a result of this adsorption and elution process the activity of the dry substance from the malt extracts is increased fifteen to seventeen times and the loss of amylase is 38-40%. W. MCCARTNEY.

Invertase from honey. P. E. PAPADAKIS (J. Biol. Chem., 1929, 83, 561-568).—The acceleration of the hydrolysis of sucrose by invertase from honey in presence of β -glucose (cf. Nelson and Sottery, A., 1925, i, 104) was not observed in presence of *d*- and *l*-arabinose and of xylose. Mercuric chloride inhibits the hydrolysis when the $p_{\rm H}$ is between 5.7 and 4.23; this inhibition, as well as the much slighter one

caused by α -methylglucoside, may be neutralised by addition of β -glucose. C. R. HARINGTON.

Fission of lecithins. H. PAAL (Biochem. Z., 1929, 211, 244—251).—Lecithin from egg-yolk is completely hydrolysed in 6 hrs. by boiling alcoholic solution of potassium hydroxide. In alcoholic solution it is hydrolysed slightly by lipase from pig pancreas at 30° and still less at lower temperatures, but when in water or glycerol emulsions it is not attacked by the enzyme even when activators are present and the hydrogen-ion concentration is most favourable for attack. On exposure to air it is gradually oxidised. W. MCCARTNEY.

Glyceric acid monophosphoric acid. M. Vogr (Biochem. Z., 1929, 211, 1—16; cf. Neuberg and others, A., 1928, 1215).—The properties of salts of glyceric acid monophosphoric acid have been investigated and a crystalline *barium* salt, $C_3H_5O_7PBa, H_2O_7PBa, H_2O_7PB, H_2O_7PB$

Thermolability of glycerophosphodehydrogenase. N. ALWALL (Skand. Arch. Physiol., 1929, 55, 100—103; Chem. Zentr., 1929, i, 2543—2544).— Muscle-glycerophosphodehydrogenase does not differ from succinodehydrogenase in thermolability. If muscle-fumarase is first destroyed by heat, the succinodehydrogenase contains less nitrogen and is less active than Anderssen's product.

A. A. ELDRIDGE. Correlation of synthesis and breakdown of active substances of muscle. E. LEHNARTZ (Z. physiol. Chem., 1929, 184, 1—55).—The enzymic synthesis of phosphocreatine is considerable in muscle press-juice at suitable $p_{\rm H}$ (about 7). At the same time at alkaline reaction there is a breakdown of lactacidogen and pyrophosphoric acid. The adenylic acid ion is found to be specific for the synthesis of pyrophosphoric acid. Under its influence the synthesis takes place more quickly than any other ionically-stimulated chemical process in muscle. This ionic action is a property of muscle-adenylic acid only. Inosic acid and adenosine are quite inactive. J. H. BIRKINSHAW.

Lactic acid fermentation of warm-blooded tissue. II. Effect of potassium and calcium ions on the existence of the extra-fermentation of salivary gland and liver tissue of rats. O. ROSENTHAL (Biochem. Z., 1929, 211, 295—322; cf. this vol., 722).—An extension of previous experiments on the extra-fermentation of the liver to that of the salivary glands. The action of potassium and calcium ions is substantially the same for both types of tissue. The extra-fermentation is greatly restricted by the absence of calcium and potassium during the aërobic period. The cation effect is reversible. Both cations have a favourable effect on the extra-fermentation, and differences of degree only between liver and submaxillary are found in the effect of the cations, indicating that the mechanism is the same in both cases. J. H. BIRKINSHAW.

Formation and isolation of methylglyoxal in glycolysis by animal enzyme. M. Vogr (Biochem. Z., 1929, 211, 17–39).—Methylglyoxal is formed during the glycolysis of animal organs and (assuming that 1 mol. of hexose gives 2 mols. of keto-aldehyde) yields of 17.9-27.4% are obtained. In the case of alcohol-ether preparations of liver and kidney of pigs and of extracts of liver, kidney, and muscle of pigs and rabbits, the best conditions for producing good yields of methylglyoxal have been determined. Methylglyoxal accumulates only if coenzyme is absent or not present in large amounts. Hexoscdiphosphate is a suitable substrate for the production of methylglyoxal, but none was obtained from dihydroxyacetone or from glyceraldehyde.

W. MCCARTNEY.

Glycolytic power of various organs and its dependence on co-enzyme content. H. KRAUT and E. BUMM (Z. physiol. Chem., 1929, 184, 196— 204).—The addition of co-enzyme from rat sarcoma to mouse carcinoma and to brain, spleen, kidney, and muscle of rats and human blood causes an increase in glycolysis. In carcinoma tissue the glycolysis is not increased beyond the ordinary maximum, but the value in the case of the brain reaches double the normal. The co-enzyme can be almost completely washed out of the kidney and spleen.

J. H. BIRKINSHAW. Rennin coagulation. Influence of hydrogen ions on the separation of casein by the action of electrolytes. C. LA ROTONDA (Annali Chim. Appl., 1929, 19, 310-328).-The effect of addition of various inorganic and organic acids on the coagulation of de-fatted milk by three different salt solutions of similar reaction has been investigated. The milk was de-fatted either immediately after milking or after being heated. The results show either that the coagulation of the casein does not occur at the isoelectric point or that the isoelectric point for case in is not $p_{\rm H}$ 4.7-4.6. The process thus depends, not merely on the degree of acidity, but also on the nature of the acid present. T. H. POPE.

Non-specificity of proteolytic organ-enzymes. X. UTKINA-LJUBOVZOVA and O. STEPPUHN (Biochem. Z., 1929, **211**, 426–444).—The liver, thyroid, kidneys, lungs, heart, brain, muscle, spleen, erythrocytes, and leucocytes of the ox and rabbit's liver contain three proteolytic enzymes with optima at $p_{\rm H}$ 3.4, 5.4, and 7.4. These enzymes are identical whatever their source and non-specific in their action. J. H. BIRKINSHAW.

Action of pepsin-hydrochloric acid after trypsin-kinase. K. FELIX and A. LANG (Z. physiol. Chem., 1929, 184, 205—208).—By subjecting a trypsin-kinase digestion of oxyhæmoglobin at various stages of hydrolysis to the action of pepsinhydrochloric acid no increase in the linkings hydrolysable by pepsin is observed. From the beginning the trypsin acts on the "pepsin linkings."

J. H. BIRKINSHAW.

The $p_{\rm R}$ optimum in the action of trypsin on fibrin. H. J. VONK and A. HEYN (Z. physiol. Chem., 1929, 184, 169—182).—The optimum $p_{\rm R}$ for the action of trypsin on fibrin is 11.3, in accordance with Ringer's results. This optimum is not displaced when the time of action is increased. There is a second small optimum at $p_{\rm R}$ 8.

J. H. BIRKINSHAW.

Plant proteases. XIV. Proteases of higher plants. O. AMBROS and A. HARTENECK (Z. physiol. Chem., 1929, 184, 93—107; cf. this vol., 606).—The action of hydrocyanic acid on various plant proteinases was examined after removal of the peptidases by adsorption. All the proteinases belong to the papain type, activated by hydrocyanic acid. According to the distribution of the proteinase and the dipeptidase in the plant a complex activated or inhibited by hydrocyanic acid predominates.

J. H. BIRKINSHAW.

Specificity of animal proteases. XVII. Proteinase and carboxypolypeptidase from pan-creas. E. WALDSCHMIDT-LEITZ and A. PURR (Ber., 1929, 62, [B], 2217-2226).-Pancreas trypsin is not homogeneous, but consists of a proteinase and a polypeptidase termed carboxypolypeptidase. The separation of the two enzymes in their natural mixtures depends on the choice of adsorbent and the hydrogen-ion concentration of the solution. In an acid medium, both enzymes are absorbed only to a slight extent by aluminium hydroxide C_7 , whereas in neutral solution the carboxypolypeptidase is mainly adsorbed. Complete separation of the tryptic enzyme mixture is thus readily effected. Proteinase and carboxypolypeptidase are specifically activated by enterokinase, which does not change in activity towards the two enzymes after protracted purification. The action towards the enzymes differs. Proteinase, free from activator, is inactive towards all substrates investigated, whereas carboxypolypeptidase under similar conditions is able to hydrolyse a series of substances. The actions of activator-free carboxypolypeptidase are identical with those of "non-activated pancreas trypsin." As far as the degradation of complex substrates such as protamines is concerned, the activator causes an extension of the range of specificity and not simply an increase in the rate of action. The action of proteinase is confined to the fission of actual proteins, for example, caseinogen, histone, and the protamines, whereas that of carboxypolypeptidase includes the hydrolysis of polypeptides of definite composition, acylated aminoacid, and peptides and protamines. The action of carboxypolypeptidase is greatly influenced by the degree of ionisation of the free carboxyl group in the substrates, which is increased by the introduction of acid residues in amino-acids and peptides or of definite amino-acid residues, for example, tyrosine. A configurative influence of the amino-acid containing the free carboxyl group is also observed. The hydrolysis of certain substrates, such as protamines, by proteinase and carboxypolypeptidase does not denote an identity in enzyme action. In the case of clupeine it is found that the individual enzyme actions are independent from one another and consequent.

1338

H. WREN.

Specificity of peptidases. III. Affinity measurements on animal dipeptidase. E. WALDSCHMIDT-LEITZ and G. VON SCHUCKMANN (Z. physiol. Chem., 1929, 184, 56—68; cf. A., 1928, 672).—The dissociation of enzyme-substrate complex for dipeptidase from pig's intestine on glycyltyrosine is smallest at $p_{\rm H}$ 7.8 (the maximum of activity— $p_{\rm H}$ curve). The form of this curve is determined by the position of the equilibrium between enzyme and substrate. The dissociation constants of dipeptidase from intestine, pancreas, and spleen all have the value 0.0026, indicating a close relationship of the chemically active groups.

J. H. BIRKINSHAW.

Hydrolysis of glycylglycine, alanylglycine, and leucylglycine by intestinal and malt peptidases. K. LINDERSTRØM-LANG and M. SATO (Z. physiol. Chem., 1929, **184**, 83—92).—Of the two peptidases from intestinal erepsin, one (optimum $p_{\rm H}$ 7·3) hydrolyses alanylglycine about forty times as fast as the other (optimum $p_{\rm H}$ 8·1). Malt also contains two distinct enzymes. One (optimum $p_{\rm H}$ 7·8) contained in proteinase-free peptidase is inactive to glycylglycine and the other (optimum $p_{\rm H}$ 8·6) from the glycerol extract is active towards glycylglycine, alanylglycine, and leucylglycine, also to leucylglycylglycine. J. H. BIRKINSHAW.

Influence of hydrogen-ion concentration on enzymes. IV. Cause of the erepsin-decomposing action of acids. K. HISHIKAWA (Exp. J. Digestive Dis., 1928, 3, 167—177).—In 0.25N—N-acid erepsin is completely decomposed in 1 hr., independently of the degree of dissociation of the acid; with more dilute acid, the velocity of decomposition is parallel to the degree of dissociation. The resistance of erepsin to acids is greatest at $p_{\rm H}$ 5.5—6.8.

CHEMICAL ABSTRACTS. Specificity of enzymic fission of dipeptides. H. von EULER, S. MYRBACK, and K. MYRBACK (Ber., 1929, 62, [B], 2194—2199).—Extract from germinated barley hydrolyses leucylglycine about 15—20 times as rapidly and alanylglycine about 8 times as rapidly as glycylglycine. The relationship differs markedly from that observed with other extracts of germinated seeds and other animal organs. Hydrolysis of leucylglycine is restricted 3 times as strongly by leucine as by glycine and very markedly by glycylglycine. H. WREN.

Physiological selection of enzymes by alcohol. L. SEMICHON (Ann. Inst. Pasteur., 1929, 43, 1210– 1218).—Only one of the four groups of micro-organisms of the ripe grape, namely, Saccharomyces ellipsoideus, can increase the concentration of alcohol in sterile grape juice above 5% and thrive in concentrations up to 14% of alcohol. To effect continuous fermentation alcohol to a concentration of 4% should be added to the must which has been previously treated with sulphur dioxide in order to kill the bacteria, when a selection of the ferments takes place exclusively in favour of *S. ellipsoideus*. Similar results have been obtained when solid media containing alcohol are inoculated. C. C. N. VASS.

Manometric determination of gas in fermentations. A. L. RAYMOND (J. Biol. Chem., 1929,

83; 611-618).—A manometric apparatus for the determination of gas formed in fermentations is described. C. R. HARINGTON.

Fermentation products. IV. Relation of the acetyl group to fermentation. T. HIGASI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 627-639).-Attention is directed to the fact that many products of fermentation contain the acetyl group. A colorimetric (nitroprusside) method for the qualitative detection of the acetyl group is given.

A. A. GOLDBERG.

Effect of various preparations on growth of baker's and brewer's yeasts. R. J. WILLIAMS, M. E. WARNER, and R. R. ROEHM (J. Amer. Chem. Soc., 1929, 51, 2764-2773) .- Six strains of yeast (three baker's and three brewer's) are compared in their behaviour towards " α - and β -bios" (Eddy and Kerr, Proc. Soc. Exp. Biol. Med., 1928, **25**, 340), " bios I " (inositol) (Eastcott, A., 1928, 1056), and the preparation (A) previously described (Williams, Wilson, and von der Ahe, A., 1927, 592). The various yeasts grow at different rates and it is found that addition of yeast extract to the authors' synthetic medium stimulates growth, maximum crops being obtained when the largest amounts of extract are added. A short growth period (18 hrs.) is better than a long one (48 hrs.) for quantitative measurements. Adsorption of A on fuller's earth gives two fractions, (B) adsorbed, (C) unadsorbed. When B is used in conjunction with C growth in two cases is stimulated very markedly by very small doses of B. In absence of C little effect is shown by B. With C and " α - and β -bios " no appreciable increase in growth is observed, and the action of B is not supplemented by either " α -" or " β -bios." Inositol, in the doses used, has little effect on the growth of any of the yeasts in absence or presence of B, and Eastcott's conclusion (loc. cit.) that " bios I " and inositol are identical does not appear justified. H. BURTON.

Separation of nitrogen during yeast fermentations. N. N. IVANOV and F. A. KRUPKINA (Biochem. Z., 1929, 212, 255—266).—In short fermentations of sugar solutions with pure cultures of Saccharomyces cerevisiæ, apiculatus, Pastorianus, and Ludwigii, nitrogen passes into solution as a result of decomposition of yeast protein. The process of nitrogen separation is bound up with that of fermentation, since in presence of unfermentable sugar (S. Ludwigii and maltose) no such separation of nitrogen occurs, and it must be distinguished from the smaller nitrogen liberation obtained during autolysis of yeast in water. P. W. CLUTTERBUCK.

Sulphite fermentation. F. POLAK (Biochem, Z., 1929, 212, 363—398).—The effect on the yield of glycerol and aldehyde and on the rate of fermentation, of variations in the medium, saturation with carbon dioxide, and variations in the rate of increase of sulphite concentration is investigated. The most suitable medium for sulphite fermentation (18% of sulphite) contains 1% of potassium phosphate, 1% of magnesium sulphate, 0.5% of animonium sulphate, and 0.5% of calcium carbonate, the yeast sowing being 8% (all figures calculated on the sugar content). Using this medium, the same yeast can be employed for nine successive fermentations. With large amounts of ammonium sulphate, the yeast suffers injury and fermentation takes much longer. On the other hand, with a high sulphite concentration (54%) and saturation with carbon dioxide, a somewhat better yield of glycerol is obtained with higher concentrations of ammonium sulphate, *e.g.*, with 0.2% and 1.2% of ammonium sulphate the yields are 30.80 and 37.84%, respectively, but the time of fermentation is longer, and with still greater amounts of sulphate the yield falls away. Even when the most suitable conditions are chosen (*i.e.*, using calcium carbonate, small amounts of ammonium salts and gradual increase of sulphite concentration) it was not found possible to increase the yield of aldehyde above 17%. In the initial stages the aldehyde content is always equal to and the alcohol greater than the free carbon dioxide. The results favour the view that the sulphite fermentation is based on a coupled reaction. P. W. CLUTTERBUCK.

Behaviour of sodium glucosesulphite with yeast. C. NEUBERG (Biochem. Z., 1929, 212, 477-489).-The mechanism of sulphite fermentation by coupled reaction (see preceding abstract) is adversely criticised. Sodium glucosesulphite is unfermentable in all concentrations by either top or bottom yeast and it retards the fermentation of added hexose. If a quantity of base be added to sodium glucosesulphite, typical fermentation is obtained, the result being as if free sugar was formed and the liberated toxic hydrogen sulphite converted into the non-toxic neutral sulphite. If sodium glucosesulphite (2 mols.) is fermented along with sugar (1 mol.) and sodium hydrogen carbonate (2 mols.) the sulphur dioxide distributes itself between fixed and free sugar and the aldehyde formed is the same as from 3 mols. of sugar and 2 mols. of sodium sulphite. The fixation of aldehyde is a true fixation of a product of fermentation and is not due to the breakdown of an initially ation and is not due to the formed stable sugar sulphite. P. W. CLUTTERBUCK.

Production of coproporphyrin by yeast. H. FINK (Biochem. Z., 1929, 211, 65-130).-Experiments with two strains of yeast (Saccharomyces anamensis) which were propagated for more than a year in a medium and under conditions which led to the accumulation of coproporphyrin gave the following results. More than 30 generations were grown, but the great accumulation of porphyrin did not cause the death of the yeasts. During satisfactory growth and good fermentation the $p_{\rm H}$ falls from the neutral point to 4. The number of cells which give red fluorescence, measured in alternate generations, is proportional to the number of dead cells present. The glycogen content of the cells is high and is always accompanied by low protein con-tent. The respiratory properties and fermenting powers of the yeasts, compared with those of ordinary yeast, show that an alteration in the type of metabolism has taken place. Accompanying great accumulation of porphyrin there is a formation and disappearance of intensely red dyes in the production of which light seems to play a part. The dyes may be originally present as uncoloured substances which are subsequently transformed by the action of light. In all the yeasts, even in the oldest cultures, the spectrum of cytochrome is recognisable. In the neighbourhood of $p_{\rm B}$ 4 there is an isoelectric region for coproporphyrin and in this region its properties assume critical values. Most of the coproporphyrin (70-80%) of the yeastcells exists adsorbed on their surfaces and is easily removed without damage to the cells. The remainder exists within the cells. Conversely, yeast will remove coproporphyrin quantitatively by adsorption from very greatly diluted solutions. The porphyrin does not penetrate the living cells. W. McCARTNEY.

Physical and biological study of the dextrorotatory sterol isolated from beer yeast. R. FABRE and H. SIMONNET (J. Pharm. Chim., 1929, [viii], 10, 289-291).—See this vol., 809.

Co-zymase and vitamin-B. H. VON EULER and K. MYRBACK (Svensk Kem. Trdskr., 1929, 41, 209—211; cf. A., 1928, 1158).—From a co-zymase preparation (activity about 75,000) a barium salt (activity 58,000) of composition Ba 20.7, P 4.82, N 11.95, pentose 17.2%, corresponding approximately with the atomic ratios N: P: Ba=5:1:1, has been prepared. Both the activity and the composition of the salt are unchanged by reprecipitation from aqueous solution with alcohol and co-zymase of unchanged activity can be regenerated from it. Co-zymase is probably a nucleoside, and lowering of its activity runs parallel with fission of organic phosphorus from the preparations. It is very similar to but not identical with vitamin-B.

J. W. BAKER.

Co-zymase. XVI. Further isolation experiments. H. von EULER and K. MYRBĀCK (Z. physiol. Chem., 1929, 184, 163—168).—See preceding abstract.

Metabolic effects of mitogenetic rays. H. GESENIUS (Biochem. Z., 1929, 212, 240).—When cultures of *Saccharomyces ellipsoideus* are exposed to the action of mitogenetic irradiation the metabolism of the cells undergoes alterations.

W. MCCARTNEY.

Cytochrome. I. Reduction time of normal tissue and yeast. II. Reduction time of benignant and malignant tumour tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1929, 184, 246—256).—I. The tissue is suspended in isotonic sodium chloride solution and the cytochrome and hæmoglobin present are oxidised by shaking with air. The time necessary for the oxidised pigment to return to the reduced state is termed the reduction time. This varies with different normal tissues (rats) and depends also on various physical and chemical factors. The effects of temperature, hydrogen-ion concentration, and added reagents have been studied. With decrease in temperature the reduction time is prolonged (cf. Keilin, A., 1925, i, 1112). The $p_{\rm H}$ of the medium has little effect on the time so long as the buffer action of the tissue protein suffices; when this does not suffice a retardation is observed. With added urethanes (to testicle) and alcohols (to yeast), increase in the homologous series causes an increase in the reduction time. Heavy metals, arsenic, and potassium cyanide prolong the

reduction time; yeast extract counteracts the effect of arsenic, whilst glycine (causes acceleration alone) neutralises the poisoning effect of copper sulphate.

II. The reduction time of benignant and malignant tumour tissue is invariably longer than that of the normal tissue. The glutathione content of the normal or diseased tissue has no direct relationship to the reduction time. Addition of glycine causes a diminution in certain cases (ovarial and gastric) of carcinoma. H. BURTON.

Intracellular oxidising substances. W. LOELE (Arch. path. Anat. Physiol., 1926, 262, 39-60; 1927, 264, 809-827; Chem. Zentr., 1929, i, 2430).-A study of the α -naphthol, benzidine, and indophenol reactions with vegetable and animal cells.

A. A. ELDRIDGE.

Relation between oxidases, vital staining, post-mortal staining, and morphology of cells. W. LOELE (Arch. path. Anat. Physiol., 1927, 265, 827-843; Chem. Zentr., 1929, i, 2430).

A. A. ELDRIDGE.

Relation of oxidising substances in bacteria and yeasts to cellular oxidases. W. LOELE (Arch. path. Anat. Physiol., 1928, 267, 733-745; Chem. Zentr., 1929, i, 2430) .- Naphthol- and benzidineoxidases are found in yeasts; the appearance of the reaction is dependent on the nutrient medium and the age of the culture. Certain groups of bacteria give the oxidase reaction. A. A. ELDRIDGE.

Role of carbohydrates in biological oxidations and reductions. Experiments with pneumococcus. R. DUBOS (J. Exp. Med., 1929, 50, 143-160).-Washed cells of pneumococcus can reduce dyes and oxidised thiol compounds only in the presence of metabolites, such as dextrose. The reduction of 1 mol. of methylene-blue appears to require almost 1 mol. of dextrose. The reduction is accelerated by meat infusion. Those systems which can reduce methylene-blue are able to form peroxides.

E. BOYLAND.

Bacterial oxidation of compounds of the p-phenylenediamine series. S. ELLINGWORTH, J. M. McLEOD, and J. GORDON (J. Path. Bact., 1929, 32, 173-183).-The ease of bacterial oxidation of p-phenylenediamine derivatives increases with the number of methyl groups in the molecule. When oxygen is allowed access to bacterial colonies previously exposed to a solution of the diamine, the monomethyl compound is the least, and the tetracthyl CHEMICAL ABSTRACTS. compound the most, toxic.

Bacterial oxidation of phenanthrene. V. O. TAUSSON (Planta, Arch. wiss. Bot., 1928, 5, 239-273; Chem. Zentr., 1929, i, 2066).-Bacteria which can utilise phenanthrene as a source of carbon occur in the soil of oil-bearing districts. Bacillus phenanthrenicus bakiensis, B. gurikus, and Bacterium phenanthrenicum oxidise phenanthrene between $p_{\rm H}$ 4.0 and 8.7 without marked production of acid. Since all three varieties can utilise pyrocatechol, salicylic acid, saligenin, and quinic acid, two can utilise quinol, and one phenol, the reaction probably proceeds in the following stages : phenanthrene, saligenin, o-hydroxybenzaldehyde, salicylic acid, pyrocatechol.

A. A. ELDRIDGE.

Biochemical reactions of streptococci. G. J. HUCKER (Zentr. Bakt. Par., 1929, I, 111, 31-64; Chem. Zentr., 1929, i, 2545) .- Two groups of streptococci are differentiated. The first (aromatic) group, represented by S. Kefir, forms l-lactic acid and fairly large quantities of volatile acids; lactose is first hydrolysed. Lævulose is preferred to dextrose as a source of carbon. The second group, typified by S. lactis and S. pyogenes, forms d-lactic acid and comparatively small quantities of volatile acids. Streptococci from milk and milk products form acetic acid and traces of propionic and higher acids, whilst human pathogenic streptococci form acetic and probably formic acids. A. A. ELDRIDGE.

Production of carbon dioxide by streptococci. G. J. HUCKER (Zentr. Bakt. Par., 1929, II, 77, 145-150; Chem. Zentr., 1929, i, 2435).-With most of the streptococci examined the production of carbon dioxide was increased correspondingly with the peptone content of the nutrient medium, whilst addition of sugar did not affect it. Exceptions are recorded. A. A. ELDRIDGE.

Respiration of luminous bacteria and the effect of oxygen tension on oxygen consumption. C. S. SHOUP (J. Gen. Physiol., 1929, 13, 27-45).--Luminous bacteria suspended in *Limulus* scrum consume oxygen and produce carbon dioxide at a rate independent of the oxygen pressure provided that this is between 152 and (approx.) 22.8 mm. At a lower oxygen pressure the respiratory activity gradually decreases until at 2 mm. it is reduced to 50% and at this point luminescence becomes dim. Pure nitrogen stops respiratory activity and pure oxygen irreversibly inhibits oxygen consumption. The curve for rate of oxygen consumption with oxygen concentration agrees with the Langmuir equation expressing the amount of gas adsorbed in unimolecular layer at catalytic surfaces at various gas pressures. W. O. KERMACK.

Reducing intensity of luminous bacteria. E. N. HARVEY (J. Gen. Physiol., 1929, 13, 13-20) .---The oxidation-reduction potential of a suspension of B. Fischeri, a fluorescent bacterium, in 0.25M-phosphate buffer at $p_{\rm H}$ 7.6 has been investigated by observing its effects on a series of "Redox " indicators. All indicators used, with the exception of indigomonosulphonate, were ultimately reduced by the bacteria, the more positive quickly even in presence of air, the more negative ones slowly and after the luminescence had disappeared and the available oxygen was practically exhausted. Under anaerobic conditions the reduction potential may be placed at $r_{\rm H}$ 8—10, whilst under acrobic conditions it appears to be about $r_{\rm H}$ 18-20. Potassium ferricyanide does not cause the luminescence to disappear and this is taken to indicate that this strong oxidising agent does not penetrate into the bacteria. The disappearance of the fluorescence after the addition of small quantities of quinone indicators may be due either to the oxidation of a luciferin-like compound in the bacteria or to a toxic effect of the indicator.

W. O. KERMACK.

Fermentation of dextrose and xylose by nodule bacteria from lucerne, clover, pea, and soya bean. M. FOOTE, W. H. PETERSEN, and E. B. FRED (Soil Sci., 1929, 28, 249—256).—Cultures of *Rhizobium* meliloti, R. trifolii, R. leguminosarum, and R. japonicum grown in sugar media with chalk or basic slag produced greater sugar destruction than when grown in the absence of these substances. The rate of fermentation declined with increasing age of the cultures. The maximum number of organisms per culture usually developed about 10 days after inoculation. A. G. POLLARD.

Fixation of atmospheric nitrogen by *Phoma* radicis callunæ, and a new method for investigating nitrogen fixation by micro-organisms. W. N. JONES and M. L. SMITH (Brit. J. Exp. Biol., 1928, 6, 167—189).—*Calluna vulgaris* can utilise sufficient atmospheric nitrogen to prevent nitrogen starvation. An apparatus for studying the fixation of nitrogen by micro-organisms is described. The mycorrhizal fungus of *C. vulgaris*, when grown in a nitrogen-free medium, utilises more dextrose when molecular nitrogen is available.

CHEMICAL ABSTRACTS. Biological production of nitrite in organic media. E. RUNOW (Zentr. Bakt. Par., 1929, II, 77, 193—205; Chem. Zentr., 1929, i, 2435).—A strain of bacteria which, when grown on an organic medium with ammonium sulphate, forms nitrite has been isolated; the amount of nitrite produced depends on the presence of a nutrient medium containing carbon, on the quantity of ammonium sulphate, on the temperature, and on the aëration. Tyrosinase is present. A. A. ELDRIDGE.

Conditions of amine production by B. coli. G. ROSKE (Jahrb. Kinderheilk., 1928, 120, 186— 195; Chem. Zentr., 1929, i, 2435).—In dextrosebouillon, but not in peptone-bouillon unless acid, B. coli produced tyramine and histamine. Buffering with lactate diminishes the production of amine.

A. A. ELDRIDGE.

Lipins of tubercle bacilli. IV. Purified wax of tubercle bacilli. R. J. ANDERSON (J. Biol. Chem., 1929, 83, 505-522).—The crude wax obtained from tubercle bacilli (A., 1927, 1114) was purified by precipitation with methyl alcohol from its solution first in ether and then in toluene, yielding a substance with m. p. 200–205°. This material was subjected to exhaustive hydrolysis with alcoholic potassium hydroxide; at an early stage a substance separated which was soluble in water and, after hydrolysis by acid, reduced Fehling's solution. The other hydrolytic products were separated in the usual manner, yielding an unsaponifiable saturated sub-stance, having C 81.7%, H 13.64%, m. p. $57-58^{\circ}$, and possessing both acidic and alcoholic properties, which is regarded as possibly a mixture of higher alcohols and fatty acids, and a mixture of fatty acids containing palmitic, stearic, oleic, and cerotic acids together with a liquid unsaturated acid having $[\alpha]_{1}^{\infty}$ —1.65°, which is analogous to phthioic acid (this vol., 1108). When hydrolysed with alcoholic hydrochloric acid, the original wax yielded a watersoluble fraction containing glycerophosphoric acid and a mixture of reducing sugars giving pentose reactions. The original material is therefore regarded

as a complex phosphatide containing a large proportion of carbohydrate. C. R. HARINGTON.

Bacteria. XXIX. De-fatted residue of avian tubercle bacilli. A. G. RENFREW (J. Biol. Chem., 1929, 83, 569—577).—Avian tubercle bacilli were dried, pulverised, and de-fatted; the material was extracted with water and the filtrate yielded 0.35%of coagulable protein and 1.4% of carbohydrate together with an alcohol-insoluble fraction of undetermined nature. Extraction of the residue with dilute alkali and treatment of the extract with acetic acid yielded 2.9% of protein. The avian strain therefore differs from the human strain (cf. Coghill, A., 1926, 1277) chiefly in its lower content of carbohydrate and of alkali-soluble protein. Acid hydrolysis of the residue yielded further amounts of waxy material.

C. R. HARINGTON.

Tuberculin fractions prepared from nonprotein culture media. F. EBERSON and E. WOLFF (Amer. Rev. Tuberculosis, 1929, **19**, 327-349).—The preparation of clinical test material is described. Of the original tuberculin, 3:44% was insoluble in alcohol, 1:6% was insoluble and 0:86% soluble in ether.

CHEMICAL ABSTRACTS. Separation of invertase from cells. N. N. IVANOV and M. A. KUDRJAVZEVA (Biochem. Z., 1929, 212, 241-254).-Separation of invertase from Aspergillus niger is very small in acid medium and increases as the $p_{\rm H}$ approaches neutrality, decreasing on adding oxalic acid and increasing with calcium carbonate. It occurs both as a result of growth of the mould and to a greater extent as a result of autolytic processes which bring about decrease of the weight of the mycelium. Separation of the enzyme occurs when the mould is grown on peptone, starch, or glycogen, but occurs to the greatest extent on sucrose and inulin, and to the least on a mixture of dextrose and lævulose or on invert-sugar. The results favour the view that the hydrolysis of sucrose occurs on the surface P. W. CLUTTERBUCK. of the mycelial protoplasm.

Heart hormone. XI. L. HABERLANDT (Pflüger's Archiv, 1929, 221, 576—590; Chem. Zentr., 1929, i, 2197—2198).—A study of sensitivity.

A. A. ELDRIDGE.

Heart hormone. Active constituent of Haberlandt's frog's heart hormone. R. RIGLER (Pflüger's Archiv, 1929, 221, 509-525; Chem. Zentr., 1929, i, 2197).—The Haberlandt effect is caused by two distinct substances; one is potassium, and the other is an ether-soluble substance.

A. A. ELDRIDGE.

Assay of insulin. K. SARGIN (Arch. exp. Path. Pharm., 1929, 144, 173—189).—Methods for the biological assay of insulin are discussed and criticised. W. O. KERMACK.

Action of insulin on the free muscle-sugar of the normal and diabetic heart. E. W. H. CRUICK-SHANK and S. PROSAD (Indian J. Med. Res., 1928, 16, 473—477).—The addition of insulin to the normal heart reduces the free sugar. When the diabetic heart is treated with normal blood which contains insulin the effect in reducing the sugar is greater than the change due to merely perfusing the diabetic heart with normal blood. CHEMICAL ABSTRACTS. Regulation of carbohydrate metabolism. Renal excretion of insulin. A. PARTOS (Pflüger's Archiv, 1929, 221, 562—570; Chem. Zentr., 1929, i, 2437).—Experiments on rabbits and man show that insulin is a constituent of the urine, but is lacking in hunger, alimentary hyperglycæmia, and pancreas diabetes. Adrenaline glycosuria in fasting animals does not cause an increase in the production of insulin. A. A. ELDRIDGE.

Glycogen of the internal ear of the guinea-pig. VI. Changes due to the injection of insulin. VII. Post-mortem changes. H. TANAKA (Sci-i-Kwai Med. J., 1929, 47, No. 12, 1-11, 12-26).— The effect of insulin is identical with that on the glycogen of other organs. After death, the glycogen of the internal ear disappears almost completely within 30 min. CHEMICAL ABSTRACTS.

Tissue respiration. V. Effect of thyroxine, adrenaline, and insulin on the oxygen uptake of the surviving rat's diaphragm. G. PAASCH and H. REINWEIN (Biochem. Z., 1929, 211, 468— 474; cf. A., 1928, 1287).—No increase in the oxygen uptake of the surviving rat's diaphragm was caused by addition of thyroxine, adrenaline, or insulin.

J. H. BIRKINSHAW.

Presence, distribution, and mode of excretion of the thyroid secretion in experimental hyperthyroidism, and corresponding observations on adrenaline and other hormones. E. GIACOMINI (Boll. Soc. Ital. Biol. sperim., 1927, 2, 955—1001; Chem. Zentr., 1929, i, 2198).—With animals overfed with thyroid gland, thyroxine or a substance having a similar action can be detected in almost all organs, particularly the liver and bile; the substance is present in the urine. After adrenal feeding, adrenaline can be detected in the urine and bile.

A. A. ELDRIDGE. Method of action of the thyroid hormone. II. Serum-proteases. R. WEIL and M. LANDSBERG (Biochem. Z., 1929, 211, 144—153; cf. this vol., 725).—The method of Utkin-Ljubovzov (A., 1926, 648) for the determination of tryptase in serum is not quantitative and it was not found possible in this or other ways to detect an increase in the proteolytic enzymes in serum following administration of thyroxine. The results of investigations on the behaviour of enzymes in hyperthyroidism support the physicochemical theory of the action of the thyroid hormone. W. MCCABTNEY.

Relation of the pituitary to carbohydrate metabolism. A. K. PICKAT (J. Méd.-biol., 1927, 4, 40-62; Chem. Zentr., 1929, i, 917).—The pituitary secretion is considered to stimulate sugar metabolism. Pituitary deficiency is associated with a disturbance of the hormonal equilibrium. A. A. ELDRIDGE.

Purification of extracts containing the growthpromoting principle of the anterior pituitary. H. M. TEEL (Science, 1929, 69, 405-406).—The growth-promoting principle may be salted out by addition of anhydrous sodium sulphate to a neutralised alkaline extract of the glands at 35°. Attempts to fractionate further the globulin group of proteins in which the growth-promoter is precipitated resulted in a division of the substance between the fractions. L.S. THEOBALD.

Effect of extracts containing the growth principle of the anterior pituitary on the blood chemistry of dogs. H. M. TEEL and O. WATKINS Amer. J. Physiol., 1929, 89, 662—685).—The injection of these extracts reduced the non-protein-nitrogen of the blood. E. BOYLAND.

Melanophore hormone in the human pituitary. K. EHRHARDT (Münch. med. Woch., 1928, 76, 321; Chem. Zentr., 1929, i, 2548).—Except in certain pathological conditions, the human pituitary contains the melanophore hormone. A. A. ELDRIDGE.

Relationship between vitamin-A and carotinoids. H. von EULER, P. KARRER, and M. RYDBOM (Ber., 1929, 62, [B], 2445-2451).--Examination of the action of lycopin, bixin, capsanthin, α -crocetin, dihydro- α -crocetin, xanthophyll, di-iodocarotin, dihydroisonorbixin, dihydro- α -crocetin methyl ester, fucoxanthin, zeaxanthin, lutein, and tri-iodocarotin towards antimony chloride shows that the Carr-Price test (A., 1926, 870) is given by many carotinoids which do not promote growth and hence that the reaction is not generally applicable to the investigation of vitamin-A. The depth of colour is very greatly influenced by oxidation of the carotinoid and a sensitive method for the examination of carotinoid preparations may be founded on this observation.

Lycopin, bixin, capsanthin, norbixin, dehydronorbixin, fucoxanthin, and dihydro-a-crocetin methyl ester do not promote growth in rats. Carotin, m. p. 182-183°, in daily doses of 0.03 mg. causes continuous growth. The nature of the preparation does not exclude the possibility of the presence in the carotin of a very active substance, but the purest carotin preparations are the most active vitamin-A preparations yet obtained. Carotin from stinging nettles is found to be slightly less active than that from carrots; it is thus evident that, if accompanying impurities are responsible for biological activity, they do not occur solely in the carrot. Experiments with dihydro-acrocetin have not given well-defined results, possibly owing to the unusually ready oxidisability of the compound even in oil solution. Di-iodocarotin is found to be active and the probability is indicated that it is not the carotin derivative itself, but a product derived from it after resorption which is the growth-promoting factor. Results with lutein are variable. H. WREN.

Relation of carotin to vitamin-A. T. MOORE (Lancet, 1929, ii, 380-381).—Carotin fed to rats does not accumulate as such in the liver, but there is a marked increase in the vitamin-A content of the liver, as measured by the antimony trichloride colour reaction. E. BOYLAND.

So-called vitamin-A reactions. G. MONASTERIO (Biochem. Z., 1929, 212, 66-70).—Although the various reactions believed to be characteristic of vitamin-A are always given by cod-liver oil, experiments with butter, olive oil, and eggs show that these reactions are, in their present form, unsatisfactory for the purpose for which they are intended. Biological tests must always be applied. W. MCCARTNEY. Relation of soil fertility to vitamin-A content of leaf lettuce. M. DYE and J. W. CRIST (J. Nutrition, 1929, 1, 335-338).—The vitamin-A content increased with the chlorophyll content, but was not otherwise necessarily associated with plant vigour. CHEMICAL ABSTRACTS.

Action of gallosterin. M. MATSUORA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 723—734).— Biological experiments show that, contrary to the statement of Shimidzu, gallosterin (vitamin-A-cholic acid) does not possess the activity of vitamin-A. A. A. GOLDBERG.

Vitamin-A and -D content of cod-liver meal. E. M. CRUICKSHANK (Rep. World's Poultry Cong., 1928 (1927), 246—247).—Experiments on chickens are described. CHEMICAL ABSTRACTS.

Vitamin-A and -D content of cod-liver meal. E. M. CRUICKSHANK, E. B. HART, and J. G. HALPIN (Poultry Sci., 1927, 7, 9-16).

Influence of vitamins-A, -B, -D, iron, copper, ox muscle, and liver on the course of and regeneration from the anæmia of rice disease. R. W. WHITEHEAD and O. W. BARLOW (Amer. J. Physiol., 1929, 89, 542—547).—Rats fed on polished rice and salts develop a secondary anæmia which is prevented by the addition of 2% of compressed yeast to the diet, but not by the addition of vitamins-A and -D, or of iron and copper. Ox liver or muscle prevents this anaemia, but yeast is not active as a curative agent. E. BOYLAND.

Activity and nitrogen content of fractions obtained in the concentration of antineuritic vitamin of brewer's yeast. A. SEIDELL (Rec. trav. chim., 1929, 48, 855—859).—Extraction of brewer's yeast (nitrogen content of dry product 9.4%) with water and subsequent adsorption of the extracted vitamin on fuller's earth affords a preparation containing about 55% of the original vitamin; subsequent adsorption of the mother-liquor affords only slightly active products. About 28% of the vitamin originally present is retained by the insoluble yeast protein (nitrogen content of dry product 8.83%). H. BURTON.

Isolation of anti-beriberi vitamin. B. C. P. JANSEN (Rec. trav. chim., 1929, 48, 984—985; cf. A., 1927, 382).—Silicotungstic acid is a more specific precipitant for the vitamin than phosphotungstic acid, and alcoholic platinum chloride solution can be replaced by alcoholic cadmium chloride (provided the solution is not too dilute). H. BURTON.

Vitamin-B content of various yeasts and of the wheaten bread prepared with them. A. SCHEU-NERT and M. SCHIEBLICH (Biochem. Z., 1929, 212, 80—86; cf. this vol., 221).—Observation of pigeons and rats fed with various kinds of yeast and with bread made with the yeasts showed that the influences of the two factors present in vitamin-B must be considered separately. Brewer's yeast contained two or three times as much antineuritic factor as did baker's yeasts, but there was the same amount of growth-promoting factor in both kinds. In order to keep alive pigeons which received all the bread they could eat, the amount of yeast in the bread had to be

increased to three times that usual in bakeries. Similarly, normal amounts of yeast in bread had to be increased if growth was to be promoted in rats. W. MCCARTNEY.

Differentiation of vitamins- B_1 and $-B_2$ in yeast by heat and ultra-violet irradiation. C. KENNEDY and L. S. PALMER (J. Biol. Chem., 1929, 83, 493— 496).—The claim of Hogan and Hunter (A., 1928, 1059) that ultra-violet irradiation causes differential destruction of vitamin- B_2 in yeast could not be confirmed. C. R. HARINGTON.

Differences in vitamin-B and -C content of cereal grains during germination. C. KUCERA (Compt. rend. Soc. Biol., 1928, 99, 967-970; Chem. Zentr., 1929, i, 2065).—During germination wheat, rye, and barley contain similar quantities of vitamin-C, whilst with oats a smaller quantity was produced. A. A. ELDRIDGE.

Vitamin content of cereals and legumes. J. BUCEK (Compt. rend. Soc. Biol., 1929, 100, 427–428; Chem. Zentr., 1929, i, 2791).—Antipolyneuritic doses for pigeons of wheat, rye, barley, oats, maize, beans, and vetch are recorded. A. A. ELDRIDGE.

Vitamin-C content of legumes during germination. F. SIMONIK (Compt. rend. Soc. Biol., 1929, 100, 431-432; Chem. Zentr., 1929, i, 2788).--Legumes form vitamin-C during germination more rapidly than do cereals. A. A. ELDRIDGE.

Diminution of the vitamin-B content of cereals and legumes during germination. C. KUCERA (Z. Tierzücht., 1929, **13**, 387—390; Chem. Zentr., 1929, i, 2788).—In rye and wheat the vitamin-B cannot be detected after germination for 6 and 18 days, respectively. Legumes, after germination for 28 days, still contain 15% of their original vitamin.

A. A. ELDRIDGE.

Vitamin-B content of the polished rice "koji." R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 626-627).--- "Koji" is a product of cereals on which Aspergillus oryzæ is grown. The contents of growthpromoting and antineuritic vitamins in the koji prepared from polished rice are determined by using young albino rats and pigeons, respectively. The rats (32-46 g.) fed with 76% of the koji as the sole source of these vitamins grew somewhat below the normal rate, reaching 105-142 g. in 3 months. Then the growth stopped and their weights began to decrease, whilst those fed with 76% of polished rice died within 2 months. The pigeons fed with 78% of the koji died in 30-41 days, showing the symptoms of polyneuritis, whilst those fed with polished rice died in 23-35 days. As the polished rice, which is the raw material of the koji, is devoid of vitamin-B, A. oryzæ can synthesise this vitamin.

K. KASHIMA.

Calcium in urine and blood during administration of lemon juice. A. LEVI (Boll. Soc. Biol. sper., 1928, 3, 67-70; Chem. Zentr., 1929, i, 2199).— After administration of lemon juice the calcium content of the urine is markedly increased, whilst the blood-calcium falls somewhat. A. A. ELDRIDGE.

Vitamins and light. I. Relation between rickets, ultra-violet light, and the Russell effect (photoactivity) with various substances, particularly lipins. J. KŘIŽENECKÝ (Sbornik Českoslov. Akad. Zeměd., 1928, 3, 587—682; Chem. Zentr., 1929, i, 2202).—Photoactivity is not a characteristic of animal and vegetable fats. Photo-activation is an oxidation process, the active particles being oxidation products. A. A. ELDRIDGE.

Quantitative response to varying intake of vitamin-D. H. C. SHERMAN and H. K. STIEBELING (J. Biol. Chem., 1929, 83, 497-504).—Rats at the age of 3-4 weeks were transferred to a diet adequate in all respects except for its content of vitamin-D; normal calcification, as determined by the calcium content of the fresh femurs, occurred in those cases where the diet was supplemented with dried whole (summer) milk to the extent of 5% of the total calories. When smaller amounts of dried milk were given the degree of calcification bore an approximately quantitative relationship to the amount of supplement. In such tests it is unnecessary to subject the animals to preliminary vitamin-D starvation.

C. R. HARINGTON. Mode of action of irradiated ergosterol on the myelin forms of lecithin. C. J. BOND (Lancet, 1929, ii, 328—329).—Irradiated ergosterol increases the production of myelin forms of lecithin in water. E. BOYLAND.

Biological inactivity of ergosterol peroxide. W. HEUBNER and F. HOLTZ (Klin. Woch., 1929, 8, 456-457; Chem. Zentr., 1929, i, 2439).—Ergosterol peroxide, $C_{27}H_{42}O_3$, produced by irradiation of ergosterol in an atmosphere containing oxygen, does not possess biological activity. A. A. ELDRIDGE.

Effect of X-rays on ergosterol. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 640-644).—Vitamin-D, formed by irradiation of ergosterol with ultra-violet light, is destroyed by 4 hrs.' exposure to X-rays. The spectrum of ergosterol and activated ergosterol extends further into the ultra-violet region after irradiation with X-rays.

A. A. GOLDBERG.

Influence of cold periods on the respiration of plants. A. HEE (Compt. rend., 1929, 189, 370-372).—Measurements of respiratory activity of both old and young leaves were made in the dark, and the results expressed in mg. of carbon dioxide expired per hour per g. dry weight. With old leaves the value rises from about 0.558 to 1.411 mg. after subjecting the material to cold lasting 12 days, with a minimum of -13° . The amount of the rise in respiratory activity varies according to the intensity of the cold. With young leaves a temperature of 0° to -2° produces a lowering of respiratory activity, and even after intense cold the rise is of less significance than with old leaves. In all cases the respiratory activity soon becomes normal again at temperatures above 0°. P. G. MARSHALL.

Transformation of sugars in the ripening of the fruits of the water melon. N. N. IVANOV, R. S. ALEXANDROVA, and M. A. KUDRJAVZEVA (Biochem. Z., 1929, 212, 267-279).—During the ripening of water melon fruits, dextrose is formed in the early stages and is gradually transformed into lævulose. When the latter begins to preponderate, the two sugars begin to combine, giving sucrose. Cultivation of the wild form of water melon also leads to the appearance of sucrose.

P. W. CLUTTERBUCK. Transformation of carbohydrates during the ripening of bananas. M. BRIDEL and C. BOURDOULL (Compt. rend. 1929, 189, 543-545).—Starch is converted into sucrose in ripening bananas.

A. A. GOLDBERG.

Methods for the determination of the nitrogenous constituents of a cyanophoric plant, *Prunus laurocerasus*. M. E. ROBINSON (Biochem. J., 1929, 23, 1099—1113).—Methods for the determination of total, insoluble, non-coagulable, proteose-, cyanide-, ammonia-, amide-, and nitrate-nitrogen are described. These were studied on the leaves of *Prunus laurocerasus* and seedlings of *Sorghum vulgare*. The methods are applicable to small quantities (10— 20 g.) of material. S. S. ZILVA.

Origin of ethereal oils in plants. L. FRANCES-CONI (Annali Chim. Appl., 1929, **19**, 333–343).— A scheme is suggested for the course of the reactions giving rise to the various terpene derivatives found in pelargonium oil (cf. A., 1925, i, 759). T. H. POPE.

Effect of some salts on the germination of the seeds of Amarantus retroflexus, L. B. N. AXENTSEV (Biochem. Z., 1929, 211, 454-467).--Solutions of potassium and calcium nitrate stimulate the germination of the seeds of A. retroflexus. These salts do not affect the seed hulls, but the inner portions; they also lessen the swelling and protect against the poisoning effect of ether and phenol. The cations and anions are arranged in a lyotropic series by their protective action. Aluminium nitrate shows strong protective power. The stimulating action of the salts is not connected with the increase in hydration of the colloids. J. H. BIRKINSHAW.

Enzyme content of seeds of different sources. M. J. LISCHKEVITSCH and S. P. PRIZEMINA (Biochem. Z., 1929, **212**, 280—290).—The enzyme content of wheat and barley seeds varies with the climatic conditions of growth, the catalase, amylase, and protease contents being considerably greater when the seeds are grown in northern or mountainous southern districts. Relationships are obtained between the catalase, amylase, and protease contents and also between the lipolytic power and high acid value of the oil of the castor-oil plant.

P. W. CLUTTERBUCK.

The seeds of the earth, their coming and going. W. KINZEL (Arch. Pharm., 1929, **267**, 455–465).— Chiefly botanical, dealing with the effects of light, temperature, and nature of environment on germination. S. COFFEY.

Influence of the iodine ion on the growth and cell increase of halophytes. J. STOKLASA (Biochem.

Z., 1929, 211, 213-228).-The effect of the addition of potassium iodide to the nutrient medium supplied to sugar-beet plants growing in pure sand has been studied at all stages of growth. For the formation of new living plant material in halophytes the presence of iodine is indispensable, and plants which receive iodine (in addition to that which is present naturally) grow better, produce more sugar, and their leaves contain more chlorophyll than do controls. The absorption of iodine is greatest in the early stages of growth. At the stage where chlorophyll begins to decompose there is a great decrease in the iodine content of the leaves and when the chlorophyll disappears the iodine also disappears and collects in the upper part of the roots. At other times there is always more iodine in the leaves than in the roots. The acidity of the sap of the leaves and roots of plants receiving added iodine is very much reduced. This reduction is due to the presence of an oxidase which, in the presence of iodine (and of iron), decomposes organic acids. Oxalic acid, which plays a specially important part in the growth of sugar beet, is much more plentiful in plants poor in iodine than in those rich in iodine. The leaves and roots of sugar-beet plants contain a substance which yields furfuraldehyde and is much more plentiful in plants rich in iodine than in controls. Plants which receive toxic amounts of iodine contain great amounts (up to 10%) of compounds yielding furfuraldehyde.

W. MCCARTNEY.

Iodine liberator from Laminaria. G. LUNDE and K. CLOSS (Nature, 1929, **124**, 578).—The "iodine liberator" in L. digitata (cf. Dillon, this vol., 360; Kay, this vol., 612) is not an iodide oxidase nor potassium iodate; it liberates only in acid solution most of the iodine present in the fresh aqueous extract. A. A. ELDRIDGE.

X-Ray photography of mineral accumulations in plants. C. L. CRUTCHFIELD (Plant Physiol., 1929, 4, 145—154).—X-Ray photography is more sensitive than microchemical methods for the detection of accumulations of aluminium and iron in the nodes of maize stalks. The method is available for the study of the translocation of salts in plants.

CHEMICAL ABSTRACTS.

Mineral constituents of fungi. W. FRIESE (Z. Unters. Lebensm., 1929, 57, 604-613).—The ash contents of fungi calculated on the dry substance was found to increase during growth from 6-9% in the young organism to 9-11.6% at the beginning of decay. The composition of the ash varied in individuals of the same species according to the nature of the soil and woodlands. Boletus edulis from a Dolomite region contained much more lime and magnesia and much less silica than the same species grown in a sandstone country. The ash of the species examined contained 46-55% K₂O and 20-33.4% P₂O₅. The stalks contained less ash than the pileus, the epidermis of the latter being richest in ash. All the species contained iron and manganese and in all but one (Amanita phalloides) the pileus was richer in manganese than the stalk. The saps of the species examined in this respect (Lactaria deliciosa and L. volema) were low in ash content, but contained both iron and manganese. W. J. Boyp.

Mineral constituents of lucerne. B. W. DOAK (New Zealand J. Sci. Tech., 1929, **11**, 108—111).— Analyses of lucerne grown on variously fertilised soils are recorded. The proportion of mineral constituents varied considerably with the nature of the fertiliser used and with weather conditions. The calcium content of lucerne was greater than that of grass pasture. In feeding values, grass pasture and lucerne in its younger stages have similar protein and carbohydrate contents, but the crude fibre of lucerne is the smaller. A. G. POLLARD.

Effects of storage on alcoholic extracts of plant tissues. Amino-acid changes. J. E. WEBSTER (Plant Physiol., 1929, 4, 141—144).—Under all the conditions examined, storage of alcoholic extracts of spinach resulted in a decrease of amino-nitrogen.

CHEMICAL ABSTRACTS.

Assimilation of carbamide by higher plants. K. PIRSCHLE (Biochem. Z., 1929, 212, 466—474).— Fourteen different kinds of plants were grown in water culture using on the one hand carbamide and on the other ammonium nitrate as source of nitrogen. After 4—5 weeks, the roots were cut in small pieces and incubated with carbamide and the ammonia formed was titrated. The roots of the carbamide cultures showed a greater power to liberate ammonia than those of the nitrate cultures. Similar behaviour in respect of the leaves of the plants was not obtained. P. W. CLUTTERBUCK.

Mineral content of grain. J. E. GREAVES and C. T. HIRST (J. Nutrition, 1929, 1, 293—298).—The following maximum, minimum (and average) values % are recorded: Ash: wheat 2.94, 1.35, (1.85); oats 4.87, 1.68, (4.05); barley 3.71, 2.08, (3.00); maize 1.79, 1.65, (1.73). Calcium: oats (0.117), wheat (0.09), barley (0.086), maize (0.15). Magnesium: wheat (0.184), oats (0.181), barley (0.181), maize (0.203). Sulphur: wheat (0.204), oats (0.19), barley (0.155). Potassium: wheat (0.476), oats (0.57), barley (0.561), maize (0.39). Phosphorus: wheat (0.331), oats (0.364), barley (0.351), maize (0.334). Iron: wheat (0.005), oats (0.007), barley (0.006).

CHEMICAL ABSTRACTS.

Distribution of nitrogen in some fruits. P. R. v. D. R. COPEMAN (Proc. Dept. Conf. S. Africa, Div. Chem., 1929, 394-399).-Grapes of the Hanepoot variety contained in 1925 0.017-0.034% of nitrogen in the juice, 0.060-0.072% in the berry, 0.211-0.446 g. in 100 berries, whilst in 1926 the berries contained 0.046-0.070% of nitrogen. The proportion of nitrogen in the berry is greatest at maturity. Nitrogen in apricot pulp varied from 0.108 to 0.218%, and the weight of nitrogen per 100 fruits from 3.71 to 4.68 g. In this case the proportion of nitrogen in the pulp decreased during ripening, but the absolute amount in the whole fruit showed little change. Washington Navel oranges from the Eastern Province (S.A.) averaged 0.188, 0.201, and 0.120% of nitrogen in the skin, rag, and juice, and one sample of pips contained 0.807%. Pears of the Louise Bonne variety contained 0.125, 0.063, 0.053, and 2.81% of nitrogen in the skin, pulp, juice, and pips, respectively. Spraying apricots and oranges with lead arsenate and nicotine sprays had no significant effect on the nitrogen content of the fruits. E. HOLMES.

Agar. M. LUDTKE (Biochem. Z., 1929, 212, 419-429).-Examination of the hydrolysate of agar showed that besides galactose, a second reducing substance was present in considerable amount. After quantitative removal of galactose by phenylmethylhydrazine and of the excess of hydrazine with benzaldehyde a reducing syrup was obtained which gave the same reducing value by Fehling's and by the hypoiodite methods and did not therefore contain ketose. If the hydrolysis is effected by dilute sulphuric acid and the acid removed with barium, the neutral filtrate contains barium. The barium content after removing galactose and decolorising rose to 16% of the dry substance. The acid content of the hydrolysate increased with duration of heating and the reducing value simultaneously decreased, but the hydrazine value remained practically constant. The acid was therefore formed from the second reducing substance. The substance is not of the uronic acid type. It contains a small amount of lævulic acid. A substance containing sulphur can also be obtained in solution by treatment of the agar with ammoniacal hydrogen peroxide or on hydrolysis by hypochlorite, the preparation therefrom containing 3% of sulphur.

P. W. CLUTTERBUCK. Chemical composition of Alaskan lichens, G. C. SPENCEB and O. F. KRUMBOLTZ (J. Assoc. Off. Agric. Chem., 1929, 12, 317—319).—An indication of the value of Alaskan lichens as fodder is afforded by the analyses of 21 varieties, chemical composition being recorded under the headings moisture, fat, fibre, protein, ash, and nitrogen-free extract.

H. J. DOWDEN. Pectins of fruits. F. EHRLICH and A. KOSMAHLY (Biochem. Z., 1929, 212, 162-239).—Oranges, red currants, and strawberries were investigated. The pectins from these fruits (the peel of the oranges was used) are built up from the same units-galacturonic acid (4 mols.), arabinose (1 mol.), galactose (1 mol.), acetic acid (2 mols.), and methyl alcohol (2 mols.)as are those from sugar beet. As regards the products of hydrolysis of the various pectins, those of orange peel and sugar beet are equal in amount, whilst the differences found between the sugar beet and the other two fruits are due to the influence of enzymes and of the method of preparation. The constitution of the pectic acids of the fruits is probably the same as that of the pectic acid of sugar beet (cf. this vol., W. MCCARTNEY. 1273).

Pectic acid and methyl alcohol contents of Russian tobacco. G. GABEL and G. KIPRIANOV (Biochem. Z., 1929, 212, 337—346).—The amount of pectic acid in a number of kinds of tobacco varied from 13 to 20% of the dry weight. The acid is present in unfermented cigarette tobacco as the dimethyl and in fermented as the monomethyl ester. The mean methyl alcohol content of unfermented tobacco is 0.945%, of fermented Russian cigarette tobacco 0.411-0.717%, of cigarette tobacco 0.228-0.401, and of pipe tobacco 0.074-0.158, whilst the ratio of methyl alcohol to pectic acid (as percentage) is of unfermented tobacco 5.5-6.4, of fermented Russian cigarette tobacco 2.9—3.2, of cigarette tobacco 1.2—2.6, and of pipe tobacco 0.4—0.7 (cf. A., 1927, 385; 1928, 95). P. W. CLUTTERBUCK.

Tobacco fermentation. T. ANDREADIS (Biochem. Z., 1929, 211, 378—394).—The tobacco was ripened in a closed system so that the volatile products (methyl alcohol and carbon dioxide) could be collected and measured. The pectin methyl alcohol in the tobacco diminished by about 30% during fermentation, the lignin methyl alcohol increased by about 100%. In unfermented tobacco pectase, hexosediphosphatase, lipase, and amylase were found, but no glyoxalase. J. H. BIRKINSHAW.

Carbohydrates of the phosphatides [of soya bean]. B. REWALD (Biochem. Z., 1929, 211, 199-201).-If phosphatide from soya bean after purification by precipitation with acetone and ethyl acetate is brought into colloidal solution in water, the solution shaken with ether until no more material goes into solution, and the emulsion which is formed destroyed with alcohol and salt, a clear aqueous solution, free from fat and phosphatide, is obtained. This solution does not reduce Fehling's solution, but after boiling with acid reduction takes place and dextrose can be identified in the solution. The phosphatide in the ether can be completely freed from carbohydrate by repetition of the process. No directlyreducing sugar is found during the process and the phosphorus content of the phosphatide rises. Experiment shows that lecithin from yolk of egg may contain very small amounts of a di- or poly-saccharide. It follows that no pentoses or hexoses are naturally associated with phosphatides and that there is no chemical combination between them and the carbohydrates with which they are found. W. MCCARTNEY.

Constituents of Arctium Lappa. I. J. SHINODA and M. KAWAGOYE (J. Pharm. Soc. Japan, 1929, 49, 94-97).-From the ethereal extract of the crushed seeds of Arctium Lappa, an oil is obtained from which, on keeping, crystals of palmitic acid separate. The alcoholic extract of the seeds which have previously been extracted four times with ether contains a compound, C₂₈H₃₈O₆, H₂O (from hot water), m. p. 112°, to which the name arctiin has been given. When arctiin is heated with 29% sulphuric acid for 2 hrs., dextrose is split off and arctigenin, C₂₂H₂₆O₆, m. p. 102°, is obtained, which reduces ammoniacal silver solution, gives a bluish-green colour with ferric chloride, and is soluble in sodium hydroxide but insoluble in sodium carbonate solution. This compound is also obtained from the ethereal extract of the seeds of A. Lappa after these have been kept for 8-9 months. When arctigenin is oxidised by potassium permanganate in acetone solution it yields veratric acid and, probably, formic acid, and when fused with alkali, protocatechuic acid and formic acid. Arctigenin gives a tribromo-derivative, C22H23O6Br3, m. p. 194-195°, which when oxidised with potassium permanganate vields 6-bromoveratric acid and on reduction with copper and zinc is reconverted into arctigenin. By treatment of arctigenin with methyl sulphate or diazomethane, a compound, $C_{23}H_{28}O_6$, m. p. 125—127°, is obtained which on nitration yields nitromethylarctigenin, 23CH24O6(NO2)4, m. p. 204206°. Treatment of arctigenin with alcoholic alkali followed by acidification yields a *compound*, m. p. 117—118°, soluble in sodium carbonate, from which arctigenin is recovered on recrystallisation. This reaction indicates the presence of a lactone ring.

W. O. KERMACK.

Examination of roots and leaves of Saussurea Lappa, Clarke. I. S. GHOSH, N. R. CHATTERJEE, and A. DUTTA (J. Indian Chem. Soc., 1929, 6, 517— 522).—The dry root contains 1.51% of essential oil (cf. Semmler and Feldstein, A., 1915, i, 429), about 6% of resin, 18% of inulin, small amounts of a bitter substance, tannins, fixed oil, potassium nitrate, and sugars, and 0.05% of an alkaloid (termed saussurine), isolated by extraction with alcoholic ammonia. The dry leaves contain 0.02% of saussurine but no essential oil. H. BURTON.

Ligno-cellulose group. I. Constituents of water hyacinth (Eichornia crassipes). H. K. SEN, P. P. PAL, and S. B. GHOSH (J. Indian Chem. Soc., 1929, 6, 673-690).-The green plant (ash content 1.1%; organic matter 3.7%) contains starch in all its parts, but the air-dried plant (moisture 13.46%; ash 19.75%; fats 7.7%; α -, β -, and γ -cellulose 42.23%; lignin 11.1%; nitrogenous matter 5.55%) is starch-free. The ash contains appreciable amounts of potassium chloride, calcium phosphate, aluminium oxide, and alkali carbonate. Acetylation of the fatfree, dried plant with boiling acetic anhydride and subsequent separation of the lignin by treatment with 2% chlorine dioxide solution gives a cellulose acetate (30.27% Ac) containing hemicellulose. When the product is first delignified and then acetylated the acetyl content of the cellulose acetate is 20.82%. Treatment of these partly acetylated derivatives with 17.5% sodium hydroxide solution removes the hemicellulose and acetyl groups, affording a-cellulose. Acetvlation of the crude or chlorine peroxide-treated cellulose with a mixture of acetic acid, acetic anhydride, and sulphuric acid gives a cellulose triacetate. Extraction of the dry plant with boiling water and subsequent hydrolysis with sulphuric acid of varying concentration under pressure affords varying amounts of reducing sugars, mainly pentoses. Preliminary ex-traction with boiling 5% sulphuric acid and subse-quent hydrolysis yields only small amounts of fermentable sugars. Other experiments on the hydrolysis of the plant are described. Destructive distillation of the dry plant at 500° and 1000° yields mainly oxides of carbon, hydrogen, methane, nitrogen, and a residue of charcoal. Preliminary experiments on the bacterial decomposition (by septic tank fluids) of the green plant are described. H. BURTON.

Alkaloid content of chlorophyll from Datura stramonium leaves. M. JANICSEK (Ber. ungar. Pharm. Ges., 1929, 5, 86—95; Chem. Zentr., 1929, i, 1840—1841).—Extracts of the leaves with alcohol followed by benzene contained 0.58—2.76% of alkaloid; extraction in a Soxhlet apparatus removes almost the whole of the alkaloid. A. A. ELDRIDGE.

Colouring matters of Carthanus. V. ASTRADA (Rev. farm. Buenos Aires, 1929, 2, 159–160).— Carthanus flowers contain H₂O 9·10, nitrogenous

substances 17.50, resin 42.50, cellulose 13.0, fat 3.90, starch 2.90, ash 11.10° . The yellow colouring matter, probably a quinoline derivative, is soluble in water but not in the usual organic solvents. Another yellow substance, contained in the cell membrane of the petals, is soluble in alkali.

CHEMICAL ABSTRACTS.

Modification of Mayer's "hæmalum." J. E. SASS (Stain Tech., 1929, 4, 127—129).—A satisfactory strain for botanical work is made as follows. To a hot solution of 50 g. of ammonium alum in 1 litre of water are added 1 g. of hæmatoxylin and 1 g. of sodium iodate. The mixture is then cooled and filtered. The stain is best when freshly prepared, but keeps for at least 6 months. H. W. DUDLEY.

Inversion method for determination of hydrogen-ion concentration of wine. G. AGABALIANZ (Biochem. Z., 1929, 211, 373—377).—An improved thermostat for high temperatures, specially adapted to the determination of $p_{\rm fl}$ by inversion of sucrose, is described. J. H. BIRKINSHAW.

Determination of p_{Π} , particularly of blood, using the antimony electrode and by colorimetric methods. H. G. K. WESTENBRINK, J. A. A. PIETERS, and J. J. L. PIETERS (Arch. Néerland. Physiol., 1929, **14**, 386—393).—Satisfactory results in the micro-determination of the p_{Π} of blood cannot be obtained with antimony electrodes, whether in the compact metallic form or electrolytically deposited on platinum as described by Brinkman and Buytendijk (A., 1928, 1391). The colorimetric method of Hawkins (J. Biol. Chem., 1923, **57**, 493) is shown to give results closely agreeing with that of Cullen (A., 1922, ii, 672), and is regarded as the most satisfactory method for micro-determination. K. V. THIMANN.

Determination of hydrogen exponent by means of the step-photometer. I. A. JANKE and S. KROFACSY (Biochem. Z., 1929, 213, 154—169).—The use of the photometer for determination of $p_{\rm H}$ depends on the equilibrium between the pseudo- and the ionised form of the indicator. The indicators recommended for use around neutrality are the nitrophenols. The step-photometer of Pulfrich gives $p_{\rm H}$ values correct to 0.05 and can be used for cloudy or coloured solutions, since no standard is necessary. The method is described. J. H. BIRKINSHAW.

Micro- and histo-chemical identification of alkaloids. A. NIETHAMMER (Biochem. Z., 1929, 213, 138—141).—Reinecke salt gives characteristic crystalline precipitates with many alkaloids and is recommended as a specific group reagent. In the tissue the reaction is seldom obtained, more frequently in the tissue juice. Saponins give a red colour. J. H. BIRKINSHAW.

Twin tubes with membrane filters. I. N. ASHESHOV (Biochem. Z., 1929, 211, 202–206).—An account is given of the construction and uses of a simple apparatus to be employed in experiments involving diffusion through semipermeable membranes. Errors due to the employment of membranes of unequal permeability are eliminated by the use of the apparatus. W. MCCARTNEY.