# BRITISH CHEMICAL ABSTRACT A.—PURE CHEMISTRY OCTOBER, 1929.

# General, Physical, and Inorganic Chemistry.

Hydrogen spectra excited by electronic shock. S. VENCOV (Compt. rend., 1929, 189, 279-280; cf. this vol., 968).—Continuous and secondary spectra of hydrogen were obtained together in the neighbourhood of the ionisation potential of the hydrogen molecule (16.5 volts). Variations in gas pressure or in the accelerating field produced the strong Fulcher bands in the latter spectrum, whilst the former appeared as a homogeneous band. Further variations in conditions of excitation produced independent effects on the intensities of the two spectra. The appearance below 20 volts of the first Balmer lines indicates that ionisation of the hydrogen molecule at 16.5 volts is accompanied by dissociation. J. GRANT.

Separation of hydrogen lines in parallel and crossed electrical and magnetic fields. N. R. SEN (Z. Physik, 1929, 56, 673-683).-Mathematical. The theory of Dirac and Darwin is used to calculate the separation of the hydrogen lines in parallel and crossed electric and magnetic fields, small relativity effects being neglected. For parallel fields the same conclusion is reached as with the older quantum mechanics. For crossed fields the arrangement of the separated  $H_{\alpha}$  lines and the possible switches are A. J. MEE. given.

Densities of hydrogen spectral lines as a function of the electronic velocity of excitation. C. J. BRASEFIELD (Physical Rev., 1929, [ii], 34, 431-437).—The densities of the principal lines of the singlet and triplet systems of molecular hydrogen, as well as  $H_{\alpha}$ ,  $H_{\beta}$ , and  $H_{\gamma}$ , were measured and plotted against electronic velocities for a range of 19-220 equivalent volts, at constant electron emission and gas pressure. The triplet lines approach a maximum density below 19 volts; the singlet lines show a maximum between 30 and 35 volts. The densities of  $H_a$ ,  $H_\beta$ , and  $H_\gamma$  decrease rapidly below 30 volts, indicating that the number of dissociating collisions producing an excited atom must be very small at 19 volts. N. M. BLIGH.

Terms of the hydrogen molecule. G. H. DIEKE (Z. Physik, 1929, 55, 447-450).-Suggestions towards a complete theory of the origin of the various hydrogen terms are made. R. W. LUNT.

Structure of the band spectra of hydrogen and helium molecules. G. H. DIEKE (Nature, 1929, 123, 979).—The author's interpretation (cf. preceding abstract) of regularities in the spectrum of the hydrogen molecule was based on an incomplete

analogy with the helium band spectrum. The missing helium bands have now been observed, and the author's views are strengthened. The new bands consist of three groups, all belonging to the triplet system, one in the red, one near 535 m $\mu$ , and one near 495 m $\mu$ . A. A. ELDRIDGE.

Electron terms in the singlet systems of the fine line spectrum of hydrogen. W. WEIZEL. (Z. Physik, 1929, 55, 483-501).-A complete analysis of the electron terms of the hydrogen molecule is described in which these are attributed to a photoelectron, whilst a second electron always remains in the lowest state; the ultra-violet bands, for example, are then symbolised thus:  $A \leftarrow B$ ,  $1_s\sigma^{21}\Sigma = 1_s\sigma^{2}_p\sigma^{1}\Sigma$ ;  $A \leftarrow C$ ,  $1_s\sigma^{21}\Sigma = 1_s\sigma^{2}_p\pi^{1}\Pi$ . In this way it has been possible to evaluate all the electron terms. The ionisation potential is found to be 15.75 in agreement with experiment, 15.9 volts. The calculated value for the heat of dissociation  $H_2^+ \rightarrow H + H^+$ , for the first vibrational quantum, and for the nuclear spacing of  $H_2^+$  are, respectively, 46.5 kg.-cal./mol., about 2100 cm.<sup>-1</sup>, and about  $H_2^+ = R_1 + R_2 + R_2$ 1.06×10-8 cm. R. W. LUNT.

Doppler effect with homogeneous hydrogen canal rays. W. RIEZLER (Ann. Physik, 1929, [v], 2, 429-444).—The positive-ray stream contains  $H^+$ ,  $H_2^+$ , and  $H_3^+$ , but when a variable magnetic field is applied it is possible to determine the Doppler effect for homogeneous beams. The velocity calculated from the deflexion by means of an electric or a magnetic field agrees with that calculated from the magnetic neid agrees with that calculated from the Doppler effect, according to which the velocities observed are in the ratio  $1:\frac{1}{2}:\frac{1}{3}$ , agreeing with  $H^+$ ,  $H_2^+$ , and  $H_3^+$ . The Doppler distribution for inhomogeneous positive rays observed by Krefft is in fair agreement with the superposed effects of all the homogeneous beams obtained by magnetic resolution. The intensity distribution of the Doppler effect for the complete stream is conditioned by processes occurring in the beam itself.

R. A. MORTON.

New connexion between the absorption spectrum of hydrogen and the many-lined spectrum. O. W. RICHARDSON (Nature, 1929, 124, 408) .- A number of band systems ending on Dieke and Hopfield's C level have been found; they all have initial states which are identical with one or other of the initial states of the bands ending on the  $2^{1}S$  level, and they have the character of band sequences similar to those of the  $\alpha$ ,  $\beta$ , and other systems ending on  $2^{3}S$ . They all have P', Q, and R'1115

branches. The correctness of Hori's analysis of the Werner  $(C \longrightarrow A)$  bands is confirmed. There are four, or probably five, 2-levels in the H<sub>2</sub> spectrum. A classification of a number of the more important levels is suggested. A. A. ELDRIDGE.

Band spectra of light molecules. I. Spectra of helium and hydrogen. W. WEIZEL (Z. Physik, 1929, 56, 727-739).—The characteristic features shown by the band spectra of light molecules are : (a) their approximate conformity to one or other of the two expressions deduced by Hund (A., 1926, 657), according to the rotational energy involved; (b) the complete decoupling of the spin, the *l*-decoupling attaining a very high degree; (c) the nonappearance of spin-multiplet structure, and (d) the rare appearance of intercombination between term systems of different multiplets. From this point of view the molecular spectra of hydrogen and helium are discussed, new terms being identified and previous interpretations corrected. The decoupling is dealt with in detail. An explanation is offered for the relative intensities of the Lyman and Werner bands of hydrogen and the interpretation of the former as singlet-singlet combinations is discussed.

J. W. SMITH.

Near infra-red spectra of helium and mercury. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 131–137).—Using a method of heating a plate sensitised with neocyanine, and also by phosphoro-photography, the near infrared spectra of helium and mercury were studied. With a strong-current Geissler tube as a source of light the helium line  $2^3S-2^3P$  could be photographed with 5 min. exposure. The mercury arc spectrum showed a group of lines in the region  $0.7-1 \mu$ . The remarkable intensity of the two oxygen lines 0.846and  $0.777 \mu$  appearing as impurity is noted and its possible bearing in astrophysics is mentioned.

N. M. BLIGH.

Helium band spectrum. III. S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 139—149; cf. this vol., 616).—New measurements on the higher members of the helium  $2^{3}\sigma\Sigma$ — $m^{3}\pi\Pi$  series bands in the ultra-violet region were made. Two new bands,  $2s^{1}$ — $8p^{1}$  and  $2s^{1}$ — $9p^{1}$ , were found and analysed. Constants are calculated for these bands, and a Rydberg formula is suggested which expresses the electronic frequencies accurately, especially of the higher members. The convergence value of  $\omega_{0}$ , the vibrational constant for the *p*-states, is found to be  $1627\cdot2\pm0\cdot2$  cm.<sup>-1</sup> N. M. BLIGH.

Properties of a class of molecular terms, especially terms of the helium molecule. G. H. DIEKE (Z. Physik, 1929, 57, 71-105).—Mathematical. The rotational structure of the terms of a molecule is investigated. A calculation due to Hill and Van Vleck is used to follow the transition from stronger to weaker rotation or from weaker to stronger coupling. The results obtained are tested on the terms of the helium band spectrum. A. J. MEE.

Electron distribution in normal helium. H. BETHE (Z. Physik, 1929, 55, 431-436).—An exceptionally good agreement is to be found between the values of the energy terms and the eigenfunk-

tion of the normal helium atom calculated by the self-consistent field method of Hartree and by the analysis of Hylleras. R. W. LUNT.

R. O. R. W. A. R.

Measurement of excitation [functions] of the helium spectrum. W. HANLE (Z. Physik, 1929, 56, 94-113).—The principle of the design of an apparatus for examining the spectrum of helium may be examined as a function of the velocity of the exciting electrons; this is discussed at length together with the errors involved in the procedure finally adopted. The gas pressure was adjusted to a value below that at which pressure effects become appreciable, and spectrograms were taken of the luminescence in the range 6678-3819 Å. produced in a fieldfree space by electrons of velocity up to 450 volts. The curves for the intensity as a function of the electron velocity show the following characteristics : a welldefined maximum lying at or below about 100 volts; lines of the same spectral series have curves of the same type, characterised by the sharpness and position of the maximum; and the triplet lines exhibit a very much sharper maximum than do the singlet lines, the 2p-ms series having the sharpest maximum. R. W. LUNT.

Spectroscopic observations of the low-voltage nitrogen arc. H. HAMADA (Sci. Rep. Tôhoku, 1929, 18, 155—164).—The distribution of spectra over the region 3800—7000 Å. in the low-voltage nitrogen arc produced in a two-electrode hot-cathode tube has been studied. From the intensity distribution in the negative band system, it would appear that the greater is the voltage applied the greater is the probability of transition from the initial states at which the molecule has the greater vibrational quantum number. R. CUTHILL.

Excitation of the arc spectrum of nitrogen. O. S. DUFFENDACK and R. A. WOLFE (Physical Rev., 1929, [ii], 34, 409—420).—The complete arc spectrum of nitrogen was excited and measured in the region 8800—3400 Å. with a low-voltage arc in a mixture of helium and nitrogen. The first step of the excitation process is probably the dissociation of nitrogen molecules into neutral atoms by impacts of the second kind with metastable helium atoms, and the second step the excitation of neutral nitrogen atoms by second impacts with metastable helium atoms. Wavelengths, classifications, and a number of new lines are tabulated. N. M. BLIGH.

Classification of the arc spectra of nitrogen and carbon. S. B. INGRAM (Physical Rev., 1929, [ii], 34, 421-430).—The wave-lengths and approximate intensities of about 125 lines of the arc spectrum of carbon between 9000 and 20,000 Å. were measured. About 90 of these lines are classified as combinations between terms in CI and NI; new terms are fixed in both of these spectra and many identifications made by Fowler and Selwyn in CI (cf. A., 1928, 450) and by Compton and Boyce (cf. this vol., 365) are confirmed. Using the data of Duffendack and Wolfe (cf. preceding abstract) a number of lines is classified in the visible spectrum of NI. The designations of the <sup>2</sup>P and <sup>2</sup>D terms found by Kiess (cf. A., 1925, ii, 911) at 5100 and 6800 Å., respectively, are corrected by

1116

assigning them to the  $2s^22p^2 \cdot 3p$  configuration, basing them on the  $^{1}D$  term of N n. A complete N. M. BLIGH. term table of N I is given.

Additional series lines in the spectra of C II and N II. I.S. BOWEN (Physical Rev., 1929, [ii], 34, 534-536).—Several of the strong lines of C II were identified as combinations of the  ${}^{4}P$  term of the sp<sup>2</sup> configuration with the quadruplet terms observed by Fowler and Selwyn (cf. A., 1928, 1165). This fixes the term values  ${}^{4}P_{1}=206810\cdot7$ ,  ${}^{4}P_{2}=206789\cdot2$ ,  ${}^{4}P_{3}=206760\cdot6$ . In N II the term value  ${}^{1}S$  term of the  ${}^{2}p^{2}$  and the  ${}^{1}P$  term of the  ${}^{3}p^{3}$  configurations were fixed at 206,159 and 72,084, respectively, relative to Fowler and Freeman's term values (cf. A., 1927, 489). The  ${}^{1}S$  term combines with the  ${}^{1}D$  term of the same configuration to give the nebular line at 5754.8 Å. The relative term values are recorded for a number of terms, including those designated "a" by Fowler and Freeman, and these were shown to belong to N. M. BLIGH. the quintuplet system.

Nitrogen afterglow. E. J. B. WILLEY (Nature, 1929, 124, 443-444).—The decay of the afterglow is only partly a homogeneous reaction in clean glass vessels, the amount of divergence from homogeneity being determined by the purity of the nitrogen. The influence of the necessary traces of electronegative gas is confined to the surfaces. Under conditions of minimised wall decay no appreciable change in the order of the reaction takes place with time, and no apparent alteration occurs in the afterglow spectrum so far as 4000 Å. No simple relationship exists between the intensity of the glow and the concentration of chemically active nitrogen, except possibly under certain conditions determined by the state of the walls. Addition of small amounts of oxygen or nitric oxide to a stream of glowing nitrogen causes a large development of radiation in the blue and regions of shorter wave-lengths. The intensity of the green flame with nitric oxide (5%) is related to the concentration of chemically active nitrogen as is that of the luminosity of the nitrogen alone. The decay of a stream of luminous nitrogen can be varied by addition of photogens without affecting the amount of the chemically active species present. It therefore appears that atoms are concerned in both phenomena, and it is suggested that the chemical activity is probably due to 2.3-volt metastable atoms.

# A. A. ELDRIDGE.

Rotational structure of the red bands of sodium. W. R. FREDRICKSON (Physical Rev., 1929, [ii], 34, 207-212).-Three bands of the red band system of sodium photographed at high dispersion were measured. Two strong series of lines run through the bands and these series are shown to be P and R branches, and the combination constants are evaluated. The final state values and those of the blue-green system agree closely and the constant for the upper state gives  $I_0' = 255 \cdot 3 \times 10^{-40}$  g.-cm.<sup>2</sup> and  $r_0' = 3 \cdot 52 \times 10^{-8}$  cm. The electronic transition is concluded to be of the  ${}^{1}S - {}^{1}S$  type. N. M. BLIGH.

Ultra-violet spectrum of magnesium hydride. II. Many-lined γ-system. R. W. B. PEARSE (Proc. Roy. Soc., 1929, A, 125, 157-179; cf. this vol., 376).—The bands of the  $\gamma$ -system of magnesium

hydride have been measured in the region 2560-3240 Å. The distribution of band origins about the origin of the system is represented by the equation  $v_0 = 35904 \cdot 5 + 1138 \cdot 4(n' + \frac{1}{2}) - 9 \cdot 5(n' + \frac{1}{2})^2 - 1702 \cdot 2(n'' + \frac{1}{2}) + 34 \cdot 2(n'' + \frac{1}{2})^2$ . The rotational structure has been analysed and the bands have been found to consist of a single R and P branch, with one line missing at the origin. The structure is characteristic of the  ${}^{1}S \longrightarrow {}^{1}S$  type of transition, and the values for the vibrational constants show definitely that the two new S levels are quite distinct from the <sup>2</sup>S level of the  $\alpha$ - and  $\beta$ -systems. Using a rotational energy term of the form  $F(j_k) = B_n j_k (j_k+1) - D_n [j_k (j_k+1)]^2$ , the following values are calculated:  $B_n' = 4.3020 - 0.0492(n+\frac{1}{2}) - 0.0050(n+\frac{1}{2})^2$ ,  $B_n'' = 6.3782 - 0.1854(n+\frac{1}{2})$ ,  $D_n' = 2.16 \times 10^{-4}$ ,  $D_n'' = 3.45 \times 10^{-4}$ ,  $I_0' = 6.439 \times 10^{-40}$  g.-cm.<sup>2</sup>,  $I_0'' = 4.343 \times 10^{-40}$  g.-cm.<sup>2</sup>,  $r_0' = 2.02 \times 10^{-8}$  cm.,  $n_0'' = 1.65 \times 10^{-8}$  cm. The observed values for the isotope effect, measured for the (0.2) and (0.1) the (0,2) and (0,1) bands, are in good agreement with those calculated on the assumption that the bands are emitted by the diatomic molecule, MgH, magnesium having isotopes of weights 24, 25, and 26. L. L. BIRCUMSHAW.

Optical excitation of phosphorus vapour. A. JAROVLEV and A. TERENIN (Nature, 1929, 124, 337).—Fluorescence emitted in the region 3500-1900 Å. was observed in phosphorus vapour (0.1 mm.) at 600-700° illuminated by spark radiation Cd 2195, 2144 Å., Zn 2100, 2062 Å., or Al 1990, 1935 Å. The first vibration quantum and the dissociation energy of the normal  $P_2$  molecule are estimated, respectively, to be 775 cm<sup>-1</sup> and 6 volts. A. A. ELDRIDGE.

Spark spectra of sulphur. L. BLOCH and E. Вьосн (Ann. Physique, 1929, [x], 12, 5-22).-А more detailed account of work already published (this vol., 225).

Arc spectrum of chlorine and its structure. C. C. KIESS and T. L. DE BRUIN (Bur. Stand. J. Res., 1929, 2, 1117-1136).-More than 200 lines between 4000 and 9900 Å. have been measured in the arc spectrum of chlorine excited by an uncondensed discharge in a Geissler tube at low pressure. Of these lines 62%, together with those observed by Turner in the Schumann region, have been classified as resulting from combinations between terms of the doublet and quadruplet systems. They arise mainly from the basic term <sup>3</sup>P of the ion, the terms coming from <sup>1</sup>S and <sup>1</sup>D not being definitely established, owing to the faintness of the lines. From these, the distance separating <sup>2</sup>P<sub>2</sub> from <sup>3</sup>P<sub>2</sub> is 104,991 cm.<sup>-1</sup>, giving 12.96 volts as the ionisation potential of neutral chlorine. C. J. SMITHELLS.

Arc spectrum of chlorine. K. MAJUMDAR (Proc. Roy. Soc., 1929, A, 125, 60-68).—From a consideration of the fact that in the arc spectra of a group of successive elements (e.g., aluminium, silicon . . potassium) the wave-numbers of the strongest lines of the elements due to the transition  $N_1 - N_2$ increase linearly with the atomic number (cf. Saha and Mazumdar, A., 1928, 1296), it is found that the group of chlorine lines due to the transition  $4M_2$   $(N_1 \leftarrow N_2)$  should lie in the region 93007700 Å. Therefore the group at 4700–4200 Å., identified by Laporte (A., 1928, 805) as being due to the transition  $4M_2$  ( $N_1 \leftarrow N_2$ ), must be actually ascribed to  $4M_2$  ( $N \leftarrow O_2$ ). With a view to discover these predicted infra-red lines the spectrum of chlorine has been photographed in the region 6400– 8700 Å. The means taken to surmount the experimental difficulties are discussed. The new lines observed in the infra-red are identified as belonging to the transition  $N_1 \leftarrow N_2$  and are tabulated in the form of multiplets. The ionisation potential is calculated to be 13·1 volts. L. BIRCUMSHAW.

Spectrum of trebly-ionised argon. D. S. Joc. (Nature, 1929, 124, 303).—The lines of treblyionised argon have been classified; all the quadruplet multiplets due to the transition  $2M_2(N_2 \leftarrow N_1)$ have been obtained. A. A. ELDRIDGE.

Number of excited atoms and the absorption spectrum of nickel vapour. A. T. WILLIAMS (Nature, 1929, 124, 373).—The equation  $N'/N = e^{-E/RT}$ , where N' is the number of excited atoms, N the total number of atoms, and E the energy, is modified to  $N'/N = e^{-(E + \Delta E)/RT}$ , since it is necessary to consider also the energy consumed in passing from one normal configuration to another :  $(3d)^8(4s)^2 \longrightarrow$  $(3d)^9(4s) = \Delta E$ . A. A. ELDRIDGE.

New zinc hydride bands in the ultra-violet. E. BENGTSSON and B. GRUNDSTRÖM (Z. Physik, 1929, 57, 1—10).—The new band system investigated extends from  $\lambda 2500$  to 2000 Å., and five bands at 2092, 2152, 2240, 2332, and 2351 Å. are analysed. These bands have only simple *P* and *R* branches, the *P*-branch being always somewhat more intense. The term-differences of the initial and end states are obtained. They represent a  ${}^{1}\Sigma' \longrightarrow {}^{1}\Sigma$  electron switch of an ionised Zn<sup>+</sup>H dipole. From these five bands it is possible to place a large number of bands in a level scheme. The dissociation energies of both electron states are calculated from the convergence limit to be D'=4.4 and D''=2.5 volts. A. J. MEE.

Regularities in the arc spectrum of arsenic. K. R. RAO (Proc. Roy. Soc., 1929, A, 125, 238-246). -The spectrum of arsenic has been photographed between 8800 and 1370 Å., using as source the arc between metallic arsenic contained in poles of carbon or aluminium. No lines have been observed in the infra-red region. The arc in nitrogen was used for investigating the Schumann region down to 1650 A. and below this region the arc in a vacuum between carbon poles containing arsenic and the spark between metallic arsenic in hydrogen. Several new lines have been measured which have led to the identification of combinations due to the electron transitions from the deepest 4p state to the higher 5s, 4p', and 4d states. The resonance triplet corresponds with the combin-L. L. BIRCUMSHAW. ation  $4p^4S - 5s^4P$ .

Magnetic separation in the spectrum of ionised krypton. C. J. BAKKER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 565—577).— The magnetic separation of the Kr II spectrum has been investigated. The g-values of the terms arising from the coupling of the 5s and 5p electron have been fixed and it is shown that g-values with strong "anomaly" appear. The g-sum rule has been confirmed. A comparison of the g-values of analogous terms in the spectra of Ne II, A II, and Kr II is given. R. A. MORTON.

First spectrum of krypton. W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Bur. Stand. J. Res., 1929, 3, 129-162).-About 200 lines (3302.54 to 9751.77 Å.) characterising the spectrum of neutral krypton atoms have been photographed, and a list of estimated intensities and measured wave-lengths has been obtained. The main spectral terms. analogous to those in the related neon and argon spectra, have been identified and nearly all the Kri lines classified in series of various types. From the combinations and series limits absolute terms are derived and the ionisation potential of 13.940 volts is deduced. The Kr I spectrum is closely analogous to NeI and AI and good agreement with theory is obtained. The proposed substitution of the krypton line 5649.56 A. for the cadmium line 6438.4696 A. as a primary standard of wave-length is open to objection because the krypton line has relatively low intensity and involves a metastable level. The line 5870.92 Å. is in these respects preferable, but it cannot be recommended as a standard until it has been re-examined for hyperfine structure.

R. A. MORTON. Extension of the Cd I-like isoelectronic sequence to Sb IV and TeV. R. C. GIBBS and (MISS) A. M. VIEWEG (Physical Rev., 1929, [ii], 34, 400—405). —The spectra of tin, antimony, and tellurium were photographed with a vacuum spectrograph. New Sn III lines, additional to those classified by Green and Loring (cf. A., 1928, 2), were identified, particularly second members of series. Sb IV lines were identified arising from transitions  $5s5p-5s^2$ , and from  $5p^2$ , 5s5d, and 5s6s to 5s5p; some second members were also found. The Cd I-like isoelectronic sequence was extended through Te V by the classification of lines resulting from transitions as in Sb IV.

N. M. BLIGH. First spectrum of xenon. W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Science, 1929, 69, 406; Chem. Abstr., 1929, 2655).—A preliminary notice of a new list of estimated intensities and measured wave-lengths for about 300 lines of the Xe I spectrum between 3442.7 and 9923.10 Å. Spectral terms accounting for most of the lines have been identified; the largest term,  ${}^{1}S_{0}$ , represents the normal state of the neutral atom and has a value 97,835, from which an ionising potential of 12.078volts is derived. L. S. THEOBALD.

Arc spectrum of platinum. J. J. LIVINGOOD (Physical Rev., 1929, [ii], **34**, 185–198).—Eight new levels and 44 new combinations were found in Pt I, and 56 new lines were measured in the ultra-violet. Many levels were interpreted from an examination of the Zeeman effect and from the g-values. Low structures are  $d^9s$ ,  $d^8s^2$ , and  $d^{10}$ ; middle terms arise from  $d^9p$  and  $d^8sp$ ; high configurations are  $d^9$ .s,  $d^8s$ .s, with an indication of  $d^8s$ .d. Quintuplet terms appear in the middle and high sets. Evidence shows that the Russell-Saunders coupling has almost completely broken down. Similarity with the theoretically analogous spectrum of NiI is only approximate. The ionisation potentials calculated approximately are 8.9 for  $d^9s$  to  $d^9$  and 9.7 volts for  $d^9s$  to  $d^8s$ . N. M. BLIGH.

Mean life for the mercury spark spectrum. L. R. MAXWELL (Physical Rev., 1929, [ii], 34, 199— 206; cf. this vol., 112).—Mean life values found for the lines 3114 and 2572 of Hg IV were  $9 \times 10^{-7}$  and  $8 \times 10^{-7}$  sec., and for the lines 3090, 3312, and 4797 Å. of Hg III were  $6 \times 10^{-7}$ ,  $4 \times 10^{-7}$ , and  $4 \times 10^{-7}$  sec., respectively. The prominent lines of Hg II have an estimated mean life of the order  $10^{-8}$  sec. These results indicate that the greater the charge of the ion producing the line the longer is the mean life. Spark lines are produced by single electron collisions.

N. M. BLIGH.

Line absorption of mercury vapour for the line 2537 A. H. KOPFERMANN and W. TIETZE (Z. Physik, 1929, 56, 604-616).-The total absorption of the 2537 Å. mercury resonance line by a layer of mercury vapour was measured by a photo-electric method at five different temperatures between  $-11^{\circ}$ and 20°. The f-values for the line were calculated by the use of a formula connecting it with the product of the maximal absorption coefficient and the layer length. For the comparison of this f-value with that derived by other methods, e.g., measurement of the absorption of the pressure-widened lines and anomalous dispersion, it must be remembered that the 2537 Å. line has a complex structure, being made up of five lines at a distance of about 0.01 Å. from each other. The f-value is intermediate between those obtained for the extreme lines and is practically equal to one fifth of the total f-values. The normal life-period of the  ${}^{3}P_{1}$  state of mercury calculated from five times the f-value is in good agreement with the life-value obtained by other methods. A. J. MEE.

Efficiency of excitation by electron impact and anomalous scattering in mercury vapour. W. H. BRATTAIN (Physical Rev., 1929, [ii], 34, 474–485; cf. Messenger, A., 1927, 85; Maxwell, A., 1926, 989; Jones, A., 1928, 1168).—The efficiency of excitation by electron impact of the 6.67-volt resonance level in the mercury atom was studied as a function of the energy of the incident electrons. The electrons which have lost energy are separated out by a small retarding field and measured. The number of collisions is calculated from the experimental value of the mean free path. For the range 6.67-7.07 volts the maximum efficiency is 0.06 at 6.77 volts, falling to 0.04 at 7.0 volts. The number of electrons scattered elastically at large angles by mercury vapour as a function of their energy was measured for an energy range of 2—10 volts. Singularities were found corresponding with an increase in large angle scattering, the most prominent being at 4.9, 5.7, and 6.3 volts, and the less prominent at 9.6, 10.3, and 11.1 volts.

N. M. BLIGH.

Origin of long infra-red radiation of mercury. W. KROEBEL (Z. Physik, 1929, 56, 114–130).—In order to test the speculations of Franck and Grotrian as to the origin of the radiation from mercury vapour in the region 400–200  $\mu$  the conditions under which this radiation is emitted and absorbed have been

investigated. The method consisted in measuring the indications of a radio-micrometer on which was allowed to fall the total long wave radiation from a specially designed mercury arc lamp, the whole being contained in an atmosphere of dry air to avoid absorption by water vapour. Radiation of wave-length below 200 µ was removed by a series of filters, the final one being blackened cardboard, for which Rubens gives a transmissibility of 9% for  $\lambda \ge 200 \mu$ . It was found that the radiation  $\lambda \ge 200 \mu$  was quenched by the addition of hydrogen to the arc source, but slightly increased by the addition of nitrogen; the radiation is absorbed by excited mercury vapour which is produced in the arc, and by mercury vapour excited by 4.9-volt electrons. It is therefore concluded, in agreement with the theory of Franck and Grotrian, that the radiation in question arises from a metastable excited Hg, molecule. R. W. LUNT.

Relation between the intensities of multiplets of mercury and of neon and the energy of the exciting electrons. W. ENDE (Z. Physik, 1929, 56, 503-515).-The relative intensities of multiplets of mercury and of neon have been determined from spectrograms of the luminescence excited in these gases in an approximately field-free space by electrons of energy from 12 to 40 volts. The relative intensities of the components of the mercury triplet  $2^{3}P - 2^{3}S_{1}$ , 5461, 4358, and 4047 Å. were 60:100:49±5%; the ratios were independent of the electron energy and almost independent of the strength of the electron beam. For the triplet  $2^{3}P_{2}-3^{3}D$ , 3663, 3655, 3650 Å. the ratios were 53:51:100, again independent of the electron energy. The measurements in neon were carried out at a constant pressure of 0.8 mm. and relate to the red and yellow groups of lines. The relative intensities differ widely from those observed by Dorgelo in the positive column. R. W. LUNT.

Spark spectrum of thallium, TI III. J. C. MCLENNAN, A. B. MCLAY, and M. F. CRAWFORD (Proc. Roy. Soc., 1929, A, 125, 50—53; cf. Carroll, A., 1926, 214).—The term structure of the second spark spectrum of thallium has been investigated, and the real F and G first members and members of each of the S, P, and D series higher than those already located by Carroll (*loc. cit.*) have been identified. The term values are based on the value zero for the state  ${}^{1}S(5d^{10})$  reached at ionisation. The ionisation potential, computed from the value 240,600 cm.<sup>-1</sup> for  $6s^{2}S_{\frac{1}{2}}$  term, is 29.7 volts. The wave-lengths assigned to TI III, together with their wave-numbers, intensities, and series designations, are tabulated.

L. L. BIRCUMSHAW.

Second spark spectrum of lead, Pb III. S. SMITH (Physical Rev., 1929, [ii], 34, 393-399; cf. this vol., 113, 227).—The multiplets  $6^{3}P_{0,1,2}-8^{3}S_{1}$ ,  $6^{3}P_{0,1,2}-7^{3}D_{1,2,3}$ ,  $7^{3}P_{0,1,2}-7^{3}D_{1,2,3}$ , and  $6^{3}P_{0,1,2}-pp^{3}P_{1}$ arising from combinations between triplet terms of Pb III were found. Twenty-one lines arising from combinations between singlet terms and intercombinations between singlet and triplet terms were identified. The  $pp^{1}D_{2}$  term is found in combination with  $6^{3}P_{1,2}$ ,  $6^{1}P_{1}$ ,  $6^{3}F_{2,3}$ , and  $6^{1}F_{3}$ . Seven new lines of Tl II are given, corresponding with some of the Pb III combinations. N. M. BLIGH.

Band spectra. R. RUEDY (J. Phys. Radium, 1929, [vi], 10, 129-160).-A theoretical review based on Hund's theory slightly modified in regard to rotatory "doubling." The phenomenon is a general property of molecular electronic levels  $i_e > 0$  and is not characteristic merely of symmetrical molecules. The relationships between the spectra of copper, silver, and gold atoms and the spectra of compounds of these metals disclose evidence of transitions between metastable states. The theory of the intensities of the bands of molecular oxygen is in agreement with experience concerning the vibration state. The selection rules for transitions between rotation levels (P,Q, and R branches) are not as strict as for atoms and depend on the speed of rotation and the nature (electric moment) of the molecule. R. A. MORTON.

Spectrum of the aurora borealis. J. KAPLAN (Science, 1929, 69, 296–297).—Two weak lines of wave-length 5176 and 5149 Å. in the auroral spectrum can be accounted for by assuming that collisions of the second kind take place between nitrogen atoms in the  $^{2}D$ -state and metastable nitrogen molecules in the  $A_{0}$  and  $A_{1}$  levels. L. S. THEOBALD.

Spectrum of sunlit aurora rays as compared with the spectrum of lower aurora in the earth's shadow. C. STORMER (Nature, 1929, **124**, 263—264).

Form and structure of sparks. **VI.** T. TERADA, U. NAKAYA, and R. YAMAMOTO (Sci. Papers Inst. Phys. Chem. Res., 1929, 10, 271-290).-The effects of various volatile organic compounds on the form of long sparks in air has been investigated. The vapours of methyl iodide, ethyl iodide, chloroform, carbon tetrachloride,  $\beta\beta$ -dichloropropane, and ethylene dichloride smooth out a zigzag spark; ethyl bromide has no effect. Alcohols, ether, and acetone cause branching of the spark and a gap in luminosity near the negative electrode. Benzene vapour is supposed to favour the formation of positive brush discharges. A transition stage in the type of spark is produced by benzoyl chloride and benzotrichloride—a smooth part of the spark near each electrode only. Halogen compounds in general, particularly those of chlorine, have the effect of smoothing zigzag sparks if their concentration exceeds a critical value depending on the ratio of the mass of the halogen atom to the mol. wt. of the compound. This effect is held to be due to enhanced ionisation near the electrodes favouring the formation of brush discharges. C. W. GIBBY.

Temperature and the Compton effect. G. E. M. JAUNCEY and H. BAUER (Physical Rev., 1929, [ii], 34, 387—392).—On Debye's theory the intensity of the unmodified X-rays scattered by crystals should increase with rise of temperature, and the ratio of modified to unmodified rays should decrease. This was investigated, using De Foe's method (*ibid.*, 1926, 27, 675). An aluminium absorbing sheet was transferred from the primary to the scattered beam and the ratio of the two ionisation currents was found at  $-140^\circ$ , 25°, and 565°. X-Rays for the wave-length range 0.32-0.62 Å. were scattered by carbon at angles of  $60^\circ$ , 75°, and 90°, and by aluminium and copper at 90° and 130°. No effect of temperature on the ratio of modified to unmodified

rays was detected within the limits of experimental error. N. M. BLIGH.

Compton scattering and the new statistics. S. CHANDRASEKHAR (Proc. Roy. Soc., 1929, A, 125, 231-237).—Mathematical. The Compton scattering by an electron gas is considered on the Fermi-Dirac statistics. Equations are derived which indicate that the distribution of intensity of the radiation scattered by a degenerate electron gas follows a parabolic and not an exponential law. The theory predicts the peak of maximum intensity at a place where the Compton theory for a free-stationary electron predicts a line. Evidence is obtained that the Compton scattering of an electron gas should not be influenced by temperature or by the presence of a magnetic field. L. L. BIRCUMSHAW.

Reflexion and absorption of X-rays of large wave-length. M. A. VALOUCH (Compt. rend., 1929, 189, 283—285).—The reflecting powers of mirrors of different materials (lead and flint glasses, aluminium) have been measured as a function of the angle of incidence for the monochromatic  $K\alpha$  carbon rays (44.9 Å.) produced at 320 volts. Prins' formula (A., 1928, 451) was applied to the experimental results, and the refractive indices and absorption coefficients were obtained. J. GRANT.

Continuous X-ray spectrum. C. ECKART (Physical Rev., 1929, [ii], 34, 167—175).—By the method of wave mechanics the quantum theory is shown to be capable of accounting for the various characteristics of the continuous X-ray spectrum. The theoretical principles are deduced from a schematic model, assuming that the target of an X-ray tube is a plane mirror which completely reflects the electron waves. N. M. BLIGH.

Resolution of the line  $L\beta_2$  into its diagram components and the relative widths of some X-ray spectrum lines. S. K. ALLISON (Physical Rev., 1929, [ii], 34, 176—180).—The line  $L\beta_2$  in iridium, thallium, and uranium was investigated using the double spectrometer. Theoretically the line should be double, its weaker component being designated  $L\beta_{15}$ . In iridium no separation was obtained owing to the width of  $L\beta_2$ ; in thallium an incomplete resolution was obtained. In uranium practically complete separation, averaging 1.86 against a theoretical 1.94 Å., was found. Some experiments were made on the intrinsic widths of certain lines in the *L* series of thallium and lead. N. M. BLIGH.

K-X-ray absorption spectra of some chlorine compounds in aqueous solution. O. STELLING (Naturwiss., 1929, 17, 689).—The wave-length values for the K-absorption spectrum of chlorine are slightly different when solid sodium chloride, potassium chloride and chlorate are used. The results for nearly saturated solutions of chlorides differ, not only among themselves, but also from those of the solids. The values for potassium chlorate in solution and in the solid state are almost the same. R. A. MORTON.

Scattering of X-rays in mercury vapour. P. SCHERRER and A. STÄGER (Helv. phys. Acta, 1928, 1, 518-533; Chem. Zentr., 1929, i, 1081).—The F-curve taneously by an improved form of Foote and Mohler's space-charge method (A., 1925, ii, 919), and an

A. A. ELDRIDGE. Motion of an electric arc in a magnetic field under low gas pressure. R. TANBERG (Nature, 1929, 124, 371---372).

Use of series inductance in vacuum spark spectra. R. C. GIBBS, (MISS) A. M. VIEWEG, and C. W. GARTLEIN (Physical Rev., 1929, [ii], 34, 406— 408).—An inductance was used in series with the spark gaps and condenser, as an aid to the identification of lines in the spark spectra of antimony and tin in the region below 2600 Å. The general effect is to strengthen lines arising from lower states of ionisation and to weaken those from higher states. Line identifications for the two elements are corrected.

N. M. BLIGH.

Electric arc in mixed gases. F. H. NEWMAN (Phil. Mag., 1929, [vii], 7, 1085-1091).-The author's third electrodemethod has been found to be inadequate for the starting of arcs in helium and neon atmospheres at pressures of 10-3 to 1 mm. This difficulty was eliminated by the fusing to the cathode of a small bead of borax, the effect of which is assumed to be a reduction in the cathode potential fall, which is then sufficient to ionise the molecules. With the arcs in the pure gases the characteristic radiations were absent, the arc core being white in colour with a surrounding column of yellow radiation showing only the D-lines. The Balmer lines were present with the CN bands. The effect of the addition of water vapour to either neon or helium was to enhance the Balmer lines and other lines of impurities while reducing considerably the spectra of the main gases.

A. E. MITCHELL.

New electroscope. B. F. J. SCHONLAND (Proc. Camb. Phil. Soc., 1929, 25, 340—343).—A new type of ionisation electroscope is described which combines a high voltage-sensitivity with a small capacity, and has a sensitivity for quantity of electricity of the same order as a combination of an ionisation chamber and a Compton electrometer. J. W. SMITH.

Photo-electric threshold of a doubly-evaporated film. R. B. JONES (Physical Rev., 1929, [ii], 34, 227-232).-An investigation was made to determine what energy fraction is spent in separating the electron from the original atom, and what work is done to take the electron through the outer surface when light is incident on a metallic surface. The preparation of a platinum, nickel, and platinumnickel film by evaporation, simultaneously and under the same conditions, is described. Threshold wavelengths found from saturation photo-electric currents obtained with monochromatic light of different wavelengths were Ni 3333, Pt 2804, Ni-Pt 3318 Å. Similar investigations with platinum and tungsten gave W 2338, Pt 2831, Pt-W 2804 Å. It is concluded that the threshold of the mixtures of two metals is the same as that of the constituent having the threshold of lower frequency. N. M. BLIGH.

Photo-ionisation of the vapours of cæsium and rubidium. E. O. LAWRENCE and N. E. EDLEFSEN (Physical Rev., 1929, [ii], **34**, 233-242).—Light intensities and photo-ionisation were measured simultaneously by an improved form of Foote and Mohler's space-charge method (A., 1925, ii, 919), and an equation is given connecting the ionisation per unit light intensity and the frequency in the case of cæsium and rubidium over the range 2200—3130 Å. The equation is in agreement with the relation that the effective collision capture cross-section of the ions for electrons varies inversely as the square of the energy of the electrons relative to the ions, or the Thomson recombination law, confirmed by Oppenheimer by wave mechanics (A., 1928, 456). Photoionisation by absorption of principal series lines in cæsium was confirmed and was observed also in rubidium. N. M. BLIGH.

Longitudinal distribution of photo-electrons. A. CARRELLI (Z. Physik, 1929, 56, 694-701).--Mathematical. The longitudinal distribution of photoelectrons is calculated by applying the new wavemechanics with the theoretical treatment of Sommerfeld. The Sommerfeld expression is only a first approximation for the case when the wave-length is large compared with atomic dimensions, but the formula here derived applies without restriction of wave-length. The formula shows a dependence hitherto unknown on the atomic number of the substance. A. J. MEE.

Effect of hydrogen on the thermionic emission from potassium. H. R. LAIRD (Physical Rev., 1929, [ii], 34, 463-473).-The thermionic currents at a given temperature were observed for a potassium surface successively cleaned by distillation and contaminated by hydrogen, and it was concluded that the large currents frequently observed from potassium are due to hydrogen contamination. A uniform field appeared to be an essential condition for the saturation of the thermionic currents at 150-185°, and probably to below 100°. The Richardson-type equation was obeyed over the range 150-210°. A value of approximately 1.3 volts for the thermionic work function  $\phi$  was characteristic of the potassium surface after hydrogen contamination of a certain type (cf. Richardson and Young, A., 1925, ii, 343). This value was concluded to be due to a layer of KH on the potassium surface, and the emission being due to its decomposition was chemical rather than thermionic in origin. Values of  $\phi$  of 0.26 volt were found at 100-110°. The conductivity of a thin layer of potassium on a pyrex insulating tube was greatly decreased by exposure to hydrogen. N. M. BLIGH.

Distribution of electrons between the plate and grid of a three-electrode tube as determined by positive cæsium ions. J. M. HYATT (Physical Rev., 1929, [ii], 34, 486—492).—Previous work was continued (cf. this vol., 228) using a plane-anode type of tube containing cæsium vapour, the source of ions being a tungsten filament. The plate current and positive ion current emitted from the filament were observed for several negative grid potentials as the plate potential was varied; the number of electrons emitted from the cæsium-covered grid per positive ion was calculated and found to increase uniformly from zero at 95 volts to 0.24 at 600 volts. An investigation of the ratio of the positive ion current to the plate to the positive ion emission from the filament is described. N. M. BLIGH.

Effect of light on the secondary electron emission of aluminium. E. FREY (Helv. phys. Acta, 1928, 1, 385-416; Chem. Zentr., 1929, i, 1084).—Illumination of non-outgassed aluminium plates with a quartz mercury lamp causes a diminution of secondary electron emission in a high vacuum. A. A. ELDRIDGE.

Critical potentials of methane. E. PIETSCH and G. M. SCHWAB (Z. Physik, 1929, 55, 231-233).— The decomposition of methane by 15·4-volt electrons is discussed in relation to the recent work of Hogness and Kvalnes (this vol., 242), in which it was concluded that  $CH_3^+$  ions were produced by electrons of this energy. It is shown that the authors' earlier results could be attributed either to direct decomposition of the methane molecule and the simultaneous but independent formation of  $CH_3^+$  ions, or to a rapid secondary reaction between  $CH_3^+$  ions and monatomic hydrogen adsorbed on the electron source. R. W. LUNT.

Emission of electrons from metals on irradiation with X-rays. W. ESPE (Ann. Physik, 1929, [v], 2, 381-426).—The action of X-rays in liberating electrons from metals has been studied quantitatively in relation to the different variable factors. On the basis of Einstein's law of equivalence formulæ have been derived for the number of electrons set free when the X-rays strike the metal at 90° and at  $\phi^{\circ}$ , and it is found that the emission should increase as  $1/\cos \phi$ . For the rapid electrons this proportionality is strictly in accord with experiment, but for the slower secondary electrons the theoretical value is too low, the error amounting to 10% when  $\phi$  is 50°. The error is less for roughened surfaces than for highly polished metal. Comparison of the strength of the electron emission for smooth and roughened surfaces shows that the emission of slow secondary electrons from a polished plate is at a minimum and increases with increasing roughness. The emission of rapid electrons decreases a little when a smooth plate is roughened. The electron emission increases with the atomic number of the metal irradiated, up to a point when the frequency of the radiation in use is exceeded by the excitation frequency of the metal. The relation between electron omission and the wave-length of the incident radiation has also been studied. The results disclose deviations from the Einstein law of equivalence which are accounted for by variable absorption of electrons by the metal. Since emission is proportional to the intensity of the exciting radiation, it is possible indirectly to determine the relation between intensity of X-rays and voltage applied to the tube. Electron emission E (for anticathodes of iron, nickel, and copper) varies as  $V^3$  (V=voltage) minus a constant. Palladium charged with hydrogen shows no measurable increase in emission of slow or rapid electrons as compared with uncharged palladium. R. A. MORTON.

Radii and collision probabilities of metastable neon and mercury atoms. M. W. ZEMANSKY (Physical Rev., 1929, [ii], 34, 213—226).—Theoretical. Assuming that metastable atoms either diffuse to the

walls of the container and give up their energy there, or are raised to a higher or lowered to the normal state by impact with other atoms, it is deduced that for large values of the time clapsing after the cut-off of the excitation the average number of metastable atoms per c.c. decays exponentially with the time.

N. M. BLIGH.

Analysis of electronic velocities by electrostatic means. A. L. HUGHES and V. ROJANSKY (Physical Rev., 1929, [ii], 34, 284—290).—Theoretical. From the equation of the electronic orbits it is shown that an analysis of electronic velocities should be possible by a radial electrostatic field as well as by the usual magnetic field. The plane of the receiving slit should be at an angle of 127° 17' to the plane of the entrance slit. Expressions are found for the resolution at this angle, between two electrons with slightly different velocities, and for the departure from perfect re-focussing of two electrons with the same velocity. N. M. BLIGH.

Distribution of mobilities of ions in moist air. J. ZELENY (Physical Rev., 1929, [ii], 34, 310—334).— A method which was used to measure the mobilities and distribution of the ions in air for various degrees of humidity is described, and a critical study of the effects of diffusion on the distribution of ions moving in an electric field was made; the results obtained were in fair agreement with theory. The mobilities of ions varied from 45% greater than the slowest for positive ions to 30% for negative ions. Groups of ions having different mobilities were not detected. Theoretical explanations of the distribution are discussed. The average mobility found for the negative ions was 2.00 and for positive ions 1.22 cm./sec. per volt/cm. for water contents of 3.2 and 2.7 mg. per litre of air, respectively. N. M. BLIGH.

Longitudinal magnetic effect on beams of slow electrons. Periodic concentration and dilatation. J. THIBAUD (J. Phys. Radium, 1929, [vi], 10, 161-176).—See this vol., 231.

Quantum theory of electronic scattering by helium. N. F. Morr (Proc. Camb. Phil. Soc., 1929, 25, 304-309).—The approximations introduced by Born (Z. Physik, 1926, 38, 803) in the calculation of the variation of electron scattering with angle in the case of hydrogen are discussed. Using the same approximations, similar calculations are made for the case of helium, the results being in good agreement with the measurements of Dymond and Watson (this vol., 368). J. W. SMITH.

Dispersion electrons in the one-electron problem. J. HARGREAVES (Proc. Camb. Phil. Soc., 1929, 25, 323—330).—Mathematical. Dirac's relativity quantum mechanics is used to derive the Kramers-Heisenberg dispersion formula for an atom with one electron and the dipole moment to which is due the incoherent scattering. The formulæ obtained are similar to those obtained by Klein (Z. Physik, 1927, 41, 407) for the case of a central field, but are not limited to this case. This yields an expression for f (the number of dispersion electrons for any line of the optical spectrum) in terms of the solutions of the four wave equations of Dirac's theory. For any state of the atom  $\Sigma f$  is not equal to unity as deduced by London (cf. A., 1926, 1191) from the original simple wave equation of Schrödinger, but, owing to the relativistic treatment, differs from it by an amount of the order of  $10^{-4}$ . J. W. SMITH.

Layers of cæsium and nitrogen on tungsten. N. A. DE BRUYNE (Proc. Camb. Phil. Soc., 1929, 25, 347-354).-When a tungsten filament is heated in cæsium vapour in the presence of a trace of nitrogen, the curve of emission against temperature shows two maxima, one being at the usual position observed in the presence of cæsium, whilst the other occurs at a higher temperature. The minimum energy which the electrons must be given for this peak to appear lies between 4 and 9 volts, which is lower than the work of dissociation of the nitrogen molecule and much lower than its ionisation potential. Hence it is concluded that the effect must be due to excited atoms or molecules. As it seems impossible that an electro-negative element such as nitrogen could itself cause increased emission, it is suggested that the function of the activated nitrogen is to hold the cæsium atoms to the surface to a temperature above that at which a cæsium atom alone can adhere.

J. W. SMITH. Ionisation of hydrogen by its own radiations. J. THOMSON (Phil. Mag., 1929, [vii], 7, 970-980).-The indications previously obtained (A., 1928, 1067) that hydrogen could be ionised by its own radiations have been confirmed, it having been found that the pure dry gas is ionised by radiations emitted by a point discharge within it. It is suggested that the ionisation is effected in stages, the molecules absorbing two or more energy quanta either from the radiations or by collisions with other active molecules. Some of the peculiar phenomena observed by Chattock and Tyndall (Phil. Mag., 1910, [vi], 19, 449) in their investigations of the pressure of the electrical wind are explained from a consideration of the ionising radiations emitted by the gas in the immediate vicinity of metallic points charged to high potentials. A. E. MITCHELL.

Effective cross-section of the heavy inert gases with respect to electrons below 1 volt. C. RAMSAUER and R. KOLLATH (Naturwiss., 1929, 17, 671).—Preliminary. The curve effective crosssection/electron velocity in volts has been plotted for xenon, krypton, and argon for the region 0—2 volts, particular attention being given to the range 0·1— 1·0 volt. R. A. MORTON.

Ramsauer effect in argon. J. HOLTSMARK (Z. Physik, 1929, 55, 437-446).—The elastic scattering of electrons in argon has been evaluated by the method of Faxén and Holtsmark (*ibid.*, 1928, 52, 485) using the data of Hartree for the atomic field. It is shown that the Ramsauer curve for the effective target area as a function of the electron velocity may be considered as equivalent to the supposition of the target areas corresponding with zero, first, and second orders of the monochromatic  $\psi$ -waves by which a homogeneous electron beam may be represented. R. W. LUNT.

Absorption coefficient for slow electrons in mercury vapour. R. B. BRODE (Proc. Roy. Soc.,

1929, A, 125, 134-142; cf. A., 1925, ii, 1020).-The absorption coefficient  $\alpha$  in mercury vapour for electrons with energies of 0.5-400 volts has been determined, using a modification of Ramsauer's apparatus for measuring the effective cross-sectional area of a gas. By employing as the source of electrons a tungsten filament in the centre of a cylinder with a fine longitudinal slit in the side, a very fine beam of electrons could be produced. No indication of a Ramsauer effect, *i.e.*, small values of  $\alpha$  for lowvelocity electrons, was observed. The value of  $\alpha$  was high at 0.5 volt and decreased rapidly with increasing velocity, a small change in the decrease being observed at about 5 volts. A minimum was reached at 20 volts and a maximum at 35 volts, followed by a regular decrease. Comparison with the results of previous investigators shows that Maxwell's measurements (A., 1926, 989) are on the whole in best agreement with the present values. Beuthe's recent work (A., 1928, 213) is criticised on the ground of inadequate experimental conditions. L. L. BIRCUMSHAW.

Activation of oxygen by electron impact. R. H. DALTON (J. Amer. Chem. Soc., 1929, 51, 2366—2374).—Besides the critical potential of 7.9 volts, oxygen in presence of carbon also shows, more particularly between 0.2 and 0.4 mm., a critical potential of 10.6 volts. Oxygen excited by electron impact between these critical potentials reacts readily with carbon to yield mainly carbon dioxide. It is suggested that the critical potential of 10.6 volts may be due to carbon dioxide and not to oxygen (cf. A., 1927, 187). S. K. TWEEDY.

Mass-ratio of proton and electron. R. FÜRTH (Naturwiss., 1929, 17, 688—689).—The fact that the numbers z and  $\mu$  ( $z=hc/e^2$ ,  $\mu=m_P/m_E$ , h being Planck's constant,  $m_F$  and  $m_E$  the respective masses of protons and electrons) are of the same order has been studied. Assuming the interconversion of radiation and matter  $r_P+r_E=\lambda=c/\nu$  ( $r_P$  and  $r_E$  being the radii of protons and electrons), and equating energies  $m_Pc^2+m_Ec^2=h\nu$ ; assuming a purely electrostatic origin of kinetic energy,  $m_Pc^2=e^2/kr_P$  and  $m_Ec^2=e^2/kr_E$ , k being a numerical constant. The above equations lead to  $\mu^2+\mu(2-kz)+1=0$ , and since z is great compared with 1,  $\mu_1=kz-2$ ,  $\mu_2=1/$ (kz-2). Putting k=2 and  $z=861\cdot5$ ,  $\mu=1721$ , whilst if evidence in favour of k=32/15 is accepted  $\mu=1836$ as against the experimental value of 1846. Thus the ratio of  $m_P$  and  $m_E$  follows from general quantum theory considerations. R. A. MORTON.

theory considerations. R. A. MORTON. Electron counting tube. H. GEIGER and W. Müller (Physikal. Z., 1929, 30, 489–493).—Experimental (cf. this vol., 114). R. A. MORTON.

Investigation of natural *H*-rays with the tube electrometer. E. A. W. SCHMIDT and G. STETTER (Z. Physik, 1929, 55, 467–482).—By using the electrometer method of Ortner and Stetter the specific ionisation produced by beams of *H*-particles of approximately uniform velocity has been measured. Over a wide range of velocity it was found that the specific ionisation was one quarter of that produced by  $\alpha$ -particles. Discrepancies between the electrometer and scintillation methods are discussed.

R. W. LUNT.

Gyro-magnetic effect and the magnetic deflexion of atomic rays from the viewpoint of the new theory of magnetism. K. HONDA (Z. Physik, 1929, 56, 857-861; cf. A., 1928, 454).---Assuming a nucleus of a ferro-magnetic atom to possess a magnetic moment but no appreciable moment of momentum, an explanation is given for the observed fact that the gyro-magnetic ratio is half that expected on the simple electron theory. This conception is also used to provide an explanation for experimental results on atomic rays obtained by experiments such as those of Gerlach and Stern (Ann. Physik, 1924, [iv], 74, 673; 1925, 76, 163).

J. W. SMITH. At. wt. of helium. A. UPMARK (Z. Physik, 1929, 55, 569—574).—The at. wt. of normal and ionised helium is discussed in the light of the author's electrostatic theory of atomic structure; the calculated values are 4-00106 and 4-00216, respectively, the latter being in agreement with Aston's mean value.

R. W. LUNT. Isotope effect in spectra and precise atomic weights. W. F. GIAUQUE (Nature, 1929, 124, 265). —A brief discussion. A. A. ELDRIDGE.

Detection of the isotopes of lead by the band spectrum method. S. BLOOMENTHAL (Science, 1929, 69, 229; cf. Grebe and Konen, A., 1922, ii, 4).-A comparison of the band spectrum of ordinary lead (at. wt. 207.2 and containing the isotopes 208, 207, and 206) with that of uranium lead (at. wt. 206.1) gives results in agreement with theory on the basis of lead monoxide as the emitter of the spectra. The separation expected on theoretical grounds between the lines due to Pb208O and Pb207O near the head of  $\gamma$  5678.3 is -0.37 wave number; that actually measured is -0.43 wave number. The negative sign indicates that the lines from the molecules of the lighter isotope are displaced towards lower frequencies with respect to those from the heavier isotope. L. S. THEOBALD.

Approximate method of determining the highvelocity limits of continuous  $\beta$ -ray spectra. J. A. CHALMERS (Proc. Camb. Phil. Soc., 1929, 25, 331-339).-By observing the thickness of aluminium sheet at which a kink occurs in the absorption curve of  $\beta$ -rays from the disintegration products of thorium, measurements have been made of the high-velocity limits of the continuous  $\beta$ -ray spectra of these elements. The results are discussed theoretically and the possibility of further application of this simple electroscopic method is indicated. The absence of y-rays from thorium-C, as in the case of radium-E (Bastings, A., 1925, ii, 9), is evidence against the supposed connexion between  $\beta$ - and  $\gamma$ -ray hardness; the softness of the  $\beta$ -rays from thorium-C" relative to the very hard y-rays is also contrary to this idea.

J. W. SMITH. Condensation of radioactive substances on solid surfaces. G. H. HENDERSON (Proc. Camb. Phil. Soc., 1929, 25, 344—346).—If a parallel beam of atoms of radon be allowed to impinge on a cooled copper disc, the latter on testing photographically is found not to show a spot representing the geometrical image, but to be fairly uniformly covered with active deposit. This is explained by supposing that the atoms remain adsorbed on the surface only a short time and again fly off. In the case of polonium a deposit was also found spread over the disc, but with a greater density opposite the geometrical image of the source. Distributed over the disc, however, were intensely active aggregates of polonium (cf. Chamié, A., 1927, 605, 1120, 1928, 103); aggregates of the same type were also found on attempting to secure polonium by recoil from radium-E. J. W. SMITH.

Destructive action of  $\alpha$ -rays on thin films of various substances. C. PAWLOWSKI (J. Chim. phys., 1929, 26, 374—378).—The action of  $\alpha$ -rays on thin films of collodion, cellophane, and mica has been examined. The rays cause the conglomeration of water into drops in collodion and cellophane, producing opacity. Mica is thus the most suitable substance for covering the radioactive source in disintegration experiments. J. A. V. BUTLER.

Ionising effect of  $\alpha$ -rays in solid dielectrics. H. FOLMER (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 759—769).—An apparatus is described with which, in conjunction with a Wulf electrometer, attempts were made to obtain evidence of ionisation when polonium rays and intermittent polonium radiation falls on solid paraffin in an electric field. Ions formed would show a tendency to move relative to the field. Current measurements against time were made and the phenomena observed are discussed. Results are inconclusive, but there is some evidence of ionisation. N. M. BLIGH.

Evaluation of radium preparations with the electron counting tube by the  $\gamma$ -ray method. H. NEUFELDT (Physikal. Z., 1929, 30, 494—495).—The method allows amounts of radium down to  $10^{-6}$  mg. to be determined to within 10%. The sensitivity is 1000 times that of other methods. An automatic counting device is used. R. A. MORTON.

**Preparation of radium emanation.** K. PETERS and K. WEIL (Naturwiss., 1929, 17, 690).—If the preparation of radium emanation is carried out under conditions permitting the  $\gamma$ -activity of the residue and the emanation to be determined during the progress of the separation, evidence is obtained of the existence of  $\gamma$ -radiation of about 1 minute life period arising from a volatile carrier. The material is condensed at —185°, and is apparently a gas. The work is being carried out on radium from other sources in order to ascertain if the particular material used contained an unusual constituent.

R. A. MORTON. Use of radioactive recoil atoms for diffusion measurements. G. von HEVESY and W. SEITH (Z. Physik, 1929, 56, 790—801).—The emission of  $\alpha$ -ray recoil atoms from a film of the chloride of thorium-*B* deposited on a surface of lead chloride diminishes on warming to temperatures between 160° and 270°. This change affords an accurate method of measuring velocities of diffusion in lead halides down to diffusion constants of 10<sup>-13</sup> cm.<sup>2</sup> per day. The values obtained for the diffusion constants of lead ions in lead chloride and lead iodide are  $D=1.06 \times 10^{7} e^{38120/RT}$  and  $D=3.43 \times 10^{4} e^{3000/RT}$ , respectively. In the case of the iodide a value of the same order has been obtained by measurements of the decrease of  $\alpha$ -ray activity. The transport number of the lead ion is calculated to be 10<sup>-5</sup>. These values are in good agreement with the observations of Tubandt (Z. Elektrochem., 1928, 34, 482). The high value of the heat of relaxation of the lead ion (38120 g.-cal.) compared with that of the chlorine ion (11180 g.-cal.) explains the observation made by Tubandt that the conductivity in the solid state is due almost entirely to the chlorine ion. J. W. SMITH.

[Radio]activity of lead obtained from the roof of Paris Observatory. A. SMITS and (MISS) C. H. MACGILLAVRY (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 610—613).—The observation of Maracineanu (A., 1925, ii, 348) that  $\alpha$ -particles are emitted from lead, but only from the surface exposed to the sun's rays, has been confirmed with a sample cut from the roof of Paris Observatory two years previously. Lead is being subjected to solar radiation in sealed quartz vessels in order to establish whether the effect is due to irradiation or to atmospheric dust. R. A. MORTON.

Calculation of radioactive decay constants by wave mechanics. T. SEXL (Z. Physik, 1929, 56, 62-71).—The suggestions of Gamow, Gurney, and Condon have been elaborated into an exact analysis by means of which the decay constants of the three radioactive groups have been calculated; the values are in good agreement with experiment.

R. W. LUNT.

The differential equations of the treatment of radioactive α-particle emission in wave mechanics. T. SEXL (Z. Physik, 1929, 56, 72-93). --Mathematical. R. W. LUNT.

Reflexion of atoms from crystals. A. ELLETT, H. F. OLSON, and H. A. ZAHL (Physical Rev., 1929, [ii], **34**, 493—501; cf. A., 1928, 566).—The specular reflexion of beams of cadmium atoms from clean cleavage surfaces of rock-salt was investigated, and an expression is given for the velocity of the reflected beam; the conditions for specular reflexion from a second crystal are considered. Results indicate that associated with motion of translation of uncharged atoms and molecules there is a wave phenomenon of the type postulated by de Broglie. N. M. BLIGH.

Wave-mechanics of an atom with a non-Coulomb central field. IV. Further results relating to terms of the optical spectrum. D. R. HARTREE (Proc. Camb. Phil. Soc., 1929, 25, 310-314; cf. A., 1928, 216, 933).—Mathematical.

J. W. SMITH.

Derivation of the dispersion formula according to the Dirac theory of the electron. K. NIKOLSKY (Z. Physik, 1929, 56, 709-712).—Mathematical. The form of the dispersion expression is the same as is obtained by the use of the older theory.

A. J. MEE.

Lattice energy of LiH and the normal potential of H-. R. S. BRADLEY (Phil. Mag., 1929, [vii], 7, 1081—1084).—Lithium hydride is assumed to have an ionic lattice and the lattice energy is determined from the force constants calculated by the method of

Lennard-Jones assuming that the repulsive exponents of Li<sup>+</sup> and H<sup>-</sup> are unchanged. The value 230.5 kg.-cal. so obtained leads to an internuclear distance of 2.18 Å., as compared with the experimental value 2.01 Å. found by Bijvoet (A., 1923, ii, 857). Calculations based on a thermodynamic cycle involving known thermochemical quantities give 245.2 kg.-cal. as the lattice energy, the discrepancy between the values being attributed to the uncertainties regarding the ionic radius of H<sup>-</sup> and the repulsive exponent in the crystal. The heat of hydration of  $H^++H^-$  is assumed to be the same as that of  $H^++F^-$ , whence the normal potential of H - is found to be -1.70 volts, which value is used to calculate equilibrium concentrations of H-aq., and it is shown that whilst the  $p_{\mu}$ of a solution may be about 14 the concentration of H- is still of the order 10-14 to 10-15, but may be increased by the aid of an oxidation-reduction system such as  $Fe^{++} \rightarrow Fe^{+++} + e$ . A. E. MITCHELL.

Effect of retardation on the interaction of two electrons. G. BREIT (Physical Rev., 1929, [ii], 34, 553-573).

Potential thresholds and radioactive disintegration in quantum mechanics. E. H. KEN-NARD (Physikal. Z., 1929, 30, 495–497).—Theoretical. R. A. MORTON.

Radioactive decomposition and relativity theory. C. Møller (Z. Physik, 55, 451-466).— The quantum mechanical analysis of radioactive process by Gamow and Kudar is discussed from the point of view of relativity. R. W. LUNT.

Rigid theory of diffusion of electrons in gases. H. BARTELS (Z. Physik, 1929, 55, 507-532).—A rigid theory of electron diffusion in rare gases has been derived by developing the analogy between this process and the optical theory of scattering; in contradistinction to Hertz' theory, it leads to integral equations. The application to the special case of diffusion through a finite layer of infinitely diluted gas is discussed in relation to the theory of Hertz, and it is shown that by careful choice of boundary conditions a valuable approximate solution may be obtained. R. W. LUNT.

Wave function and velocity distribution in degenerate gases. W. LENZ (Z. Physik, 1929, 56, 778-789).-Mathematical. J. W. SMITH.

Quantum theory and special relativity. M. S. VALLARTA (Nature, 1929, 124, 336).

Relationship between h, c, and  $e^2$ . W. N. BOND (Nature, 1929, 124, 408–409).—A study of probability, and of the agreement of evidence, throws doubt on the validity of Eddington's relationship ch/ $2\pi e^2 = 136$ , and tends to confirm the equation  $1.0968 \times$  $10^5 = (e^5/h^3)[2\pi^2/c(1+m/M)(e/m)].$ 

A. A. ELDRIDGE.

Second-order wave equations of the spinning electron. G. TEMPLE (Proc. Roy. Soc., 1929, A, 125, 152—156).—Mathematical. The general theory of a system of second-order equations satisfied by a wave tensor of the first rank is given.

L. L. BIRCUMSHAW. New quantum theory of the ideal monatomic gas and Avogadro's law. G. POLVANI (Nuovo Cim., 1928, 5, 307-309; Chem. Zentr., 1929, i, 616-617).

Appearance of noble gases in vacuum tube discharges. D. DOOLEY (Nature, 1929, 124, 372).— No evidence for the production of noble gases from a magnesium nitride film on the electrodes was obtained (cf. Riding and Baly, A., 1925, ii, 925). The appearance of such gases, particularly helium, is probably due to diffusion from the atmosphere.

A. A. ELDRIDGE.

Turbulence in the sun's atmosphere. W. H. MCCREA (Nature, 1929, 124, 442-443).

Packing of atoms in alloys. A. WESTGREN and A. ALMIN (Z. physikal. Chem., 1929, B, 5, 14-28).-The variation of the linear lattice dimensions with composition of the alloy has been investigated in the a-phases of the systems Ag-Al, Cu-Al, and Ni-Al, and in all cases the parameters are less than those calculated by Vegard's addition law from the parameters of the components. From calculations of the volume occupied per atom in the various phases of the above systems, and of the systems Cu-Zn, Ag-Zn, Ag-Cd, Cu-Mg, and Fe-W, it is shown that, in general, a contraction in atomic volume accompanies the formation of the intermediate phases. The atomic volumes in contiguous phases of any system differ only slightly, so that the curves of volumes drawn for a series of phase regions are almost continuous. The volume contraction is especially marked in nickel-aluminium alloys, and it is suggested that this depends on the fact that such alloys are formed by the union of an atom which is deficient in a nuclear electron with one of normal type. F. L. USHER.

Relation between colour and molecular structure in organic compounds. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Indian J. Physics, 1929, 4, 57-78).-Existing theories of colour in relation to structure for organic compounds are reviewed, and a new generalisation is proposed to cover the facts supporting the various older theories. The theory is suggested by a comparison of the structure and physical properties of diamond and graphite. A general parallelism is shown to exist between the colour or light absorption and the degree of optical, electrical, and magnetic anisotropy of molecules from an examination of data on light absorption and scattering, electric and magnetic birefringence, magnecrystalline behaviour, and crystalline birefringence of carbon compounds. Structures and groups favouring colour development tend generally to enhance the degree of optical, electrical, and magnetic anisotropy of the molecule. A theoretical basis for the generalisation is given by the electron theory of dispersion and theories of the origin of optical anisotropy. The mechanism of light absorption is briefly discussed, with reference to electrical conductivity, and the special type of photoconductivity observed in illuminated crystals of high refractive index. N. M. BLIGH.

Intensities in the harmonic band of hydrogen chloride. J. L. DUNHAM (Physical Rev., 1929, [ii], 34, 438-452).—The intensities of the first 9 lines of the negative branch of the first harmonic absorption band of hydrogen chloride at  $1.76\mu$  were measured with a prism spectrograph, using a galvanometer and thermo-relay to observe thermopile voltages. The positive branch, not being resolvable, was measured as a whole. The integrated absorption coefficient of each line was calculated by Bourgin's methods (cf. A., 1928, 1076). A calculation of the intensity ratio of the band as a whole to that of the fundamental from the Schrödinger equation for an anharmonic oscillator shows satisfactory agreement with experiment. The relative intensities of the lines in a band are calculated from an analysis of the effect of rotation, in agreement with experiment. N. M. BLIGH.

Spectrophotometric study of micas. T. YOSHIMURA (Suppl. Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 1—4).—The extinction coefficients of various coloured micas for different wavelengths and different thicknesses of mica have been determined. The extinction coefficients of thinner layers were always greater than those of thicker layers, probably on account of the greater effect of reflexion in the former case. The colour is probably due to colloidal particles, as no characteristic absorption bands were found. C. W. GIBBY.

Rare earths associated with uraninites. J. K. MARSH (Phil. Mag., 1929, [vii], 7, 1005—1011).— An examination of six uraninites from different localities and of ages 205— $900 \times 10^6$  years has shown that the proportion of rare earths associated with the uraninites is greatest in those of greatest age. There is, however, no relationship between the quantities of the different rare-earth metals associated in each uraninite, and it is suggested that the rare earths are intimate associates rather than real constituents of these. The occurrence of the rare earth is attributed to imperfections in the chemical or physical separations which occurred during magmatic segregation and the greater amount of the rare earths in the older minerals is attributed to greater magmatic turbulence and volcanic activity in the earlier geological times.

A. E. MITCHELL.

Absorption spectrum of praseodymium compounds in various term and aggregation conditions. R. BRUNETTI (Nuovo Cim., 1928, 5, 391-403; Chem. Zentr., 1929, i, 1307-1308).--The absorption spectrum of praseodymium compounds in dilute liquid and in solid solution consists of four bands in the visible region between 6000 and 4000 Å. The spectra of various compounds in equal small concentrations show only small differences. The absorption spectrum of the solutions and superimposed polarised multiplets of the crystal show the mean position of the characteristic radiations of the Pr<sup>III</sup> ion. A. A. ELDRIDGE.

Band spectrum of magnesium oxide. P. N. GHOSH, B. C. MOOKERJEE, and P. C. MAHANTI (Nature, 1929, 124, 303).—The spectrum contains eight groups of bands extending from 4372 to 5700 Å.; the 61 band heads have been arranged in the usual n', n'' progression. The vibrational constants (cm.<sup>-1</sup>) of the molecule are :  $\omega_0'$  817.01,  $\omega_0'x'$  2.378,  $\omega_0''$  773.85,  $\omega_0''x''$  2.86. The molecule is of the normal type with small change in the moment of inertia.

A. A. ELDRIDGE.

Spectra of mercury, cadmium, and zinc halides. K. WIELAND (Helv. phys. Acta, 1928, 1, 442—434; Chem. Zentr., 1929, i, 1081—1082).— The spectra of the three chlorides, bromides, and iodides were studied in the region 4000—2300 Å. The mercuric chloride spectrum between 2650 and 2380 Å. consists of nearly 100 bands. The isotope effect for chlorine and bromine was detected.

A. A. ELDRIDGE.

Parameters characterising partial polarisation of light emitted by fluorescence. P. SOLEILLET (Ann. Physique, 1929, [x], **12**, 23—97).—A more detailed treatment of work already published (this vol., 120).

Duration of fluorescence of uranyl salts in the solid state and in solution. R. DELORME and F. PERRIN (J. Phys. Radium, 1929, [vi], 10, 177-186).--Uranyl salts excited by blue light emit intense green fluorescence, the intensity of which has been determined in relation to time by means of a phosphoroscope and a photometric arrangement. The time  $\tau$ , defined by  $I = I_0 e^{-t/\tau}$ , indicating the mean life period of the molecules in the excited state, has been determined at  $20^{\circ}$  and at  $-180^{\circ}$ . For the solid uranyl salts the following values illustrate the results : sulphate (cryst.)  $\tau \times 10^4$  sec. equals 2.5 at 20° and 3.5 at  $-180^{\circ}$ ; nitrate (cryst.  $6H_{2}O$ ) 6·1 and 8; chloride 1.54 and 3.6, respectively. The increased duration effected by cooling in liquid air is therefore relatively small. Dilute solutions of uranyl sulphate in pure sulphuric acid (viscosity 0.2) show fluorescence characterised by  $\tau = 1.4 \times 10^{-4}$  sec. at 17°, the value decreasing with rise of temperature, with increasing concentration, or addition of water. Traces of added substances, e.g., hydrochloric acid, greatly reduce the value of  $\tau$ . Solutions of uranyl metaphosphate in metaphosphoric acid show values of  $\tau$ varying greatly with the viscosity,  $\tau$  being  $0.9 \times 10^{-4}$ sec. for a solution twice as viscous as water, and  $7 \times 10^{-4}$  for a thick glassy solution. The results support the hypothesis that the luminescence is due to simple fluorescence of long duration, i.e., electronic activation followed by spontaneous deactivation.

### R. A. MORTON.

Resonance-fluorescence phenomenon in the cyanogen spectrum. H. T. BYCK (Physical Rev., 1929, [ii], 34, 453-456).-Experiments were made to test Herzberg's view that the intensification of certain pairs of lines in the violet CN bands was due to the absorption of radiation of short wave-length from nitrogen bands in the far ultra-violet (cf. A., 1928, 813, 931; this vol., 489). Radiation from the nitrogen discharge was found to have no effect on the appearance or non-appearance of the doublets; the intensification was found to depend on the pressure under which the excitation of the CN spectrum occurs, and appears to result from collision with some higherenergy atomic or molecular species the formation of which is suppressed at higher pressures. Herzberg's explanation is not supported. N. M. BLIGH.

Diffusion of photoluminescence by repeated absorption and radiation processes. G. A. GAM-BURZEV (Z. Physik, 1929, 55, 533-545).—The changes resulting from diffusion of radiation on the increase or decrease of the duration of luminescence of molecules are considered.

[Observation of] fluorescence. M. HAITINGER and V. REICH (Chem. Fabr., 1929, 379—380).—The exciting ultra-violet light falls vertically on to the surface of the liquid and the resulting fluorescence is observed laterally. The breadth of the fluorescence band at the surface is determined by the nature and concentration of the fluorescent substance and by the solvent used. The intensity of the fluorescence is increased by interposition of a water lens.

J. S. CARTER.

Raman effect. A. DADIEU and F. KOHLRAUSCH (Monatsh., 1929, 52, 220-240).—See this vol., 976.

Does the nitrogen nucleus conform with the Bose statistics ? W. HEITLER and G. HERZBERG (Naturwiss., 1929, **17**, 673-674).—The observations of Rasetti (this vol., 975) on the Raman effect with molecular nitrogen indicate that the nitrogen nucleus complies with the Bose statistics. Important theoretical significance concerning the quantum mechanics of the nucleus is attached to this fact, but the conclusions stand or fall with the correctness of the analysis of the Raman spectrum. R. A. MORTON.

Incoherent scattered radiation in diatomic molecules. F. RASETTI (Physical Rev., 1929, [ii], 34, 367-371).—Using a tube suitable for gases at 10-15 atm. pressure, the Raman spectra excited in hydrogen, nitrogen, oxygen, and nitric oxide by the mercury line 2536 Å. were photographed with a quartz spectrograph. Very complete results were obtained for hydrogen. The constants  $B_0=h/8\pi^2 I_0c$ , for zero rotation, and  $\omega_{0/1}$ , the frequency of transition from the zero to the first vibrational state, are found respectively to have the values  $59\cdot4\pm0.03$  and  $4162\cdot1\pm0.3$  for hydrogen,  $1\cdot992\pm0.005$  and  $2330\cdot7\pm0.2$  for nitrogen, and  $1\cdot436\pm0.005$  and  $1554\cdot7\pm1.0$  for oxygen. The spectra were in accordance with theoretical deductions (cf. this vol., 627, 975; Hill and Kemble, *ibid.*, 865). N. M. BLIGH.

Fine structure of infra-red absorption in organic compounds and the Raman effect. R. B. BARNES (Nature, 1929, 124, 300-301).—The infra-red absorption bands of benzene, toluene, o., m., and p-xylene, ethylbenzene, butylbenzene, chlorobenzene, and bromobenzene have been studied. The benzene band at  $3.25 \mu$  consists of three components at 3.231, 3.253, and  $3.291 \mu$ , respectively. For toluene, intensity changes and new bands which combine to produce an apparent shift to  $3.35 \mu$  are detailed. In o-xylene only one benzene vibration is possible, and it has been shifted by  $0.007 \mu$ . In m-xylene only the band at  $3.291 \mu$  occurs. In p-xylene the bands at 3.231 and  $3.291 \mu$  occurs. In the xylenes a group of strong, complex bands, apparently due to the two methyl groups, occurs in the region  $3.3-3.5 \mu$ . Similar results were obtained with the other compounds. For each Raman line a corresponding infrared band was found, but many of the infra-red bands have not been predicted by the observation of Raman lines. A. A. ELDRIDGE.

Raman spectrum and fluorescence of benzene. C. V. SHAPIRO (Nature, 1929, **124**, 372).—Since the

frequencies concerned in the Raman effect may be attributed to vibrational frequencies, or combinations of such frequencies, of the normal electronic state of the molecule, it is to be expected that these levels will appear as end states in the process of emission or fluorescence. This is confirmed for benzene. All the bands recorded by Riemann (A., 1926, 660) can be arranged in series according to the general equation  $v = v_0 + n'a - n''_1b_1 - n''_2b_2 - n''_3b_3 - n''_4b_4$ , where  $v_0 = 37494$ , a = 921, and the *b* levels (with corresponding Raman values in parentheses) are :  $b_1$  998 (991),  $b_2$ 600 (605), b<sub>3</sub> 855 (853), b<sub>4</sub> 1180 (1176)

### A. A. ELDRIDGE.

Method for measuring the dielectric constants of conducting liquids. A. ASTIN (Physical Rev., 1929, [ii], 34, 300-309).—In view of the wide divergence of reported results, a modified resonance method for determining the dielectric constants of conducting liquids has been applied to dilute solutions of potassium chloride for various concentrations, and also to check values for sugar solutions. The dielectric constant of benzene determined by a method devised for non-conducting liquids and giving absolute values directly was  $2 \cdot 239 \pm 0.005$  at 25°; the value for water by comparison is  $79.5\pm0.5$  at  $25^{\circ}$ 

## N. M. BLIGH.

Dielectric constants of imperfect conductors. R. T. LATTEY and O. GATTY (Phil. Mag., 1929, [vii], 7, 985-1004).-The corrections to be applied, for the inductance of the leads and the effects of leakage, in the determination of the capacity of a condenser are discussed and the results applied in the measurement of the dielectric constants of a number of liquids at different temperatures; the corrected values of the dielectric constants are compared with those obtained by other observers. In some cases there are wide discrepancies between the different values. For liquids of high dielectric constant the temperature coefficient of the dielectric constant is found to conform with Abegg's formula. A. E. MITCHELL.

Dielectric constant of carbon dioxide as a function of its density. J. G. KIRKWOOD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 56-58).-The dielectric constant,  $\varepsilon$ , of gaseous and liquid carbon dioxide under high pressures has been measured at various temperatures. With the gas at 35°, the molecular polarisation, as given by  $(\varepsilon - 1)V/(\varepsilon + 2)$ , where V is the molecular volume, rises continuously at first with increasing density, but just beyond the critical density there is a sharp discontinuity and the value begins to fall rapidly; at 100° the values are rather greater, but show a similar variation with density. The Clausius-Mosotti formula, as modified by Debye, on the other hand, would require the molecular polarisation to be independent of the temperature and density. This discrepancy is probably due to it being inadmissible to neglect the field due to neighbouring molecules when calculating the total polarising field at a point within a gas at high pressure when an external field is applied, and furthermore change in density has an effect on the structure of the molecules. At low densities the gas appears to contain at least two kinds of molecules; if one form had a permanent electric moment and were formed in increasing

amounts with rise in either density or temperature. the results obtained would be partly explained. R. CUTHILL.

Dielectric constant of ethyl ether in the critical state. N. LITVINOV and V. LITVINOV (Z. Physik, 1929, 57, 134-144).- A resonance method is used for the determination of the dielectric constant of liquid ethyl ether at high temperatures, up to the critical temperature. The results are compared with the theoretical expectations from the work of Gans and Debye. Up to 180° there is agreement, but not in the neighbourhood of the critical point. A. J. MEE.

Some applications of electric moments to electronic theories of valency. C. P. SMYTH (J. Amer. Chem. Soc., 1929, 51, 2380-2388).-Absence of an electric moment in the paraffins and also of any variation in the moments of the higher ketones and alkyl halides indicates absence of measurable alternate polarity in the hydrocarbon chain, or of inherent dissymmetry in the electronic linkings of alkyl radicals. No measurable polarity is transferred through more than two atoms in the chains. The ethylene double linking has no measurable polarity and appears to be comparatively rigid; polarity may arise when different radicals are attached on opposite sides of the linking. It is suggested that the directive influences and effects on chemical activity commonly attributed to differences in polarity may be due to differences in the energy levels occupied by the valency electrons, which may or may not give rise to measurable polarity. S. K. TWEEDY.

Characteristic regularity in the molecular polarisation of some pure dipole substances. P. GROSS (Physikal. Z., 1929, 30, 504—506).—The molecular polarisation  $P_m = (\varepsilon - 1)M/(\varepsilon + 2)d$  ( $\varepsilon$  being the dielectric constant, M the mol. wt., and d the density) for a given type of organic halogen derivative is a constant, independent of the particular halogen substituted. In some cases the constancy of  $P_m$  in a series is less clearly shown, but the deviations do not exceed the known errors in determining dielectric constants. The electron polarisation  $P_E$ , determined from the molecular refraction, increases whilst  $P_m$ decreases if the halogen derivatives from chlorine to iodine are compared. The total polarisation of the free molecule is approximately constant in some cases, R. A. MORTON. but not in others. 984-231

Measurement of the magnetic rotation of gases and vapours. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1929, 189, 281-282).-The magnetic rotations of carbon dioxide, sulphur dioxide, carbon disulphide, ethylene, and ethyl chloride have been determined in an improved apparatus which enables measurements to be made at pressures up to 2-3 atm. The results are compared with those of other workers. In partleuiar, the constant for gaseous carbon disulphide is two thirds that of the liquid, and the relatively large value obtained for acetylene is an example of the influence of the carbon triple linking. J. GRANT.

Magnetic birefringence in liquids of the aliphatic series. M. RAMANADHAM (Indian J. Physics, 1929, 4, 15-38).-Apparatus is described by which, in conjunction with a Rayleigh compensator, the magnetic birefringence was observed and measured

for the first time for 30 liquids of the aliphatic series. Saturated compounds and their derivatives generally showed negative double refraction. Compounds containing the carbonyl group showed positive birefringence. Water was negatively birefringent. Values were found for  $(n_p - n_s)/\lambda H^2$ , the Cotton-Mouton constant, where  $n_p - n_s$  is the difference of the two refractive indices,  $\lambda$  is the wave-length of the light employed, and H is the strength of the magnetic field. Some approximate calculations are given of magnetic anisotropy of organic molecules obtained from birefringence data and the optical anisotropy of the molecules found from the work of Krishnan on lightscattering (A., 1928, 461). Aliphatic molecules are very feebly anisotropic compared with aromatic molecules. N. M. BLIGH.

Anisotropy of the polarisation field in liquids. K. S. KRISHNAN and S. R. RAO (Indian J. Physics, 1929, 4, 39-55).—It was supposed that the Lorentz expression for the polarisation field acting on any molecule in a refracting medium, due to the doublets induced in the surrounding ones, was applicable to liquid media consisting of optically anisotropic molecules only if the molecular distribution round the single molecule should be spherically symmetrical and if their orientations with respect to it should be entirely fortuitous. The validity of these two conditions is discussed on the basis of recent evidence on the fine structure of liquids by X-ray diffraction, and for highly asymmetric molecules the former condition is not found to be justified. The anisotropy of the polarisation field is evaluated for various liquids from X-ray data and shows good agreement with results calculated from measurements on light scattering. The influence of the molecular density is discussed. The anisotropy tends asymptotically to a maximum value determined by the asymmetry of the molecule, at high densities, and to zero at low densities, in agreement N. M. BLIGH. with theoretical considerations.

Anomalous diamagnetism. C. V. RAMAN (Nature, 1929, 124, 412).—The assumption of the existence of closed electron orbits of dimensions larger than atomic in association with the crystal lattice of bismuth furnishes an explanation of the pronounced diamagnetic anisotropy, the large Hall effects, and the changes of electrical resistance exhibited by bismuth. Kapitza's results (this vol., 989) are also in accord with Ehrenfest's hypothesis.

A. A. ELDRIDGE. Electrical spectrum of water with undamped oscillations in the wave-length range 3000— 2200 mm. N. Novosilzev (Ann. Physik, 1929, [v], 2, 515—536).—An apparatus is described whereby the refraction of undamped waves in the region 2—4 m. by liquids can be measured to within 0.15%. For water  $n^{17}$  has the following values : 8.996 at 3000— 2800 mm., 9.003 at 2800—2600 mm., 9.0065 at 2600— 2200 mm. No anomalous dispersion was detected in the region studied The dielectric constant  $(n^{17})^2$  is 81.02—81.07, in good agreement with other data.

R. A. MORTON.

Dispersion and absorption line width in the alkali vapours. S. A. KORFF (Physical Rev., 1929, [ii], 34, 457-462; cf. this vol., 635).-Measurements were made photographically at various vapour densities of the widths in absorption of the sodium-D lines, and of rubidium 4201 and 4215 Å. Stewart's linewidth equation (Astrophys. J., 1926, 59, 30) was verified for higher series members for the first time. Photographic measurements of the refractivity of sodium vapour near the D-lines were made, using the interferometer-spectroscope method (cf. A., 1928, 1310), with increased accuracy over previous visual measurements. The dispersion conforms to the classical curve; the form of the dispersion to line width relation remains unchanged for higher series members. A short theoretical summary of dispersion and quantum modifications is given. N. M. BLIGH.

Anomalous dispersion of lithium vapour. A. FILIPPOV (Naturwiss., 1929, 17, 689).—Preliminary. The anomalous dispersion in the region of the first 25 members of the principal series of lithium has been observed and measured interferometrically for 14 lines. R. A. MORTON.

Anomalous dispersion of sodium vapour. A. FILIPPOV and V. PROKOFIEV (Z. Physik, 1929, 56, 458—476).—The anomalous dispersion associated with the doublets of the principal series of sodium has been measured in 16 out of 25 observed cases, using a fluorspar interferometer; from these measurements the transition probabilities in the principal series have been calculated. The values for the first four doublets agree with those calculated by wave mechanics.

R. W. LUNT.

Chemical combination as an electrostatic phenomenon. X. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 402-406; cf. this vol., 983).—The influence of atomic deformation on the energy associated with a binary compound is discussed with a view to derive the most probable configuration of the ions in the molecule. Types of molecule containing atoms bearing a different number of charges, e.g., water and ammonia, are considered, with special reference to molecules wherein the outlying ions exert considerable deformatory action on a polarisable central ion. The energy relationships of the water molecule are calculated and from the results the probable atomic orientation is deduced.

H. F. GILLBE.

Theory of complex compounds. I. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1927, No. 5, 118— 156).—The "trans influence" is employed in explanation of the behaviour of complex compounds.

CHEMICAL ABSTRACTS.

Electronic interpretation of oxidation and reduction. W. A. NOYES (J. Amer. Chem. Soc., 1929, 51, 2391-2396).—Consideration of electronic oxidation mechanisms in the light of principles which have been used to reconcile the positive-negative valency theory of Noyes, Stieglitz, etc. with the theories of Lewis, Langmuir, and others leads to the formulation of three types of oxidation processes. (i) Oxidation by transfer of an electron from one atom to another (e.g., oxidation of sodium by chlorine; dissolution of aluminium in sodium hydroxide solution). (ii) Addition of a positive hydroxyl group to an unshared pair of electrons either of a negative ion or of an electrically neutral molecule, in the latter case with separation of a hydrogen ion and formation of a semipolar union (e.g., oxidation by hydrogen peroxide of trimethylamine to its oxide). (iii) Separation of an electrically neutral semipolar oxygen atom (which may preserve its semipolarity in the new compound or may form a hydroxyl group), followed by its union with an unshared pair of electrons (e.g., thermal conversion of potassium chlorate into perchlorate). S. K. TWEEDY.

New chemical theory and its thermodynamical consequences. A. Gosselin and M. Gosselin (J. Chim. phys., 1929, 26, 349-367).- A theory of chemical combination based on the conception that the molecules of gaseous elements, e.g., H2, N2 (doublets), and compound molecules remain intact in compounds. Thus ammonia is HN-H2, methane H2C-H2, hydroxylamine NH-H<sub>2</sub>O. Three kinds of linkings are distinguished; polar (ionisable), steric (similar to Werner's co-ordination linking), and mixed. The formulæ of a large number of compounds on this basis are given. Heats of formation obtained from these formulæ by assuming that every linking has a constant value, independent of others present in the molecule, agree with the experimental values. J. A. V. BUTLER.

Surface tension of mercury in the presence of gas under varying pressures. S. G. Cook (Physical Rev., 1929, [ii], **34**, 513—520).—Using a slight modification of Poindexter's apparatus (cf. A., 1927, 1132) the maximum surface tension was reached only when mercury vapour was present. For hydrogen, oxygen, air, and carbon dioxide the surface tension was investigated in relation to time of exposure to the gas and to gas pressure. For a given pressure as the gas is adsorbed, the tension falls to an equilibrium value, which rises, as the pressure is reduced, to a maximum depending on the nature of the gas. The maximum value for mercury-hydrogen was 441, and for mercury-mercury vapour 515 dynes/cm.

N. M. BLIGH.

Size of the molecules of fatty acids. F. J. HILL (Phil. Mag., 1929, [vii], 7, 940-946).-A combination of du Nouy's tensimeter and Ferguson's sphere method is used to replace Langmuir's balance method for determining the change in surface tension of water on the surface of which small quantities of fatty acids are spread. The acid is added to the water in ether solution of known concentration. The results of measurements from which are deduced the dimensions of the molecules of oleic, palmitic, and stearic acids are in fair agreement with those obtained by Langmuir, with discrepancies in the values for palmitic and stearic acids, the ratios of length to breadth being respectively 2.3 and 3.8, whilst Langmuir obtained A. E. MITCHELL. 5.2 and 5.3.

Scattering of X-radiation by two-dimensional gratings. W. LINNIK (Z. Physik, 55, 502-506).— The experimental difficulties which beset attempts to observe scattering from two-dimensional crystal gratings have been resolved by passing an X-ray beam through a number of thin sheets of the material under examination. These sheets are arranged so that they all project on to the position they held in the crystal from which they were cut, and are spaced at irregular distances. Spectrograms are given for mica, gypsum, and calcite. R. W. LUNT.

X-Ray investigation of statistical anisotropy in crystal masses. W. E. SCHMID (Z. Physik, 1929, 56, 740-750).—The statistical anisotropy of crystal masses has been investigated by an X-ray method. The interpretation of the diagrams is discussed. J. W. SMITH.

Anomalous dispersion in the X-ray region. R. FORSTER (Helv. phys. Acta, 1928, 1, 18-46; Chem. Zentr., 1929, i, 969-970):—The refractive index of X-rays as a function of the wave-length between 0.5 and  $2\cdot3$  Å. was studied for glass, silver, and copper. A. A. ELDRIDGE.

X-Ray investigation of some mixed crystal systems having monoxides as components. Systems CoO-MgO, NiO-MgO, and CoO-NiO. S. HOLGERSSON and A. KARLSSON (Z. anorg. Chem., 1929, 182, 255-271).—For the three systems investigated there exists complete miscibility, Vegard's law of the additivity of the linear dimensions of the interchangeable elements in the lattice being confirmed. H. F. GILLBE.

X-Ray investigation of iron and zinc alloys. A.  $\hat{O}$ sawa and Y. Ogawa (Sci. Rep. Tôhoku, 1929, **18**, 165–176).—X-Ray examination of iron-zinc alloys shows the existence of two compounds, Fe<sub>3</sub>Zn<sub>10</sub> and FeZn<sub>7</sub>. The former has a cubic lattice with a parameter of 8.93 Å. and 52 atoms per unit cell, and the latter has a hexagonal closely-packed lattice of the magnesium type. Iron-zinc alloys are closely similar in their crystalline forms to silver-zinc, copperzinc, and gold-zinc alloys. R. CUTHILL.

Crystal analysis of solid  $\alpha$ -nitrogen. J. DE SMEDT, W. H. KEESOM, and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 745—748; cf. A., 1926, 1082).—Carefully purified nitrogen was submitted at the temperature of liquid hydrogen to the  $K\alpha$  radiations from copper. Analysis of the photographs obtained points to a quadratic crystal structure. N. M. BLIGH.

**Crystal structure of solid nitrogen.** L. VEGARD (Nature, 1929, 124, 267, 337, and Naturwiss., 1929, **17**, 672; cf. this vol., 987).—The unit cubic cell, of side 5.65 Å., contains 8 atoms. The space-group is  $T^4$ ; the distance between the two atoms of a molecule is 1.06 Å., and (the molecules being considered spherical) the minimum distance between the centres of the molecules is about 4.0 Å. A. ELDRIDGE.

Lattice structure of nickel. S. VALENTINER and G. BECKER (Naturwiss., 1929, **17**, 639—640).—The statement of Bredig and Allolio (A., 1927, 502) that nickel sputtered in hydrogen exhibits a close-packed hexagonal lattice is not confirmed. The normal facecentred cubic lattice of edge 3.51 Å. is shown under all conditions investigated. R. A. MORTON.

X-Ray determination of structure of metasilicates. B. E. WARREN (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 74–75).—Diopside has the lattice constants a=9.71, b=8.89, c=5.24 Å., and

 $\beta = 74^{\circ}$  10'. The space grouping is 2Ci-6, the unit cell containing 4 mols. of  $CaMg(SiO_3)_2$ . The silicon atoms are each surrounded by four oxygen atoms, two of each four being held in common with neighbouring groups, so that the linked tetrahedra form chains parallel to the c axis of the crystal and held together by the calcium and magnesium atoms. Tremolite has the constants a=9.7, b=17.8, c=5.26 Å., and  $\beta=74^{\circ}$ 48'. The silicate chain consists of two diopside chains one above the other and separated by a reflexion plane, part of the intermediate oxygen being removed and the remainder shared between two tetrahedra, one in each chain. This new chain lies parallel to the c axis and there are 4 chains per unit cell. The calcium and magnesium atoms are on the 2-fold axis, the former in a group of 8 oxygen atoms and the latter in a group of 6. The 4 oxygen atoms which are outside the chains lie in the reflexion planes and are bound between magnesium atoms. The formula cannot be CaMg(SiO<sub>3</sub>)<sub>4</sub>; either there is isomorphous replacement by tervalent ions or else water is introduced, and the correct formula is H<sub>2</sub>Ca<sub>2</sub>Mg<sub>5</sub>(SiO<sub>3</sub>)<sub>8</sub>. It is probable that in respect of structure diopside and tremolite are typical of the pyroxenes and amphiboles, respectively. R. CUTHILL.

**Crystal structure of tricalcium aluminate.** F. A. STEELE and W. P. DAVEY (J. Amer. Chem. Soc., 1929, **51**, 2283—2293).—X-Ray powder photographs show that tricalcium aluminate,  $3CaO,Al_2O_3$ , has a body-centred cubic structure, the unit cube having an edge of 7.624 Å. and containing 3 mols. The results indicate three possible structures for the substance, in none of which ionic groups occur. The structure is mixed ionic. S. K. TWEEDY.

X-Ray study of minerals of the spinel group, and synthetically prepared substances of the spinel type. S. HOLGERSSON (Lunds Univ. Årsskr., [ii], Avd. 2, 23, 9; Kungl. Fysiogr. Sällskapets Handl., 1927, [ii], 38, No. 9, 1-112; Chem. Zentr., 1929, i, 372-373).-The following values (A.) for the edge of the unit cube were obtained : spinel (Ceylon, red)  $8.102 \pm 0.003$ ,  $8.099 \pm 0.004$ ; spinel (Aka, blue)  $8.108 \pm 0.002$ ; chlorospinel (Achmatovsk)  $8.103 \pm$ 0.004; spinel (Amity, black)  $8.126\pm0.004$ ; herynite (India)  $8.120\pm0.003$ ; herynite (Ronsberg)  $8.130\pm$ 0.004; gahnite (Falun)  $8.085 \pm 0.003$ ,  $8.092 \pm 0.003$ ; kreittonite (Bodenmais)  $8.115 \pm 0.003$ ,  $8.118 \pm 0.003$ ; magnesiaferrite  $8.356 \pm 0.004$ ; magnetite (Dalarna)  $8.400 \pm 0.003$ ; magnetite (Nordmarken)  $8.412 \pm 0.003$ ; manganomagnetite (Silfberg) 8.408±0.003; jacobsite (Silfberg)  $8.402 \pm 0.003$ ; jacobsite (Jakobsberg)  $8.424 \pm 0.003$ ; franklinite (New Jersey)  $8.432 \pm$ 0.003; chromite (Ural)  $8.358 \pm 0.003$ ,  $8.355 \pm 0.004$ . The aluminates are thus differentiated from the ferrites; moreover, values of n are 1.716-1.80 and 2.35-2.42, respectively, chromite again occupying an intermediate position. The hardness is a function of the lattice dimensions. Synthetic substances possessed the following dimensions (Å.): MgAl<sub>2</sub>O<sub>4</sub>  $8.090 \pm 0.003$ ; MnAl<sub>2</sub>O<sub>4</sub>  $8.263 \pm 0.007$ ; ZnAl<sub>2</sub>O<sub>4</sub>  $8.099 \pm 0.003$ ; CoAl<sub>2</sub>O<sub>4</sub>  $8.059 \pm 0.003;$ NiAl<sub>2</sub>O<sub>4</sub>  $8.045 \pm 0.005;$ CuAl<sub>2</sub>O<sub>4</sub>  $8.072 \pm 0.007;$ MgFe<sub>2</sub>O<sub>4</sub>  $8.342 \pm 0.005;$ MnFe<sub>2</sub>O<sub>4</sub> ZnFe<sub>2</sub>O<sub>4</sub>  $8.572 \pm 0.006;$  $8.403 \pm 0.004;$  $8.359 \pm 0.005;$ CoFe<sub>2</sub>O<sub>4</sub> FeFe<sub>2</sub>O<sub>4</sub>

Crystal structure of sesquioxides and compounds XYO<sub>3</sub>. W. H. ZACHARIASEN (Norske Videnskaps Akad., Mat. Nat. Kl., 1928, No. 4, 1–165 : Chem. Zentr., 1929, i, 8–14).—Values of the parameter (r),  $\alpha$ , c/a, and d, respectively, of oxides of the corundum type, ditrigonal-scalenohedral, space-group  $D_{3,4}^{e}$ , with 2 mols. in the unit cell, are : Al<sub>2</sub>O<sub>3</sub>  $5 \cdot 13 \pm 0 \cdot 02$  Å.,  $55^{\circ} 16' \pm 5'$ ,  $1 \cdot 366$ ,  $3 \cdot 96$ ; Ti<sub>2</sub>O<sub>3</sub>  $5 \cdot 42 \pm 1000$  Å. 0.01 Å., 56° 50′  $\pm$ 5′, 1.317, 4.58; V<sub>2</sub>O<sub>3</sub> 5.45  $\pm$ 0.03 Å.,  $\begin{array}{l} 53^{\circ} \, 49^{\prime} \pm 8^{\prime}, \, 1{\cdot}4\overline{13}, \, 5{\cdot}04 \; ; \; \mathrm{Cr}_{2}\mathrm{O}_{3} \; 5{\cdot}35 \pm \overset{\circ}{\underline{0}}{\cdot}03 \; \overset{\circ}{\mathrm{A}}{\cdot}, \, 55^{\circ} \; 0^{\prime} \pm 8^{\prime}, \; 1{\cdot}374, \; 5{\cdot}25 \; ; \; \mathrm{Fe}_{2}\mathrm{O}_{3} \; 5{\cdot}42 \pm \overset{\circ}{\underline{0}}{\cdot}02 \; \overset{\circ}{\mathrm{A}}{\cdot}, \; 55^{\circ} \; 14^{\prime} \pm 5^{\prime}, \end{array}$ 1.367, 5.25;  $Ga_{2}O_{3}$  5.31 $\pm$ 0.02 Å., 55° 50' $\pm$ 5', 1.347, 6.44;  $\operatorname{Rh}_2O_3$  5.45 $\pm$ 0.03 Å., 55° 43' $\pm$ 8', 1.351, 8.20. The average separation of metal and oxygen atoms, and the minimal separation of oxygen atoms, respectively, are:  $Al_2O_3$  1.92, 2.495;  $Ti_2O_3$  2.04, 2.68;  $V_2O_3$  2.00, 2.56;  $Cr_2O_3$  1.99, 2.57;  $Fe_2O_3$ 2.02, 2.545;  $Ga_2O_3$  1.99, 2.59;  $Rh_2O_3$  2.03, 2.66 Å. The following are the lattice constants of cubic, bodycentred sesquioxides:  $Sc_2O_3 9.79 \pm 0.03$ ,  $Mn_2O_3 9.41 \pm 0.01$ ,  $Y_2O_3 10.60 \pm 0.02$ ,  $In_2O_3 10.12 \pm 0.03$ ,  $Sm_2O_3 10.85 \pm 0.02$ ,  $Eu_2O_3 10.84 \pm 0.02$ ,  $Gd_2O_3 10.79 \pm 0.02$ ,  $Tb_2O_3 10.70 \pm 0.02$ ,  $Dy_2O_3 10.63 \pm 0.02$ ,  $Ho_2O_3 10.58 \pm 0.02$ ,  $Er_2O_3 10.54 \pm 0.02$ ,  $Tm_2O_3 10.52 \pm 0.02$ ,  $Yb_2O_3 10.39 \pm 0.02$ ,  $Lu_2O_3 10.37 \pm 0.02$ ,  $Tl_2O_3 10.57 \pm 0.02$ ,  $Tb_2O_3 10.57 \pm 0.02$ ,  $Tb_2O_3 10.57 \pm 0.02$ ,  $Th_2O_3 Th_2O_3 T$ 0.03 Å., the calculated densities being 3.89, 5.00, 5.00, 7.07, 7.21, 7.30, 7.62, 7.81, 8.20, 8.36, 8.65, 8.77, 9.28, 9.42, 10.11. The unit cell contains 16 mols. R<sub>2</sub>O<sub>3</sub>; space-group (thallium oxide)  $T^5$ . Lithium nitrate has r 5.74 $\pm$ 0.02 Å.,  $\alpha$  48° 3' $\pm$ 10' and is isomorphous with sodium nitrate. Cadmium carbonate, isomorphous with calcite, has  $r \ 6.112 \pm 0.006 \text{ Å.}, \ \alpha \ 47^{\circ} 24' \pm 5'.$ Rhombic lead, barium, and strontium carbonates are isomorphous with aragonite. Lead carbonate (cerussite) has a 5.14, b 8.45, c 6.10 Å., a:b:c=0.609:1:0.723; space-group  $V_{h}^{16}$ , with 4 mols in the unit cell. Barium carbonate has a 5.29, b 8.88, c 6.41 ( $\pm 0.05$ ) Å. Strontium carbonate has a 5.13, b 8.42, c 6.10 Å. Silver nitrate, rhombic-bisphenoidal, has a:b:c=0.9430:1:1.3697;  $a \ 6.97$ ,  $b \ 7.34$ , c 10.14 Å., with 8 mols. in the unit cell; space-group  $V^1$ ,  $V^2$ ,  $V^3$ , or  $V^4$ . Rubidium nitrate,  $D_{2d}$ ,  $D_3$ , or  $C_{3r}$ , has r 4.36 Å.,  $\alpha 90^{\circ}$  or r 7.37 Å.,  $\alpha 109^{\circ} 28'$ , with 4 mols. in the unit cell; space-group probably  $C_{\rm ar}^5$ . Potasium chlorate has a:b:c=0.8331:1:1:2673, β 109° 42'; a 4.64, b 5.58, c (calc.) 7.07 Å.; spacegroup C<sub>2h</sub>. Potassium bromate, ditrigonal-pyramidal. has  $r 4.403 \pm 0.005$  Å.,  $\alpha 86^{\circ} 0' \pm 5'$ , with 1 mol. in the unit cell; space-group  $C_{av}^{s}$ ; atomic separations are recorded. Iodic acid is rhombic, a 5.53, b 5.92, c 7.75 Å., with 4 mols. in the unit cell; space-group V1, V2, V3, or V4. Sodium iodate, rhombic-bipyramidal, has a:b:c=0.9046:1:1.2815; a 5.75+0.01, b  $6.37 \pm 0.01$ ,  $c 4.05 \pm 0.01$  Å., with 2 mols. in the unit cell; space-group  $V_h^{19}$ . Cæsium iodate, apparently cubic, has a  $4.662 \pm 0.002$  Å., with 1 mol.

4 E

in the unit cell. The compound SrZrO<sub>3</sub> is cubic,  $a 4.094\pm0.003$  Å, with 1 mol. in the unit cell. The compound CdTiO<sub>3</sub>, of the perowskite type, has  $a 3.75\pm0.05$  Å. Potassium nitrate has the aragonite structure: a 5.40, b 9.14, c 6.41 Å. Silver chlorate has  $a 8.475\pm0.004$ ,  $c 7.90\pm0.01$  Å. The unit cell of silver bromate, space-group probably  $V_{11}^{11}$ , bodycentred, contains 8 mols. The compounds MgTiO<sub>3</sub> and LiNbO<sub>3</sub> possess the ilmenite structure; the rhombohedral unit cell contains 2 mols. and has the dimensions, respectively,  $r 5.40\pm0.02$  Å,  $\alpha 55^{\circ}1'$ ;  $r 5.47\pm0.03$  Å.,  $\alpha 55^{\circ}43'$ . The above observations are examined theoretically, and the various crystal types are classified. A. A. ELDRIDGE.

X-Ray observations on cellulose. V. Lattice of cellulose hydrate. A. BURGENI and O. KRATKY (Z. physikal. Chem., 1929, B, 4, 401-430).-An experimental method is described for the determination of the lattice constants of cellulose hydrate with greater accuracy than has been possible hitherto. Films of higher orienting power than usual were prepared by converting cellulose xanthate into cellulose hydrate. The X-ray analysis attempts to estimate the statistical symmetry of the crystalline aggregates, the crystalline arrangement, i.e., the position of the translation lattice of the aggregates relative to the macroscopic form of the film, and the translation group of single crystals. It is assumed that as the statistical symmetry of the xanthate film is rhombic holohedral (anisotropic class 4), that of the hydrate film will be the same. This is proved by X-ray observations. As regards the crystalline arrangement, it may be described to a first approximation as a twin crystal with two mirror images, monoclinic in structure, one on each side of the plane of symmetry. The digonal axis coincides with the direction of extension. The plane  $A_0$  makes an angle of between  $0^{\circ}$  and  $15^{\circ}$  with the plane of symmetry. The exact determination of the crystalline arrangement is also attempted. To a first approximation the following conclusions are reached with regard to the translation lattice.  $A_0$ ,  $A_3$ , and  $A_4$  are probably unique planes in the lattice. The angle between  $A_3$ and  $A_4$  is between 20° and 45°. The angle between  $A_0$  and  $A_3$  and  $A_4$  is larger than 45°. The translation lattice has rhombic or monoclinic symmetry.

### A. J. MEE.

Structure of the crystalline part of cellulose. III. H. MARK and G. VON SUSICH (Z. physikal. Chem., 1929, B. 4, 431—439).—Preparations of tunicin (animal cellulose) and  $\beta$ -cellulose can be obtained which give the ring thread structure with (101) parallel to the plane of symmetry, and the simple thread structure with [010] parallel to the direction of stretching. The X-ray diagrams of these substances agree with the monoclinic form of cellulose. A. J. MEE.

Diffraction of X-rays in liquids and solutions. J. A. PRINS (Z. Physik, 1929, 56, 617-648).—The general theory of diffraction of X-rays is summed up and applied to concrete cases. The mathematical expressions of Zernike and Prins are used. In some cases it is sufficient to assume that the arrangement of molecules is purely a question of geometrical prob-

ability; in other cases it is necessary to take into account the kind of intermolecular forces which are brought into play. Strong diffraction beneath the principal maximum is connected with a tendency towards association. A consideration of the diffraction by monatomic and polyatomic molecules leads to the following conclusions. For monatomic molecules the whole diffraction pattern depends on the arrangement of the molecules. For polyatomic molecules for which the origin of diffraction is concentrated mainly in the neighbourhood of the centre, the principal maximum is favoured; above the principal maximum the inner structure predominates. For polyatomic molecules for which the origin of diffraction is concentrated more at the edge of the molecule, the diffraction pattern is strongly influenced by the inner structure where the principal maximum is to be expected. These results become unsatisfactory only if the molecules are strongly anisotropic and also if the anisotropic axes are correlated with those of neighbouring molecules. Solutions are also dealt with. The effect of the Coulomb force on the diffraction patterns of ionic solutions is investigated. Comparisons with experiment agree, at least qualitatively. An apparatus is described which enables photographs of the diffraction of X-rays at free liquid surfaces to be taken. A. J. MEE.

Crystallisation of gold from the liquid state. C. O. BANNISTER (Inst. Metals, Sept., 1929, Advance copy, 4 pp.).—Cupellation beads of pure gold solidify with the occurrence of "flashing," and the crystalline surface shows an irregular polygonal structure caused by solidification from the labile region. If traces of metals such as platinum, iridium, and ruthenium be present, or if the bead be touched with a gold wire, flashing is prevented, and solidification takes place in the metastable region by radial growth from centres, with velocities which are approximately equal in all directions. The phenomenon is illustrated photographically, and the formation of boundaries is discussed. W. HUME-ROTHERY.

Structure of Heusler's alloy. E. PERSSON (Z. Physik, 1929, 57, 115-133).-The crystal structure of copper-manganese-aluminium alloys was determined by the X-ray method. The  $\beta$ -phase which is responsible for the magnetism of the alloy has a space-centred cubic fundamental lattice, the aluminium atoms being situated at points forming a face-centred cubic superstructure. The manganese concentration must reach a definite limiting value before the alloy becomes magnetic. Experiments were carried out with a series of alloys with compositions corresponding with the formula (Cu,Mn)3Al, with varying manganese content. X-Ray diagrams were obtained for specimens in the ordinary state and after tempering at 210° for 15 days. The former consisted mainly of the  $\beta$ -phase, of which the parameters increased with increasing manganese content. With still greater manganese content some β-manganese was present with some aluminium in solid solution. The highest manganese content of the  $\beta$ -phase coincides with the highest magnetic effect. The tempered specimens showed the presence of the  $\beta$ -phase in two similar crystalline forms; one consisting of manganese-free

 $\beta$ -Cu-Al phase, and the other of a  $\beta$ -phase with maximum manganese content. The composition of the latter, or  $\beta'$ , phase corresponds with the formula Cu<sub>2</sub>MnAl. Alloys containing the  $\beta'$ -phase are all ferro-magnetic. An X-ray analysis of Heusler bronzes of the composition Cu<sub>2</sub>MnSn shows the presence of a phase of analogous structure to the  $\beta$ -Cu-Mn-Al phase. A. J. MEE.

Theory of isomorphous overgrowth in ionic crystals. I. N. STRANSKI (Z. physikal. Chem., 1929, 142, 453—467).—The method previously used (cf. A., 1928, 1178; Kossel, this vol., 18) is applied to find the conditions for the deposition on an ionic crystal of an overgrowth of a salt differing only in the charges carried by its ions. It is estimated that a supersaturation of 3% is necessary before sodium bromide is deposited on lead sulphide crystals. The conditions of formation of mixed crystals between salts having ions of different charges are discussed and an explanation is given of the separation of minute crystals of salts of doubly-charged ions.

J. A. V. BUTLER.

Isomorphous overgrowth in ionic crystals. I. N. STRANSKI and K. KUHELIEV (Z. physikal. Chem., 1929, 142, 467—475).—The degree of supersaturation required for the deposition of sodium nitrate on crystals of calcite, siderite, and rhodochrosite and of sodium bromide on galena has been determined at different temperatures. Sodium bromide is deposited only below  $50.7^{\circ}$  as NaBr,2H<sub>2</sub>O, since sufficient supersaturation for the deposition of NaBr above this temperature could not be obtained. The dependence of the degree of supersaturation on the temperature agrees with the theory (see preceding abstract).

J. A. V. BUTLER.

Hall effect in single metal crystal. P. I. WOLD (Science, 1929, 69, 72).—The Hall effect in a large single crystal of zinc of the close-packed hexagonal system is approximately 50% greater than in polycrystalline zinc (cf. *ibid.*, 1928, 68, 183).

L. S. THEOBALD.

Magnetic behaviour of some organic crystals. S. BHAGAVANTAM (Indian J. Physics, 1929, 4, 1— 14).—A simple direct method is described by which, through the mechanical force on a crystal for different orientations in a magnetic field, the ratio of the principal magnetic susceptibilities was measured for iodoform, carbamide, succinic acid, azobenzene, *p*-nitrotoluene, and anthracene. The aliphatic compounds were in general feebly anisotropic and the aromatic highly anisotropic. The crystals form classes in which the axes of maximum optical moment and of maximum diamagnetic susceptibility coincide or are crossed respectively; they are similar chemically to those which, as liquids, exhibit negative and positive birefringence. The results are discussed in relation to chemical constitution and crystal structure. N. M. BLIGH.

Saturation of the electric and magnetic polarisation of gases in quantum mechanics. K. F. NIESSEN (Physical Rev., 1929, [ii], 34, 253-278).—An extension of the work of Van Vleck (A., 1928, 572). On the basis that the electric polarisation of a gas results from the effects of a change in the spatial orientation of the rigid or permanent moment of the molecule, and of the inducing of an elastic polarisation or deformation of the molecule, a complete formula is derived, including a correction for rotation, in the cases respectively of gases of rigid molecules with a permanent electric moment and of gases of deformable molecules in a strong field. In the former the classical Langevin function is found to be valid. The divergence between Langevin's and Brillouin's function (J. Phys. Radium, 1927, 8, 74) is shown to be due to the non-commutativeness of the magnetic moment or angular momentum matrices.

N. M. BLIGH. Absence of change in magnetic susceptibility with crystallisation in strong magnetic fields. L. A. WELO (Physical Rev., 1929, [ii], 34, 296—299).— Lead, tin, bismuth, nickel chloride, and potassium ferricyanide were crystallised in strong magnetic fields and examined, against specimens similarly crystallised in absence of the field, for changes in the magnetic susceptibilities. The changes if any were of the order of 0.4—0.04%. N. M. BLIGH.

Magnetisation diagram of single iron crystals. G. J. SIZOO (Z. Physik, 1929, 56, 649-670).—A number of determinations was carried out with single iron crystals of very pure iron. All mechanical strains were eliminated by a process of long heating. In order to obtain the magnetisation curve a magnetometric method was used. In many cases there were sudden changes of direction or discontinuities in the curve. Hysteresis was present without exception in all the crystals only in the region of low field strength. In the region above the last discontinuity in the curve the specimen is completely magnetised. At this point the hysteresis branch forms the continuation of the reversible part of the magnetising curve. The retentivity has the same general value as for ordinary polycrystalline iron.

A. J. MEE.

Intensity of magnetisation in iron-nickelcobalt alloys. H. MASUMOTO (Sci. Rep. Tôhoku, 1929, 18, 195—229).—For the reversible iron-nickel alloys the magnetisation curves, obtained by plotting the magnetising field against the intensity of magnetisation, are similar in form to those for pure iron and nickel, but the irreversible alloys and those with hexagonal close-packed structure are magnetised much less readily. The iron-cobalt  $\alpha$  and  $\gamma$  solid solutions and the nickel-cobalt  $\gamma$  solid solution are magnetised much more easily than the corresponding solid solutions with hexagonal closely-packed lattices. Irreversible ternary alloys and the *H*-solid solutions are very difficult to magnetise, but the reversible alloys are magnetised quite easily. R. CUTHILL.

Magnetisation diagram of single nickel crystals. G. J. Sizoo (Z. Physik, 1929, 57, 106— 114).—A new method was used to obtain long wirelike crystals of nickel. The method used is also applicable to the preparation of nickel-iron alloys. The magnetisation diagrams of a number of these nickel crystals were obtained. Since the crystals were mechanically very soft, high values for the coercive force were obtained. In order to reduce this the specimens were heated for 24 hrs. at 900°.

formula. An interpretation on the lines of a Paschen-Back effect due to an internal electric field is discussed. N. M. BLIGH.

Anomalous magnetic properties at low temperatures : anhydrous ferrous chloride. H. R. WOLTJER and E. C. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 735—738).—The specific magnetic susceptibility of anhydrous ferrous chloride was found to depend on the absolute temperature T according to the formula  $\chi(T-0)=$ const., down to about 63° Abs. The formula is obeyed by many paramagnetic substances. The value of  $\theta$  was found to be 20.4° Abs. Above 63° Abs. the susceptibility is independent of the intensity of the magnetic field. At the temperature of liquid hydrogen anomalies occur, the susceptibility becomes dependent on the intensity of the field, and the dependence on temperature is opposite to that at higher temperatures. N. M. BLIGH.

Determination of the susceptibility of erbium sulphate at low temperatures. W. J. DE HAAS, E. C. WIERSMA, and W. H. CAPEL (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 739-744).-The susceptibility of erbium sulphate was determined for the range 290-14.3° Abs. to ascertain whether results previously found for gadolinium sulphate are specific or are general to the sulphates of all the rare earths. It appears that erbium does not follow the Curie law, but that 0 has the value 1.9° Abs. in the formula  $\chi(T+\theta) = \text{const.}$  The magnetisation plotted against field strength shows that the susceptibility is nearly independent of the field strength for liquid hydrogen temperatures, and no saturation was definitely N. M. BLIGH. observed.

Magnetic susceptibility of praseodymium sulphate solutions. O. SPECCHIA (Nuovo Cim., 1928, 5, 432—440; Chem. Zentr., 1929, i, 1313).— The magnetic susceptibility of the salt  $Pr_2(SO_4)_3, 8H_2O$ is  $18.625 \times 10^{-6}$ ; the Bohr magneton number is 3.56, using the value 19900 for the magnetic moment of the Pr<sup>...</sup> ion. A. A. ELDRIDGE.

Electrostriction in non-conducting liquids. B. BRUHAT and M. PAUTHENIER (J. Phys. Radium, 1929, [vi], **10**, 209—218).—New expressions are derived for the adiabatic and isothermal electrostrictions of non-conducting liquids in terms of experimentally determinable quantities and independent of the Lorentz-Lorenz formula (cf. A., 1928, 695). The agreement between theory and experiment is good for carbon tetrachloride, approximate for benzene, and poor for carbon disulphide. The deviation in the last case is discussed in the light of several hypotheses, but is finally attributed to dissolved gases. J. GRANT.

Dielectric breakdown in solids. P. BÖNING (Z. Physik, 1929, 56, 446—457).—Measurements of the dielectric strength of sylvine as a function of the thickness of the test specimen and of the temperature are described which are in good agreement with extensions of Semenov's theory. R. W. LUNT.

Influence of rolling and recrystallisation on the structure of regular surface-centred metals.

The coercive force was thus reduced to 1-2 gauss. The characteristic magnetisation diagram was similar to that for iron (cf. this vol., 1133). Above a certain point there was no hysteresis. Below this point, however, hysteresis was present for all the crystals, and the curve showed one or more discontinuities. All the crystals showed a certain amount of retentivity. A. J. MEE.

Law of paramagnetisation of a crystal and the law of the paramagnetic rotatory dispersion. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 578-589, Z. Physik, 1929, 57, 11-29, and J. Phys. Radium, 1929 [vi], 10, 283-293; cf. A., 1928, 823; this vol, 633).-Ladenburg's mathematical theory of paramagnetic rotatory dispersion (A., 1928, 348) has been verified experimentally for tysonite and parisite. Both substances appear to give a single paramagnetically active band only, and even if several bands exist they cannot be independent. The enormous paramagnetic rotation of tysonite is related to the presence of a band (or group of bands) near 2370 Å. greatly exceeding the visible bands in intensity. Tysonite contains a high percentage of cerium, only a little neodymium, and less praseodymium, and as the visible bands are due to the minor constituents, the intense ultra-violet band and the large rotation are ascribed to cerium<sup>+++</sup>. The paramagnetic rotatory power of tysonite in the direction of the optical axis is given by  $\rho = \rho_{p}$  tanh  $\mu_{B}H/RT$ , where H is the magnetic field strength, T the absolute temperature, and  $\rho_{r}$ , the saturation-rotation, is a function of rotatory dispersion and temperature, whilst  $\mu_B$  is a magnetic moment which in this case is one Bohr magneton. This result is made clear by the demonstration that the paramagnetic rotatory power is due to a single element. The hyperbolic tangent indicates with certainty a reversal of the sense of the magnetic moment. R. A. MORTON.

Law of the paramagnetic rotation of tysonite and tables of the paramagnetic rotatory power of some crystals. J. BECQUEREL and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 590—596; cf. preceding abstract).—The law of the hyperbolic tangent may not be general, as the value of one Bohr magneton for the moment may be a very special one, corresponding possibly with simplified conditions. Full data on paramagnetic rotation of tysonite, parisite, and bastnæsite are given. R. A. MORTON.

Introduction to a theory of magneto-optical phenomena in crystals. J. BECQUEREL (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 749—758).— With the view of developing a general theory of the magneto-optics of crystals the ordinary and extraordinary spectra in uniaxial crystals are considered. Data and characteristics are reviewed and interpreted for the Zeeman effect in crystals; the rule for the asymmetries in the intensities of paramagnetic origin and its quantum treatment is discussed. The rareearth crystals show fine distinct absorption bands, and in the Zeeman effect give doublets of abnormally large separation, and circularly polarised in two opposite senses, results not explained on the Landé von Göler and G. SACHS. III, IV, and V (Z. Physik, 1929, 56, 447-484, 485-494, 495-502).

Compressibility and pressure coefficient of resistance of zirconium and hafnium. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1928, 63, 347—350).—Expressions for the values at 30° and 75° are given. CHEMICAL ABSTRACTS.

Has pure iron allotropic modifications? T. D. YENSEN (Science, 1928, 68, 376-377).—The amount of silicon required to prevent the change of  $\alpha$ - to  $\gamma$ -iron decreases as the carbon content decreases, and assuming the absence of oxygen, the silicon content necessary to eliminate the change is zero at zero carbon content, indicating that pure iron exists only in one form. Equilibrium diagrams based on this view are in accord with experimental evidence.

L. S. THEOBALD.

Isodimorphism of sodium bromide and sodium chloride. Preparation of pure sodium bromide. A. V. RAKOVSKI and V. V. POLYANSKI (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 5—9).— Sodium chloride and bromide exhibit isodimorphism of Roozeboom's fifth group. Sodium chloride and bromide can be separated by means of methyl alcohol.

CHEMICAL ABSTRACTS. Thermodynamics and kinetics of the thermoelectric effect in crystals, especially the Bridgman effect. P. EHRENFEST and A. J. RUTGERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 698-706).—Theoretical.

Temperature dependence of electrical conductivity. W. V. HOUSTON (Physical Rev., 1929, [ii], 34, 279—283).—It is shown that the zero resistance of a pure metal at 0° Abs. can be explained by taking into account the restriction of the transition probabilities on account of the degeneration of the electron gas, using the Fermi statistics and Brillouin's equations of wave scattering as treated by Frenkel and Mirolubov (A., 1928, 933). A satisfactory law of temperature variation of resistance is also obtained. N. M. BLIGH.

Dependence of ionic conductivity in crystals of salts on field strength. A. SMEKAL (Z. Physik, 1929, 56, 579-596).—The relationship between field strength and ionic conductivity in crystals is discussed. The normal case of inner transverse field for electrical transfer in pure crystals provided with "soluble" electrodes is a linear field distribution. The conditions for this normal case are stated. The differences which have been previously noticed in the results of experiments in non-homogeneous fields are due to the presence of electrolytic impurity conduction, which causes the conductivity of a crystal to exceed that of the pure crystal by a large amount. The crystals which have been used in most cases, i.e., quartz, calcite, and mica, belong to this class of substances. The increase in the "continued" conductivity of a crystal with increase in the field strength, first observed by Poole, also occurs with ervstals with linear potential fall. This has been shown to be true for rock-salt. A method of finding the " true " ionic conductivity of crystals is outlined. Making use of a previously determined general temperature law of "continued" conductivity, it is possible to

find the "true" conductivity without knowing the field strength or the current, the latter being found indirectly from measurements of the "continued" conductivity and temperature with a vanishing field. The increase in the "continued" conductivity with the field strength is discussed theoretically. Two possibilities are given which lead to the same qualitative result. A. J. MEE.

Dependence of electrical ionic conductivity of single crystals on field strength. F. QUITTNER (Z. Physik, 1929, 56, 597-603).-The conductivity of rock-salt and sylvine crystals is investigated. The continued conductivity of natural rock-salt and the crystals of salt obtained after melting shows, after electrolytic purification of the crystals, an increase with increase of field strength. The temperature at which these experiments were carried out was 90°. Curves are given showing the specific conductivity of crystals from various sources as a function of the field strength. In the lower potential regions the increase in conductivity is large, but with higher field strengths there seems to be an exponential relationship between the conductivity and the field strength. There is a very marked difference between the increase in conductivity of natural crystals and those obtained by melting and cooling, and differences exist between crystals obtained by rapid and slow cooling. The increase in conductivity of natural crystals is greater than that of artificial crystals, which, however, possess a conductivity 10-1000 times as great. Natural sylvine crystals were investigated, and it was found that the conductivity is considerably greater than that of rock-salt, but the effect of alteration of the field strength was smaller. At high field strengths the distribution of the potential in the interior of the crystal is linear. A. J. MEE.

Superconductivity of gallium. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 733-734).—In a previous investigation (this vol., 496) a trace of indium as impurity was suspected. The experiments were repeated with spectroscopically pure gallium, using Keesom's new low-temperature cryostat (this vol., 1136). Previous conclusions on the superconductivity of gallium are confirmed. N. M. BLIGH.

New superconductors. Resistance of alloys at the temperatures of liquid hydrogen and liquid helium. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 715—723).—Eutectic mixtures of the systems Sn-Bi, Sn-Zn, Sn-Cd, Tl-Au, Tl-Cd, Pb-Ag, Pb-Cd, Pb-Sb, and Pb-Bi were examined, and the influence of small admixtures of non-superconductors with superconductors was investigated. Values of the resistances are tabulated and plotted against temperatures in each case, and the displacement of the temperature interval of fall in resistance with respect to the thermal transition curve of the pure metal given first in each group is shown.

N. M. BLIGH.

A superconductor, consisting of two non-superconductors. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 724-730; cf. this vol., 652).—Previous work was extended to a number of gold-bismuth alloys of varying composition. The resistances of each with respect to temperature were determined, and the results interpreted with the help of the m.-p. diagram for the system. It is concluded that the solid solution of about 4% of bismuth in gold becomes superconductive at  $1.9^{\circ}$  Abs. N. M. BLIGH.

Change of the electric resistance of pure hafnium and zirconium between  $1\cdot3^{\circ}$  and  $90^{\circ}$ Abs. W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 707—709).—The specific resistance of hafnium was found to be  $0\cdot0000296$ . The ratio  $R/R_0$  found for zirconium and hafnium is tabulated and plotted against temperature for the range  $1\cdot3$ —90° Abs. No minimum is found in the curves. There was no evidence of superconductivity. N. M. BLIGH.

Resistance of compounds of metals at the temperature of liquid hydrogen and liquid helium. W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 731-732; cf. this vol., 496).—The resistances of the compounds of two metals,  $Sb_2Tl_7$ ,  $AuPb_2$ , and  $Cu_4Sn$ , were measured over a small range of very low temperatures. The first two compounds were found to become superconductive above the b. p. of helium  $4\cdot 2^{\circ}$  Abs.  $Cu_4Sn$  showed no superconductivity, as previously found in the case of  $Cu_3Sn$ .

N. M. BLIGH.

Conductivities of solid lead chloride and lead iodide. W. SEITH (Z. Physik, 1929, 56, 802—808).— The variations with temperature of the conductivities of solid lead chloride and lead iodide may be expressed in the forms  $x = 6 \cdot 55e^{-10900/RT}$  and  $x = 2 \cdot 99 \times 10^{-2}e^{-10500/RT} + 2 \cdot 69 \times 10^{4}e^{-27480/RT}$ , respectively. In accordance with the views of Phipps, Lansing, and Cook (A., 1926, 231), this is interpreted as indicating that in the chloride only one ion takes part in the conduction, whilst with lead iodide both are mobile. This is in agreement with the observations of Tubandt (Z. Elektrochem., 1928, 34, 482). J. W. SMITH.

Thermoelectric phenomena and resistance in metallic single crystals. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1929, 63, 351-360).—The thermal E.M.F. against copper of single crystals of zine, cadmium, antimony, tin, and bismuth between  $20^{\circ}$  and  $88^{\circ}$  was measured, and the calculated thermal E.M.F., Peltier heat, and difference of Thomson heat for rods of the same metal with different orientations are discussed. CHEMICAL ABSTRACTS.

Cause of the thermo-triboelectric anomaly of mercury. M. C. MONTO (Nuovo Cim., 1928, 5, 347-351; Chem. Zentr., 1929, i, 1421).

Sound propagation in gas mixtures. D. G. BOURGIN (Physical Rev., 1929, [ii], 34, 521—526).— Mainly mathematical. Previous results on a single gas and a mixture of two gases (cf. this vol., 637) are simplified and extended to a mixture of any number of gases. N. M. BLIGH.

Methods and apparatus used in the cryogenic laboratory. XXII. A cryostat for temperatures below 1° Abs. W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 710-714).-With the object of diminishing as far as possible the pressure over a quantity of liquid helium large enough to allow measurements to be made in the space so cooled, two large-capacity vacuum pumps were arranged in parallel and connected to a cryostat filled with liquid helium through cryostats connected to the helium liquefier by vacuum siphon tubes. It was found possible to make measurements down to about  $0.85^{\circ}$  Abs. in a space of about 300 c.c., thus extending downwards by about  $0.3^{\circ}$  the range in which measurements can be made. N. M. BLIGH.

The null heat point and the heat of bodies. I. MAJDEL (Arh. Hemiju, 1929, 3, 93-105).-A body emits heat when the frequency of vibration of its atoms lies between 35 and  $281 \times 10^{12}$ /sec.: the temperature  $T_0$  at which thermal vibrations cease, and at which the specific, atomic, and molecular heats are zero, although kinetic energy is still possessed by the atoms, is termed the null heat point. The functional relation between the actual specific atomic heat,  $\mu$ , and the temperature is for solid elements given by  $\mu = \gamma - \alpha/(t+\beta)$ , where  $\alpha$  is a constant (939.8) and  $\beta$  and  $\gamma$  are constant parameters characteristic for a given element. At low temperatures,  $\mu = 0$  and  $T_0 = \alpha/\gamma - \beta$ .  $T_0$  is shown to be a periodic function of the atomic number. It is proposed to abandon the use of the absolute zero temperature in physics, using in its place  $T_0$ , which is a specific and characteristic constant of each element. The validity of this conception is supported by the periodicity of  $T_0$ ,  $\gamma$ , and  $\beta$ , by the agreement of a classification of the elements based on this principle with that of Goldschmidt, and by the derivation of Dulong and Petit's law from the above equations.

R. TRUSZKOWSKI. Heat of dissociation of diatomic hydride molecules. W. W. WATSON (Physical Rev., 1929, [ii], 34, 372—374).—Heats of dissociation for the hydrides of lithium, beryllium, magnesium, and calcium are given as found by extrapolation from vibrational band spectra data, and are compared with results from a conservation of energy formula. The apparent discrepancy between the values and those from the phenomenon of instability at high rotational speeds is discussed. This rotational distortion is attributed to an uncoupling action on the electronic angular momenta. N. M. BLIGH.

Ebullioscopic paradox. J. E. VERSCHAFFELT (J. Chim. phys., 1929, 26, 379–384).—Polemical with Berthoud, Briner, and Schidlof (this vol., 635).

J. A. V. BUTLER.

Joule-Thomson effect and heat capacity at constant pressure for air. O. C. BRIDGEMAN (Physical Rev., 1929, [ii], 34, 527-533).—The constants for air in the equation of state (cf. A., 1927, 819) are evaluated, and the equation is used to compute  $\mu C_p$  at various temperatures and densities, and to calculate  $C_p$  for various pressures from accurate data at one atmosphere. The two sets of values of  $\mu$  are plotted along isotherms against pressures. These values, the computed  $C_p$  data, and the Joule-Thomson inversion curve obtained from the equation of state are in good agreement with available experimental data. N. M. BLIGH. Thermal conductivity of ice. S. ARZYBYSCHEW and L. PARFIANOWITSCH (Z. Physik, 1929, 56, 441— 445).—The thermal conductivity of ice at 0° has been redetermined,  $55\pm0.8\times10^{-4}$  g.-cal. cm.<sup>-1</sup> sec.<sup>-1</sup>; this value is approximately the same as the older determinations of Neumann and of Straneo, and the value of Forbes (0.0021) is therefore traversed.

R. W. LUNT.

Abnormally high heat production with the thorium mineral orangite. H. HERSZFINKEL (Naturwiss., 1929, 17, 673).—Poole's observation (Phil. Mag., 1912, 23, 183) that the heat emitted from orangite considerably exceeds that corresponding with the thorium content has been confirmed, the material from Arendal giving 34 times and that from Langesund 30 times as much heat as the thorium present would require. Control experiments indicate that the heat evolution from mixtures of radioactive materials is additive. R. A. MORTON.

Specific heat of tungsten between  $90^{\circ}$  and 2600° Abs. C. ZWIKKER and G. SCHMIDT (Physica, 1928, 8, 329—346; Chem. Zentr., 1929, i, 1313).— At 92° and 290° Abs. the atomic heat of tungsten is 3.48 and 5.88, respectively; at 2220° Abs. the value is 7.9. Another method gave  $8.3_6$  for 2500° Abs.

A. A. ELDRIDGE. Variation of latent heat of vaporisation with temperature. V. KIREJEV (Z. anorg. Chem., 1929, **182**, 177—181).—Mathematical. The function L/RT = f(0) = K, where L is the molecular heat of vaporisation and 0 the reduced temperature, affords a simple means of investigation of the relationship between L and T. For various substances and for the temperature interval over which 0 lies between 0.90 and  $\theta_c$ , the approximation formula  $K = (1\cdot 1 - \theta)K_c/(1\cdot 1 - \theta_c)$  is valid. H. F. GILLBE.

Fusion curves of some salt hydrates. G. TAMMANN (Z. anorg. Chem., 1929, 179, 186—192).— The curves obtained by Geller (Z. Krist., 1924, 60, 415) for sodium sulphate decahydrate and magnesium chloride hexahydrate are incorrect, as the method employed is unsatisfactory, especially at high temperatures and low pressures. H. F. GILLBE.

Vapour pressures of piperidine and  $\alpha$ -picoline. Application of Dühring's rule to compounds of the pyridine group. F. T. RILEY and K. C. BAILEY (Proc. Roy. Irish Acad., 1929, 38B, 450— 453).—The b. p. of  $\alpha$ -picoline and piperidine have been determined over a range of pressures between 760 and 6 mm., and those of pyridine, quinoline, and isoquinoline have been redetermined over the same range. When the b. p. of pyridine at a series of pressures are plotted against those of the other liquids straight lines are obtained, as is required by Dühring's rule. C. W. GIBBY.

Entropy and specific heat of solid inorganic compounds. W. HERTZ (Z. anorg. Chem., 1929, 182, 189—191).—The quantity  $Sc^1$ , where S is the entropy and c the specific heat, is for all solid inorganic compounds containing the same number of atoms constant and equal to the value of  $Sc^1$  for the elements multiplied by the number of atoms in the compound. H. F. GILLEE.

Heat capacity of oxygen from  $12^{\circ}$  Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 2300– 2321).—The transition temperatures between the three solid forms of oxygen are  $23.66^{\circ}$  and  $43.76^{\circ}$  Abs.; the m. p. is  $54.39^{\circ}$  and the b. p.  $90.13^{\circ}$  Abs. The molal latent heats of transition at these four points are, respectively: 22.42, 177.6, 106.3, and 1628.8g.-cal. The molal entropy of oxygen, corrected to the state of a perfect gas by means of Berthelot's equation, is 40.74 g.-cal./1° at the b. p., in substantial agreement with the value derived from spectral observations. The significance of this agreement is interpreted. The molal entropy at  $298.1^{\circ}$  Abs., calculated from spectroscopic data, is 49.03 g.-cal./1°. The Tetrode equation, suitably extended, leads to the accurate value, as is to be expected. The results show that the magnetons in solid oxygen at liquid hydrogen temperatures have little random distribution; they may be coupled into a sort of magneton crystal within the molecular lattice, and the strong paramagnetism of the oxygen may be due to destruction of these couplings by the applied magnetic field (Paschen-Back effect). S. K. TWEEDY.

Limiting density of matter and energy. W. ANDERSON (Z. Physik, 1929, 56, 851-856).— Theoretical (cf. Stoner, Phil. Mag., 1929, [vii], 7, 63). J. W. SMITH.

Zero volume of metal alkyls. W. HERZ (Z. anorg. Chem., 1929, **182**, 173-176).—The zero volumes  $v_0$  of a large number of metal alkyl compounds have been calculated from the refractive indices, and the results agree with those previously deduced. In each homologous series  $v_0$  diminishes as the mol. wt. increases, whereas for corresponding compounds of different metals  $v_0$  increases with increase of at. wt. of the metal; mercury is anomalous. The first law applies also to compounds containing mixed radicals; isomeric compounds usually exhibit but slight variations of  $v_0$ . H. F. GILLBE.

Molecular theory of friction. G. A. TOMLINSON (Phil. Mag., 1929, [vii], 7, 905-939).-The theory of dry solid friction is based on the assumed existence of molecular attractions and repulsions such that the repulsive force varies much more rapidly with the distance than does the attractive force and that its effective range is considerably less than the molecular dimensions. It follows that when two bodies move relatively one on the other and there is in consequence a continuous change in the molecules bearing the load, a loss of energy occurs which is manifest as friction. The force of friction is thus a statistical average of the repulsive forces between successive groups of molecules bearing the load between two bodies. Equations deduced for the coefficients of limiting and rolling friction indicate the characteristic properties of these factors. A number of experimental determinations of limiting and rolling friction are described the results of which are in fair agreement with the deductions from the theory. The theory indicates that, contrary to older ideas, there should be friction between bodies in normal contact, but the magnitude

of this is so small as not to be measurable by ordinary means. A. E. MITCHELL.

Expansion of gases on mixing, especially at very low pressures. I. Its relation to the empirical calculation of the fugacities in gaseous mixtures. L. J. GILLESPIE (Physical Rev., 1929, [ii], 34, 352-366).-The expansion of a gas in a mixture and the expansion of gases on mixing to form a mole of mixture from the pure gases at constant temperature and pressure are plotted as a function of the pressure for mixtures of ethylene and argon, ethylene and oxygen, nitrogen and hydrogen, and nitrogen and methane, and it is shown that these quantities do not vanish at zero pressure. A method is given for calculating the values for zero pressure from the equation of state for the mixture. The fugacity of a gas, or its pressure corrected for deviations from the ideal gas law, can be more accurately calculated when account is taken of data for expansion N. M. BLIGH. at zero pressure.

Determination of the softening interval of glasses and the abnormal change of specific heat and volume over the interval. G. TAMMANN and A. KOHLHAAS (Z. anorg. Chem., 1929, 182, 49–73).—By experiments with salicin, brucine, piperine, and various sugars and gums it has been shown that the temperature interval over which softening takes place has for its upper limit the lowest temperature at which thin threads may be drawn from the material, and for its lower that at which minute cracks appear in the surface when touched with a glass rod; these temperatures may be determined with ease to within  $\pm 0.5^{\circ}$ . At the lower limit the abnormal increase of specific heat commences and the volume isobars simultaneously exhibit a marked change of slope.

H. F. GILLBE.

Ceramic mixtures of high m. p. Systems kaolin-alumina-felspar and kaolin-zirconiafelspar. R. SCHWARZ and E. REIDT [with K. CHUDOBA] (Z. anorg. Chem., 1929, 182, 1-18).—The softening points of mixtures of felspar and alumina, and of kaolin, alumina, and felspar, have been determined over a wide range of concentrations. The coefficients of linear expansion of certain mixtures have been determined, the results showing that increase of either the felspar or the alumina content of the three-component mixtures produces an increase of the coefficient of expansion. The resistance of the sintered mixtures to chemical action, measured by the loss of weight after heating with fusion mixture at 950° and treatment with hydrochloric acid, is roughly proportional to the porosity, and is a maximum when the ratio  $Al_2O_3$ : SiO<sub>2</sub> is unity. The microscopic appearance of various specimens is described. Zirconia lowers the softening point of felspar in kaolin mixtures, and decreases the resistance to chemical action. H. F. GILLBE.

Structure of gold-nickel alloys. W. HEIKE and H. KESSNER (Z. anorg. Chem., 1929, 182, 272— 280).—Hafner's view (Diss., Freiberg-i.-S., 1927) of the mode of breakdown of gold-nickel mixed crystals appears in the light of microscopical investigation to be correct, in contradiction to Fraenkel and Stern's observations. Alloys rich in nickel undergo a farreaching change of structure when heated for a long period at 500—1000°. The most satisfactory etching solution for gold-nickel alloys is a hot solution of potassium sulphide. H. F. GILLBE.

Stability of the hysteresis of iron-nickel alloys. G. GOSSELS (Z. anorg. Chem., 1929, 182, 19–27).— The resistance isotherms of nickel-iron alloys containing up to 46% Ni have been determined from 0° to 900°. The maximum resistance is at 33.2% Ni, and has at 900° the value  $132 \times 10^{-6}$  ohm. Investigation of the stabilisation of alloys containing 9.6% Ni indicates that the resistance is unaltered by heating for several hours at  $650-700^\circ$ . H. F. GILLBE.

Effect of pressure on the resistance of three series of alloys. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1928, 63, 329—345).—The pressure and temperature coefficients of electrical resistance and the specific resistance at 30° have been determined for iron-cobalt, iron-nickel, and copper-nickel alloys. The results are discussed. CHEMICAL ABSTRACTS.

Dilatometric study of some univariant two-phase reactions. P. A. CHEVENARD, A. M. PORTEVIN, and X. F. WACHÉ (Inst. Metals, Sept., 1929, Advance copy, 29 pp.).—The changes taking place on the quenching and annealing of aluminiumrich aluminium-copper and aluminium-silicon alloys have been studied by dilatometric methods. The precipitation of silicon from solid solution in aluminium is accompanied by an expansion, an increase in hardness, and a decrease in the coefficient of expansion of the alloy. The precipitation of Al<sub>2</sub>Cu from a supersaturated (quenched) solid solution by annealing above 175° causes an expansion, but ageing below 175° results in a contraction. It is concluded that most of the age-hardening of the aluminium-copper alloys at low temperatures cannot be due to the precipitation of Al<sub>2</sub>Cu, but is the result of a reaction causing contraction; the nature of this is obscure, but is probably due to the combined influence of silicon and copper. The effect of the addition of copper to austenitic ferronickel alloys has been studied similarly. If sufficient copper be present two-phase alloys are formed, but the solubility increases with temperature, so that alloys can be obtained which are homogeneous on quenching, but precipitate a copper-rich constituent on annealing. These changes are in addition to the magnetic transformations, and the boundaries of the two-phase region in the equilibrium diagram have been determined for the iron-nickel-copper system.

W. HUME-ROTHERY.

X-Ray analysis of the iron-boron system. T. BJURSTRÖM and H. ARNFELT (Z. physikal. Chem., 1929, B, 4, 469—474).—An X-ray analysis of ironboron alloys, obtained by melting together technical ferroboron (19% boron) with iron, shows that within the range 0—19% B two phases, Fe<sub>2</sub>B and FeB, occur. The first has a body-centred tetragonal lattice in agreement with the results of Wever. The lengths of the edges of the elementary parallelepipeds are  $a_1=5\cdot099, a_3=4\cdot240$  Å. The unit cell contains four Fe<sub>2</sub>B groups. The phase FeB has a rhombic lattice of which the parameters are  $a_1=5\cdot495, a_2=4\cdot053.$  $a_3=2\cdot946$  Å. The elementary parallelepiped contains four FeB groups. A. J. MEE.

X-Ray analysis of the copper-antimony and the silver-antimony systems. A. WESTGREN, G. HAGG, and S. ERIKSSON (Z. physikal. Chem., 1929, B, 4, 453-468).—The observations are in agreement with the equilibrium diagram for the system obtained by Carpenter. Antimony can dissolve in copper up to a considerable concentration. The parameter of the copper lattice increases from 3.608 A. for pure copper to 3.66 Å. for the alloy saturated with copper. At the ordinary temperature in the homogeneous region from 19 to 25 at.-% Sb there is a copperantimony phase with hexagonal close packing, of which the lattice dimensions increase with increasing antimony concentration from  $a_1 = 2.72$ ,  $a_3 = 4.32$  Å., to  $a_1 = 2.750$ ,  $a_3 = 4.349$  Å. The Cu<sub>2</sub>Sb phase has a simple tetragonal lattice with six atoms in the unit cell, of which the dimensions are  $a_1=3.992$ ,  $a_3=$ 6.091 Å. The alloy Cu<sub>2</sub>Sb has obviously an analogous structure to  $Fe_2As$ . On this basis its structure can be calculated. The X-ray analysis of a series of silver-antimony alloys shows that the equilibrium diagram of Petrenko is incorrect. The maximum solubility of antimony in silver is about 5 at.-% Sb. The lattice parameter of the silver phase increases in the homogeneous region from 4.078 Å. for pure silver up to 4.113 Å. for the saturated phase. At the ordinary temperature between 10 and 16 at.-% Sb there is a phase with hexagonal close packing. The there is a phase with hexagonal close packing. lattice dimensions increase with increasing antimony concentration from  $a_1 = 2.921$ ,  $a_3 = 4.775$  Å., up to  $a_1 = 2.959$ ,  $a_3 = 4.786$  Å. Between 20 and 25 at.-% Sb there is another intermediate phase which has a structure very similar to hexagonal close packing, but is really rhombic. The values for the parameters are : for 20%,  $a_1=2.981$ ,  $a_2=5.196$ ,  $a_3=4.802$  Å.; for 25%,  $a_1=2.988$ ,  $a_2=5.239$ ,  $a_3=4.842$  Å. A. J. MEE.

Determination of solubility of slightly soluble liquids in water and the solubilities of the dichloroethanes and dichloropropanes. P. GROSS (J. Amer. Chem. Soc., 1929, 51, 2362—2366).—A saturated solution of the slightly soluble liquid is analysed by means of a liquid interferometer which has previously been calibrated against solutions of the liquid of known concentration. The following solubilities (g. per 100 g. of water at 25°) were determined : s-dichloroethane, 0.506; as-dichloroethane, 0.865;  $\alpha\beta$ -dichloropropane, 0.280;  $\alpha\gamma$ -dichloropropane, 0.273; carbon tetrachloride, 0.077 (provisional). S. K. TWEEDY.

Solubility of sodium and potassium hydroxides in methyl and ethyl alcohols. A. G. MURRAY (J. Assoc. Off. Agric. Chem., 1929, 12, 309).— Sodium or potassium hydroxide in excess was allowed to remain in contact with ethyl or methyl alcohol for a period of 3 weeks at about 28°. The clear supernatant liquid was decanted, diluted ten times, and titrated with N-sulphuric acid. The following solubilities (g. per 100 c.c.) are recorded : potassium hydroxide in ethyl alcohol 29, in methyl alcohol 40·3; sodium hydroxide in ethyl alcohol 13·6, in methyl alcohol 23·9. The densities and the solubilities expressed as percentages and normalities are also given. H. J. DOWDEN.

Influence of strong electrolytes on the solubility of potassium chlorate. J. HOLLUTA and F. PETER (Z. physikal. Chem., 1929, 143, 119-134).-The solubility of potassium chlorate in water and in solutions of potassium chloride, nitrate, and sulphate, and sodium chloride and chlorate, has been measured at 25°, and at concentrations extending to the saturation point of the added salt. The solubility was raised by sodium chloride, and lowered by the remaining salts. The curves connecting the square root of the ionic strength with the reciprocal of the total molar concentration approximate to straight lines at low concentrations, except in the case of potassium nitrate, and from these curves the activity coefficients of potassium chlorate in the solutions were calculated. Calculation of the mean atomic radii by means of the Debye-Hückel expression lead to values considerably in excess of those calculated by Hückel, and of those arrived at by Goldschmidt from the results of crystal measurements, the differences being attributed partly to hydration. The solubility  $(\eta)$  of potassium chlorate in solutions of each of the salts (concentration = c) can be calculated by means of the expression  $\eta = A +$ Bc, A and B being constants the values of which are given. F. L. USHER.

Relation between sizes of ions and salting-out of quinol and quinone. K. LINDERSTRØM-LANG (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 13, 1--6).—The effect of ammonium chloride and the alkylammonium chlorides on the solubility of benzoquinone and quinol in water at 18° can be represented fairly satisfactorily by the equation  $\log(s_0/s) = kc$ , where s is the solubility in a salt solution of concentration c, and  $s_0$  is the solubility in pure water (cf. A., 1925, ii, 30). With quinol the value of the constant k decreases regularly with increase in the size of the salt cation, whilst with benzoquinone k scarcely varies at all. R. CUTHILL.

Theory of gas adsorption. A. MAGNUS (Z. physikal. Chem., 1929, 142, 401-430; cf. A., 1927, 105).—A kinetic theory of the adsorption of gas molecules on surfaces is based on the assumption that the forces are purely electrostatic, due to either permanent or induced dipoles in the gaseous molecules. It is inferred that at very low pressures the amount adsorbed is proportional to the pressure, but this condition is rarely realised. By the use of Volmer's equation of state for the adsorbed substance, adsorption equations are obtained which are in good agreement with experiment. The dependence of the heat of adsorption on the gas pressure, predicted by the theory, corresponds qualitatively with that observed. J. A. V. BUTLER.

Heat of adsorption of oxygen and nitric oxide on charcoal. H. I. BULL and W. E. GARNER (Nature, 1929, 124, 409).—Repetition of the work of Garner and McKie (A., 1927, 1134), in which it is now shown that carbon is a relatively bad conductor in high vacua and that at low concentrations of oxygen the gas does not become uniformly distributed throughout the mass of the charcoal grains. For oxygen absorbed on charcoal the heat rises from 46 g.-cal. per mol. to 100 g.-cal. per mol., then falls to 65 g.-cal. per mol., and thereafter remains constant except for a curious type of alternation (cf. Marshall and Bramston-Cook, this vol., 999). For the same charcoal the maximum heat of absorption of nitric oxide occurs at higher surface concentrations than for oxygen, and alternation does not occur beyond the maximum. The presence of areas of different activities on the charcoal surface is indicated. The phenomena are probably due to incompleteness of the reaction between oxygen and carbon at low surface concentrations. A. A. ELDRIDGE.

Adsorption phenomena in solutions. XVIII. Gas-free carbon as adsorbent. N. SCHLOV and K. TSCHMUTOV (Z. physikal. Chem., 1929, 143, 41— 54).—In the adsorption of oxygen by gas-free carbon, carbon dioxide is always formed except at low pressures. Although oxygen, carbon dioxide, and hydrogen chloride are adsorbed by gas-free carbon, this material seems to be incapable of adsorbing potassium chloride from its aqueous solution. The primary stage of the adsorption is the formation of a film containing negatively charged ions, and the hydrolytic adsorption which follows has been studied by determination of the  $p_{\rm H}$  changes. H. F. GILLBE.

Adsorption of organic acids by charcoal. C. FROMAGEOT (Nature, 1929, 124, 412).—The author's results are correlated with those of Phelps and Peters (this vol., 1000). A. A. ELDRIDGE.

Adsorption of fumaric and maleic acids by pure charcoals. H. J. PHELPS (J.C.S., 1929, 1724-1727; cf. Phelps and Peters, this vol., 1000) .- The relation between the adsorption on pure charcoal and the ionisation of maleic and fumaric acids has been examined. The adsorption of both acids is zero at  $p_{\rm H}$  7, that of maleic acid rising steadily to  $p_{\rm H}$  1.5 (the most acid solution with which it was possible to work) with no indication of a maximum, whilst that of fumaric acid reaches a maximum at  $p_{\rm H}$  3.7. These results suggest that doubly-ionised molecules are not adsorbed in either case, and that the singly-ionised molecule of maleic acid is adsorbed, but to a smaller degree than the neutral molecule. These facts are consistent with the hypothesis that it is the oxygen of the un-ionised carboxyl group which holds the molecule on the charcoal surface, this attachment being effected probably by the presence of an electric charge, and, in the case of maleic acid, by the close proximity of the two carboxyl groups. Possibly also adsorption is hindered by the presence of the water sheath supposed to surround most ions.

C. A. SILBERRAD.

Adsorption hysteresis. A. R. URQUHART (J. Text. Inst., 1929, 20, 117—123T).—Previous work on adsorption hysteresis is reviewed and experimental results are described which show that the assumption of McGavack and Patrick (A., 1920, ii, 417), according to which hysteresis phenomena may be explained by the presence of residual traces of non-condensable gases in the material, is incapable of satisfying the conditions which obtain with cotton. That hysteresis in general cannot be so explained is proved experimentally by an investigation of the adsorption of water by silica gel in such circumstances that there could be no doubt about the removal of the last

traces of non-condensable gas. Two samples of the gel were used which gave different isotherms of the same general form, and definite hystercsis was observed in both cases. B. P. RIDGE.

Adsorption by metallic hydroxides. VI. Adsorption of anions in relation to their coagulative action and their strength. VII. Adsorption isotherms and the mechanism of the adsorption of acids and bases by hydroxides. K. C. SEN (Z. anorg. Chem., 1929, **182**, 118–128, 129–138).—Study of the adsorption of various acids, bases, and salts by ferric, aluminium, and chromic hydroxides shows the last-named to have the greatest adsorptive power. In all cases the adsorption follows a logarithmic law, but the quantity  $\alpha$  adsorbed per unit weight of adsorbent is in certain cases dependent on the quantity of adsorbent used, the volume and concentration of the solution, and the physical nature of the hydroxide; with chromic hydroxide  $\alpha$  varies also with time. For a fixed quantity of dissolved material  $\alpha$  increases with increase of the quantity of adsorbent; heating decreases the adsorptive power. The adsorption of arsenious acid is irreversible only in the case of chromic hydroxide; different specimens of ferric and chromic hydroxides show different values of the adsorption constant. Arsenious acid and sodium arsenite are adsorbed to the same equivalent extent by aluminium hydroxide, but the acid is more readily adsorbed than the salt by chromic hydroxide. The adsorption of acids by the three hydroxides increases with the basicity of the acid, probably on account of complex formation. Citric acid, anomal-ously, is adsorbed by chromic hydroxide to a smaller extent than are oxalic and sulphuric acids. Other factors which influence the adsorption of acids, although to a smaller degree, are the strength and structure of the acid and the nature of the anion. Weiser's observations on the effect of neutral particles are confirmed. The second stage of the coagulation of a colloid by an electrolyte, viz., adsorption of ions by the neutralised particles, is a specific effect. The constant of the adsorption isotherms varies for each of the three hydroxides and even for different specimens of the same hydroxide. The mechanism of the adsorption process is ascribed to surface chemical activity, which is most in evidence when there is a tendency to salt formation between the adsorbent and material adsorbed. Chemical combination and adsorption are thus regarded as manifestations of the H. F. GILLBE. same forces.

Adsorption of methylene-blue by lead sulphate. W. D. BANCROFT and C. E. BARNETT (Coll. Symp. Mon., 1928, 6, 73—76).—Lead sulphate crystals adsorb methylene-blue. For any concentration of dye, the amount adsorbed by a powdered solid is a function of the apparent  $p_{\rm II}$  of the solution. The maximum adsorption of a dye by a crystal is not a measure of the total surface.

### CHEMICAL ABSTRACTS.

Mechanism of the adsorption of water by cotton. A. R. URQUHART (J. Text. Inst., 1929, 20, 125-132T).—A theory is outlined which explains not only the hysteresis, but also most of the other hitherto unexplained phenomena observed with cotton; it may also be applied to starch and to many elastic gels. It assumes that adsorption takes place in accordance with the number of free active hydroxyl groups on the micellar surfaces of the cellulose, and that absorption of water tends to restore the original orientation of the surface, so that the number of active groups increases. This increase is not so great as the original decrease which occurs when the cellulose is first formed in the cotton hair, since the amplitude of vibration of a molecule held to another by the attraction of one or more active groups will be less than that of a molecule with the active groups free, so that there is less tendency for a group to return to the surface than there was originally for it to leave it. Hence the adsorbing surface will be in a less active condition during adsorption than during desorption, and hysteresis will result.

B. P. RIDGE.

Two-phase theory of the absorption of water vapour by cotton cellulose. F. T. PEIRCE (J. Text. Inst., 1929, 20, 133—150T).—It is assumed that there are two distinct ways in which water molecules are held in the cellulose: (a) in which one water molecule is definitely associated with one hexose unit, as in a chemical compound, and (b) in which the water molecules fill the spaces available under attractive forces like those in a liquid. Mathematical treatment indicates how absorption isotherms and other experimental relations may be derived on the basis of the theory propounded. B. P. RIDGE.

Absorption and adsorption of iodine by soils, and its elutriation. K. SCHARRER and J. SCHWAI-BOLD (Z. anorg. Chem., 1929, 182, 193—206).—A variety of soils have been treated with iodine, iodides, iodates, and periodates, and considerable variation is found to exist in the quantities absorbed. By washing for many hours only a part of the iodine taken up is removed. Moor soils absorb greater quantities of iodine than do mineral soils, the quantities in the latter case being determined principally by the amount of colloidal material present. The quantity absorbed decreases in the order periodate, iodate, iodide, iodine following periodate in the case of mineral soils. H. F. GILLBE.

Adsorption of sodium oleate at the air-water interface. M. E. LAING, J. W. MCBAIN, and E. W. HARRISON (Coll. Symp. Mon., 1928, 6, 63-72).--Contrary to the predictions of Gibbs' theorem, sodium oleate is positively adsorbed in the air-water interface. The adsorbed soap is in hydrolytic equilibrium with the solution, but its hydrolysis is completely suppressed by a small excess of alkali.

CHEMICAL ABSTRACTS.

Activity and adsorption of *p*-toluidine on the surface of its aqueous solution. J. W. MCBAIN, W. F. K. WYNNE-JONES, and F. H. POLLARD (Coll. Symp. Mon., 1928, 6, 57—62).—The partial pressure and activity of aqueous *p*-toluidine are proportional to the concentration. This supports the view that even in solutions far from saturated the surface is covered with a unimolecular film of solute, of which there is also an excess in the neighbourhood of the surface. Gibbs' thermodynamic treatment is insufficient. CHEMICAL ABSTRACTS. Interfacial tensions of water-n-butyl alcohol, water-isobutyl alcohol, and glycerol-isobutyl alcohol. K. SILBEREISEN (Z. physikal. Chem., 1929, 143, 157—166).—The interfacial tensions have been determined with a view to the use of these liquids in determining the pore diameter of ultrafilter membranes by Bechhold's method. A new apparatus making use of the capillary-rise method is described, and the interfacial tensions at temperatures from 1° to 37° are given. F. L. USHER.

Relation between surface energy of liquids and saturation pressure. N. BARBULESCU (Bul. Soc. Stiinte Cluj, 1928, 4, 251—262; Chem. Zentr., 1929, i, 1427).—For non-associated liquids the surface tension is calculated from the molecular heat of vaporisation by a simplified method. For associated liquids a modified expression leads to good results with methyl alcohol, ethyl alcohol, and acetic acid.

A. A. ELDRIDGE.

Liquid-solid interface tension. M. LOEWEN-THAL (Nature, 1929, 124, 301).—Experiments are described which demonstrate that the interfacial layer of mercury at the surface of a containing vessel is the seat of tension and potential energy. A. A. ELDRIDGE.

Electrical relations at surfaces, spreading of liquids, thickness of surface films, and the dropweight and ring methods for the determination of surface tension. W. D. HARKINS [with B. GINSBERG, D. M. GANS, and H. F. JORDAN] (Coll. Symp. Mon., 1928, 6, 17-40).—The behaviour of hexane emulsified in sodium oleate solution on passing a current through the liquid is discussed. Formulæ for the spreading coefficient are developed and applied to the behaviour of films of benzene on water. Improvements in the ring method for determining surface tension are suggested.

CHEMICAL ABSTRACTS.

Internal pressures in adsorbed films. R. G. NUTTING (J. Wash. Acad. Sci., 1929, 19, 295-300).-An attempt is made to deduce energies of association and relations between internal and external pressures from weight-pressure and weight-temperature curves for dissolved or adsorbed vapours and gases. Expressions are deduced connecting the kinetic and cohesive pressures with concentration and temperature; these do not involve the use of an equation of state. Relations are also derived which connect surface tension with vapour pressure, and cohesive pressure in an adsorbed film with (i) vapour pressure and temperature, and (ii) osmotic pressure. The relations between adsorption and humidity and temperature are also discussed, the former with reference to silica (A., 1927, 509), and it is concluded that in the case of silica and water the inner layers are so compressed that the concentration is about 1.3. corresponding with an additional cohesive pressure of about 17,000 atm. C. A. SILBERRAD.

Spreading of proteins. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 770-771; cf. A., 1926, 790, 1094).—It has been found that various proteins have the same spreading-number, indicating that the surface occupied by 1 mg. of the substance is 1 sq. m. In aqueous

solution the molecules probably have their polar groups oriented towards the outer surface; when spread on an acid solution these groups are drawn to the surface and form a horizontal layer. The radius of the molecule is found to be 22.5 Å, and it appears that the spherical molecules are transformed into flat plates. Casein, hæmoglobin, and egg-albumin show the same transformation at the isoelectric point. The phenomenon is reversible.

### N. M. BLIGH.

Preparation of dichroic gold-gelatin films. P. A. THIESSEN (Z. anorg. Chem., 1929, **182**, 187– 188).—In about 100 c.c. of a gold hydrosol, prepared by using sodium citrate as the reducing agent, 0.2 g. of gelatin is dissolved and the whole is evaporated to dryness. After washing free from electrolytes the material is dissolved in hot water, spread on a glass plate, and partly dried; it is then stretched to about double its length and dried, whereupon red and blue dichroism is clearly exhibited. H. F. GILLBE.

Ionic exchange peculiar to permutit. G. WIEGNER and K. W. MULLER (Z. Pflanz. Düng., 1929, 14A, 321-347).—In alcohol-water solution ionic exchange in permutits is reduced owing to the limited hydration of the ions. In aqueous sugar solutions the exchange of ions is but little affected. The dielectric properties of the dispersion medium cannot be correlated with altered ionic exchange as in the case of the alcohol-water mixtures. The capacity of these gels for ion exchange is largely influenced by their degree of dispersion. The molecules of sucrose and dextrose do not penetrate the fine framework of the gel because of their large diameters, and no regularised absorption is possible. The cations of methylene-blue undergo very little exchange with the permutit complex.

### A. G. POLLARD.

Electrical method of measuring the concentration of suspensions. A. SLAWINSKI (J. Chim. phys., 1929, 26, 368—373).—Two glass tubes of the same size, with metal ends, are filled with the same suspension and one is placed vertical and one horizontal. The electrical conductivities are measured after the deposits have settled. Formulæ and tables are given for calculating the concentration. The method is more accurate than direct calculation from the conductivity (A., 1926, 1211) and is applicable to blood and to oil emulsions. J. A. V. BUTLER.

Dispersoid synthesis of gold by means of alkaline formaldehyde solutions. P. P. von WEIMARN (Kolloid-Z., 1929, 48, 346-352).—A summary of several years' work on the synthesis of gold sols, the details of which have been published elsewhere (cf. this vol., 760). E. S. HEDGES.

**Refractive indices of hydrosols.** A. DUMANSKI and B. S. PUTSCHKOVSKI (Kolloid-Z., 1929, 48, 338— 342).—The authors' formula for the refractive index of a hydrosol,  $n=c_1^{n_2-n_1}/d_2+n_1$ , where  $n_1$  and  $n_2$  are respectively the refractive indices of the dispersion medium and of the disperse phase, c is the concentration, and  $d_2$  the density of the disperse phase, agrees with the formula given by Wiegner (A., 1917, ii, 185). Data have been worked out for silicic acid, stannic acid, molybdic acid, zinc hydroxide, casein, and dextrin. E. S. HEDGES.

Wo. Ostwald's "solid-phase rule" and the solubility of casein in sodium hydroxide. S. P. L. SøRENSEN and I. SLADEK (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 14, 1-35).—The fact that in the equilibrium between certain proteins and their saturated solutions in solutions of electrolytes the concentration of protein in the liquid phase is dependent on the ratio of the amount of solid to that of solvent can be explained by the assumption that the proteins are loose compounds of substances of differing solubilities just as satisfactorily as by Ostwald's "solid-phase rule " (A., 1927, 310). When casein is treated with an aqueous solution of sodium hydroxide and sodium chloride at 18°, the proportion which dissolves, Q, decreases with increase in the relative amount of solid, Z, and increases with increase in the hydrogen-ion activity,  $pa_{\rm H}$ , of the solution. The concentration of casein in the solution at equilibrium, C, increases with increase in Z up to a point, after which it tends to fall again, probably owing to sodium hydroxide being bound by the solid phase. With a given salt concentration and value of Z, Qincreases with increase in the concentration of sodium hydroxide, and the pan increases at the same time. For a fixed value of Z and  $pa_{\rm H}$ , Q rises with the salt concentration, a result which, taken in conjunction with those of Linderstrøm-Lang and Kodama (A., 1925, ii, 1056), shows that the salt shifts the isoelectric point of casein towards the acid side. In general, the ratio of the amount of sodium hydroxide to that of casein is greater in the solution than in the solid phase. With a fixed concentration of alkali and a fixed value of Z, both Q and C rise continuously with the salt concentration up to about 2N, beyond which they start to fall again; the pa<sub>H</sub> decreases with increasing solubility. R. CUTHILL.

Structure viscosity of aqueous "solutions" of sulphonated oils have been made by means of the overflow viscosimeter. Solutions of sulphonated castor oils exhibit considerable structure viscosity at  $p_{\rm H}$  7.8-8.0. In strongly alkaline solutions ( $p_{\rm H}$ > 10.0) the phenomenon is less marked. The structure viscosity becomes observable at a definite concentration of solution. An emulsion of toluene with sulphonated castor oil and alkali has less structure viscosity than a solution of the sulphonated castor oil of the same concentration. Sulphonated train oil exhibits structure viscosity over a narrower range of hydrogen-ion concentration and in less intensity than sulphonated castor oil. E. S. HEDGES.

Dielectric polarisation of solutions of eggalbumin. (MLLE.) Y. GARREAU and N. MARINESCO (Compt. rend., 1929, 189, 331—333).—The  $\varepsilon$ - $p_{\rm H}$  curve at 20° for solutions of egg-albumin (fractionally precipitated by ammonium sulphate and purified by electro-dialysis) can be explained by the superposition of two opposite effects, namely, the amphoteric and hydrophilic effects for which  $\varepsilon$  is a minimum and maximum, respectively, at the isoelectric point,  $p_{\rm H}$  4.7 (cf. Marinesco, A., 1928, 1321). The presence in the sample of traces of adsorbed electrolytes may also modify the curve. J. GRANT.

Mechanism of gelatinisation. F. L. USHER (Proc. Roy. Soc., 1929, A, 125, 143-151).-Three possible types of mechanism for the gelation of sols are briefly discussed, and it is suggested that the behaviour of certain gelatinising lyophobic sols supports the theory which postulates a modification of the properties of the solvent in the vicinity of the disperse phase so as to produce a rigidity of the whole system, without necessitating any particular spacial arrangement of the solid units. From a consideration of the change in the disperse phase it is shown that, over a limited range of electrolyte concentration, collisions will result in the formation of linear aggregates rather than compact clusters, and if sufficiently close together these will tend to form a tangled network holding the liquid in its meshes. The above views are supported by microscopical observations on the formation of gels prepared from gamboge and cadmium sulphide by the addition of suitable concentrations of sodium chloride. A gel is regarded as an intermediate stage in the formation of a precipitate-a stage which, however, is realised only when the volume of the solid phase bears a large enough proportion to that of the liquid, and in the presence of a suitable electrolyte at a concentration lying between rather narrow limits. The suggested mechanism of gelatinisation is not applicable to turgescible substances, like gelatin or agar, or to gels formed in non-ionising liquids.

L. L. BIRCUMSHAW.

Swelling of gelatin in aqueous solutions of acids, bases, and salts and in mixtures of these. A. KÜNTZEL (Biochem. Z., 1929, 209, 326-437).-The swelling of gelatin in presence of electrolytes represents the result of "charge swelling," i.e., the absorption of electrolytes and their charges, and of " peptisation swelling "; the former predominates in acid and alkaline solution and the latter in salt solutions. The former reaches a maximum for that concentration of electrolyte at which there is maximum adsorption. The amount of "charge swelling" is determined by the degree of adsorbability of both ions and is therefore small with neutral salts when both ions are approximately equally adsorbed and large with acids and bases. The union of gelatin with ions is regarded as one of adsorption and not of salt formation. According to their behaviour towards gelatin electrolytes can therefore be divided into cationophile (the cation is here more strongly adsorbed than the anion, e.g., with acids, calcium chloride, etc.) and anionophile (the anion is more strongly adsorbed, e.g., sodium hydroxide or chloride). Electrolytes of the same group show additive and of different groups antagonistic effects. If two antagonistic electrolytes added to gelatin are of such a kind that the protein adsorbs equal amounts of positive and negative charges, the gelatin is then in the isoelectric condition. This depends therefore on the concentration of the ions present and not merely on the concentration of hydrogen ions. The so-called second isoelectric point obtained with phosphate buffers corresponds

with a charge minimum and not with an inversion of charge. It is obtained only when the concentration of phosphate is greater than 0.005M. Peptisation occurring simultaneously with charge swelling causes a considerable increase of that effect. Different electrolytes have different peptising powers; the greater is the molar solubility the greater is the peptising power. The absolute amount of swelling is also affected by changes of dissolution swelling, *e.g.*, by increasing the time of the experiment and by changes of temperature, of ash and gelatose content, and of acid peptisation (cf. A., 1928, 237). P. W. CLUTTERBUCK.

Influence of volume in swelling. D. J. LLOYD (Kolloid-Z., 1929, 48, 342—345).—Measurements of the swelling of purified isoelectric gelatin in water, salt solutions, acids, and alkalis have been made. In pure water and in solutions of salts and acids the degree of swelling is independent of the volume, provided that no hydrolytic degradation of the gelatin occurs. In alkalis, a certain amount of hydrolysis always proceeds and the swelling therefore increases with greater volumes of swelling liquid. The influence of the volume of liquid on the swelling of commercial samples of gelatin is due to alteration of the relative concentration of electrolytes and degradation products present as impurities.

E. S. HEDGES.

Rôle of dielectric constants, polarisation, and dipole moments in colloid systems. V. Swelling of cellulose acetate in binary mixtures. I. I. SAKURADA (Kolloid-Z., 1929, 48, 353-361; cf. B., 1929, 713).—The swelling of acetone-soluble cellulose acetate in binary liquid mixtures of varying composition has been investigated by both volumetric and gravimetric analytical methods and has been compared with the polarisation curves of these mixtures. Weakly dipolar liquids, such as benzene, carbon tetrachloride, and carbon disulphide, do not cause swelling either singly or in pairs; the polarisation curves are linear and practically horizontal. As examples of mixtures of a non-polar with a dipolar liquid the following were examined : benzene with ethyl ether, toluene, chlorobenzene, nitrobenzene, chloroform, or ethyl acetate, and carbon tetrachloride with ethyl ether, ethyl acetate, or acetone. Certain mixtures (carbon tetrachloride with ethyl ether, ethyl acetate, or acetone) gave linear curves, but the majority of curves showed a bend. In these cases there was a correspondence between the swelling and polarisation curves, although in some instances (benzene with chloroform, carbon tetrachloride with ethyl acetate or acetone) the bends in the two curves are in opposite directions. The main result of the experiments is the establishment of a close relation between swelling and polarisation. E. S. HEDGES.

Effect of temperature on the coagulation of a colloidal solution of copper. E. F. BURTON and (MRS.) B. R. DEACON (Coll. Symp. Mon., 1928, 6, 77— 82).—When a colloidal solution of copper is heated in a copper tube a critical temperature above which coagulation takes place is observed.

CHEMICAL ABSTRACTS.

Coagulation of colloids by electrolytes. VI. Use of the glass electrode in the potentiometric

study of the coagulation process. A. J. RABINO-VITSCH and V. A. KARGIN (Z. physikal. Chem., 1929, 143, 21-40).-The properties of the Haber glass electrode have been studied in regard to its employment in the absolute determination of the  $p_{\rm H}$  of solutions of weak acids. With change of the  $p_{\rm H}$  of the solution the potential of the glass electrode exhibits a linear change which is, however, less than the change observed with the platinum electrode, and a further error is introduced by the difference of potential exhibited in solutions of the same  $p_{\rm ff}$  containing two acids of different dissociation constants. The errors may be eliminated by calibration of the electrode in buffer solutions of suitable  $p_{ii}$  containing an acid having approximately the same dissociation constant as that of the acid to be investigated. With these precautions the glass electrode may be employed for the study of colloidal solutions. The end-point of a potentiometric acid-alkali titration obtained with the glass electrode agrees closely with that obtained when the platinum-hydrogen electrode is used, and  $p_{\rm H}$  determinations correspond approximately with those calculated from conductivity data. Investigation of arsenious oxide sols with the aid of the glass electrode indicates the incorrectness of the view that at the conductimetric end-point of the titration all cations, irrespective of valency, are adsorbed to the same extent. For univalent cations the adsorption maximum is reached at considerably higher concentrations. If the curves showing the replacement of hydrogen ions by cations of various valency are assumed to be of approximately similar form to the adsorption isotherms for the corresponding cations, it is found that for cations of different valencies these curves are of different form, in contradiction to Freundlich's assumption. An abnormally high value has been established for the dissociation constant of the hydrogen sulphide adsorbed on the colloidal particles. H. F. GILLBE.

Inhibitive effect of starch on the velocity of coagulation of goethite sols by electrolytes. H. FREUNDLICH and B. S. GREENSFELDER (Kolloid-Z., 1929, 48, 318-325).-The time-course of the coagulation by sodium sulphate of a goethite sol prepared from iron pentacarbonyl was followed by centrifuging the precipitate and titrating the remaining sol. Small amounts of starch have little effect on the rate of coagulation of the sol by sodium sulphate and sodium chloride, but larger amounts decrease the velocity greatly; still greater amounts of starch exert little further influence. The results suggest that a layer of starch of definite thickness is formed at the surface of the goethite particles and that protection reaches a maximum as soon as the layer is completed. The effect of the starch is irreversible, for subsequent dilution has little influence. The coagulation velocity of sols free from starch undergoes a steep rise over a small region of electrolyte concentration and reaches a constant value at a higher concentration of electrolyte. In presence of large amounts of starch, high concentrations of electrolytes give rise to a peptisation of the goethite sol. E. S. HEDGES.

Periodic precipitation in presence and absence of colloids. R. J. DOYLE and H. RYAN (Proc. Roy.

Irish Acad., 1929, 38B, 435-449).-Periodic precipitation of calcium phosphate occurs in the absence of colloids when capillary tubes containing calcium chloride solution are suspended with their open ends dipping in saturated sodium phosphate solution. The presence of glycerol or of a plug of gelatin in the tube reduces the speed of diffusion, but has no influence on the disposition of the rings. Experiments with lead nitrate and potassium iodide, also in the absence of gels, show that the distances of the bands from one another are in a geometrical progression (cf. Jabłczyński, A., 1926, 473) and also proportional to the square root of the time. It is shown that the formation of the bands does not take place at the head of the diffusion wave, but behind it. Various suggested theories are discussed : that of Fischer (A., 1925, ii, 853) is the most satisfactory. The use of carrageen moss jelly for the preparation of Liesegang rings is described. C. W. GIBBY.

The Maxwell-Clausius relation without reference to Carnot's principle. V. KARPEN (Compt. rend., 1929, 189, 359-360).—A reply to Verschaffelt (cf. this vol., 648), explaining in particular the term *Kdv* as representing the variation in intramolecular or kinetic energy. C. A. SILBERRAD.

Electrometric titration curves of dibasic acids. III. Substituted malonic acids. GANE and C. K. INGOLD (J.C.S., 1929, 1691-1700) .-The methods previously adopted (A., 1928, 846, 1083) have been applied to the determination of the distances (r) between the carboxyl groups of a series of alkylated malonic acids in order to examine the internal polar influences of the alkyl groups on the carboxyl groups, as these should in such a series constitute the main cause of disturbance in the spacial relations deduced from the valency deflexion hypothesis. The effects of solvation in augmenting, and of inductive electron attraction of the carboxyl groups in diminishing, the values of r are (as before) assumed to be nearly constant throughout the series, assumed to be nearly constant throughout the series, and practically eliminated by treating the results comparatively. The values obtained for  $K_1 \times 10^4$ ,  $K_2 \times 10^7$ , and r are, respectively : malonic acid 17.7, 43.7, 1.54; methyl- 10.7, 34.3, 1.64; ethyl- 12.6, 28.1, 1.50; n-propyl- 10.7, 20.8, 1.47; isopropyl- 11.7, 15.9, 1.37; dimethyl- 8.27, 15.3, 1.45; diethyl- 62.3, 0.590, 0.71; di-n-propyl-malonic acid 86.7, 0.342, 0.64. The values of r are shown to be in accordance with expected results both as regards order and relative with expected results both as regards order and relative magnitude. The qualitative relations between the dissociation constants are also shown to be in accordance with those anticipated by the valency deflexion theory. C. A. SILBERRAD.

Idiomorphic crystals of cuprous oxide in copper. C. BLAZEY (Inst. Metals, Sept., 1929, Advance copy, 4 pp.).—The microstructure of a sample of copper containing 0.05% O showed small particles of cuprous oxide with well-developed crystal faces, in contrast to the usual rounded forms. The sample was found beneath the brick floor of a furnace, and must have melted with absorption of oxygen, and flowed between the furnace bricks, after which it was protected from surface oxidation, and remained for nearly a year at a temperature which may have been more than 800°. W. HUME-ROTHERY.

Hydrates of lithium chlorate. L. BERG (Z. anorg. Chem., 1929, 181, 131–136; cf. Kraus and Burgess, A., 1927, 627).—An investigation of the system lithium chlorate-water has furnished further evidence of the existence of the hydrate  $3\text{LiClO}_3, \text{H}_2\text{O}$  (A., 1926, 1014). J. S. CARTER.

Thermal analysis. Systems containing lead chloride or mercuric iodide as solvent. H. PELABON and (MME.) LANDE (Bull. Soc. chim., 1929, [iv], 45, 488-492).-Eutectic points have been observed in the following systems, at the temperatures and molecular compositions indicated : lead chloride-lead fluoride, 461.5°, 8.6% lead fluoride; lead chloride-litharge, 402°, 30% litharge; lead chloride-lead iodide, 338°; lead chloride-silver chloride, 291°, 61% silver chloride; lead chloride-cuprous chloride, 258°. The mean value of the cryoscopic constant of lead chloride is 464°. Cadmium iodide and mercuric iodide form a continuous series of mixed crystals. Mercuric iodide and mercurous iodide form a eutectic at 227°, containing 47.5 mol.-% of mercurous iodide. The curve could not be followed above a concentration of 70 mol.-% of mercurous iodide, on account of increasing decomposition of the latter above 290°. C. W. GIBBY.

System sodium hydrogen carbonate-potassium hydrogen carbonate-water. N. E. OGLESBY (J. Amer. Chem. Soc., 1929, 51, 2352-2362).--Observations were made at 20°, 25°, and 30°, the sum of the partial pressures of the carbon dioxide and the water being maintained at 1 atm. The only solid phases found were sodium and potassium hydrogen carbonates. The solubility of the latter per 100 g. of water is 36.57 g. at 25° and 39.92 g. at 30°.

S. K. TWEEDY.

Ternary systems. VIII. Potassium carbonate, potassium sulphate, and water at 25°. A. E. HILL and S. MOSKOWITZ (J. Amer. Chem. Soc., 1929, 51, 2396—2398).—The solubility of the potassium sulphate is reduced to below 0.1% when the solution is still far from saturation with respect to carbonate, and to 0.03% at the saturation point. Solid solutions do not occur in the system.

S. K. TWEEDY.

System mercuric iodide, potassium iodide, and acetone. (MLLE.) M. PERNOT (Compt. rend., 1929, **189**, 326—328).—Earlier experiments (this vol., 400) repeated at 20° give a curve with six instead of five branches; the results are said to be dependent on the method of preparation of the saturated solutions. The salt  $HgI_{2,1}KI_{,0}.25C_{3}H_{6}O$  is indicated, but not  $HgI_{2,2}KI$  and  $2HgI_{2,3}KI$  (loc. cit.). J. GRANT.

Equilibria in the reduction, oxidation, and carburation of iron. VIII. System ironoxygen. R. SCHENCK, T. DINGMANN, P. H. KIRSCHT, and H. WESSELKOCK (Z. anorg. Chem., 1929, 182, 97-117).—The oxidation of iron by carbon monoxidecarbon dioxide mixtures at 700°, 800°, and 1000° has been studied. Stable equilibrium between wüstite and oxoferrite is attained at these temperatures when the gaseous phase contains 40.3%, 35.1%, and 28.5% of carbon dioxide, respectively. The solubility of oxygen in the oxoferrite phase does not exceed 0.5% at 800° and 1000°, whilst the higher value, viz., 0.8%, observed at 700° is probably due to equilibrium not having been attained owing to the slowness of the reaction. Corrections have been made in the ironoxygen diagrams previously given (Schenck and Dingmann, A., 1927, 1030). The question of the preparation of pure ferrous oxide is discussed; the stability of this compound is greatly increased by the presence of manganous or magnesium oxide. A state of stable equilibrium during the oxidation of iron by small quantities of carbon dioxide is reached much more readily in presence of small quantities (0.5-4.0%) of copper or nickel, whilst metastable phases are apparently not formed in appreciable quantity. The equilibrium is shifted somewhat towards the side of higher carbon dioxide percentages, and the oxygen content of the solid phase is considerably reduced, probably owing to the replacement by copper or nickel of the iron oxide in the mixed crystals.

H. F. GILLBE.

Heterogeneous equilibria in the gaseous phase in presence of appreciably volatile solids. K. JELLINEK (Z. physikal. Chem., 1929, **143**, 69—78).— Mathematical. The equation of the reaction isochore of a heterogeneous gas equilibrium in presence of a solid of appreciable vapour pressure is discussed, particularly with reference to the relation between the calculated heat change and that observed calorimetrically. H. F. GILLBE.

Thermodynamic consideration of certain reactions. I. BRICHTA (Arh. Hemiju, 1929, 3, 106— 113).—The value of the Nernst theorem for the examination of certain reactions is pointed out, and the application of this theorem to a number of reactions, such as the synthesis of methane, of acetaldehyde, of methyl alcohol, etc. from carbon monoxide, hydrogen, and methane, is given. R. TRUSZKOWSKI.

Heats of dissociation of the molecules CH, NH, OH, and HF. D. S. VILLARS (J. Amer. Chem. Soc., 1929, 51, 2374–2377).—By utilising principles discovered by Kuhn (A., 1926, 1192) and Mecke (A., 1927, 495) the above heats of dissociation are respectively calculated from band spectra data to be 82-0, 108-3, 138-0, and 172 kg.-cal.

S. K. TWEEDY.

Theoretical evaluation of the entropies of aqueous ions. W. M. LATIMER and C. KASPER (J. Amer. Chem. Soc., 1929, 51, 2293-2299).-The entropy change,  $\Delta S$ , of the process : ion (g)=ion (aq.)is a function of  $e^2/r$ , where e is the ionic charge and r the radius of the ionic cavity in the water solution (Latimer and Buffington, A., 1926, 1102). Now  $\Delta S$ . is the sum of the entropy change,  $\Delta S_1$ , arising from the polarisability of the medium and of  $\Delta S_2$  due to the compressibility of the water arising from the electrostatic attraction of the water molecules.  $\Delta S_1$  cannot be calculated satisfactorily (Born's equation fails; Z. Physik, 1920, 1, 4) and in any case is very small compared with  $\Delta S_2$ , which is calculated thermodynamically, using Born's expression for  $\Delta F_1$  (F=free energy) for evaluating r, with the aid of Zwicky's relation between pressure, e, and r (A., 1926, 462). For large ions in water  $\Delta S_2 = -22e^2/r$ . In this way  $\Delta S_2$  (approximately  $\Delta S$ ) is calculated for alkali metals, thallium, silver, and barium. For large ions  $\Delta S = 1.35 \times 10^{-4} \Delta F$ , which is Latimer and Buffington's straight line relation. The electron affinities of chloride, bromide, and iodide ions, as calculated from the crystal lattice energies, lead to calculated values of  $\Delta S$  which substantially agree with the experimental values. S. K. TWEEDY.

Calculation of heats of dilution of salts. J. B. GOEBEL (Z. physikal. Chem., 1929, 143, 167—171; cf. A., 1915, ii, 156).—The heat of dilution (U) of a salt solution can be calculated by means of a simple empirical formula  $U=-13000(k_0'-k_0)(1-0.017t)(c_1-c_2)+(209+4.5t)(\sqrt{c_1}-\sqrt{c_2})$ , where  $k_0$  is the equilibrium constant at 0° as determined by cryoscopic measurements,  $k_0'$  is an ideal equilibrium constant to which is assigned the value 0.265,  $c_1$  and  $c_2$  are respectively the initial and final concentrations, and t is the temperature. The heats of dilution of lithium, sodium, and potassium chlorides and of sodium and potassium nitrates are calculated for 33- and 50-fold dilutions over a temperature interval 0—26°, and compared with those measured by Naudé (cf. A., 1928, 1097). The formula is also applied to the calculation of heats of dissociation.

F. L. USHER.

Reduction potential of selenious acid, free energy of aqueous selenic acid, and free energy of trichloride ion. E. F. IZARD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 53-56).—The equilibrium constant for the reaction  $X_2+H_2SeO_3+H_2O=$  $H_2SeO_4+2HX$ , where X is either chlorine or bromine, has the value  $1.4 \times 10^9$  for the chlorine system and 0.88 for the bromine system, at 25°. From these figures the reduction potential of the reaction  $H_2SeO_3+H_2O=3H'+HSeO_4'$  is calculated to be -1.088 volts, which gives -107,710 g.-cal. for the free energy of HSeO<sub>4</sub>'.

The equilibrium constant of the reaction  $Br_2+Br'=Br_3'$  has been obtained by a distribution method, and that of the reaction  $Cl_2+Cl'=Cl_3'$  by determining the solubility of chlorine in aqueous solutions of sulphurie and hydrochloric acids and the chlorides of sodium, potassium, and barium at 25°. The equilibrium constant for the latter reaction has the value 0.010, which gives the figure of -28,637 g.-cal. for the free energy of the trichloride ion.

### R. CUTHILL.

Electrical conductivity of ethyl alcohol and its aqueous solutions. M. CHANOZ and G. CLUZET (Compt. rend. Soc. Biol., 1929, 99, 1999—2001; Chem. Zentr., 1929, i, 1661).—The electrical conductivity of absolute alcohol is smaller than that of distilled water; it increases on dilution, being maximal at 3% of alcohol. The simple ionisation  $C_2H_5^+$ , OH<sup>-</sup> is impossible. A. A. ELDRIDGE.

Effect of adsorbed water on the electrical conductivity of powders. F. B. KENRICK and F. J. GIFFEN (Coll. Symp. Mon., 1928, 6, 53-56).

Surface conductance. D. R. BRIGGS (Coll. Symp. Mon., 1928, 6, 41-52).—In aqueous solutions of low specific conductivity present in the interstices of a diaphragm, the electrical conductance through the interface phase is greater than that through an equal volume of liquid in bulk. A method for the determination of surface conductance of diaphragms is described. Salt solutions show definite valency and lyotropic effects. CHEMICAL ABSTRACTS.

Capacity of certain saturated complex compounds for further combination. O. E. ZvJAGIN-STSEV (J. Russ. Phys. Chem. Soc., 1929, **61**, 515—519). —Measurements of the electrical conductivity of solutions of Wilm's salt,  $(NH_4)_3[RhCl_6], NH_4NO_3$ , indicate that this dissociates with the formation of five ions, viz.,  $3NH_4$ ,  $NO_3$ , and  $[RhCl_6NH_4]''$ . This bivalent complex ion appears to act as a secondary complexforming radical. R. TRUSZKOWSKI.

Mechanism of ionic conduction in solid compounds [of the class of] "good conductors." A. SMEKAL (Z. physikal. Chem., 1929, B, 5, 60—80; cf. A., 1928, 1330; this vol., 871).—A theoretical discussion of the mechanism of electrical conduction in solid salts, of which the greater part has been previously abstracted. The large differences observed in the conduction by silver and sodium halides are due, not to different mechanisms, but to the relative importance of the contributions of the lattice ions and the "pore" ions to the total conductivity in the two cases. The mobile "pore" ions are identified with the "edge" ions of Blüh and Jost (cf. this vol. 32). F. L. USHER.

Spectroscopic and chemical investigation of the phenomena at the boundary of an aqueous electrolyte and a gas space on the passage of a discharge. W. R. COUSINS (Z. physikal. Chem., 1929, B, 4, 440-452) .- If in the electrolysis of sulphuric or phosphoric acid, sodium hydroxide, or silver nitrate, the anode is placed in the electrolyte and the cathode in the gaseous space above the liquid, which contains only water vapour corresponding with the saturation pressure of the electrolyte and its decomposition products brought about by the passage of the discharge, the light appearing in the gaseous layer at the surface of the liquid contains the spectra of the hydroxyl group and of atomic hydrogen. If the position of the electrodes is reversed, the anode being placed in the gas space, the spectrum of the singlycharged oxygen ion together with the weak spectrum of the uncharged oxygen atom is obtained. This has some bearing on the formation of persulphuric acid and Caro's acid observed by Haber and Klemenc in the electrolysis of concentrated sulphuric acid by this method. The probable explanation of the reaction is as follows. In the first case, with the cathode in the gaseous space, very little of these acids is obtained. In the second case, where the anode is outside, large quantities are formed. This may be due to the fact that in the former case there is very little oxidising action due to the hydroxyl group in the gaseous space, whilst in the latter there will be a very much greater oxidising effect owing to the presence of oxygen ions and atoms. A. J. MEE.

Contact potential between [pieces of] the same metal. W. ENDE (Physikal. Z., 1929, 30, 477– 480).—Contact potential differences between pieces of the same metal have been measured for brass, nickel, and platinum in air and in a vacuum (with and without cooling by means of liquid air) the surface condition being varied with the object of finding conditions for minimum P.D. values. Satisfactory results (P.D.<0.05 volt) are obtained when the surface layer of a hard metal is removed by sawing, turning, scraping, or treatment with a sand blast. Unsatisfactory results are given by washing, corrosion, and especially by treatment with all grades of emery paper. Reproducible contact potential differences below 0.05 volt could not be obtained with platinum. R. A. MORTON.

Potential of carbohydrate solutions. (MLLE.) N. MAYER (Compt. rend., 1929, 189, 319–321).—The results obtained by Wurmser and Geloso (A., 1928, 846) for dextrose and lævulose apply also to lactose, galactose, mannose, xylose, arabinose, and dihydroxyacetone. Variations in concentration of xylose (0.1-2.5%) do not appreciably affect the potential.

Reduction potential of thiosulphate. J. SCHEFFER and F. BÖHM (Z. Elektrochem., 1929, 35, 484-486).-The potential between a platinised platinum electrode and a solution containing thiosulphate and tetrathionate ions and buffered with phosphate mixture at  $\cdot p_{\rm H}$  7 changes considerably on keeping the solution in an atmosphere of nitrogen. Values of the normal oxidation-reduction potential, varying from 0.346 to 0.405 volt referred to the normal hydrogen electrode were obtained by extrapolation from the observed potentials of platinum electrodes in solutions prepared from sodium thiosulphate and potassium ferricyanide and buffered at H. T. S. BRITTON. pn 7.

Oxidation-reduction potentials of some vital stains. L. RAPKINE, A. P. STRUYK, and R. WURMSER (J. Chim. phys., 1929, 26, 340-348).— The oxidation potentials of cresol-blue, toluidineblue, azure-blue I, Nile-blue, cresol-violet, Janusgreen, neutral-red, and Unna's neutral-violet have been determined by electrometric titration with titanous chloride solutions over a range of  $p_{\rm H}$  values. The potential corresponding with an equimolecular mixture of oxidant and reductant is plotted against  $p_{\rm H}$  for each substance. The results show that these substances give sufficiently definite oxidation potentials for use in determining the potentials of living cells. J. A. V. BUTLER.

Polarisation in standard cells. W. S. NIEDER-HAUSER and G. S. HULETT (J. Amer. Chem. Soc., 1929, 51, 2327-2344).-Neutral saturated and unsaturated cadmium cells and zinc cells all behave similarly during the passage of current through the cell, the bulk of the polarisation occurring at the mercury electrode. On discharge, the greater polarisation occurs at the amalgam electrode. When polarisation is produced by large currents (1.7 milliamp., higher in presence of acid) a persistent recovery effect is observed at the mercury electrode, which markedly changes the subsequent behaviour of the cell during polarisation. This recovery effect disappears if the solid mercurous sulphate is removed; it is attributed to increase in the rates of dissolution and crystallisation at the surfaces of the sulphate crystals. The polarisation is diminished on addition

of acid and is always unaccompanied by any appreciable change in the resistance of the cell. A full discussion is given; the electrolytic actions at the mercury electrode of the standard cell appear not to be strictly reversible. The currents used when measuring cell potentials by the deflexion method are sufficient to produce polarisation, but the error introduced thereby is usually negligible.

S. K. TWEEDY.

Hysteresis in standard cells. W. E. NIEDER-HAUSER and G. A. HULETT (J. Amer. Chem. Soc., 1929, 51, 2345-2351).-The hysteresis of the separate electrodes of the cadmium cell has been investigated experimentally for the sudden temperature drop from 35° to 25°. The magnitude of the hysteresis at the anode depends on the size of the cadmium sulphate crystals; it is practically zero when this size is very small. The effect is much more persistent at the cathode, but is completely absent when no solid mercurous sulphate is present. Hysteresis at the anode is explained by the rise in temperature producing a more concentrated, and therefore denser, cadmium sulphate solution, which descends to the amalgam surface; on cooling, the more concentrated solution can deposit its excess salt only on the crystals. and since it can reach these crystals only by slow upward diffusion a hysteresis effect occurs. When the crystals are large the diffusion distances are greater and the available surface is less, so the effect is prolonged. An analogous explanation, referred to mercurous sulphate, probably also holds for the cathode. Acid appears to diminish the hysteresis by decreasing the rates of crystallisation and dissolution at the crystal surfaces. Decrease in the magnitude of the hysteresis due to age is attributed to the crystals assuming a more perfect shape on keeping, with a consequent lowering in the rate of dissolution or crystallisation. The high E.M.F. of freshlyprepared cells is due, at least in part, to hysteresis consequent on the overheating of the cells during preparation. A method of avoiding this overheating is described; by this cells were made which show normal constant values within a few hours of assem-S. K. TWEEDY. bling.

Flame speeds and their calculation. W. PAY-MAN and R. V. WHEELER.—See B., 1929, 666.

Gaseous combustion at high pressures. XIII. Molecular heats of nitrogen, steam, and carbon dioxide at high temperatures. D. M. NEWITT (Proc. Roy. Soc., 1929, A, 125, 119-134; cf. A., 1928, 847).—Data accumulated during previous researches are analysed, with the object of obtaining a quantitative estimate of the energy distribution at the moment of maximum pressure in typical explosions at high pressures, and also of calculating the mean heat capacities of the various explosion products over a temperature range from 15° up to various definite points between 2600° and 3000°. Data derived from explosions at high initial pressures (1) of theoretical hydrogen-oxygen mixtures diluted with either argon or nitrogen and (2) of carbon monoxide-oxygen mixtures containing excess of the combustible gas are used to calculate the mean molecular heats of carbon dioxide, steam, and nitrogen. The method used to

J. GRANT.

calculate  $C_v$  for nitrogen depends on the assumption that  $C_v$  for the monatomic gas argon is independent of temperature. By exploding a series of  $2H_2+O_2$ mixtures diluted with argon or nitrogen in varying proportions, the compositions of pairs of mixtures which on explosion will attain the same mean maximum temperature may be found by interpolation. In this way values are obtained for the apparent mean molecular heats of nitrogen at the various temperatures, but in order to allow for the fact that the heat losses for the two mixtures are not the same, a second series of explosions of the nitrogen mixtures must be carried out at a different initial pressure. An equation is given from which the true  $C_{\epsilon}$  may be calculated. From this value and from a knowledge of the heat of combustion of hydrogen and the degree of dissociation of steam, the mean molecular heat of steam may be calculated. In the case of carbon dioxide, the results of a series of explosions of the mixture 2CO+O2+4CO between initial pressures of 50 and 150 atm. are utilised. The results are discussed and compared with those obtained by previous investigators. The values for steam are by no means concordant. In the case of nitrogen, the values are in general higher than those found by Pier and Bjerrum and may be represented by  $C_r = 4.87 + 0.000387T$  in place of  $C_v = 4.85 + 0.000375T$ .

L. L. BIRCUMSHAW.

Ignition of electrolytic gas. L. FARKAS, P. GOLDFINGER, and F. HABER (Naturwiss., 1929, 17, 674; cf. this vol., 11, 278).—Earlier work on the suggested chain mechanism for the ignition of electrolytic gas has been confirmed and extended. Atomic oxygen or atomic hydrogen present in minute amount renders electrolytic gas immediately explosive. Further control experiments strengthen the case in favour of the chain mechanism. R. A. MORTON.

Rate of dissociation of nitrogen tetroxide. A. R. OLSON and C. E. TEETER, jun. (Nature, 1929, **124**, 444—445).—For nitrogen tetroxide containing 0.1% of air the velocity of sound is 192.6 m. per sec. at 25° and 565 mm., at a frequency of 51570 vibrations per sec., corresponding with a velocity coefficient 5630.

A. A. ELDRIDGE.

Unimolecular decomposition of some ethers in the gaseous state. J. V. S. GLASS and C. N. HINSHELWOOD (J.C.S., 1929, 1804-1814).-The rates of decomposition of methyl ethyl, methyl propyl, and diisopropyl ethers in the gaseous state have been investigated (cf. A., 1927, 212, 630). The decomposition of methyl ethyl ether is mainly homogeneous, but partly heterogeneous at lower temperatures. The reaction is not a simple unimolecular one, acceleration by the products and intermediate formation of aldehyde causing the coefficient to increase for the first 25% of the reaction, but the times required for a given fraction to decompose are independent of the initial pressure. The heat of activation is 47,000 g.-cal. per mol. Methyl propyl ether decomposes, giving mainly carbon monoxide, methane, and ethane, not more than 10% giving carbon monoxide, hydrogen, and propane. The reaction is mainly homogeneous in an empty silica bulb, a 16-fold increase in the surface : volume ratio causing but little disturbance. The heat

of activation is 49,000 g.-cal. per mol. Diisopropyl ether can decompose in three ways:  $C_3H_7 \cdot O \cdot C_3H_7$  $(a)=CO+3CH_4+0\cdot 5C_2H_4+C$ , a homogeneous unimolecular reaction,  $(b)=2CH_3 \cdot CH \cdot CH_2+H_2O$ , a surface reaction,  $(c)=CH_3 \cdot CO \cdot CH_3+C_3H_8$ , probably homogeneous, accompanying (a) to a slight extent. The velocity of (a) is independent of pressure between 327 and 29 mm. With methyl ethyl ether and methyl propyl ether the presence of hydrogen raises the velocity coefficients, which diminish at low pressures. C. W. GIBBY.

Hydration of ions and molecules. III. Velocities of hydration and dehydration. N. E. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 375-380).—The velocity coefficient  $K_1$  for the hydration of green chromic chloride remains constant at 0.0055 until 1 mol. of water has been added, when it suddenly falls to  $K_{0}=$ 0.00030 and again remains constant until another molecule of water has been added. From the formula  $L=SF(KT/2\pi m)^{\frac{1}{2}}e^{-W/RT}$  it is possible to calculate the number of mols. of water liberated on crystallisation of a particular salt when a crystallisation centre is present in the solution. In this equation L is the number of mols. striking the crystallising centre in unit time, *i.e.*, the number of mols. which can be dehydrated, S is the number of mols. present in solution, F the area of the solid phase, K is Boltzmann's constant, m the mass of a molecule, and W the energy of dehydration which can be calculated from the observed velocities of crystallisation at different temperatures. From the values of W calculated from the results of Marc (A., 1909, ii, 798) and of Fischer the following values for m are calculated : potassium sulphate, 4; ammonium oxalate, 3; sodium oxalate, 3; sodium pierate, 3; potassium alum, 4; and ammonium alum, 3. The results are of the same order as those found by other workers by different methods. A. FREIMAN.

Mechanism of oxidative processes. XVII. Ratio of oxidation velocities of molecular oxygen and hydrogen peroxide. H. WIELAND and W. FRANKE (Annalen, 1929, 473, 289-300).-When a solution of potassium hexacyanocobaltiate is shaken with oxygen, air, or a 3% oxygen-nitrogen mixture, diminishing amounts of oxygen are absorbed with decrease in oxygen concentration. The amounts of hydrogen peroxide produced decrease in the same order; almost the theoretical amount is obtained with pure oxygen. With the dilute oxygen mixtures, the peroxide formed takes part in the oxidation. Simultaneous oxidation with hydrogen peroxide and oxygen and determination of the amount of peroxide used shows that the reaction velocity for oxygen is about five times as great as for hydrogen peroxide. With benzoquinone (in an atmosphere of nitrogen) and methylene-blue as hydrogen acceptors oxidation of the cobaltiate also occurs. Autoxidation of a cuprous chloride solution with oxygen at various  $p_{\rm H}$  values (cf. A., 1924, ii, 35) shows that in strongly acid solution oxygen is consumed more rapidly than at  $p_n 2 \cdot 3 - 7$ ; the formation of hydrogen peroxide is detectable only in acid solution (cf. loc. cit.). The velocity of oxidation with peroxide decreases with increasing acidity, and oxidation is more rapid with oxygen at all hydrogen-ion concentrations. The velocity of oxidation of ferrous sulphate with hydrogen peroxide at  $p_{\rm H} < 7$  is much greater than for autoxidation. Thus, at  $p_{\rm H}$  5 and 4 oxidation is 2000—3000 times as great as with peroxide. In strongly acid solution autoxidation is extraordinarily slow (cf. A., 1928, 965), and the results show that intermediate formation of detectable amounts of hydrogen peroxide during autoxidation is excluded. H. BURTON.

Velocity of oxidation of hydrogen bromide by chromium trioxide in presence of chlorides, and the catalytic influence of the manganous ion. II. M. BOBTELSKY and A. ROSENBERG (Z. anorg. Chem., 1929, 182, 74-92).-At low concentrations all chlorides exert a retarding influence on the oxidation of hydrogen bromide by chromium trioxide, the optimum chloride concentration being about N. No specific action has been observed, even hydrogen chloride acting as an ordinary univalent chloride; the activity decreases as the valency of the cation In highly concentrated solutions the increases. retardation produced by the alkali chlorides is but slight, whereas that caused by zinc, cadmium, and mercuric chlorides is very great; other chlorides accelerate the reaction, their influence diminishing in the order nickel, magnesium, ferric iron, hydrogen, aluminium, chromic chromium. The only chlorides which tend to be attacked by the chromium trioxide are those of magnesium, ferric iron, and manganese, and there appears to be no relationship between this phenomenon and the catalysis of the oxidation process. The influence of the two neutral chlorides when present simultaneously is less than the sum of their The catalytic influence of the separate influences. manganese ion in dilute solution is exceptional, being greatly increased by the presence of neutral chlorides but nevertheless influenced by the nature of the neutral salt present; the order in which chlorides which have when alone a retarding action increase the activity is that in which they accelerate the reaction in concentrated solution. H. F. GILLBE.

Reaction velocity of iodine with sodium formate in presence of concentrated electrolytes. M. BOBTELSKY and D. KAPLAN [with (FRL.) C. DIESENHAUS] (Z. anorg. Chem., 1929, 182, 382-394).—The reaction between iodine and sodium formate is exceedingly sensitive to hydrogen ions, which at N concentration reduce the reaction velocity coefficient to less than 2% of its value in neutral solution. The influence of other cations is thus largely, if not entirely, governed by the extent to which the salt is hydrolysed. In general chlorides and sulphates at concentrations from N to 6N retard the reaction, the specific influence of the cations decreasing in the order aluminium, nickel, zinc, magnesium, calcium, strontium, barium, sodium, potassium; cobalt and manganese have approximately the same activity as nickel, and ammonium the same as sodium. At concentrations below about 3N, cadmium salts accelerate the reaction, but at higher concentrations retardation is produced. The retarding influence of anions is relatively small, and for the halogens decreases with increase of at. wt., fluorine having a slight accelerative influence, whilst

the reaction velocity in presence of the sulphate, acetate, and perchlorate ions scarcely differs from that of the uncatalysed reaction. The presence at high concentrations of electrolytes which have a powerful retarding influence tends to arrest the retardation produced by the cation.

H. F. GILLBE.

Velocity of reaction between sodium hydroxide solution and carbon dioxide. S. MITSUKURI (Sci. Rep. Tôhoku, 1929, 18, 245-297).-The velocity of the reaction between carbon dioxide and aqueous solutions of sodium hydroxide of concentrations varying from N to about 9N has been investigated between 10° and 30° by observations on the absorption of gas from bubbles rising in a stationary solution and from bubbles stationary in a moving solution and the absorption at the surface of falling drops of solution and at the surface of stationary solutions in bulk. The results can be qualitatively accounted for by supposing the rate of absorption to depend on the rate of the chemical reaction at the interface and the rate of diffusion of alkali through a thin film of liquid at the interface, the thickness of which increases with increase in the viscosity of the solution. It is assumed that the chemical reaction is truly heterogeneous in character. In the absorption by the surface of solution in bulk, the rate of diffusion from the body of the solution is so rapid that the concentration of alkali on the lower side of the surface film, and therefore on the surface itself, is kept appreciably constant. If, however, the solution is stiffened with gelatin, diffusion is retarded, and the concentration of alkali in the surface falls gradually at first as absorption proceeds. R. CUTHILL.

Different reduction velocities of gold chloride by arsenious oxide, dissolved as glass or crystal. E. JENCKEL (Z. anorg. Chem., 1929, 182, 314—318).— Solutions of arsenious oxide prepared from the vitreous modification reduce gold chloride four to five times as rapidly as do solutions prepared from the crystalline form. Although the rate of dissolution in water of the vitreous oxide is much greater than that of the crystalline material, there is no appreciable difference in the velocity of deposition from supersaturated solutions. It is concluded that there exist anisotropic molecules which only slowly lose their anisotropic properties. H. F. GILLBE.

Esterification of formic acid in methyl alcohol. H. GOLDSCHMIDT and R. S. MELBYE (Z. physikal. Chem., 1929, 143, 139-156).-The rate of esterification of formic acid in methyl alcohol in the presence of hydrogen chloride, picric acid, trinitro-m-cresol, or trichlorobutyric acid as catalyst is proportional to the hydrogen-ion concentration of these substances in the respective solutions. Water exercises a powerful retarding influence on the esterification in the presence of hydrogen chloride. In the absence of any catalyst the reaction is bimolecular, and is very sensitive to traces of water or basic impurities. Addition of sodium formate causes a large diminution in the velocity up to a concentration of 0.025N, above which it remains sensibly constant. It is concluded that the hydrogen ions arising from the dissociation of the formic acid play the same part in the esterification

as those furnished by the catalysts named above. The degree of dissociation of formic acid in methylalcoholic solution, obtained from the results of measurements of the alcoholysis constant, is given as  $\alpha = (5 \cdot 07 \times 10^{-9}/c)^{\frac{1}{2}}$ , where c is the concentration of the acid. F. L. USHER.

Possibility of characterising kinetic processes in heterogeneous systems by a single stirring factor. W. HELLER (Z. physikal. Chem., 1929, 142; 431-452).—The influence of temperature and rate of stirring on the velocity of dissolution of tin and cadmium in ferric chloride solutions and of magnesium in ammonium chloride solutions has been studied. The results can be expressed by equations of the type  $k = (An + C_0)(t - \tau)$ , where k is the velocity coefficient of the reaction, t the temperature, and n the rate of revolution of the stirrer.  $A, C_0$ , and  $\tau$  are constants,  $C_0$  and  $\tau$  being characteristic of the reaction and independent of the form of the apparatus, whilst A depends on both the reaction and the apparatus. The values of A in two different types of apparatus vary in the same proportion for different reactions, so that  $A = A_0 k$ , where  $A_0$  is the value in a "normal apparatus" and k is a constant which depends on the type of apparatus only. This constant can be found for a given type of apparatus, so that measurements may be referred to the " normal apparatus " only.

J. A. V. BUTLER.

Optical investigation of the passivity of metals. L. TRONSTAD (Nature, 1929, 124, 373).—The oxide film on passive iron or nickel is not totally destroyed on activation, but becomes porous and spongy; on re-passivation the holes are refilled with oxide, and the film becomes thicker. A. A. ELDRIDGE.

Atmospheric corrosion of metals. J. C. Hubson.—See B., 1929, 684.

Corrosion of steel in dilute acids. H. ENDO and K. NAKAWAGA.—See B., 1929, 751.

Homogeneous catalysis of a gaseous reaction. Kinetics of the catalytic decomposition of *iso*propyl ether. J. V. S. GLASS and C. N. HINSHELwood (J.C.S., 1929, 1815—1819).—The decomposition of gaseous *iso*propyl ether in accordance with the equation  $C_3H_7 \cdot O \cdot C_3H_7 = CH_3 \cdot CO \cdot CH_3 + C_3H_8$  is catalysed by *iso*propyl iodide, in virtue of the iodine produced by the decomposition of the latter.

The reaction is homogeneous, and the rate is proportional to the concentrations of ether and of *iso*propyl iodide. The heat of activation is  $28,500 \pm$ 500 g.-cal. per mol. C. W. GIBBY.

Air oxidation of hydrocarbons catalysed by nitrogen oxides. C. H. BIBB and H. J. LUCAS.— See B., 1929, 667.

Combination of hydrogen and oxygen on the surface of platinum. R. P. DONNELLY and C. N. HINSHELWOOD (J.C.S., 1929, 1727—1733).—The rate of combination of hydrogen and oxygen on the surface of platinum at ordinary pressures is independent of the hydrogen pressure, and increases with the oxygen pressure, the effect being the more marked the higher is the pressure. This differs from the behaviour observed at low pressures by Langmuir (A., 1922, ii, 629). It is concluded that in general, if

the law followed by a heterogeneous reaction changes with pressure; the centres on which reaction predominates also change with pressure. The presence of nitrogen or argon reduced the temperature to which the platinum could be heated without causing explosion; the presence of nitrogen peroxide reduced the rate. C. W. GIBBY.

Reduction of azoimide by hydrogen in presence of colloidal palladium. B. RICCA and F. PIRRONE (Gazzetta, 1929, 59, 379–384).—The reducing action of molecular hydrogen on an alkaline solution of azoimide in presence of colloidal palladium is very slight, but in acid solution reduction takes place to completion with the formation of ammonia and hydrazine. The latter product is recognised after separation of the colloidal palladium by dialysis. The same result is obtained by the action of nascent hydrogen from zinc or iron and hydrochloric acid. The equation  $HN_3+6H=NH_3+N_2H_4$  is suggested (cf. Raschig, A., 1925, ii, 223). R. K. CALLOW.

Mechanism of the catalytic decomposition of hydrogen peroxide on colloidal silver. E. WIEGEL (Z. physikal. Chem., 1929, 143, 81-93; cf. this vol., 643).—When a highly disperse Carey Lea silver sol prepared with alkaline dextrin is added gradually to excess of 5-10% hydrogen peroxide, the silver at first dissolves until a saturated (true) solution of Ag-O-OH is produced. The quantity thus dissolved varies inversely with the concentration of alkali. After the saturation point has been reached further addition of the sol leads to deposition of silver from the solution on the particles introduced, with simultaneous liberation of oxygen. Evidence is given in support of the view that the dissolved silver hydrogen peroxide, when adsorbed at the silver interface, dccomposes into hydrogen peroxide and silver peroxide, the latter then losing its oxygen. Since the metal is dissolved by hydrogen peroxide, so long as any of the latter remains this cycle is repeated, until the whole of the peroxide is decomposed. The process is accompanied by a large decrease in the total silver surface. F. L. USHER.

Topochemistry of contact catalysis. IV. Experimental proof of adlineation by topochemical reactions. E. PIETSCH, A. KOTOWSKI, and G. BEREND (Z. physikal. Chem., 1929, B, 5, 1—13; cf. this vol., 519).—A number of topochemical changes occurring on the surfaces of various crystals, in which the reaction products contrast in colour with the attacked crystals, have been observed microscopic-ally and photographed. Definite proof is obtained that the active centres of reaction are linear discontinuities in the surface (as assumed in the general theory of surface catalysis of Schwab and Pietsch), since in all cases the reaction is sharply localised at these parts before the entire surface becomes involved.

F. L. USHER.

Organic inhibitors in the acid corrosion of iron. J. C. WARNER.—Sec B., 1929, 751.

Decomposition of carbon monoxide in the silent electric discharge. III. R. W. LUNT and L. S. MUMFORD (J.C.S., 1929, 1711-1723; cf. A., 1925, ii, 1178; 1927, 531).—The velocity of
decomposition of carbon monoxide in the silent electric discharge is independent of the nature of the electrodes when the latter consist of mercury or dilute sulphuric acid. This is in agreement with the results of Berthelot (A., 1890, 691, 692), but not with those of Schutzenberger (A., 1890, 691, 692, 1358). With either kind of electrode carbon monoxide decomposes readily, even when very carefully dried. The brown solid produced during the discharge is not entirely polymerised malonic anhydride (cf. Ott, A., 1925, ii, 579; 1928, 720), but is probably a mixture containing carbon. C. W. GIBBY.

Activation of sulphur. R. SCHWARZ and P. W. SCHENK (Z. anorg. Chem., 1929, 182, 145-158).--Activation of sulphur has been accomplished by the silent electric discharge. No increase of volume takes place and it is inferred that rupture of the molecule does not occur, and further, on account of the extremely short life of the active substance, that triatomic sulphur, analogous to ozone, is not produced. The activated sulphur shows an increased reactivity towards hydrogen and carbon monoxide.

H. F. GILLBE. Structure of electro-deposited metals. F. FOERSTER and K. KLEMM.—See B., 1929, 685.

Production of electrolytic deposits of beryllium from molten electrolytes. H. FISCHER.—See B., 1929, 723.

Influence of the composition and temperature of the electrolyte in the preparation of beryllium by the Stock-Goldschmidt and Siemens & Halske methods. H. FISCHER.—See B., 1929, 723.

Preparation of beryllium by electrolysis. K. ILLIG, M. HOSENFELD, and H. FISCHER.—See B., 1929, 722.

Polarographic studies with the dropping mercury cathode. IV. Deposition of zinc from cyanide solutions. I. PINES (Coll. Czech. Chem. Comm., 1929, 1, 429-442; cf. this vol., 1015).-Zinc is deposited at the dropping mercury cathode from solutions of zinc cyanide in potassium cyanide when the mol. ratio of the two cyanides does not exceed 1:4; with more potassium cyanide only potassium is deposited. From solutions containing only a slight excess of potassium cyanide zinc is deposited at three different potentials, namely, -1.03 volt from Zn<sup>"</sup> ions, -1.23 volt from the complex ions  $Zn(CN)_4''$ , and -1.4 volt from  $Zn(CN)_5'''$ ions. The equilibrium constant of  $[Zn^*][CN']^4/$  $[Zn(CN)_4'']$  is 10<sup>-16</sup> and of  $[Zn^*][CN']^5/[Zn(CN)_5'']$  $6.8 \times 10^{-21}$ . The solubility product of zinc cyanide is  $2.6 \times 10^{-13}$ . Evidence is adduced which indicates that the deposition of zinc from double cyanide solutions is hindered by the slowness of dissociation of the complexes and not by the great complexity of the anions present. A. R. POWELL.

Direct electrolytic preparation of some metal permanganates. G. RAFIN (Compt. rend., 1929, 189, 287-289).—Calcium and barium permanganates were obtained in solution by electrolysis of the hydroxide in an isolated porous vessel, with a block of silico-manganese as anode, and a platinum cathode immersed in distilled water. On electrolytic reduction the former solution was decomposed with the formation of lime and oxides of manganese, whilst green, insoluble barium manganate was obtained from the latter. J. GRANT.

Formation of perchlorate during electrolytic preparation of chlorate. II. A. V. PAMFILOV and O. S. FEDOROVA (J. Russ. Phys. Chem. Soc., 1929, 61, 363—367).—Owing to the disagreement found (A., 1928, 968) in the percentage yield values of the total products of the electrolysis as found by chemical analysis and gas analysis, the methods of analysis used are fully reviewed and discussed and possible sources of error are pointed out and eliminated; the total yields as found by gas analysis and chemical analysis agree very closely within the limits of experimental error (difference from -0.7% to +0.6%). The authors conclude that the corresponding values of perchlorate as calculated by Spitalski, Sokolov, and Veintraub (J. Appl. Chem. Russia, 1924, [i], 1, 75) are too high. A. FREIMAN.

Colloidal basic chromic chromate. Conditions for formation by cathodic reduction of chromic acid. S. TAKEGAMI (Bull. Chem. Soc. Japan, 1929, 4, 156-163) .- During the electrodeposition of chromium from an aqueous solution of chromic acid there may be formed at the cathode a membrane of colloidal chromic chromate, permeable only to hydrogen ions. By the reduction of chromic acid solutions with alcohol it is shown that this can occur only if the ratio of ter- to sexa-valent chromium at the cathode is 1:0.5. When excess of alcohol is mixed with a solution of chromic acid at the ordinary temperature the mixture shows an increase in viscosity and a decrease in conductivity, and finally becomes coagulated. The ratio,  $Cr^{III}:Cr^{VI}$ , becomes steady at 1:0.4. Colloidal properties, as judged by viscosity measurements and ultramicroscopic observations, appear only when the ratio, Cr<sup>111</sup>: Cr<sup>VI</sup>, has reached the value 1:0.5. Dialysis yields a sol in which the ratio has risen to 1:0.2. This sol is positively charged, forming a gummy mass at the cathode, and is easily precipitated by bivalent anions. By concentration in a vacuum at 50° a sol containing 18 g. Cr per litre is obtained which has at 25° a specific conductivity of  $9.4 \times 10^{-4}$  and a relative viscosity of 330, and will if cooled to 20° slowly set to a gel which again becomes fluid on warming to the original temperature. T. H. MORTON.

Photochemistry of the halogens. A. BERTHOUD (J. Chim. phys., 1929, 26, 333–339).—A reply to Plotnikov (this vol., 522). J. A. V. BUTLER.

Photochemistry of silver iodide. LÜPPO-CRAMER (Z. wiss. Phot., 1929, 27, 1—8).—When a film of silver iodide free from foreign substances such as desensitisers is exposed to diffuse light, subsequent exposure to more feeble light has a bleaching action. This is not, however, a manifestation of the Herschel effect, but is a solarisation occurring before the maximum possible blackening has been attained. A similar result is obtained even if 5% of the iodide is replaced by bromide, but not if 10% is replaced. There may also be a marked Schwarzschild effect, but this can be completely prevented by powerful iodine acceptors, thus showing it to be an intermediate regression. Thallous iodide increases the sensitivity of silver iodide in much the same way as silver bromide, so that in either case the effect of the added substance is doubtless to be ascribed to its interfering with the crystal lattice. The effect of ripening on the sensitivity of silver iodide is probably a development phenomenon; the increase in size of grain consequent on ripening presumably reduces the protective action of the gelatin in respect of the separation of silver.

R. CUTHILL.

Photochemical reductions and oxidations from the electronic point of view. A. STEIGMANN (Z. wiss. Phot., 1929, 27, 24-36).-The photochemical reduction of silver ions or other reducible groups can be effected either by transfer of electrons from another part of the molecule or by donation of electrons liberated along with hydrogen ions from gelatin or other reducing agent under the influence of light. If there is present a substance which has a greater affinity for electrons than the silver ion has, it will act as a desensitiser, whereas a substance which gives off electrons readily as well as takes them up readily will be a sensitiser. In general, in a ternary photochemical system consisting of a reducing agent or group and two oxidising agents, either of these last will be sensitised at the expense of the other being desensitised, depending on which has the stronger affinity for electrons. Neither has, however, its maximum theoretical effect, a sensitiser always having some desensitising action and vice versa. The difference in susceptibility to desensitisers between various emulsions is probably due to differences in activity of the ripening nuclei. R. CUTHILL.

Photochemistry of the silver halides. VI. Analytical and photographic investigation of the silver halides. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1929, 27, 36-47).-The disposition of the excess of silver in photographic emulsions before and after exposure is discussed. Before exposure, 75% of the silver above the amount corresponding with the halide is contained in the gelatin in a highly disperse state, and only 25% is in the grains of halide; 95% of the total quantity is not in the form of silver sulphide. Treatment with dichromate and sulphuric acid removes the whole of the highly disperse portion and most of the other portion too, and reduces the sensitivity. The effect on the sensitivity cannot, however, be explained on the assumption that the sensitivity centres are partly occluded within the grains, those on the surface being removed by the acid (cf. Kieser, B., 1929, 265), for the sensitivity is affected more in respect of chemical" development than in respect of primary physical development. It seems probable that the chromic acid does not remove the silver completely but deposits some of it as dichromate, and that dichromate ions are also adsorbed, which would presumably alter the photographic properties of the emulsion. The effect of such substances as potassium iodide in laving bare the nuclei in exposed chloride and bromide emulsions treated with chromic acid (Lüppo-Cramer, "Grundlagen des Negativverfahrens," Halle, 1927, p. 533) has been observed with iodide emulsions as

well, and is readily explained by supposing that the anion of the salt displaces the dichromate ion from the sensitivity centres. The halogen produced on exposure in a chloride or bromide emulsion is free in the gelatin, whilst with a chloride emulsion the whole of the silver formed is adsorbed in the grains, treatment with chromic acid removing 95%, without altering the threshold sensitivity to chemical development very much. R. CUTHILL.

Action of ultra-violet light on certain inorganic compounds. E. MONTIGNIE (Bull. Soc. chim., 1929, [iv], 45, 492—494).—After exposure to ultraviolet light the following potassium salts affect a photographic plate : chloride, bromide, sulphate, nitrate, chlorate, perchlorate, permanganate, chromate, dichromate, oxalate, and tartrate. Calcium fluoride and phosphate behave similarly, but ammonium chloride, ammonium phosphate, magnesium oxide, and magnesium sulphate showed no effect.

C. W. GIBBY. Phototropy in inorganic compounds. E. L. RAO, K. VARAHALU, and M. V. NARASIMHASWAMI (Nature, 1929, 124, 303).—The phototropy of compounds of the formula 2HgS,HgX<sup>I</sup><sub>2</sub> or 2HgS,HgX<sup>II</sup> is due to dissociation into the simple salts by absorption of actinic energy; on preservation in the dark, recombination, with emission of radiant energy, takes place. A. A. ELDRIDGE.

Photochemical methods of testing sources of ultra-violet radiation. F. C. HYMAS (Quart. J. Pharm., 1929, 2, 281-291).—Three chemical methods of testing the emission of ultra-violet light, namely, the decompositions of carbon tetrachloride, of aqueous solutions of oxalic acid in the presence of uranyl sulphate, and of potassium iodide-starch solutions, have been compared. Failure to obtain concordant results with the first-named method was shown to be due to the fact that the reaction is most intense in the vapour phase. The potassium iodide-starch method has a temperature coefficient between 25° and  $62^{\circ}$  of -1.042 for  $10^{\circ}$ , and for periods less than 10min. the amount of "reaction is proportional to the energy absorbed. The rate of emission of the ultraviolet radiation decreases more rapidly when measured by the potassium iodide-starch method; this is attributed to the difference in the absorption spectra of the solutions employed and the deterioration of the quartz lamp due to the deposition of silica (cf. Pettersson, this vol., 377). C. C. N. VASS.

Photochemical oxidation of ethyl alcohol by potassium dichromate. II. E. J. BOWEN and and E. T. YARNOLD (J.C.S., 1929, 1648-1655; cf. A., 1927, 1040).—The oxidation of ethyl alcohol by potassium dichromate under the influence of light of wave-lengths 4360, 4060, and 3666 Å. has been investigated with reference to the following factors: (1) Effect of neutral salts. Sodium sulphate had no effect on the photochemical rate; large quantities of calcium chloride affect the rate only slightly, but alter the concentration of alcohol which gives the maximum rate by the removal of water to form hydrated ions. (2) The order of the reaction with respect to alcohol in low concentrations. The quantum efficiency  $\gamma$  can be represented by the equation  $\gamma = k_1 a + k_2 a^2$ , a being

the percentage of alcohol by volume. It is concluded that the photoactive ions are dichromate ions solvated with one and two alcohol molecules. (3) The cause of the diminution of the rate at high alcohol concentrations. The quantum efficiency passes through a maximum at 85 vol.-% of alcohol, and then diminishes owing to the scattering of light by an amorphous precipitate, caused by the insolubility of basic chromium sulphates in concentrated aqueous alcohol. (4) The dependence of the rate on the concentrations of hydrogen ions and dichromate ions. This can be accounted for on the assumption that the ion  $HCr_2O_7$  is photochemically active. This hypothesis is supported by the results of experiments on the oxidation of glycerol by potassium dichromate, in which the quantum efficiency is proportional to the glycerol concentration when the latter is small, and at higher concentrations rises to a limiting value of 0.52, instead of to unity as for concentrated ethyl alcohol solutions. The photochemically active substance is a dichromate ion combined with one glycerol molecule. An approximate value has been determined for the second dissociation constant of dichromic acid in solutions of aqueous alcohol of various concentrations.

C. W. GIBBY.

Bromination of benzene in light. W. MEID-INGER (Z. physikal. Chem., 1929, B, 5, 29-59).-An attempt is made to explain the mechanism of a simple photochemical reaction in a liquid phase by means of the conceptions hitherto used for gaseous reactions, viz., atomic activation, chain reactions, and photo-chemical equilibrium. The factors influencing the bromination of benzenc in light at low concentrations of bromine (1-2 mg./c.c.), using carbon tetrachloride as a diluting solvent, have been experimentally determined. It is found that either bromine can be substituted directly in the ring with formation of monobromobenzene, or the double linkings can be broken and benzene hexabromide formed. A reaction scheme based on the assumption that each quantum produces two bromine atoms and that the latter are the active agents in the bromination is suggested. An expression for the reaction velocity obtained in terms of experimentally measured quantities is in satisfactory agreement with the observations. The light reaction is independent of the bromine concentration and of the wave-length of the light used. No explanation can be offered for the fact that the temperature coefficient of the reaction decreases from 1.6 to 1.0 with decreasing concentration of benzene.

F. L. USHER.

Alkali aluminosilicates. I. Synthetic study of nepheline. E. GRUNER (Z. anorg. Chem., 1929, 182, 319—331).—The synthesis of nephelines by heating mica with sodium or potassium hydroxide and water for several hours has been studied. The lowest temperature at which nephelines are formed is about 200°, and at about 400° the reaction is first observed to proceed in the reverse direction. Other products, such as natrolite and other zeolitic minerals, are simultaneously formed in small quantities. Paragonite is more readily converted into sodium nepheline than is muscovite into potassium nepheline. In both cases preliminary ignition of the mica causes the appearance of an initial slow stage, in the synthesis followed by a very rapid stage, whilst the end part of the reaction follows the same course as when the mica is not ignited. By the action of sodium hydroxide on kaolin at  $800-1000^{\circ}$  there results in addition to nepheline an aluminosilicate of the composition  $2Na_2O_Al_2O_3_2SiO_2$ , which by treatment with water

forms a nepheline monohydrate. H. F. GILLBE.

Composition of the cyanide complex radical of metals. I. Silver cyanide complex radical. K. MASAKI (Bull. Chem. Soc. Japan, 1929, 4, 190—193). —The addition of silver cyanide, chloride, thiocyanate, oxide, or chromate to excess of sodium cyanide and titration of the excess of cyanide with silver nitrate gives a molal ratio of combined cyanide to silver of I:1. L. S. THEOBALD.

Silver iodidothiocyanate. A. C. VOURNASOS (Z. anorg. Chem., 1929, 182, 37-48).-The compound Na<sub>6</sub>[AgI(CNS)<sub>6</sub>] has been prepared by refluxing an acctone solution of silver iodide and sodium thiocyanate until a clear solution is produced, cooling, and allowing the solution to evaporate at about 20°. The resulting product, after recrystallisation from acetone and drying over sulphuric acid, forms colourless prismatic needles which are unaffected by light. Acetone solutions of the complex salt form with benzene, the paraffins, liquid terpenes, aldehydes, and nitriles clear solutions from which the complex may be obtained by evaporation; on addition of water, alcohols, fatty acids, or phenols to the acetone solution decomposition immediately ensues with precipitation of silver iodide. Addition of aliphatic mono-, di-, or tri-amines results in the gradual separation of crystalline complexes such as [AgI,2NH2Me], which are readily decomposed by water and show no tendency to ionisation in dilute acetone solution. By pouring an acetone solution of the complex salt into a large excess of 10% ammonia solution the complex

 $[Ag(NH_3)_2]I, H_2O$  is produced, which is soluble in water without decomposition; sodium and potassium hydroxides cause complete decomposition of the complex. *Potassium silver iodidothiocyanate*,

 $K_6[AgI(CNS)_6]$ , and the ammonium salt,

 $(\ddot{NH}_4)_8$  [AgI( $\dot{CNS}$ )<sub>8</sub>], have also been prepared. A solution of the acid H<sub>6</sub> [AgI(CNS)<sub>6</sub>] is obtained by addition of concentrated hydrochloric acid to an acetone solution of the salt. H. F. GILLBE.

Decomposition of beryl and the preparation of beryllium salts suitable for electrolysis. K. ILLIG, M. HOSENFELD, and H. FISCHER.—See B., 1929, 722.

High-purity magnesium produced by sublimation. H. E. BAKKEN.—See B., 1929, 685.

Preparation of luminophores. L. VANINO and M. PREM (J. pr. Chem., 1929, [ii], **123**, 85--88).— The views expressed by Breteau (A., 1916, ii, 100) with regard to the preparation of phosphorescent calcium sulphide are criticised. The addition of the phosphorogen to the ground-mass, after previous ignition of the latter, is not advantageous, immediate addition producing a far greater degree of phosphorescence. The use of sodium carbonate and chloride, as recommended by Verneuil (A., 1887, ii, 539), affords no improvement in phosphorescence, but the authors

consider that the flux contributes to the fusibility of the ground-mass, and to the ultimate phosphoresence (especially in the case of lithium salts). It is found that the use of lithium carbonate or sulphate as flux is much superior to employment of a mixture of sodium, potassium, and lithium sulphates. The advantageous replacement of bismuth by vanadium, recommended by Breteau (loc. cit.), is confirmed. Cerium salts in conjunction with bismuth yield a bright phosphorescence of warm violet colour, whilst replacement of cerium by uranium nitrate gives a duller tint; use of tungsten trioxide affords a greenishyellow phosphorescence. A period of heating of 0.75 hr. is found to be sufficient (cf. Bretcau, loc. cit.), and the after-glow is more efficient the greater is the velocity of cooling (cf. Breteau, loc. cit.). Certain mixtures exhibit phosphorescence which varies in intensity with the period of heating. The results for mixtures containing calcium oxide, barium oxide or carbonate, strontium oxide, carbonate, or thiosulphate, the colours produced, and the variation of the phosphorescence or luminescence with the time of heating, are given in tabular form. C. W. SHOPPEE.

Reducing action of metals on salts in liquid ammonia solution. Action of sodium on zinc cyanide. W. M. BURGESS and A. ROSE (J. Amer. Chem. Soc., 1929, 51, 2127-2131).-The formula NaZn<sub>4</sub> (Kraus and Kurtz, A., 1925, ii, 577) for the product of the above reaction is confirmed by quantitative analysis:  $4Zn(CN)_2 + 9Na = NaZn_4 + 8NaCN$ . The compound reacts with dry oxygen in two stages : first sufficient oxygen to convert the sodium into monoxide is taken up rapidly and exothermically, and then the compound very slowly changes from black to white, apparently because of oxidation of the zinc. The second stage is so accelerated by moisture that the two stages become indistinguishable. The compound reacts with acid, yielding hydrogen equivalent to the total sodium and zinc present. Hydrogen is also formed when water acts on the compound; part of it is due to the direct decomposition of the water by the zinc. S. K. TWEEDY.

Cadmium and beryllium peroxides. T. R. PERKINS (J.C.S., 1929, 1687-1691).-Cadmium peroxides have been prepared by five different methods. (1) Cadmium hydroxide dissolved in concentrated ammonium nitrate solution reacts with hydrogen peroxide, giving a stable precipitate of  $Cd_3O_5, xH_2O$ . (2) Addition of alcoholic potassium hydroxide to an alcoholic solution of cadmium bromide containing perhydrol " gave a precipitate of  $CdO_{1.62}$ . (3) The compound  $Cd_4O_7, 2H_2O$ , a true peroxide, was obtained by adding a solution of cadmium hydroxide in ammonia to "perhydrol." (4) Addition of ethereal hydrogen peroxide to an ethereal solution of cadmium dimethyl gave the compound 3CdO,2H<sub>2</sub>O<sub>2</sub>. (5) Passing ozone through a suspension of finely-divided cadmium oxide in chloroform gave small quantities of peroxide. The compounds Cd<sub>4</sub>O<sub>7</sub>,2H<sub>2</sub>O and 3CdO,2H<sub>2</sub>O<sub>2</sub> decompose unimolecularly. An attempted preparation of beryllium peroxide by method (4) was unsuccessful. C. W. GIBBY.

Ortho- and pyro-silicic acids. P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1929, 182, 343350).—By prolonged hydrolysis of ethyl orthosilicate with water at the ordinary temperature orthosilicic acid,  $SiO_2,2H_2O$ , has been prepared, and by desiccation of this substance at 13°, pyrosilicic acid,  $2SiO_2,3H_2O$ , has been obtained. H. F. GILLBE.

Germanium. XXX. Halogen substitution products of monogermane. L. M. DENNIS and P. R. JUDY (J. Amer. Chem. Soc., 1929, 51, 2321— 2327; cf. A., 1928, 33).—Monochloromonogermane, GeH<sub>3</sub>Cl, b. p. 28°, m. p.  $-52^{\circ}$ ,  $d^{-52}$  (liq.) 1.75, log p(vapour pressure in mm.)=7.961—1527.4/T, obtained by the interaction of hydrogen chloride and monogermane in presence of anhydrous aluminium chloride, is somewhat unstable at the ordinary temperature : 2GeH<sub>2</sub>Cl=GeH<sub>4</sub>+Ge+2HCl. Dichloromonogermane, GeH<sub>2</sub>Cl<sub>2</sub>, b. p. 69.5°, m. p.  $-68^{\circ}$ ,  $d^{-68}$  (liq.) 1.90, log p=7.969-1742.7/T, was prepared similarly. Both substances are readily hydrolysed with evolution of hydrogen; the reactions with common reagents are recorded. Monobromomogermane, b. p. 52°, m. p.  $-32^{\circ}$ ,  $d^{29.5}$  2.34, log p=7.851-1614.7/T, is a colourless liquid prepared analogously to the foregoing. Dibromomonogermane, b. p. 89°, m. p.  $-15^{\circ}$ ,  $d^{\circ}$  2.80, log p=9.798-2461.9/T, resembles the monobromoderivative. Evidence of the formation of the corresponding iodine compounds was obtained; these were, however, too unstable to be isolated.

S. K. TWEEDY.

**Zirconium iodide.** E. CHAUVENET and J. DAVIDOWICZ (Compt. rend., 1929, **189**, 408—409).— Zirconyl iodide,  $ZrOI_2,8H_2O$ , heated in a vacuum or in a current of dry hydrogen, decomposes simultaneously into zirconia, and either zirconium iodide,  $ZrI_4$ , or (principally) hydrogen iodide. Iodozirconie acid,  $ZrI_4,2HI$ , a brick-red crystalline powder which is decomposed by heat into its molecular constituents and by water into zirconyl iodide, is therefore formed. Zirconium iodide, which crystallises in white needles, is also decomposed by water, and may be distilled from a mixture of dry iodine and zirconium heated to redness in a vacuum, and any sublimed iodine subsequently removed in carbon disulphide. J. GRANT.

Action of the alkali carbonates on lead chloride. (MME.) N. DEMASSIEUX (Compt. rend., 1929, 189. 333-335).—Conductometric analysis of mixtures of solutions of lead chloride and of sodium carbonate at  $17^{\circ}$  show that lead chloridocarbonate, (PbCl)<sub>2</sub>CO<sub>3</sub>, identical with phosgenite, is precipitated when the concentration is  $0.5Na_2CO_3+1PbCl_2$ , but is progressively transformed into lead carbonate on further addition of the alkali. Transformation is complete when the mixture is equimolecular, and the deposit thereafter consists of lead carbonate only. Some weeks are required to attain complete equilibrium. J. GRANT.

Periodic structures from interacting gases. E. S. HEDGES (J.C.S., 1929, 1848—1849).—Regularly spaced bands of ammonium chloride may be obtained in narrow tubing connecting, through drying trains, solutions of ammonia and hydrochloric acid (cf. Koenig, A., 1920, ii, 594; Doyle and Ryan, this vol., 1144). C. W. GIBBY.

Chemical reactions of dried substances. I. Ammonia and phosphorus pentoxide. L. HARRIS and C. B. WOOSTER (J. Amer. Chem. Soc., 1929, 51, 2121—2126).—Pure sublimed phosphorus pentoxide absorbs rapidly appreciable quantities of intensively dried ammonia; the reaction product forms a protective film on the pentoxide. S. K. TWEEDY.

Preparation of azoimide and its salts. W. Horn and G. Pyl (Z. angew. Chem., 1929, 42, 888-891).-Azoimide may be safely distilled from 5% acid solutions (made by mixing the requisite amounts of dilute sulphuric acid and crude sodium azide) at 40° under 40 mm. pressure. By collecting the distillate in well-cooled solutions of alkali hydroxide or in suspensions of alkaline-earth hydroxides the corresponding azide is readily obtained in a pure form. The excess of alkaline-earth hydroxide may be removed from the solution by passing a regulated stream of carbon dioxide through the liquid until the red colour of phenolphthalein is just discharged. Barium azide may be prepared by treating a 10% solution of sodium azide at 0° with the requisite quantity of a 27% solution of hydrofluosilicic acid and neutralising the liquor, after filtration, with barium hydroxide. For the preparation of potassium azide 80 g. of potassium are heated in a revolving tube furnace at 300° in a current of ammonia until absorption ceases, the ammonia is replaced by nitrogen, and the potassamide heated at 270-280° in a current of nitrous oxide. The resulting mass is dissolved in warm water and the azide recovered by crystallisation in almost quantitative yield. Barium azide in 30% yield may be prepared by slowly dropping ethyl nitrite into a well-stirred mixture of barium hydroxide and hydrazine hydrate. Lithium azide is obtained by double decomposition of an alcoholic solution of lithium chloride with sodium azide. A. R. POWELL.

Preparation and properties of nitryl chloride. H. J. SCHUMACHER and G. SPRENGER (Z. anorg. Chem., 1929, 182, 139-144).—Pure nitryl chloride, NO<sub>2</sub>Cl, has been prepared by treatment of gascous nitrosyl chloride with ozone, cooling in liquid air, and removing the oxygen formed according to the equation  $NOCl+O_3 \longrightarrow NO_2Cl+O_2$ . The product is at the ordinary temperature a colourless gas which condenses at  $-15^{\circ}$  (1 atm.) to a colourless liquid of  $d^{\circ}$  1.37 and f. p. -145°. The gas is non-associated at 100°. Unimolecular decomposition takes place with measur-able velocity at 120°, the products being nitrogen peroxide and chlorine. The vapour-pressure curve has been determined from  $-15^{\circ}$  to  $-80^{\circ}$ ; the slight curvature of the log p-1/T curve is ascribed not to decomposition but to association, or, less probably, to the difference between the specific heats of the liquid and vapour. The calculated latent heat of vaporisation H. F. GILLBE. is 6140 g.-cal.

Slow oxidation of phosphorus. I. Inhibition of the glow of phosphorus by phosphorous oxide. II. Oxidation products of phosphorus and phosphorous oxide. (MISS) C. C. MILLER (J.C.S., 1929, 1823—1829, 1829—1846; cf. A., 1928, 972).—I. Phosphorus trioxide prepared by the method of Thorpe and Tutton (J.C.S., 1890, 57, 545) can be freed completely from phosphorus by repeated exposure to light and distillation from the red phosphorus thus produced. Phosphorus trioxide inhibits the glow of phosphorus; moisture and ozone destroy the inhibition and the trioxide. The inhibiting effect of oxygen is small compared with that of ethylene. The work of Schenck, Mihr, and Banthien (A., 1906, ii, 326) on the vapour pressure of phosphorus trioxide is criticised.

II. Oxidation of phosphorus in moist air gives a solution containing hypophosphoric, phosphorous, and phosphoric acids. In dry air the product was a mixture of phosphorus tetroxide, phosphorus pentoxide, and small quantities of amorphous phosphorus and of a substance which on treating with water gave the reactions of hypophosphoric acid. No trioxide was found. Phosphorus tetroxide is oxidised in oxygen at 350-410°, but not appreciably at lower temperatures. The products of oxidation of phosphorus dissolved in phosphorus trioxide in the presence of a small quantity of moisture are essentially the same as those obtained in the absence of the trioxide. Oxidation of phosphorus-free phosphorus trioxide by ozonised oxygen at 25° gave a mixture of phosphorus tetroxide and phosphorus pentoxide; 1 mol. of ozone oxidised 2 mols. of  $P_4O_6$ . When phosphorus was oxidised in the presence of phosphorus trioxide and a small amount of water vapour, 5 mols. of P4O6 were oxidised for every mol. of phosphorus  $(P_4)$  oxidised. The mechanism of the reaction between phosphorus and oxygen is discussed. C. W. GIBBY.

Sulphur tetrafluoride. J. FISCHER and W. JAENCKNER (Z. angew. Chem., 1929, 42, 810-811). -Sulphur tetrafluoride has been prepared by heating at 120° a mixture of cobalt trifluoride and sulphur, diluted with powdered fluorspar, in a vacuum for 2 days, and condensing the gaseous product in a vessel surrounded by liquid air. By fractional distillation fairly pure sulphur tetrafluoride is obtained; the compound is a colourless gas, which condenses at  $-40^{\circ}$  and 1 atm. pressure to a clear mobile liquid; the m. p. at 1.3 mm. pressure is  $-124^{\circ}$ . The vapourpressure curve of the liquid is expressed by the equation log  $p = -1132/\hat{T} + 7.746$ . The pure substance, as distinct from the crude material, does not attack dry glass and is stable towards paraffin oil, rubber, and sulphur. Mercury is immediately attacked, whilst the gas dissolves in water with decomposition, forming a clear solution.

H. F. GILLBE.

Interaction of carbon tetrabromide with sulphur and selenium. H. V. A. BRISCOE, J. B. PEEL, and J. R. ROWLANDS (J.C.S., 1929, 1766— 1768).—Carbon tetrabromide reacts with sulphur to give sulphur monobromide, carbon disulphide, bromine, and carbon, and with selenium to form selenium monobromide, selenium tetrabromide, and a mixture of carbon and selenium. These observations are not in agreement with those of Bartal (A., 1905, ii, 704; 1906, ii, 746). C. W. GIBBY.

Hydrated chromic hydroxide free from electrolytic impurities. P. A. THIESSEN and B. KANDE-LAKY (Z. anorg. Chem., 1929, 182, 425—428).—By slowly dropping a solution of chromic ethoxide in ethyl alcohol into water a greyish-green chromic hydroxide hydrosol free from electrolytes may be obtained, and by permitting the concentration to exceed a certain value (about 0.02% Cr.O.) the hydrogel is precipitated. After being freed from alcohol and carbon dioxide by heating, the sol has a concentration of about 0.015%, and possesses great stability. The colloidal particles have a weak positive charge, and the sensitivity of the sol towards electrolytes resembles that of metallic sols; the stability passes through a maximum on the gradual addition of sodium hydroxide solution. The hydrogel is greyish-green in colour and is easily peptised by hydrogen chloride or chromic chloride to a deep green sol.

#### H. F. GILLBE.

Reduction of permanganate by manganous salts. M. GELOSO and P. DUBOIS (Compt. rend., 1929, 189, 296-298) .- A study of the influence of time, temperature, concentration, and of the presence of calcium carbonate on this reaction has led to the conclusion that there is no formation of definite compounds, but a continuous variation in the degree of oxidation of the pseudo-dioxides formed. Calcium carbonate serves principally to neutralise the acid formed, whilst part of it is converted into insoluble manganese carbonate, and it also exerts a surface effect which is being further studied. J. GRANT.

Manganimolybdates. F. ZAMBONINI and V. CAGLIOTI (Gazzetta, 1929, 59, 400-460).-Evidence obtained from a re-examination of the products obtainable by the oxidation of mixtures of ammonium molybdate and manganic hydroxide points to the existence of compounds of the type

 $4M_{2}^{1}O,Mn_{2}O_{3},13MoO_{3},9H_{2}O$  containing both bi- and quadri-valent manganese. Friedheim and Samelson's work (A., 1900, ii, 547) has been repeated and a crystallographic examination of the products to which they assigned the formulæ

 $\begin{array}{c} 3(\mathrm{NH}_4)_2\mathrm{O},\mathrm{Mn}_2\mathrm{O}_3,9\mathrm{MoO}_3,7\mathrm{H}_2\mathrm{O},\\ 4(\mathrm{NH}_4)_2\mathrm{O},\mathrm{Mn}_2\mathrm{O}_3,11\mathrm{MoO}_3,8\mathrm{H}_2\mathrm{O},\text{ and}\\ 2(\mathrm{NH}_4)_2\mathrm{O},\mathrm{Mn}_2\mathrm{O}_3,7\mathrm{MoO}_3,5\mathrm{H}_2\mathrm{O} \text{ showed that these are} \end{array}$ identical crystallographically, optically, and in density. Identity in chemical constitution was also proved, and the formula  $4(NH_4)_2O,Mn_2O_3,13MoO_3,9H_2O$  or  $[Mn^{---}(Mo_2O_7)_6](NH_4)_8,Mn^{--}MoO_4,9H_2O$  is suggested. From this substance the compounds

4K2O,Mn2O3,13MoO3,9H2O,

 $4Rb_2O,Mn_2O_3,13MoO_3,9H_2O$  (both reddish-orange), 2(NH<sub>4</sub>)<sub>2</sub>O,2Na<sub>2</sub>O,Mn<sub>2</sub>O<sub>3</sub>,13MoO<sub>3</sub>,9H<sub>2</sub>O, red, monoclinic, and the corresponding silver and barium compounds have been obtained by the action of the halides of the metals. A crystallographic examination has been made of most of these salts; the alkali manganimolybdates are isomorphous. It is suggested that Pechard's salt obtained by the action of potassium permanganate on the precipitate formed by mixing solutions of ammonium molybdate and manganous sulphate may be a mixture of the compounds

 $3[(NH_4)_2, K_2]O, MnO, Mn_2O_3, 13MoO_3, 9H_2O$  and

4[(NH<sub>4</sub>)<sub>2</sub>,K<sub>2</sub>]O,Mn<sub>2</sub>O<sub>3</sub>,13MoO<sub>3</sub>,9H<sub>2</sub>O in the propor-tions 5:3. Ammonium nickelimolybdate prepared as purplish-black crystals by boiling ammonium molybdate with nickel sulphate and ammonium persulphate has the formula 4(NH<sub>4</sub>)<sub>2</sub>O,Ni<sub>2</sub>O<sub>3</sub>,13MoO<sub>3</sub>,9H<sub>2</sub>O and is isomorphous with the alkali manganimolybdates. Spectroscopic evidence is adduced for the existence of quadrivalent manganese in these compounds, the intensity of the band at  $497 \,\mu\mu$  increasing with the change from Mn<sup>\*\*</sup> through Mn<sup>\*\*\*</sup> to manganimolybdate F. G. TRYHORN. solutions.

Formation of a manganese carbide decomposable by water from manganese oxide and methane at relatively low temperatures. F. FISCHER and F. BANGERT.-See B., 1929, 717.

Preparation and properties of an oxide of bromine. B. LEWIS and H. J. SCHUMACHER (Z. anorg. Chem., 1929, 182, 182-186).-Bromine oxide,  $(Br_3O_8)_n$ , has been prepared by treatment of bromine with ozone at  $-5^{\circ}$  to  $10^{\circ}$  in a closed vessel; the oxide deposits gradually on the walls of the vessel, the reaction being complete within 5-10 min. at the higher temperature. If the materials be impure or the temperature too high, the oxide fails to appear and the ozone decomposes explosively. Unless an excess of ozone be present the oxide decomposes into bromine and oxygen, but in presence of an excess of ozone slow decomposition takes place, the ozone being gradually and completely converted into bromine oxide and finally into oxygen; at  $-80^{\circ}$  the oxide is stable for several days, even in absence of ozone. Two crystalline modifications of the new compound exist, the transition point being  $-35^{\circ}\pm3^{\circ}$ . Bromine oxide dissolves in water, forming an acid solution containing neither free bromine nor bromine ions but capable of liberating iodine on addition of potassium iodide solution; titration shows the acid produced to have the formula H<sub>4</sub>Br<sub>a</sub>O<sub>8</sub>. Evidence has been obtained of the existence of a second bromine oxide, which is gaseous at the ordinary temperature. H. F. GILLBE.

Preparation of anhydrous hydrogen iodide. R. T. DILLON and W. G. YOUNG (J. Amer. Chem. Soc., 1929, 51, 2389-2391).-Concentrated hydriodic acid is dehydrated by phosphorus pentoxide and the gaseous iodide bubbled through saturated calcium iodide solution in order to remove free iodine. The gas is then dried with phosphorus pentoxide and cooled to  $-30^{\circ}$ . Light must be excluded, and the apparatus should be initially filled with nitrogen.

S. K. TWEEDY. Action of carbonic acid under high pressures on iron. E. MÜLLER and H. HENECKA.-See B., 1929, 751.

Double sulphates and their components. VI. Rhodium double sulphates and their hydrates. F. KRAUSS and H. UMBACH (Z. anorg. Chem., 1929, **182**, 411–424).—Cæsium rhodium alum,

CsRh(SO<sub>4</sub>)<sub>2</sub>,12H<sub>2</sub>O, has been prepared by slow evaporation of a solution of the mixed sulphates at the ordinary temperature; it forms orange crystals having  $d_4^{20}$  2.23<sub>8</sub>, and lattice constant a = 12.30 Å. By desiccation at temperatures below 100° the yellow hexahydrate and the brown, sparingly soluble dihydrate, d 2.72, and 3.07, respectively, are formed. If the dihydrate be heated above 100° decomposition ensues, but by heating with concentrated sulphuric acid the anhydrous salt is obtained as a rose-coloured powder which is but slightly soluble in water and has  $d_4^{20}$  3.29. By evaporation on the water-bath of a solution of the alum a dark yellow powder of composition  $CsRh(SO_4)_{2,4}H_2O$  is obtained. In cold dilute solution this does not liberate free sulphate ions, and it loses water continuously when heated. The complex rhodiosulphate ion breaks down gradually when the aqueous solution is heated. The dihydrated complex salt, obtained by heating the tetrahydrate at 165°, has  $d_4^{29}$   $3\cdot 4_1$ . The free acid,  $Rh_2(SO_4)_3, H_2SO_4, 16H_2O$ , is obtained as a yellow, crystalline powder by the slow evaporation of a concentrated solution of cæsium rhodium alum to which 0.33 vol. of concentrated sulphuric acid has been added. H. F. GILLBE.

Osmium tetroxide. E. FRITZMANN (Z. anorg. Chem., 1929, 182, 34-36).—Polemical.

H. F. GILLBE.

Complex compounds of platinous chloride with aminoacetal. L. TSCHUGAEV and B. ORELKIN (Z. anorg. Chem., 1929, 182, 28–34).—See A., 1913, i, 23. H. F. GILLBE.

Oxidation of complex compounds of platinum. II. Oxidation by persulphate and free oxygen. L. TSCHUGAEV and J. TSCHERNIAEV (Z. anorg. Chem., 1929, 182, 159-172; cf. A., 1926, 373).-By oxidation of Peyrone's salt with ammonium persulphate a black crystalline product of relatively high stability and composition and having the empirical formula  $[PtCl_2OH(NH_3)_2]$  is obtained; the same substance is produced by the cautious reduction of the compound  $[PtCl_2(OH)_2(NH_3)_2]$  with zinc dust, or by heating at 100° a mixture of the compounds [PtCl<sub>2</sub>·(NH<sub>3</sub>)<sub>2</sub>] and [PtCl<sub>2</sub>(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] with slightly acidified water. Oxidation of Peyrone's salt with ammonium persulphate in presence of potassium chloroplatinite results in the formation of a rather unstable complex containing one [PtCl4]" ion and two ions containing tervalent platinum. A very stable complex containing tervalent platinum is produced by the oxidation of ethylenediamine chloroplatinite with ammonium persulphate in presence of water and a little hydrochloric acid; this material is not decomposed by hot dilute acids nor by salt solutions containing free chlorine ions, and may readily be recrystallised from water: it has the formula [PtCl<sub>3</sub> en], and forms large red crystals. The co-ordination isomeride,

[Pt en<sub>2</sub>]PtCl<sub>6</sub>, obtained by refluxing [Pt en]PtCl<sub>4</sub> with ethylenediamine and treatment of the product with potassium chloroplatinite, is red but easily differentiated from the red tervalent platinum compound. Oxidation of the green Magnus salt with ammonium persulphate yields a golden-yellow crystalline precipitate, (Pt·4NH<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)(PtCl<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub> which is decomposed rapidly even by washing with water at the ordinary temperature; the dry substance oxidises alcohol to aldehyde, and forms with dry pyridine a bright red, amorphous substance which is fairly stable towards cold water. If nitric acid in presence of hydrogen peroxide be employed for the oxidation of Magnus' salt there results a similar unstable compound, which, however, possesses no oxidising properties; it is violet-red and of composition

 $(Pt,4NH_3,NO_3)(PtCl_4)$ , and forms a red pyridine additive compound of probable composition  $(Pt,4NH_3,NO_3,C_5H_5N)(PtCl_4)$ . The action of liquid ammonia on platinum trichloride is described.

H. F. GILLBE.

Recovery of platinum. G. J. HOUGH (Ind. Eng. Chem. [Anal.], 1929, 1, 162).-Alcoholic filtrates obtained in the determination of potassium by platinic chloride are treated with about 1 g. of ammonium chloride crystals to each 300 c.c. of filtrate and filtered after mixing and keeping. The filtrate, distilled to 0.25 of its volume, gives a distillate of 83-85% alcohol. The ammonium chloroplatinate and chloroplatinate residues are dissolved in hot water containing a few c.c. of hydrochloric acid (1:2), heated nearly to the b. p., and treated with magnesium powder in slight excess. After removal of the excess of magnesium with concentrated hydrochloric acid, the solution is boiled and the platinum-black collected, washed, and dissolved in aqua regia. Having been evaporated and redissolved three times with hydrochloric acid, the platinic chloride is finally taken up with hot water, acidified with a few drops of hydrochloric acid, and made up to standard volume.

H. J. DOWDEN.

Recommended specifications for analytical reagent chemicals. W. D. COLLINS, H. V. FARR, J. ROSIN, G. C. SPENCER, and E. WICHERS (Ind. Eng. Chem. [Anal.], 1929, 1, 171—174).—Specifications and methods of testing recommended by a Committee of the American Chemical Society are published for the following reagents : bromine, copper ammonium chloride, powdered and granulated eupric oxide, ether, potassium chromate, sodium potassium tartrate, silver sulphate, and two grades of zine.

A. R. POWELL.

Limits of applicability of indicators in simple  $p_{\rm H}$  determinations. J. EISENBRAND (Pharm. Ztg., 1929, 74, 989–992, 1009–1010).—The sources of error involved in these investigations are discussed in detail. The salt error occurring in buffered solutions is considered with reference to pieric acid, bromothymol-blue, methyl-orange, and dimethylyellow, and the actual errors introduced, which vary with different indicators and also with the concentration of salt as well as with the nature of the salt, are calculated for various concentrations of sodium and potassium chloride from N to 5N. For bromothymol-blue the error is small with high concentrations of salt and large with low concentrations (0.5-1N). potassium chloride), whereas for methyl-orange the converse is true. With unbuffered solutions the chief source of error is the degree of dissociation of the indicator, for which the following values are calculated:  $\Delta p_{II} = 0.98$ , 1.43, and 1.80 for  $K = 10^{-7}$ , 10<sup>-6</sup>. and 10-5, respectively. The limited applicability of indicators with very small dissociation constants and of neutralised indicator solutions is also discussed and it is concluded that no satisfactory method exists for measuring  $p_{\mu}$  by means of coloured indicators in unbuffered solutions. The effect of the indicator can be ignored only in those cases where the concentration is exceptionally low (10-14 mol. per litre). This may be accomplished by using fluorescent indicators such as fluorescein, umbelliferone, quinine, and naphthol in conjunction with the quartz lamp.

S. COFFEY.

Dilution method for the colorimetric determination of  $p_{\rm H}$  in coloured solutions. F. C. THOMPSON and W. R. ATKIN (J. Soc. Leather Trades Chem., 1929, **13**, 297—299).—Portions of the solutions are diluted to 2, 4, 8, 16, and 32 times their original volume, respectively, the  $p_{\rm H}$  values determined colorimetrically plotted against the logarithm of the concentration, and the  $p_{\rm H}$  value of the original solution is determined by extrapolation. D. WOODROFFE.

Acid reaction and carbon dioxide content of conductivity water. R. J. BEST (Austral. J. Exp. Biol., 1929, 6, 107-110).—The carbon dioxide content of conductivity water of specific conductivity  $0.3 \times 10^{-6}$  to  $0.75 \times 10^{-6}$  mho is calculated and its  $p_{\rm H}$ (calc.) is shown to agree fairly closely with that obtained by the indicator method.

P. W. CLUTTERBUCK. Determination of halogen [in perchlorates] by Gasparini's method. II. K. HELLER [with F. HORA and K. WILLINGSHOFER] (Z. anal. Chem., 1929, 78, 127—131; cf. this vol., 528).—Perchlorates can be quantitatively reduced to chlorides by electrolysis in Gasparini's apparatus, a solution of titanic sulphate in concentrated sulphuric acid, together with silver and potassium nitrates, being used as electrolyte. Reduction is complete after 5—6 hrs., when a further quantity of silver nitrate is added, the solution rendered ammoniacal, filtered, the filtrate acidified with nitric acid, and the silver chloride weighed. Alternatively, the excess of silver in solution may be determined volumetrically by Volhard's method.

H. F. HARWOOD.

Argentometric studies. I. Potentiometric titration of iodides. O. Tomfček (Goll. Czech. Chem. Comm., 1929, 1, 443—448).—The irregularities observed on the titration curve of potassium iodide near the equivalence point are shown to be due to the presence of bromide and not to adsorption of silver ions on silver iodide during the coagulation which takes place just before the equivalent point is reached. Even the purest samples of commercial potassium iodide contain about 0.5% of potassium bromide, so that for standardisation purposes iodide prepared by the action of a sulphite on pure resublimed iodine should be used. A. R. POWELL.

Volumetric determination of alkali fluorides and silica. W. SIEGEL (Z. angew. Chem., 1929, 42, 856-857).—Silica, in the form of the freshly precipitated gel or as a carefully neutralised solution of alkali silicate, is added to the solution of alkali fluoride and the titration effected with 0.5N-hydrochloric acid, using methyl-red as indicator. The reaction is 6MF+ $SiO_2+4HCl=M_2SiF_6+4MCl+2H_2O$ . The presence of non-alkali metals is inadmissible. The silica content of silicate solutions may be determined by this method.

In alkaline solutions of alkali fluorides carbonate and silicate may be present, but not fluosilicate. To determine carbonate the solution is titrated with acid, after addition of calcium chloride, using phenolphthalein as indicator. The silica content is determined as described above. If solutions have an acid reaction hydrogen fluoride and fluosilicate may be present, but not silicate. The hydrogen fluoride content is determined after addition of calcium chloride by titration, using methyl-red, and the fluosilicate determined by continuing the titration, using phenolphthalein, the reaction being  $M_2SiF_6+4MOH=6MF+SiO_2+2H_2O$ . J. S. CARTER.

Determination of sulphuric acid in a mixture of sulphuric acid, acetic acid, and acetic anhydride. T. Somiya.—See B., 1929, 670.

Improvements in Denigès' colorimetric method for [the determination of] phosphorus and arsenic. E. TRUOG and A. H. MEYER (Ind. tain conditions stannous chloride reduces ammonium molybdate to give a blue coloration in the absence of phosphate, whilst if the acidity is too high, the blue colour in the presence of phosphates may be repressed. To obviate these difficulties in conducting Deniges' test (cf. B., 1920, 781A), the reagents recommended are (A) 10N-sulphuric acid containing 2.5 g. of animonium molybdate per 100 c.c. and (B) a solution of 25 g. of pure stannous chloride in 1000 c.c. of 10 vol.-% hydrochloric acid. The standard phosphate solution contains 0.25 p.p.m. of phosphorus (0.2195 g. of recrystallised potassium dihydrogen phosphate in 1000 c.c. of water is equivalent to 50 p.p.m. of phosphorus), 4 c.c. of solution (A), and 6 drops of (B) in 100 c.c. In conducting the test, the liquid after dilution should contain 4 c.c. of (A) and 6 drops of(B) per 100 c.c. At this concentration the colour develops immediately but fades in 10-12 min. The test is not vitiated by the presence of less than 700 p.p.m. of silica, nor by considerable amounts of aluminium, manganese, calcium, or magnesium salts. Ferric iron markedly influences the colour and should first be reduced. Arsenates may be determined in exactly the same way as phosphates, and if both are present the two may first be determined together and then the phosphate alone, after removal of arsenic by precipitation with hydrogen sulphide.

H. J. DOWDEN. Iodometric determination of phosphorous acid. A. SCHWICKER (Z. anal. Chem., 1929, 78, 103-109; cf. A., 1919, ii, 77).—An excess of 0-1Niodine is added to the phosphite solution, followed by 5-10 c.c. of N-ammonium borate. After 15 min. the solution is acidified with 2N-hydrochloric acid and the excess of iodine titrated with 0.1N-thiosulphate. In place of ammonium borate, N-ammonia, magnesia mixture, or N-potassium hydroxide may be used, but as all these require to be added drop by drop with avoidance of excess, they are less convenient. Phosphites may also be determined by addition of 0.1N-iodide-iodate solution to the solution of the phosphite, followed by the addition of hydrochloric acid and titration with thiosulphate, but in this case the reaction mixture must be kept for 2.5 hrs. before acidification. The above time may be reduced to 20 min. by working at 50°, but special precautions are then necessary to prevent loss of iodine. Both the above methods permit the determination of phosphites in presence of hypophosphites. H. F. HARWOOD.

Colorimetric determination of phosphoric acid by Denigès' method. S. N. Rozanov (Trans. Sci. Inst. Fertilisers, Moscow, 1928, No. 55, 139–158).— The optimal limits are 0.3-0.5 mg. P<sub>2</sub>O<sub>5</sub> per litre; the quantity of aqua regia used is unimportant. The maximum deviation, in comparison with the double precipitation method, was 1%.

CHEMICAL ABSTRACTS. Volumetric determination of phosphoric acid. W. SMITH (Quart. J. Pharm., 1929, 2, 238—241).— Solutions of phosphoric acid can be titrated directly by the employment of two indicators. Dimethylaminoazobenzene is used for the first titration, cresolphthalein for the second, and cresolphthalein with neutral calcium chloride solution at 70° for the third. C. C. N. VASS.

Determination of neon in natural gases. N. P. PÉNTCHEV (Compt. rend., 1929, 189, 322—324).— The density of the helium-neon mixture obtained after removal of argon, krypton, and xenon by coconut charcoal cooled in liquid air was determined (cf. A., 1928, 987), the procedure being controlled by spectral analysis. The results obtained with natural gas of known helium and argon content from a Bulgarian spring confirm the astrophysical theory of Moureu and Lepape. J. GRANT.

Separation of calcium and magnesium by the oxalate method. Z. HERRMANN (Z. anorg. Chem., 1929, 182, 395—410).—The supersaturation of solutions of magnesium oxalate and the mechanism of its precipitation have been studied and a theoretical explanation is derived. The induction period observed when ammonium oxalate solution is added to a solution containing magnesium ions is reduced by increase of concentration or of temperature. Smoluchovski's theory of the slow coagulation of colloidal solutions is applicable also to the precipitation of crystalline compounds. H. F. GILLBE.

Effect of lead on the permanganate titration of antimony in white metal analyses. A. VASILIEV and H. STUTZER (Z. anal. Chem., 1929, 78, 97-102).-Direct titration with permanganate of the solution obtained by treating a lead-antimony alloy with sulphuric acid, with subsequent additions of hydrochloric acid and water, shows only 98-99% of the total antimony present. Satisfactory results are obtained if the precipitated lead sulphate be subsequently dissolved in dilute hydrochloric acid and this solution also titrated; a deduction of 1% must be made from the total antimony figures. In the case of white metals containing tin and copper in addition to antimony and lead this correction is unnecessary, the figures then obtained being in good agreement with those yielded by the bromate method. H. F. HARWOOD.

Electro-analytical determination of thallium as thallic oxide. A. JÍLEK and J. LUKAS (Coll. Czech. Chem. Comm., 1929, 1, 417–428).—Electrolysis of thallous nitrate solutions containing hydrofluoric acid results in the deposition of a small amount of thallium on the cathode and the remainder as the *compound*,  $Tl_2O_3$ , HF, on the anode; addition of hydrogen peroxide converts all the thallium into the anodic compound, which, however, is not pure, containing only 84.44% instead of 85.73% Tl. For the determination of the metal the solution containing less than 0.25 g. of thallium as nitrate is treated with 1-2 g. of 40% hydrofluoric acid in a Classen platinum dish which serves as anode and electrolysed at 0.2 amp., using a rotating platinum disc cathode. After 1 hr. 1 c.c. of 30% hydrogen peroxide is added to dissolve the metal deposited on the cathode and electrolysis is continued for a further 1 hr.; this operation is repeated three times or until the electrolyte gives no test for thallium with sodium sulphide. The deposit is washed with water without interrupting the current, dried at 100°, and weighed; the weight multiplied by the empirical factor 0.8444 gives the weight of thallium present. A. R. POWELL.

Determination of copper and nitrite in solutions of cuprammonium hydroxide. E. BUTTERWORTH and H. A. ELKIN.—See B., 1929, 717.

Determination of copper with 5:7-dibromo-8-hydroxyquinoline. L. W. HAASE (Z. anal. Chem., 1929, 78, 113—124).—The above reagent is well adapted for the determination of small amounts of copper (0.5—20 mg. per litre) for which the colorimetric methods are unsuitable. The reagent is employed as a 0.5% solution in 5N-hydrochloric acid, and the solution under examination must not contain more than 0.7% of free hydrochloric acid or 5% of free acetic acid. The copper precipitate is dried for 1 hr. at 105°, and then for 2—3 hrs. at 140° before being weighed. The presence of large amounts of alkali salts has no influence on the accuracy of the results, but humus and similar substances must be destroyed by treatment with hydrochloric acid and hydrogen peroxide before precipitation of the copper. An improved method for the preparation of the reagent is recorded. H. F. HARWOOD.

Quantitative oxidation with ceric sulphate. A. J. BERRY (Analyst, 1929, 54, 461-464).—The ceric sulphate solution (prepared from 25 g. of the nitrate treated with concentrated sulphuric acid and diluted to 500 c.c.) is standardised with a suitable reducing agent such as ferrous ammonium sulphate. Ferrocyanides are readily and quantitatively oxidised at the ordinary temperature, the end-point being found by means of diphenylamine sulphate. With tartrates 1 mol. of tartaric acid requires 3.51 atoms of available oxygen. In the case of thallous salts a solution of iodine in chloroform is converted quantitatively into iodine monochloride to furnish means for determining the end-point. To a few c.c. of a dilute solution of iodine in chloroform in a stoppered bottle are added about 50 c.c. of concentrated hydrochloric acid, and the solution of ceric sulphate is added until the violet colour disappears. A measured volume of the thallous salt solution is then added and the standard ceric sulphate run in until the chloroform is again colourless. The ceric sulphate is here standardised by oxidising a solution of potassium iodide of known concentration to iodine mono-D. G. HEWER. chloride.

Determination of manganese by Volhard's method. F. J. WATSON.—See B., 1929, 753.

Potentiometric determination of iron and molybdenum [in presence of each other]. H. BRINTZINGER and W. SCHIEFERDECKER (Z. anal. Chem., 1929, 78, 110—112).—The solution of the chlorides of the two metals containing 30 g. of calcium chloride and 25 c.c. of concentrated hydrochloric acid in 100 c.c. is boiled for 5 min. in a stream of carbon dioxide, cooled to 90°, and titrated with 0.1Nchromous chloride. A sharp change in potential occurs when all the ferric iron has been reduced to ferrous and all sexavalent to quinquevalent molybdenum, and on continuing the titration a second break occurs when the quinquevalent molybdenum has been reduced to the tervalent state; from these data the amounts of each metal present can be calculated. H. F. HARWOOD.

Detection of cobalt and nickel in presence of phosphates and identification of magnesium in presence of cobalt and nickel. R. Rossi (Annali Chim. Appl., 1929, 19, 255—260).—In the ordinary method of inorganic qualitative analysis, it is not the ammonium chloride but rather the ammonia, in excess and in the cold, which keeps the cobalt and nickel in solution in presence of phosphoric acid. Hence, after the subsequent boiling of the solution, these metals, particularly the cobalt, may be largely retained in the third group precipitate. A procedure is described which overcomes the difficulty thus presented and also prevents any possibility of error in the identification of magnesium. T. H. POPE.

Volumetric determination of tin. H. WOLF and R. HEILINGÖTTER (Chem.-Ztg., 1929, 53, 683).—The most satisfactory reducing agent for the iodometric determination of tin is iron nails, reduction being effected in 1 : 1 hydrochloric acid at  $90-95^{\circ}$  on a boiling water-bath. Three nails 8—10 cm. long will reduce 0.1 g. of tin from the stannic to the stannous condition in 8 min. Directions are given for the determination of tin in antimony, copper, and lead alloys by this method. A. R. POWELL.

Rapid analysis of bearing-metal alloys. J. F. ILTSCHENKO and R. M. STACHORSKI.—See B., 1929, 753.

Determination of tin and antimony in bearingmetal alloys. A. P. AFANASIEV.—See B., 1929, 753.

Preparation of antimony-free arsenious oxide and the determination of minute amounts of antimony in arsenious oxide. C. W. FOULK and P. G. HORTON (J. Amer. Chem. Soc., 1929, 51, 2416— 2419).—The impure arsenious oxide is converted into the chloride, which is then repeatedly extracted with concentrated hydrochloric acid, in which antimonous chloride is very soluble as compared with the arsenious compound. The remaining arsenious chloride is hydrolysed to the oxide, which is then purified by the usual methods. The procedure is applicable to the detection and the approximate determination of minute amounts of antimony in arsenious oxide.

S. K. TWEEDY.

Determination of bismuth [in ores]. G. J. HOUGH.—See B., 1929, 753.

Analytical chemistry of tantalum, niobium, and their mineral associates. XV. Separation of tantalum and niobium from titanium and zirconium. W. R. SCHOELLER (Analyst, 1929, 54, 453-460).—Tantalum and niobium may be qualitatively separated from titanium and zirconium by the pyrosulphate and tannin method, whereby the mixed oxides (0.1-0.2 g.) are fused with 2-3 g. of hydrogen sulphate, the mass is solidified in a thin layer round the sides of the silica crucible, and the hot reagent (1 g. of tannin dissolved in 90 c.c. of water and 10 c.c. of 1:1 sulphuric acid) added. After gentle heating the contents of the crucible are transferred to a beaker, boiled, left until clear, and the precipitate A is filtered off. The filtrate is boiled down with 5 c.c. of concentrated sulphuric acid, and treated with concentrated nitric acid, whereby the tannin is readily oxidised. After decolorisation and cooling, 50 c.c. of water are added, and titanium and zirconium identified. The precipitate A proves the presence of earth acids, and they are identified jointly by the tartaric hydrolysis method (this vol., 902) and separately by the tannin method (B., 1925, 974). The method has been worked out in a preliminary way as a quantitative test with satisfactory results. The salicylate process for the separation of titanium from tantalum, niobium, and zirconium is adversely criticised. D. G. HEWER.

Electrode holder for arc spectrum analysis. L. L. QUILL and P. W. SELWOOD (Ind. Eng. Chem. [Anal.], 1929, 1, 180).—The holder consists of two horizontal arms mounted on a rotatable fibre cylinder which can be adjusted vertically by means of a screw running through the main support and operated by a large vulcanised handle. The lower arm has also an independent vertical movement through a rack and pinion with two vulcanised handles to allow of frequent adjustment of the positive electrodes which are fixed in this arm. One pair of electrodes is made of iron and is used as a reference standard, whilst the other pair, of carbon, is used for the analysis. Either pair may be brought into the axis of collimation of the spectrograph by rotating the fibre cylinder.

A. R. POWELL.

Manipulation in intensive drying. H. B. BAKER (J.C.S., 1929, 1661-1664).-The various precautions necessary to ensure success in experiments involving intensive drying are briefly summarised. The apparatus must be constructed of good Jena glass completely free from bubbles and thoroughly cleaned before being worked in the blowpipe flame. Preliminary drying of the apparatus is best effected by heating with a waving Bunsen flame while a current of air dried by phosphoric oxide is passed through both during the heating and subsequent cooling, and a bulb of pure phosphoric oxide must be sealed on to the apparatus. The only tap lubricant permissible is metaphosphoric acid protected from atmospheric moisture by purified vaseline, whilst for experiments involving hydrogen chloride and ammonia no lubricant may be employed, the taps being hand-polished with rouge and water. In all cases it is necessary to introduce phosphoric oxide into the hole in the barrel of the tap. The purity of the materials used must greatly exceed that required for at. wt. determinations. J. W. BAKER.

Intensive drying of gaseous media. W. A. BONE (J.C.S., 1929, 1664—1666).—Additional details (cf. preceding abstract) concerning the technique of intensive drying are summarised (cf. J.C.S., 1906. 89, 652; A., 1926, 480). The possible limit of phosphorie oxide desiccation is reached in about 250 days, the explosion vessels (of Jena red-line resistance glass) being externally heated to  $150-200^{\circ}$  once a fortnight. Scaling of the explosion vessels is effected with a blow-pipe flame of dried carbon monoxide and air to avoid any absorption of steam by the glass. With such precautions mixtures of dried carbon monoxide and oxygen can be subjected to repeated condenser discharges of 0.5 microfarad at 1000 volts without the slightest combustion occurring. J. W. BAKER.

Large metal Soxhlet extractor. L. R. BRYANT (Ind. Eng. Chem. [Anal.], 1929, 1, 139—140).—A sectional electrically-heated extractor constructed of copper has been used for the preparation of large quantities of fat-free material. The boiler, the extraction chamber, and the condenser system are separable, but are bolted together when in use. The material to be extracted is held in a linen bag supported by a copper frame, which rests on a perforated plate. Drainage taps and a level gauge are provided, and in order to obviate premature siphoning it is important that the internal diameters of the solvent vapour tube and the siphon tube should be in the ratio of 2.22 to 4.77 mm. H. J. DOWDEN.

Graduated wash bottles. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1929, 1, 162).—To compensate for the loss in the washing of slightly soluble precipitates, graduated wash bottles are advocated. For hot washing media, the vessels may consist of large test-tubes, suitably calibrated and etched and provided with detachable wooden bases to act as stands. H. J. DOWDEN.

Modification of the Kjeldahl trap. G. H. W. LUCAS (Ind. Eng. Chem. [Anal.], 1929, 1, 140).—In the distillation of frothy liquids, the exit from the distillation vessel consists of a wide tube sealed through the side of a 500-c.c. Kjeldahl flask, the internal end being bent downwards. In the bottom of the flask is a hole, which is connected to the exit tube by a narrow inclined tube, so that froth entering the flask drains back slowly into the distillation vessel. The neck of the flask is constricted below the side limb in order to support a small glass funnel filled with glass wool, the replacement of which is effected through the mouth of the flask.

H. J. DOWDEN. New desiccator shapes and insertions. H. LIESEGANG (Chem. Fabr., 1929, 256—257).—A squareshaped desiccator with an internal arrangement similar to that in an egg-box is described. This insertion may be made of cardboard, metal, or porcelain and is removable. The new desiccators will hold more crucibles safely than the usual form; the internal compartments may also be used in the ordinary circular desiccator. A. R. POWELL.

Rapid-indicating continuous-reading vacuum and pressure gauges. H. G. ANDERSON (Ind. Eng. Chem., 1929, 21, 795—797).—The gauges described operate by recording the resistance of a piece of platinum ribbon supplied with a constant flow of heat. The temperature and consequently the resistance varies with the conductivity and therefore the pressure of the surrounding gases. They are capable of use at all pressures below atmospheric, but the sensitiveness increases with diminishing pressure. In

one type on which greater heat is used to give sensitiveness at higher pressures compensator bulbs for atmospheric fluctuations are necessary. For the other it is sufficient to set the zero under the conditions of measurement. The recording pointer comes to rest within 6 sec. C. IRWIN.

Differential pressure gauge. A. R. OLSON and L. L. HIRST (J. Amer. Chem. Soc., 1929, 51, 2378— 2379).—An electrically controlled gauge which enables very slow reactions at any pressure to be studied is described. S. K. TWEEDY.

Platinum resistance thermometer. T. Hsü (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 51-53). —The readings obtained at several temperatures with platinum resistance thermometers of two different types and filled with various gases have been compared. R. CUTHILL.

Apparatus for measuring the density of liquids by means of a hydrometer. P. FUCHS.—See B., 1929, 663.

Inexpensive pyrex conductivity cell. W. B. CAMPBELL (J. Amer. Chem. Soc., 1929, 51, 2419— 2420).—The electrodes are narrow strips of thin platinum foil and are fused firmly on to the surface of the glass inside the cell. S. K. TWEEDY.

Conductivity of electrolytes. II. Improvements in the oscillator and detector. G. JONES and G. M. BOLLINGER (J. Amer. Chem. Soc., 1929, 51, 2407-2416; cf. A., 1928, 595).-Although when measuring conductivity it is desirable to use a low voltage across the bridge, and a modification of the oscillator previously described is given to enable suitable low and controllable voltages to be obtained, the sensitivity of the bridge is diminished thereby, and this is best surmounted by improving the amplifier. Transformer design for oscillating valve amplifiers is discussed. An improved amplifier is recommended, but when used it is necessary to place a "wave filter" across the telephones in order to diminish extraneous noises. The error produced by the mutual inductance between the oscillator and the detector and the oscillator and the bridge is also discussed.

S. K. TWEEDY.

Three electrode lamps in electrochemical measurement. A. H. W. ATEN, (MISS) L. BOER-LAGE, and D. CANNEGIETER (Chem. Weekblad, 1929, 26, 426—430).—Various circuits, in which valves are employed for magnifying alternating and direct currents, for rectifying, and as direct-current generators, are described. S. I. LEVY.

High-temperature technique and new fluorides. O. RUFF (Z. angew. Chem., 1929, 42, 807–810).— Modifications of the earlier apparatus (A., 1914, ii, 336) employed for the study of high-temperature reactions are described. Certain earlier work has been repeated, including determinations of the vapour-pressure curves of iron, cobalt, and nickel, and of the phase diagrams of the systems  $ZrO_2$ -CaO and  $ZrO_2$ -ThO<sub>2</sub> at temperatures above 2000°. Recent work on fluorides is summarised (cf. A., 1928, 854; this vol., 40, 160, 527). H. F. GILLBE.

Fusion calorimeter. H. SACHSE (Z. physikal. Chem., 1929, 143, 94-96).—A modification of the Bunsen ice calorimeter, in which the working substance is diphenyl ether, m. p.  $26.55^{\circ}$ , is described. When the volume change is determined by weighing mercury, 0.02 g.-cal. can be measured. The instrument is particularly suitable for the measurement of slow thermal effects. F. L. USHER.

Flow meter for gases. A. V. SIVOLOBOV (J. Chem. Ind. Moscow, 1928, 5, 1429—1431).—Riesenfeld's apparatus is improved.

#### CHEMICAL ABSTRACTS.

Bottle for accurate weighing of volatile liquid mixtures. Z. BLASZKOWSKA (Ind. Eng. Chem. [Anal.], 1929, 1, 170-171).-The bottle consists of a lower container of about 100 c.c. capacity joined to a smaller upper container of 50 c.c. capacity by means of a horizontal S-shaped neck and having a narrow, long side-tube sealed into its upper part. Both side-tube and upper vessel are provided with glass stoppers. In using the apparatus one liquid is introduced into the upper container, the whole is weighed, and the apparatus tilted to transfer the liquid to the lower container, a second liquid is then placed in the upper portion and, after weighing, transferred to the lower for mixing; this operation is repeated as often as necessary and finally the mixture is transferred to the reaction vessel through the side-tube. A. R. POWELL.

Volumenometer. A. W. FRANCIS and E. P. OXNARD (Ind. Eng. Chem. [Anal.], 1929, 1, 169–170).—For the determination of the volume or density of a powder or irregular solid which is soluble or porous a weighed quantity is placed into a thick-

out the bridge is diminizhed thereby, and

walled, flat-bottomed, pyrex glass bulb, the neck of which is provided with a ground-glass collar and steel clamp which holds the collar in position above a leather or rubber washer on the top of the bulb. The cover is connected through capillary tubing with rubber joints to a pipette bulb of known volume slightly less than that of the bulb. The lower tube of the pipette is connected to a manometer about 2 m. long which is provided with two metre rules, the lower one being inverted, so that the zero points of the rules are opposite the graduation marks above and below the bulb of the pipette. A levelling bulb of 150-200 c.c. is connected by pressure tubing to the pipette below the lower graduation and readings are taken of the manometer when the mercury in the closed arm is at the lower and then at the higher graduation; the readings are repeated with the empty bulb. From the results obtained the volumes of air in the bulb with and without the sample can be calculated; the difference is the volume of the sample, which should be correct to 0.2 c.c. A. R. POWELL.

Modified Pauly receiver. J. B. BROWN (Ind. Eng. Chem. [Anal.], 1929, 1, 160).—In the base of a 250- or 500-c.c. pyrex suction flask are blown six depressions about 20 mm. in diameter and to each of these is scaled a piece of pyrex glass tubing 12 cm. long, 12 mm. in diameter, and with walls 2 mm. thick, the tubes sloping outwards on a line parallel to the side walls of the flasks. The adapter is made of ordinary glass, its lower end being at least 8 mm. outside diameter to prevent bubble formation and spattering. A. R. POWELL.

## Geochemistry.

Formation of ozone in the highest layers of the atmosphere. W. ANDERSON (Physikal. Z., 1929, 30, 485-487).-Ozone in the upper layers of the atmosphere is not primarily formed by ultra-violet solar radiation nor does it arise from storms. Dobson's view that the connexion found between the amount of ozone and magnetic disturbance might suggest some action associated with the aurora borealis is criticised on the ground that the maximum ozone concentration occurs at heights between 30 and 50 km. from the earth, whilst the aurora occurs at 80-100 km. This view involves ozone formation at great heights and a gradual sinking of the molecules. The formation of ozone is assumed to be due to the absorption of corpuscular radiation, and by making simple assumptions it is shown that ozone formation should be very small below 30 km., maximal between 40 and 50 km., and again very small beyond 70 km. It is unlikely that the penetrating height radiation contributes materially to ozone formation.

R. A. MORTON. Ground waters in Balakhani. A. KREMS (Azerbeid. Neft. Choz., 1928, No. 4, 34–37).—The chloride, carbonate, sulphate, lime, and magnesia contents of the water at various depths are recorded. CHEMICAL ABSTRACTS. Bodenbenderite, a new mineral of the Argentine. E. RIMANN (Bol. Acad. Nac. Ciencias, 1929, **31**, 5–17).—Bodenbenderite has d 3·3—3·5, H 6·0— 6·5, and fuses at 1000—1100° to a cloudy glass having d 2·8—3·0. It is of a clear red colour, with a glassy lustre, does not exhibit double refraction, and has  $n>1\cdot77$ . Finely-divided ferric oxide and minute bubbles of carbon dioxide are distributed throughout the crystals. After adjustment of the analysis for obvious impurities the chemical composition approximates to the formula  $4MO,M'_2O_3,3M''O_2$ , where M= Mn, Fe<sup>\*\*</sup>, Ca, and Mg, M'=Al, Fe<sup>\*\*\*</sup>, and Y, and M''=Si, Ti, and U. The chemical behaviour of the mineral indicates the presence of two components, viz., 1 mol. of similar composition to plazolite except that no water is present, and containing all the yttrium, magnesium, titanium, and uranium, and 3 mols., insoluble in hydrochloric acid, of vesuviana.

H. F. GILLBE. Occurrence of beryllium. M. HOSENFELD.— See B., 1929, 722.

Crystallisation of basalts. C. N. FENNER (Amer. J. Sci., 1929, [v], 18, 225-253).—The theory that the crystallisation of a basaltic magma on cooling tends to give through differentiation a residue approximating in composition to a granite or rhyolite is criticised. Numerous instances show that such a magma tends to become rich in iron through the separation of magnesia-rich pyroxenes, the iron finally appearing as magnetite. The intersertal intergrowths of quartz and felspar met with in many dolerites and adduced in support of the above theory are probably not due to differentiation by magmatic crystallisation but result from secondary reactions. The view is taken that several other processes co-operate with crystallisation in effecting differentiation, an important agency being gaseous transfer; the assumption usually made that basaltic magmas contain only insignificant amounts of gases and volatile substances is incorrect. H. F. HARWOOD.

Pleochroic haloes in biotite. D. E. KERR-LAWSON (Univ. Toronto Stud., Geol. Ser., 1928, No. 27, 15—27).—A biotite from Murray Bay indicated no anomalies in the constants of the uranium series. The persistence of a marked concentric distribution of the darkening effect in the haloes is due to a terminal reversal effect by which, in the region of the range of a given set of  $\alpha$ -particles, the development of darkening due to other sets of  $\alpha$ -particles is inhibited. CHEMICAL ABSTRACTS.

Bromine content of Solikamsk carnallites. N. N. EFREMOV and A. A. VESELOVSKI (J. Chem. Ind. Moscow, 1928, 5, 1365—1369).—Solikamsk carnallite contains 0.17—0.30% Br, apparently chiefly as the compound KCl,MgBr<sub>2</sub>,6H<sub>2</sub>O. The estimated bromine content of the deposit is  $22 \times 10^6$  tons.

CHEMICAL ABSTRACTS.

Diatomaceous earth. E. V. ROZHKOVA (Trans. Inst. Econ. Min. Met., Moscow, 1929, No. 42, 51-61). —Two deposits near Mt. Kamyshlov (Urals) contain, respectively, SiO<sub>2</sub> 78.76, 75.59; TiO<sub>2</sub> 0.27, 0.93; Al<sub>2</sub>O<sub>3</sub> 9.81, 10.57; Fe<sub>2</sub>O<sub>3</sub> 3.15, 3.74; CaO 0.69, 1.05; MgO 1.72, 1.46; K<sub>2</sub>O 0.78, 0.56; Na<sub>2</sub>O 0.27, 0.54; SO<sub>3</sub> 0.11, 0.29; loss on ignition 4.70, 4.69%.

CHEMICAL ABSTRACTS.

Iron of Sumampa and other pseudometeorites. E. H. DUCLOUX (Rev. fac. eienç. quim. La Plata, 1928, 5, i, 77—81).—Analyses of a supposed meteorite, and two specimens proved not to be meteorites, are recorded. CHEMICAL ABSTRACTS.

# Organic Chemistry.

M. p. of normal paraffins. J. H. HILDEBRAND and A. WACHTER (J. Amer. Chem. Soc., 1929, 51, 2487—2488).—When the m. p. (lit.) of the normal paraffins from  $C_{19}$  to  $C_{38}$  are plotted against number of carbon atoms a smooth curve is obtained. No alternation exists and the data given by Levene, West, and van der Scheer (B., 1915, 634) for seven of the series appear to be high. Dicetyl has m. p. 70.2° (lit. 68—75°). H. BURTON.

Synthesis of isomeric  $\Delta^{\beta}$ -butenes. W. G. YOUNG, R. T. DILLON, and H. J. LUCAS (J. Amer. Chem. Soc., 1929, 51, 2528-2534).- a-Hydroxyα-methylbutyric acid, m. p. 72·5° (lit. 66-68°; all m. p. and b. p. are corr.) (improved method of preparation from methyl ethyl ketone given), on slow thermal decomposition affords a ethylacrylic acid (11%), b. p.  $76\cdot5-83^{\circ}/12$  mm., m. p.  $-16^{\circ}$ , angelic acid (I) (20%), b. p.  $85\cdot5-87\cdot5^{\circ}/12-13$  mm., m. p.  $45-45\cdot5^{\circ}$ , and tiglic acid (II) (20%), b. p.  $95-96^{\circ}/11\cdot5$ mm., m. p. 63.5-64°. Addition of hydrogen iodide to I in chloroform solution in the dark at 3° in presence of a small amount of molecular silver affords some tiglic acid hydriodide (III), m. p. 86.2-86.3° (formed also by the addition of hydrogen iodide to II), as well as angelic acid hydriodide (IV), m. p. 57.9-58.5°. Treatment of III and IV with sodium carbonate solution at 15—50° gives  $trans \Delta^{\beta}$ -butene, b. p. 0·3—0·4°/744 mm. [dibromide (meso), b. p. 72·7— 72·9°/50 mm.,  $d_{4}^{20}$  1·7829,  $n_{10}^{20}$  1·5116], and  $cis \Delta^{\beta}$ -butene, b. p. 2·95—3·05°/746 mm. [dibromide (racemic), b. p. 75.6-75.8°/50 mm., d<sup>20</sup> 1.7916, n<sup>20</sup><sub>D</sub> 1.5147], respectively (cf. Wislicenus and others, A., 1901, i, 2; Pfeiffer, A., 1904, ii, 525).

H. BURTON. cycloPropane derivatives. N. VAN KEERSBILCK (Bull. Soc. chim. Belg., 1929, 38, 205-211).—The 4 G

preparation of δ-methyl-Δay-pentadiene by way of α-chloro-δ-methyl-Δγ-pentene from cyclopropyldimethylcarbinol (Bruylants, A., 1909, i, 226; Kijner and Klawikordoff, A., 1911, i, 635; Bruylants and Dewael, A., 1928, 518) has led to the preparation of related hydrocarbons and derivatives for comparison. δ-Methyl-Δαγ-pentadiene, b. p. 76-76.5°/759 mm.,  $d_4^{20}$  0.71814,  $n_{\rm D}^{20}$  1.45317, is prepared by the action of alcoholic potassium hydroxide on the monobromide derived from cyclopropyldimethylcarbinol. 8-Methyl- $\Delta^{\beta}$ -penten- $\gamma$ -ol, b. p. 121·6—122°/757 mm.,  $d_{4}^{\infty}$  0.83432,  $n_{\rm D}^{20}$  1.42946, is obtained by the interaction of ethyl crotonate and magnesium methyl bromide, and when warmed with a little concentrated sulphuric acid gives  $\delta$ -methyl- $\Delta^{\beta\delta}$ -pentadiene, b. p.  $75.6-76^{\circ}/760$  mm.,  $d_{1}^{20}$  0.71896,  $n_{10}^{20}$  1.44655. When cyclopropyldimethylcarbinol is distilled with a little sulphuric acid it yields vinylcyclopropane, b. p. 69.5-70°/751 mm.,  $d_4^{20}$  0.74999,  $n_D^{20}$  1.42524, accompanied by 2:5-dimethyltetrahydrofuran, b. p.  $92-93^{\circ}$ ,  $d_4^{20}$  0.8335. Dehydration of cyclopropyldiethylcarbinol yields  $\gamma$ -cyclopropyl- $\Delta^{\beta}$ -pentene, b. p. 127.5-128°/762.5 mm. Dehydration of cyclopropylmethylethylcarbinol yields both  $\beta$ -cyclopropyl- $\Delta^{\alpha}$ - and  $-\Delta^{\beta}$ -pentenes, the products having b. p.  $103.5 - 103.8^{\circ}$ ,  $d_4^{20}$  0.7772,  $n_D^{20}$  1.43901, and b. p.  $105 \cdot 5 - 106^{\circ}$ ,  $d_4^{20}$  0.7804,  $n_p^{20}$  1.44253.

R. K. CALLOW.

Additive properties of diacetylenic hydrocarbons. V. GRIGNARD and TCHHOUFAKI (Rec. trav. chim., 1929, 48, 899-903).--See this vol., 448, 907.

Formation of liquid hydrocarbons from acetylene. I. Polymerisation of acetylene. F. FISCHER, F. BANGERT, and H. PICHLER.—See B., 1929, 703.

Promoter action with oxide catalysts for the decomposition of alcohols. H. ADKINS and P. E.

MILLINGTON (J. Amer. Chem. Soc., 1929, 51, 2449-2460).-The percentage of ethylene in the products formed when alcohol is passed over a zinc oxide catalyst at 400° varies considerably when precipitated zinc oxide is used. Reproducible results are obtained when the oxide is prepared by ignition of zinc oxalate (standard catalyst). Addition of small amounts of various oxides, sodium hydroxide, and sulphuric acid to the standard catalyst shows that for ethyl, propyl, isopropyl, and butyl alcohols the effect of the added substance is never constant, but is specific for a given alcohol. With an iron oxide catalyst (from ferrous oxalate) and alcohol at 400°, only boric oxide increases the formation of ethylene and ethane at the expense of dehydrogenation; the amount of carbon dioxide produced is diminished by sulphuric acid, sodium hydroxide, and chromium oxide. With titanium oxide catalysts and alcohol at 400° added sodium hydroxide increases the amounts of ethane and hydrogen and diminishes the amounts of ethylene and methane. The ratio ethane : ethylene varies considerably using specimens of titanium oxide prepared by hydrolysis of ethyl and butyl orthotitanates; the amounts of methane and hydrogen produced are almost constant. Selective activation is possible, therefore, without addition of promoters or poisons. The results do not support Taylor's hypothesis (cf. A., 1927, 632) of the effect of acid and basic promoters on the ratio dehydration : dehydrogenation. H. BURTON.

Reactions of allyl alcohol over aluminium and zinc oxide catalysts. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1929, 51, 2430-2436).-When allyl alcohol is passed over aluminium oxide at 330° at 50 c.c. per hr. propaldehyde is formed; no acraldehyde results and only a small amount of hydrogen is produced. The change occurs presumably by intramolecular rearrangement of the alcohol (cf. Constable, A., 1927, 27). A marked lowering of activity of the catalyst is observed when 0.01 mol. of boric acid, sulphuric acid, chromic oxide, or sodium hydroxide is added. With zinc oxide catalysts at 330° both acraldehyde and propaldehyde arc produced (cf. A., 1928, 968). A decrease in the rate of flow of the alcohol increases the percentage of acraldehyde in the products formed; an increase in the volume of catalysts (for constant flow) has the same effect. When the catalyst is prepared by igniting zinc oxalate the amount of acraldehyde produced is larger than with the catalyst obtained from zinc hydroxide. Addition of 0.01 mol. of boric, tungstic, or sulphuric acid, chromic oxide, or sodium hydroxide to the catalyst (from oxalate) causes selective activation, since, with a rate of flow of the alcohol of 50 c.c. per hr., an increase in the amount of aldehydes produced results (with the exception of sulphuric acid). In all the cases there is a decrease in the percentage of aeraldehyde; this is again increased by decreasing the rate of flow of the alcohol. H. BURTON.

Relative configurations of d- $\beta$ -octanol and its dextrorotatory halides. Interconversion of the optically active  $\beta$ -octanols by a new method. A. J. H. HOUSSA, J. KENYON, and H. PHILLIPS (J.C.S., 1929, 1700—1711).—d- or l- $\beta$ -Octanol is con-

verted by the action of *dl-p*-toluenesulphinyl chloride and pyridine into  $d_{-}$ ,  $[\alpha]_{-1}^{22} + 24 \cdot 16^{\circ}$ ,  $n_{\rm D}^{23} 1 \cdot 5071$ , and  $l_{-}$ ,  $[\alpha]_{-161}^{20} - 28 \cdot 2^{\circ}$ ,  $n_{\rm D}^{20} 1 \cdot 5038$ ,  $-\beta$ -octyl  $dl_{-}p$ -toluenesulphinates, respectively, without change in configuration, the same esters being obtained by direct esterification of the alcohol with p-toluenesulphinic acid. These react with halogens (in aqueous or chloroform solution) thus:  $C_7H_7 \cdot SO_2R + Cl_2 \longrightarrow C_7H_7 \cdot SO_2Cl + RCl$ , to yield, respectively, *l*- and d- $\beta$ -chloro-octanes (the rotation values of which, compared with those of earlier investigators, are inexplicably low), a Walden inversion taking place, since, by the action of hypochlorous acid, which reacts in accordance with the similar scheme, C<sub>7</sub>H<sub>7</sub>·SO<sub>2</sub>R+  $HOCI \longrightarrow C_7H_7 \cdot SO_2CI + R \cdot OH$ , they are converted, respectively, into l- and d- $\beta$ -octanol. At the same time octenes and hence dihalogeno-octanes are formed as by-products. Oxidation of the p-toluenesulphinates with potassium permanganate converts them into the corresponding p-toluenesulphonates, again without change in configuration. These, when boiled under reflux with an alcoholic solution of lithium chloride, yield the β-chloro-octance of opposite sign, by a reaction exactly similar to that involved in the conversion of d- $\beta$ -octyl p-toluenesulphonate into l-β-octyl acetate or benzoate by boiling with alcoholic potassium acetate or benzoate (Pickard and Kenyon, J.C.S., 1914, 105, 830) and hence involving a change in configuration. Thus both methods point to the conclusion that d- $\beta$ -octanol and its dextrorotatory halides have the same configuration. This is in agreement with the views of Pickard and Kenyon (loc. cit.), but not with those of Levene and Mikeska (A., 1924, i, 940), and both the validity of the assumptions and the experimental technique of these authors are criticised. The action of thionyl chloride on d- $\beta$ octanol yields l-B-chloro-octane of the same rotation  $([\alpha]_{5593}^{20} - 31.0^{\circ})$  as that obtained in the presence of pyridine, which, therefore, does not affect the rotation. Mechanisms for these configuration changes based on the proved structure of p-toluenesulphinates (Phillips, A., 1926, 159) are suggested and it is considered probable that the Walden inversion occurs whenever a group attached to an asymmetric carbon atom is replaced, unless a phenyl group is directly linked to the asymmetric atom or a carboxyl group is present in the molecule. J. W. BAKER.

[Aliphatic (open-chain) hydroterpenes.] S. SABETAY and J. BLÉGER (Bull. Soc. chim., 1929, [iv], 45, 497—498; cf. A., 1928, 1138).—Mainly a question of priority (cf. Longuinov and Margoliss, this vol., 538). The authors recommend restricting the use of the names tetrahydrogeraniol, dihydrocitronellol, and dihydrorhodinol to dl-, d-, and l- $\gamma\eta$ -dimethyloctanol, respectively. R. BRIGHTMAN.

Manufacture of  $\gamma$ -butylene glycol. I. G. FARBENIND. A.-G.—See B., 1929, 671.

Tetramethylene glycol and tetramethylene chlorohydrin. W. R. KIRNER and G. H. RICHTER (J. Amer. Chem. Soc., 1929, 51, 2503-2506).--Fission of benzyl &-hydroxybutyl ether (Bennett, A., 1925, i, 883) with hydrobromic acid (cf. Bennett and Hock, A., 1927, 355) affords tetramethylene glycol, b. p. 107-108°/4 mm., m. p. 19-19.5°,  $d_4^{*0}$  1.0171,  $n_D^{so}$  1·4467 [bisphenylcarbimide derivative, m. p. 179·5° (lit. 180—181°)], converted by treatment with thionyl chloride and pyridine at 55—80° into tetramethylene chlorohydrin, b. p. 84—85°/16 mm.,  $d_4^{so}$  1·0883,  $n_D^{so}$ 1·4518 [*phenylcarbimide* derivative, m. p. 54°;  $\alpha$ -naphthylcarbimide derivative, m. p. 69—70° (lit. 66°)]. H. BURTON.

Crystalline acetin and diglycide. M. BATTECAY, H. BUSER, and E. SCHLAGER (Bull. Soc. chim., 1929, [iv], 45, 494—497).—See this vol., 539.

Methionic [methanedisulphonic] acid. H. J. BACKER (Rec. trav. chim., 1929, 48, 949–952).— Treatment of methylene chloride (1 mol.) with potassium sulphite (2 mols.) and water at  $150-160^{\circ}$ affords about 85% of the theoretical amount of potassium methanedisulphonate. The free acid  $+2H_2O$ , m. p.  $90.5^{\circ}$  (*thallous* salt), is obtained by decomposition of the barium salt, prepared also by Schroeter's method (A., 1898, i, 614). The solubilities of the crystalline and anhydrous acid and salts in water at  $25^{\circ}$  are given. H. BURTON.

Production of esters from acid amides. H. G. SMITH and IMPERIAL CHEM. INDUSTRIES, LTD.—See B., 1929, 671.

Acids of montan wax. D. Holde, W. Bley-BERG, and H. VORRER.—See B., 1929, 667.

Derivatives of homolævulic acid. R. LUKES (Coll. Czech. Chem. Comm., 1929, 1, 461-466).--- $\gamma$ -Acetoxy- $\gamma$ -hexolactone, b. p. 135-136°/10 mm.,  $d_4^{131}$  1·1507,  $n_B^{131}$  1·44731, is obtained by interaction of homolævulic [ $\gamma$ -ketohexoic] acid and acetic anhydride in the presence of a little acetyl chloride, and when distilled under ordinary or reduced (200-250 mm.) pressure yields acetic acid and 5-keto-2-ethyl-4:5-dihydrofuran, b. p. 75-76°/10 mm.,  $d_4^{108}$  1·0662,  $n_4^{108}$ 1·45835. The latter affords 5-keto-2-ethyl-2:5-dihydrofuran, b. p. 99-101°/10 mm.,  $d_4^{103}$  1·0704,  $n_B^{123}$ 1·46467, when heated with trimethylamine at 100°, and yields homolævulanilide, m. p. 92°, with aniline. A. I. VOGEL.

Manufacture of [alkoxy]aliphatic acids. H. DREYFUS.—See B., 1929, 671.

Polymerisation and ring formation. I. General theory of condensation polymerides. W. H. CAROTHERS. II. Poly-esters. W. H. CAROTHERS and J. A. ARVIN (J. Amer. Chem. Soc., 1929, 51, 2548-2559, 2560-2570).-I. Two types of linear polymerides,  $\{R\}_n$ , are recognised: (1) addition (A) polymerides (e.g., caoutchouc, polystyrene, polyoxymethylenes), where the polymeride has the same composition as the monomeric compound, and (2) condensation (C) polymerides (e.g., cellulose, hexaethylene glycol), where the monomeric compound differs from the structural unit (R) by  $H_2O$  (NH<sub>3</sub>, HCl). Substances of the type x·R·y are termed bifunctional (x and y are capable of interaction, forming z), and the change  $x \cdot R \cdot y \longrightarrow \cdot R \cdot z \cdot is$ a bifunctional reaction. The change  $x \cdot \mathbf{R} \cdot x + y \cdot \mathbf{R} \cdot y \longrightarrow$ ·z·R·z·R· is a bi-bifunctional reaction. Bifunctional reactions are intramolecular when five- or sixmembered ring formation is possible and the monomeric ring compound,  $R \bigcirc z$ , results. If the monomeric ring substance is larger than six-membered

intermolecular change occurs and the products are of the type  $[\cdot\mathbf{R}\cdot\mathbf{z}\cdot]_n$  or  $x\cdot[\cdot\mathbf{R}\cdot\mathbf{z}]_{n-1}\cdot\mathbf{R}\cdot\mathbf{y}$ . Various examples from the literature are discussed.

II. The bi-bifunctional reaction  $R(CO_2H)_2$ +  $R'(OH)_2 \longrightarrow [\cdot CO \cdot R \cdot CO \cdot O \cdot R' \cdot O \cdot]$  (structural unit), where all the functional groups are involved, will give rise to polymerides when the number of atoms in the structural unit is seven or more. The following esters are described : ethylene malonate, succinate, m. p. 108°, adipate, m. p. 50°, and sebacate, m. p. 79°; trimethylene succinate, m. p. 52°, adipate, m. p. 45°, and sebacate, m. p. 56°; hexamethylene succinate, m. p. 57°, adipate, m. p. 56°, and sebacate, m. p. 67°; decamethylene succinate, m. p. 68°, adipate, m. p. 77°, and sebacate, m. p. 74°. The number of atoms in the structural unit varies from 7 to 22, and all the esters are highly polymerised. The lowest mol. wt. observed is 2300 (ethylene malonate), the highest 5000 (trimethylene sebacate). The esters are nonacidic and it is assumed that alcoholic hydroxyl groups are at each end of the complex molecule (excess of glycol is used in the preparations). Ethylene phthalate (prepared from the glycol and phthalic anhydride first at 190° and then at 300°/3 mm., similarly from the glycol and ethyl phthalate, and from the glycol and phthaloyl chloride in pyridine), trimethylene, hexamethylene, and decamethylene phthalates are also described. The mol. wt. of these esters varies from about 1500 to 5000. When a mixture of ethyl fumarate and ethylene glycol is heated at 190-230° (final pressure 4 mm.) in a current of nitrogen ethylene fumarate (mol. wt. determination not possible owing to insolubility) results. Ethylene maleate is obtained from the glycol and maleic anhydride first at 195-200° and then at 200-215°/vac. These preparations differ from those described by Vorländer (A., 1895, i, 17). H. BURTON.

Determination of relationship of stercochemical structure existing between optical antipodes of different substances. J. TIMMER-MANS (Rec. trav. chim., 1929, 48, 890—894). *d*-Chloro- and *d*-bromo-succinic acids furnish a continuous series of mixed crystals, whilst *d*-chloro- and *l*-bromo-succinic acids afford a partial racemate. The stereochemical structures of both *d*-acids are therefore probably similar. The f.-p. curves of various closely related substances quoted in the literature are commented on. H. BURTON.

Formation of *l*-malic acid from fumaric acid by Aspergillus niger. F. CHALLENGER and L. KLEIN (J.C.S., 1929, 1644—1647).—The fermentation of a 1% solution of potassium fumarate at  $31-32^{\circ}$  by cultures of A. niger which have been trained to grow in this medium produces *l*-malic acid which was isolated as such and identified by the formation of its di-p-nitrobenzyl ester, m. p. 125°. The formation of *l*-malic acid must arise from asymmetric addition of water to the double linking and not by the prior formation of *dl*-malic acid, since the latter becomes dextrorotatory after attack by A. niger. This view is in agreement with various biochemical observations which are summarised. Di-p-nitrobenzyl dl-malate has m. p. 109°. J. W. BAKER. 1166

Action of phosphorus pentachloride on ethyl tartrate. T. S. PATTERSON and A. R. TODD (J.C.S., 1929, 1768-1771).-Fractional distillation of the product obtained by the action of phosphorus pentachloride on ethyl tartrate yields dichloromaleic anhydride (I), ethyl chlorofumarate mixed with ethyl dichlorosuccinate (II), and ethyl hydrogen chlorofumarate (III). The initial product is probably ethyl 3-chloromalate, which is further chlorinated to ethyl dichlorosuccinate, and this is converted by loss of hydrogen chloride into ethyl chlorofumarate (II). The latter is then converted into ethyl chlorofumaryl chloride, which yields III on pouring into water, or it may become further chlorinated to give, ultimately, dichlorofumaryl chloride, from which I J. W. BAKER. results.

Production of acetaldehyde from acetylene. I. G. FARBENIND. A.-G.—See B., 1929, 708.

Condensation of acetaldehyde with methylmalonic ester. Methylations with methyl bromide. H. J. LUCAS and W. G. YOUNG (J. Amer. Chem. Soc., 1929, **51**, 2535—2538).—Ethyl methylmalonate (I) and methylacetoacetate are conveniently prepared by passing methyl bromide into the hot alcoholic solution of ethyl sodio-malonate and -acetoacetate. Condensation of I with acetaldehyde in presence of acetic anhydride affords the ethyl ester, b. p. 100—106°/3—5 mm.,  $d_1^{\text{al}}$  1.0732, of  $\gamma$ -hydroxybutane- $\beta\beta$ -dicarboxylic acid [diamide, m. p. 209.5° (corr.; decomp.)]. H. BURTON.

Formation of cyclic acetals by the action of acetone and acetaldehyde on  $\alpha\gamma$ -dihydroxycompounds. J. BÖESEKEN (Rec. trav. chim., 1929, 48, 931—934).—An account of the formation of five- and six-membered *iso*propylidene and ethylidene ethers from  $\alpha\gamma$ -glycols, glycerol, and related compounds (cf. Böeseken and van Loon, A., 1920, i, 837; Hill, Hibbert, and others, A., 1928, 1114, 1213; van Roon, this vol., 291). H. BURTON.

Acraldehyde, anti-oxidants, coloured hydrocarbons yielding dissociable peroxides (rubrene family) and hæmoglobin. C. MOUREU (Rec. trav. chim., 1929, 48, 826—837).—A resume of the author's work on the stabilisation of acraldehyde, anticatalysts, the theory of anti-oxidation catalysis, and rubrene. The dissociation of rubrene peroxide appears to be analogous to the dissociation of oxyhæmoglobin. The respiratory function of hæmoglobin is, therefore, not necessarily a function of the iron present in the molecule. H. BURTON.

α-Bromo- and α-hydroxy-aldehydes. IV. α-Hydroxy-n-butaldehyde, α-hydroxyisobutaldehyde, and glycollaldehyde. R. DWORZAK and J. PIERRI (Monatsh., 1929, 52, 141—150; cf. A., 1927, 1055; this vol., 297).—Treatment of para-n-butaldehyde with bromine at  $-10^{\circ}$  to  $-5^{\circ}$  and subsequently with alcohol affords slightly impure α-bromo-n-butaldehyde ethylacetal, b. p. 76—81°/12 mm., which is hydrolysed by boiling with water to α-hydroxy-nbutaldehyde, b. p. 70—80°/14 mm. (p-nitrophenylhydrazone, m. p. 135°; p-nitrophenylosazone, m. p. 227°). The oil obtained by distillation crystallises after about two weeks. Similar bromination of para-

isobutaldehyde yields  $\alpha$ -bromoisobutaldehyde ethylacetal together with a substance,  $C_{12}H_{18}OBr_6$ , m. p. 85.5°, the mol. wt. of which in benzene is low. Hydrolysis of the acetal furnishes  $\alpha$ -hydroxyisobutaldehyde (p-nitrophenylhydrazone). Hydrolysis of bromoacetal and subsequent prolonged extraction of the partly neutralised reaction mixture with ether gives glycollaldehyde; this could not be isolated by distillation. The above hydroxyaldehydes are determined by Fehling's solution. The action of dilute alkali on glycollaldehyde appears to give products which are not analogous to those from lactaldehyde (cf. loc. cit.). H. BURTON.

Ketonic transformation of aldehydes at high temperatures. I. S. DANILOV (J. Russ. Phys. Chem. Soc., 1929, 61, 723-725).-The transformation of di- and tri-substituted aldehydes into ketones at elevated temperatures in the presence of catalysts, such as mercury salts, aluminium oxide, zinc chloride, etc., is discussed. The possibility of the formation according to this mechanism of the ketones resulting from the destructive distillation of cellulose substances is suggested. Trimethylacetaldehyde, b. p. 74°, which is a product of wood distillation, was found to isomerise quantitatively into methyl isopropyl ketone, b. p. 93-94°, by the action of aluminium chloride at 350° in an atmosphere of carbon dioxide. Triphenylacetaldehyde with the same catalyst, at 320-340°/ 25 mm., gave triphenylethanone, m. p. 136°.

M. ZVEGINTZOV.

Conversion of sugars into furan or hydrofuran derivatives. E. VOTOČEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1929, 1, 449-460).-Methyl 3-methoxy-5-methylfuran-2-carboxylate (I), m. p. 48°, prepared from δ-ketorhamnolactone, is converted by aqueous potassium hydroxide into 3-methoxy-5-methylfuran-2-carboxylic acid, m. p. 158-159° (potassium salt), which yields 3-methoxy-5-methyl-furan, b. p. 124-125°, on dry distillation with lime. The ester I affords on prolonged exposure to the atmosphere or more rapidly in the presence of a little hydrochloric acid a relatively unstable, optically inactive yellow compound,  $C_{15}H_{18}O_9$ , m. p. 62°, which when warmed with 0.2N-potassium hydroxide or hydrochloric acid furnishes methyl 3-methoxy-5methylfuran-2-carboxylate, m. p. 48°, and a compound, m. p. 70°. A. I. VOGEL.

Structure of a-methylxyloside. F. P. PHELPS and C. B. PURVES (J. Amer. Chem. Soc., 1929, 51, 2443-2449, and Bur. Stand. J. Res., 1929, 3, 247-253).—Methylation of  $\beta$ -methylxyloside with methyl iodide and silver oxide affords trimethyl-β-methylxyloside (I), m. p. 51°,  $[\alpha]_B^{20}$  -69.5° in chloroform. When methylation of xylose is carried out first with methyl sulphate and alkali and then with methyl iodide and silver oxide the yield of I is smaller and the product is optically impure (cf. Carruthers and Hirst, J.C.S., 1922, 121, 2299). Methyl iodide-silver oxide treatment of a-methylxyloside affords trimethyl- $\alpha$ -methylxyloside (II),  $n_{\rm D}^{\infty}$  1.4397,  $[\alpha]_{\rm D}^{\infty}$  +121.5° in chloroform, purified by distillation. Hydrolysis of I and II with 4% hydrochloric acid at 85° yields the same trimethyl- $\alpha$ -xylose, m. p. 91–92°,  $[\alpha]_{D}^{30}$  +64.5°  $\longrightarrow$  17.7° in water. It is concluded that I and II

contain the same ring structure and arc an  $\alpha$ - and  $\beta$ -pair. H. BURTON.

Sugar oxidations and decompositions. III. Theory of sugar degradation. IV. Behaviour of dextrose in sulphuric acid solution. K. BERNHAUER (Biochem. Z., 1929, 210, 175-185, 186-180; cf. this vol., 543).-III. It is suggested that there are two main methods of degradation of dextrose: (1) Non-oxidative processes characterised by formation of C<sub>3</sub> chains preceded by a rearrangement into the labile furanose form and hence taking place chiefly in alkaline solution. This includes all processes giving rise to methylglyoxal, acetaldehyde, and products derived from them by simple oxidation and reduction, e.g., acetic acid.  $(\hat{2})$  Processes depending on a primary oxidation of the stable form of dextrose. This oxidation occurs most readily at the 1- and 5-carbon atoms (ends of the pyranose oxygen bridge) and at the 6-carbon atom, principally in acid solution.

IV. In sulphuric acid solution dextrose is much less easily oxidised by hydrogen peroxide and ferrous sulphate than in originally neutral solution. The dextrose appears to be present in a more stable form. Acetic acid is not produced. J. H. BIRKINSHAW.

Glucosides. II. Preparation of a-glucosides from β-glucosyl chlorides. W. J. HICKINBOTTOM (J.C.S., 1929, 1676-1687).-The conversion of 2-trichloroacetyl-3:4:6-triacetyl- (I) and 3:4:6-trichloroacetyl- (II)  $-\beta$ -glucosyl chlorides, prepared by slight modification of Brigl's method (A., 1922, i, 225), into a-glucosides has been studied. Contrary to Brigl, I exhibits almost no mutarotation even in chloroform solution. In dry methyl alcohol, however, the rotation rapidly increases from  $[\alpha]_{p}$  +2.5° to  $+92.5^{\circ}$  in 46.8 hrs. and then slowly falls to an equilibrium value, the solution acquiring an acid reaction. If, at the point of maximum rotation, the solution is shaken with silver oxide to remove the unchanged  $\beta$ -glucosyl chloride,  $\alpha$ - (70%) and  $\beta$ -methylglucosides can be isolated. The formation of the β-glucoside cannot be ascribed in this case to the prior formation of the 1:2-anhydride, especially since the original  $\beta$ -glucosyl chloride is stable in the presence of silver chloride and silver oxide in dry benzene solution. Similar, but much slower, rotation changes occur in ethyl ( $[\alpha]_n + 7.0^\circ$  to  $+44.5^\circ$  in 165 hrs.) and n-butyl  $([\alpha]_p + 4^\circ \text{ to } + 22 \cdot 0^\circ \text{ in } 193 \cdot 5 \text{ hrs.})$  alcohols, although the change was not followed for a sufficient length of time to attain the maximum value. More rapid rotation changes of the same type occur with II; in methyl alcohol the rotation changes rapidly to  $[\alpha]_D$ +160° in 2 hrs., whilst in ethyl alcohol the maximum is reached in 9 hrs. Treatment with silver carbonate and subsequent deacetylation with anhydrous ammonia at the ordinary temperature again yields a mixture of  $\alpha$ - and  $\beta$ -glucosides. The initial rise in rotation is determined partly by isomerisation to the a-glucosyl chloride and partly by reaction of the  $\beta$ -chloride with the alcohol to yield an  $\alpha$ -glucoside. When equilibrium between the  $\alpha$ - and  $\beta$ -glucosyl chlorides is attained the reaction with the solvent becomes predominant and causes the final fall in rotation. The predominant formation of a-glucosides

requires that the rate of replacement of halogen by the alkoxy-group should be rapid compared with the rate of isomerisation of the  $\beta$ -glucosyl chloride, and should be favoured by dilution of the reactants with an indifferent solvent. Isomerisation of I into the  $\alpha$ -chloride occurs in acetone solution, but by the action of "active" silver oxide in methyl alcohol solution, the yield of a-methylglucoside never exceeds 70%. When an alcoholic solution of I or II is treated with silver nitrate and pyridine, however, the yield of α-glucoside is increased to 79.4 and 88-90%, respectively (cf. Schlubach and Schröter, A., 1928, 873). By the action of dry silver oxide on a suspension of II in a chloroform solution of phenol and subsequent deacetylation, a-phenylglucoside hydrate, m. p. 148-150°, [a]<sub>p</sub> +143°, is obtained. J. W. BAKER.

Synthesis of glucosides. II. Preparation of some galactosides. A. ROBERTSON (J.C.S., 1929, 1820—1823).—Tetra - acetylgalactosidyl bromide (Fischer and Armstrong, A., 1902, i, 263) is obtained in good yield by addition of penta-acetylgalactose to a mixture of acetic anhydride and glacial acetic acid saturated at 0° with hydrogen bromide. It reacts with quinol in acetone in the presence of aqueous potassium hydroxide to give O-tetra-acetyl- $\beta$ -p-hydroxyphenylgalactoside, m. p. 202—203°, which is deacetylated to  $\beta$ -p-hydroxyphenylgalactoside  $+1.5H_2O$ , m. p. 246—247°,  $+2H_2O$ , m. p. 246—247°,  $[\alpha]_D^n -53.2°$  in water. By similar methods are obtained O-tetra-acetyl- $\beta$ -p-anisyl-, m. p. 104°, - $\beta$ -1menthyl-, m. p. 100—101°,  $[\alpha]_D^n -48.6°$  in chloroform, and  $\beta$ -d-bornyl-, m. p. 140°,  $[\alpha]_D^n +1.3°$  in chloroform, -galactosides, from which by deacetylation are obtained, respectively,  $\beta$ -p-anisyl-, anhydrous, m. p. 161°, and  $+H_2O$ ,  $[\alpha]_D^n -40°$  in water;  $\beta$ -1-menthyl-,  $+2H_2O$ , m. p. 40—41°,  $[\alpha]_D^n -74.2°$  in alcohol,  $+0.5H_2O$ , and  $\beta$ -d-bornyl-,  $+H_2O$ , m. p. 123°,  $[\alpha]_D^n$ -6.5° in alcohol, and anhydrous, m. p. 137—138°, -galactosides. J. W. BAKER.

Sugar anhydrides. A. PICTET and H. VOGEL (Rec. trav. chim., 1929, 48, 843-846).—When a concentrated, aqueous solution of trihexosan is exposed to ultra-violet light for 56 hrs. 60% conversion into hexahexosan (I) occurs; further irradiation of I appears to have no action. Amylase converts I into maltose, whilst acetyl bromide gives hepta-acetylmaltose. When I is hydrolysed with oxalic acid a mixture of dextrinose (II) (an *iso*maltose; see Georg and Pictet, A., 1926, 823) and dextrinosan (III),  $C_{12}H_{20}O_{10}$ , m. p. 185-186°,  $[\alpha]$ +150·7°, is obtained. A very dilute solution of III gives a reddish-brown coloration with iodine; III is not converted into II by boiling with water, whilst irradiation affords I. H. BURTON.

Polysaccharides. IV. Constitution of xylan. H. A. HAMPTON, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1929, 1739–1753).—Pure xylan, containing 10.7% of moisture,  $[\alpha]_{12}^{22}$ — $109.5^{\circ}$  (calculated as anhydrous material in 2.5% aqueous sodium hydroxide solution), isolated by extraction with boiling 12% aqueous sodium hydroxide from esparto cellulose, has definitely the composition ( $C_5H_8O_4$ )<sub>n</sub>, and by hydrolysis with 3% nitric acid gives a 93% yield of crystalline xylose (cf. Heuser and Jayme, A.,

1923, i, 1061). Previous methods of methylation of xylan are shown to yield mixtures of hydrolysis products containing mono-, di-, and tri-methylxyloses. Pure dimethylxylan (I), m. p. 194-196° (slight decomp.),  $[\alpha]_{D}^{18^{15}} - 92^{\circ}$  in chloroform, is obtained by two methylations of xylan with potassium hydroxide and methyl sulphate under prescribed conditions, proof that the methyl groups occupy the 2 and 3 positions being obtained from the following reactions. Hydrolysis of I with 1.2% methylalcoholic hydrogen chloride yields dimethylmethyl-xyloside (II), b. p. about  $80^{\circ}/0.04$  mm.,  $n_{\rm F}^{\rm F}$  1.4581,  $[\alpha]_{\rm D}^{\circ3}$  +61.8° in methyl alcohol, which is further methylated with methyl iodide and silver oxide to yield trimethylmethylxyloside; this is hydrolysed to 2:3:4-trimethylxylose (Carruthers and Hirst, J.C.S., 1922, 121, 2299) in 81% yield, slight losses arising from the formation of furan derivatives as byfrom the formation of furan derivatives as by-products. Hydrolysis of II with 3% hydrochloric acid at 100° gives an 85% yield of 2:3-dimethyl-xylose,  $n_D^{20}$  1.4783,  $[\alpha]_D^{20}$  +22.6° in water, characterised as its anilide, m. p. 146°. By hydrolysis and subsequent oxidation with bromine II is converted into 115°/0.02 mm.,  $n_{\rm p}^{16.5}$  1.4640,  $[\alpha]_{\rm m}^{26.5}$  +97° (initial value in water), characterised by conversion into the phenylhydrazide and p-bromophenylhydrazide, m. p. 150-151°, of 3:5-dimethylxylonic acid. Hydrolysis of III in aqueous solution is very slow, equilibrium being approached only after 400 hrs., and on complete methylation it is converted into 2:3:5-trimethyl- $\gamma$ -xylonolactone, thus confirming its structure as a  $\gamma$ -lactone. Hence positions 4 and 5 of the original dimethylxylose from dimethylxylan must be unmethylated, the pyranose form of the sugar yielding a furanose type of lactone, and in xylan these two positions must be involved either in linking the J. W. BAKER. β-xylose units or in ring formation.

(SIR) J. C. IRVINE (Rec. trav. chim., Starch. 1929, 48, 813-816) .- Polysaccharides derived from dextrose are divided into two classes. (1) Methylation (methyl sulphate and iodide) proceeds regularly until the methoxyl content is 37%; further methylation is effected indirectly by chlorination and subsequent treatment with sodium methoxide (e.g., starch, glycogen, tetra-amylose). (2) Methylation proceeds regularly, yielding the fully methylated derivative (e.g., cellulose, hexa-amylose). Hydrolysis of the fully methylated derivatives of both classes gives 2:3:6-trimethylglucose. This has a tendency to exist in 1:4- and 1:5-ring modifications, indicating that the parent substances may be structurally different. The oxygen ring in starch probably differs from that in cellulose. Starch and cellulose may be polymerides of isomeric anhydrides of  $\alpha$ - and β-glucose (1:4- and 1:5-ring, respectively).

H. BURTON.

Dissolution and acetylation of starch. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 153—156). —Besides glycerol, starch is soluble to the extent of 10% in fused erythritol at 150—160°, less easily soluble in mannitol at 180—190°, and very slightly soluble in ethylene glycol at 190°. In methyl alcohol at 185° the starch neither swells nor dissolves. Triacetylstarch is obtained by acetylation with acetic anhydride in glycerol solution. This product, which is more soluble, less viscous in solution, and has a lower specific rotation than that obtained by acetylation in zinc chloride solution (this vol., 175), has probably suffered some depolymerisation. Untreated potato starch, dissolved in glycerol containing zinc chloride at 160—170°, and acetylated by treatment with acetic anhydride at 70°, yielded a product of  $[\alpha]_D + 164°$  in chloroform, M 4000—6000. Initial dissolution of the starch at a higher temperature gave a triacetyl compound which was further depolymerised,  $[\alpha]_D + 146°$ , M 3200. The polysaccharides obtained in either case by deacetylation were nonreducing and gave a blue colour with iodine.

T. H. MORTON. Lignin. III. Destructive distillation of lignin from corn cobs. M. PHILLIPS (J. Amer. Chem. Soc., 1929, 51, 2420-2426).-The ligning are obtained by the following methods: (a) heating the corn cobs with 2% sodium hydroxide solution under pressure and acidifying the alkaline liquors, (b) prolonged treatment with hydrochloric acid  $(d^{15} 1.21)$  at the ordinary temperature, and (c) prolonged treatment with 72% sulphuric acid at the ordinary temperature. Distillation of lignin a at 380-400° under ordinary pressure gives aqueous distillate (15.5%) of dry, ash free lignin), oil (17.7%), carbon residue (52.2%) of lignin used), and gas (13.5%) by difference). The aqueous distillate contains acetone (0.13%), methyl alcohol (1.9%), and acids (as acetic 0.05%; this small value is probably due to deacetylation during the alkali treatment), whilst the oil consists of acids (8.6%), phenols (84%), and hydrocarbons and neutral compounds (7.2%). Lignins b and c afford about the same amounts of aqueous distillates as a; these contain more acetone and acetic acid but less methyl alcohol (probably due to smaller methoxyl contents of b and c) than the distillate from a. About one half the amount of oil is formed, but the carbon residue increases. H. BURTON.

Lignin colouring matters. F. PODBREZNIK (Bull. Inst. Pin, 1928, 233—236, 245—250; Chem. Zentr., 1929, i, 1212—1213).—A study of the colour reactions of lignin. The reaction with alcoholic phloroglucinol and hydrochloric acid is not merely a chemical reaction, but is concerned with selective adsorption. The behaviour of lignin obtained in different ways was examined. A. A. ELDRIDGE.

[Preparation of] diamines and amino-alcohols. N. PUTOCHIN (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 10—21).—By the use of more concentrated sodium hydroxide solution and distillation of the liquid to dryness, nearly theoretical yields of diamines were obtained by Gabriel's method (A., 1888, 1292). The method is convenient for the preparation of primary hydroxyamines, e.g., of  $\gamma$ -hydroxypropylamine (90% yield) from  $\gamma$ -phthalimidopropyl bromide, and of  $\varepsilon$ -hydroxyamylamine, m. p. 26°, b. p. 221—222°,  $d_4^{rr}$  0.9488,  $n_{\rm B}^{tr}$  1.4618 (chloroplatinate, m. p. 180°).

CHEMICAL Abstracts. Behaviour of isomeric r- $\alpha$ -bromopropionylnorvalines and r-alanylnorvalines towards N-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1929, 11, 119-125).-Treatment of dl-norvaline with dl-a-bromopropionyl bromide and 2N-sodium hydroxide solution affords two  $\alpha$ -bromopropionylnorvalines, (A), m. p. 128.5-129.5° after sintering at 126°, and (B), m. p. 130.5-131.5° after sintering at 129°. Amination of A and B affords the corresponding inactive alanylnorvalines (I), m. p. 218-219° with darkening after sintering at 184°, and (II), m. p. 224-225° (decomp.), respectively. Fission of I and II does not occur with trypsin-kinase at  $p_{\rm H}$  8.4 and 37° or with N-sodium hydroxide at 37°. Erepsin  $(p_{\rm H}, 7.8)$  has no action on II, whilst I undergoes 25%hydrolysis. Partial hydrolysis of A and B occurs with N-sodium hydroxide; trypsin-kinase  $(p_{\rm H} 7.8)$ has some action on A but practically none on B.

H. BURTON.

Constitution of sulphur and nitrogen compounds derived by substitution of the carboxyl group. G. ODDO (Rec. trav. chim., 1929, 48, 875-879).—On the basis of his tetragonal mesohydric form of the carboxyl group I (cf. A., 1907, ii, 15; 1922, ii, 367), the author discusses the constitution of various compounds obtained by substituting the ketonic or hydroxylic functions of the carboxyl group by S or SH, and by NH or NHR, both separately and together in the latter case. These compounds are considered to possess the usual formulæ only in their alkyl derivatives, the free substances having a mesohydric form, e.g., II, which, by fission in the directions (a) and (b) affords normal and iso-alkyl derivatives.

In support, the cases of amidines, hydrazines, and hydroxylamino-oximes, the mesohydrics III (X, X= H, NH<sub>2</sub>, and OH, respectively) of which are symmetrical and can afford but one product by fission at C. W. SHOPPEE. (a) or (b), are instanced.

Synthetic carbamide from ammonia and carbon dioxide. G. A. YAKOVKIN.-See B., 1929, 707.

Carbamide series : nitrocarbamide, nitrobiuret, and dicyanic acid. K. C. BLANCHARD (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 50-51).--Carbamide and monosubstituted carbamides may be used as a source of cyanic acid or carbylamines, respectively, for the preparation of mono- and s-di-substituted carbamides, the dry reactants being heated together at 160°, or boiled in aqueous solution. Aromatic and aliphatic secondary amines similarly give very poor yields of as-disubstituted carbamides. The introduction of a nitro-group decreases the stability, nitrocarbamide readily breaking down into cyanic acid and nitramide, and hence it acts as a nitrating agent in concentrated sulphuric acid solution. The decomposition is promoted by alkalis but hindered by mineral acids. In aqueous solution nitrocarbamide reacts with ammonia and amines to yield carbamide or its derivatives. In a similar manner nitrobiuret is a source of nascent dicyanic acid which, in the absence of amines, forms allophanic acid and hence, ultimately, carbamide and carbon dioxide, whilst it reacts with amines to yield ω-substituted biuret derivatives. In moist alcohol nitrobiuret yields allophanic esters and ultimately carbamic esters, and in concentrated sulphuric acid the nitronitrogen is quantitatively evolved. By the application of these synthetic methods the following new compounds have been prepared but are not described : s-di-n-amyl-, n-amyl-, as-di-n-butyl- (picrate), as-phenyln-propyl- (picrate; oxalate), as-phenyl-n-butyl-carb-amides;  $\omega$ -n-propyl-, n-butyl-, benzyl-,  $\alpha$ -naphthyl-, ww'-dimethyl-, diethyl-, di-n-butyl-, phenylethyl-, and J. W. BAKER. phenyl-n-propyl-biurets.

Preparation of ethyl phosphinoacetate. A. E. ARBUZOV and G. C. KAMAÏ (J. Russ. Phys. Chem. Soc., 1929, 61, 619-622).-Yields of ethyl phosphinoacetate reaching 95% are obtained by the interaction of sodium ethoxide, diethyl phosphate, and ethyl chloroacetate in absolute alcoholic solution. In other solvents, such as ether or light petroleum, the yields are considerably smaller (cf. A., 1914, i, 651). R. TRUSZKOWSKI.

Syntheses with ethyl phosphinoacetate. A. E. ARBUZOV and A. I. RAZUMOV (J. Russ. Phys. Chem. Soc., 1929, 61, 623-628).-Ethyl sodiophosphinoacetate is condensed with methyl iodide to yield ethyl a-diethylphosphinopropionate, b. p. 127°/5 mm., and a-diethylphosphinopropionic acid, which could not be distilled without decomposition. These products gave on hydrolysis a-phosphinopropionic acid, m. p. 119-132°. Better yields of the phosphinopropionic ester are obtained using the potassium salt of ethyl phosphinoacetate in the above reaction, no diethylphosphinopropionic acid being obtained in this case. Ethyl benzyldiethylphosphinoacetate, b. p. 180°/3 mm., and benzylphosphinoacetic acid, m. p. 137-145°, are prepared similarly. R. TRUSZKOWSKI.

Organic additive compounds of calcium chloride and calcium iodide. F. R. GREENBAUM (J. Amer. Pharm. Assoc., 1929, 18, 784-789).—The following compounds have been prepared according to G.P. 306,804 (cf. B., 1918, 636A): calcium iodide additive products with carbamide, m. p. 95°, thiocarbamide, hexamethylenetetramine, m. p. 180°, urethane, thiosinamine, antipyrine, monoacetylthiocarbamide, monoacetylcarbamide, phenylcarbamide, and calcium chloride additive products with all the above (calcium chloride-urethane; calcium chlorideacetylcarbamide, m. p. 135-140°; calcium chloride-thiocarbamide, m. p. 175-177°). In the case of calcium chloride usually 4 mols. of the base enter into the additive combination and with calcium iodide 6 mols. The additive compounds are stable and less hygroscopic than either calcium chloride or iodide. E. H. SHARPLES.

Acetoxymercuric chloride. F. C. WHITMORE and G. J. LEUCK (J. Amer. Chem. Soc., 1929, 51, 2589-2590).-The salt, HgCl<sub>2</sub>,Hg(OAc)<sub>2</sub>, described by Donk (A., 1907, i, S19) is acetoxymercuric chloride. HgCl·OAc. It is not possible to mercurate dimethylaniline, phenol, or *p*-cresol with this salt.

H. BURTON.

Manufacture of lead tetraethyl. H. W. DAUDT. --See B., 1929, 709.

Nomenclature of organic compounds of complex function. A. M. PATTERSON (Rec. trav. chim., 1929, 48, 1012—1017).—Analysis of the nomenclature (literature) of 2557 compounds reveals an order of precedence of groups in fairly good agreement with the proposals previously made (A., 1918, i, 97).

H. BURTON.

Catalytic transference of hydrogen between organic compounds. S. AKABORI and T. SUZUKI (Proc. Imp. Acad. Tokyo, 1929, 5, 255-256; cf. Wieland, A., 1923, i, 167).-By treating a compound which is capable of splitting off hydrogen with one capable of casy reduction, in presence of an activating agent (palladium-black), transference of hydrogen takes place from the former to the latter. Cinnamic acid, oleic acid, eugenol, and coumarin when heated with tetrahydronaphthalene and palladium give good yields of hydrocinnamic acid, stearic acid, hydroeugenol, and hydrocoumarin, respectively. A mixture of tetrahydroquinoline (1 mol.) and maleic acid (2 mols.) is converted quantitatively into quinoline and succinic acid. Piperidine is not reduced by maleic acid and palladium but gives an almost theoretical yield of pyridine with safrole and palladium. Tetrahydroisoquinoline is, and tetrahydropapaverine is not, reduced by anethole and palladium; nicotine gives small quantities of nicotyrine with these A. A. GOLDBERG. reagents.

Synthesis of isoamylcyclopentane. J. McA. HARRIS, jun. (J. Amer. Chem. Soc., 1929, 51, 2591).— Magnesium isoamyl bromide converts cyclopentanone into 1-isoamylcyclopentanol, b. p. 101°/17 mm.,  $d_{*}^{*0}$ 0·8848,  $n_{11}^{*0}$ 1·4549, dehydrated by means of p-toluenesulphonic acid to 1-isoamyl- $\Delta^1$ -cyclopentene, b. p. 168—170°/760 mm.,  $d_{*}^{20}$ 0·8010,  $n_{11}^{20}$ 1·4467. Catalytic reduction (platinum-black) of this affords isoamylcyclopentane, b. p. 168—170°/760 mm.,  $d_{*}^{20}$ 0·7837,  $n_{11}^{20}$ 1·4321. H. BURTON.

Thermal reactions of pure organic substances under high hydrogen pressures. F. HOFMANN and K. LANG.—See B., 1929, 707.

**3:4-Dichlorofluorobenzene**. G. M. KRAAY (Rec. trav. chim., 1929, **48**, 1055–1057).—Diazotisation of **3:4**-dichloroaniline in a large excess of sulphuric acid and subsequent decomposition with boiling hydrofluoric acid (1 litre per mol. of base) affords a product which after removal of **3:4**-dichlorophenol and fractionation has b. p.  $170.9-171.4^{\circ}/762.6$ mm., and contains 90.6% of **3:4**-dichlorofluorobenzene. The impurity present is probably *o*-dichlorobenzene. H. BURTON.

2:5-Dichlorofluorobenzene and other aromatic fluoro-compounds. T. DE CRAUW (Rec. trav. chim., 1929, 48, 1061-1065).—Chlorination of *m*-fluoroacetanilide with 1 mol. of chlorine in acetic acid solution and hydrolysis of the mixture of products obtained with 38% hydrochloric acid affords 4-chloro-3-fluoroaniline (1), m. p. 61° (acetyl derivative, m. p. 146°), 2-chloro-5-fluoroaniline (II), m. p. 26° (acetyl derivative, m. p. 91°), and a small amount of 2: 4-dichloro-5-fluoroaniline (III), m. p. 67° (acetyl derivative, m. p. 126°, obtained also in 90% yield by dichlorination of *m*-fluoroacetanilide). Replacement of the amino-group with chlorine by the usual method gives 2:5-dichlorofluorobenzene, b. p. 168°/760 mm., m. p.  $2^{\circ}$ ; similarly, II yields 3:4-dichlorofluorobenzene (cf. Kraay, preceding abstract) and III furnishes 2:4:5trichlorofluorobenzene, m. p. 62°. When these chlorofluorobenzenes are treated with sodium methoxide the fluorine atom is replaced by the hydroxyl group, affording the appropriate di- or tri-chlorophenol. H. BURTON.

Reaction between magnesium phenyl bromide and some amides of sulphonic, sulphinic, and sulphenic acids. H. GILMAN and C. C. VERNON (Rec. trav. chim., 1929, 48, 745-747).—Under ordinary conditions no reaction occurs between magnesium phenyl bromide and substituted amides of benzene-sulphonic, -sulphinic, and -sulphenic acids. Thus p-toluenesulphondiphenylamide in boiling anisole gives 62.5% of unchanged amide, a little diphenyl, and much tar; di-p-toluenesulphimide in toluene gives 63% of unchanged imide, a little diphenyl, and a small amount of a substance, m. p. 165°, whilst 88.8% of unchanged benzenesulphin-anilide was recovered from its reaction in ether. Benzenesulphendiethylamide (Lecher and Holschneider, A., 1924, i, 728) in toluene at 70°, however, yields phenyl sulphide (69.4% yield calculated on the reacting sulphide) and diethylamine, 45.5% of the amide being recovered unchanged. J. W. BAKER.

Conjugated systems. I. Chlorination of phenylbutadiene. I. E. MUSKAT and K. A. HUGGINS (J. Amer. Chem. Soc., 1929, 51, 2496-2503). -Treatment of  $\alpha$ -phenylbutadiene with chlorine (1 mol.) in various solvents and at  $-80^{\circ}$  to  $150^{\circ}$ affords in all cases the  $\gamma\delta$ -dichloride (I), b. p.  $125^{\circ}/3$ mm. (ozonolysis product benzaldehyde). Treatment of I with aqueous potassium hydroxide at 90° yields δ-chloro-α-phenylbutadiene (II), b. p. 115.5°/3.5 mm., m. p. 53°, obtained also when I is boiled for several hours. The action of silver oxide and water on I gives  $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoic acid, formed by oxid-ation of the corresponding intermediate aldehyde. Further chlorination of I in chloroform solution yields a mixture of stereoisomeric aByd-tetrachloro-a-phenylbutanes, b. p. 155-166°/7 mm., which on treatment with zinc dust (1 mol.) at the water-bath temperature furnishes I, and with 2 mols. gives  $\alpha$ -phenylbutadiene. Treatment of II with chlorine (1 mol.) affords γδδ-trichloro- $\alpha$ -phenyl- $\Delta^{\alpha}$ -butene, b. p. 140°/5 mm. (ozonolysis product benzaldehyde), chlorinated further to αβγδδ-pentachloro-α-phenylbutane, b. p. 162°/5 mm. Straus' results (A., 1909, i, 638) on the bromination of a-phenylbutadiene are confirmed. H. BURTON.

Reactions and space formula of diphenyl. E. E. TURNER (Rec. trav. chim., 1929, 48, 821– 825).—The theory of substitution in the diphenyl molecule is discussed. The different significance of physical and chemical experiments regarding the space formula of diphenyl is stressed.

H. BURTON.

Directive effects in the diphenyl and fluorene series. C. RUIZ (Anal. Asoc. Quím. Argentina, 1928, 16, 187-196; cf. this vol., 1063).—The course of substitution in diphenyl and fluorene compounds is discussed from the point of view of Holleman's theory. In either series substitution takes place according to the usual rules in the less stable nucleus, containing an activating (o, p-directing) group. Under vigorous conditions the formation of a quinonoid conjugated system allows substitution in the second nucleus. Further support is given to the conception of fluorene as a 2 : 2'-substituted diphenyl. R. K. CALLOW.

Dicymyl [s-pp'-ditolyltetramethylethane]. E. BOEDTKER and R. KERLOV.—See this vol., 1071.

Phenylindenes. Extension of Wolff's reaction to the direct preparation of a hydrindene from the corresponding ketone. C. MOUREU, C. DUFRAISSE, and P. GAGNON (Compt. rend., 1929, 189, 217—218). —By the reduction of  $\gamma\gamma$ -diphenyl- $\alpha$ -hydrindonephenylhydrazone (or semicarbazone) with alcoholic sodium ethoxide in a sealed tube at 200° (cf. Wolff, A., 1912, i, 988) a good yield of  $\gamma\gamma$ -diphenylhydrindene is obtained. Best results are obtained by forming the sodium ethoxide *in situ*, the alcohol being introduced in a small separate tube and thus kept out of contact with the sodium until after the reaction tube is sealed. J. W. BAKER.

Synthesis of meso-alkyl and meso-aryl anthracene derivatives. VI. E. DE.B. BARNETT and N. F. GOODWAY (J.C.S., 1929, 1754-1761).--9-Benzhydrylanthrone reacts with the appropriate Grignard reagent to yield 10-benzhydryl-9-methyl-, m. p. 216°, 10-benzhydryl-9-benzyl-, m. p. 181°, and 9-phenyl-10-benzhydryl-, m. p. 222°, -9:10-dihydroanthranol-9. These are converted by heating with acetic acid containing hydrochloric acid into 10-benzhydryl-9-methyl- and 10-benzhydryl-9-benzyl-, m. p. 236°, -anthracenes: the phenyl derivative, however, could not, be purified. 2-Methyl-9-anthrone (I), m. p. 103° (Limpricht, A., 1901, i, 145, gives m. p. 100°), generally gives only resinous products with the Grignard reagent, but a poor yield of 2:9-dimethyl-anthracene (II), m. p. 85°, and a good yield of 9-benzyl-2-methylanthracene (III), m. p. 139°, are similarly obtained. Treatment of II with bromine in carbon disulphide converts it into 9-bromomethyl-2-methylanthracene, m. p. 150° (decomp.), which is readily converted into the corresponding 9-piperidinomethyl-, m. p. 128°, and 9-anilinomethyl-, m. p. 159° (164° on remelting), derivatives, and by further action of bromine gives 10-bromo-9-bromomethyl-2-methylanthracene, m. p. 190°, which also yields the corresponding 9-piperidinomethyl-, m. p. 167°, and 9-anilinomethyl-, m. p. 144°, derivatives. Similar bromination of III yields 10-bromo-9-benzyl-2-methylanthracene, m. p. 164°. By the pyridine-acetic anhydride method I is converted into 2-methyl-9-anthranyl acetate, m. p. 143°, and by methylation with methyl p-toluenesulphonate into 2-methyl-9-anthranyl methyl ether, m. p. 77°. Reduction of 2-methylanthraquinone either by tin and hydrochloric acid (Padova, A., 1909, 1, 655) or aluminium powder and concentrated sulphuric acid (G.P. 201,542) yields a mixture from which, after acetylation, 3-methyl-9-anthranyl acetate, m. p. 139°, may be separated by fractional crystallisation, and is hydrolysed to 3-methyl-9-anthrone, m. p. 101°. By reactions similar to those above this is converted into 3:9-dimethylanthracene, m. p. 85° [9-bromo-derivative (not pure), m. p. 145° (decomp.)]; 10-bromo-9-bromomethyl-3-methylanthracene, m. p. 186° (9-piperidinomethyl derivative, m. p. 140°); 9-benzyl-3-methylanthracene, m. p. 101° (10-bromoderivative, m. p. 139°). J. W. BAKER.

Sulphonation of phenanthrene. I. New monosulphonate. II. Disulphonation. L. F. FIESER (J. Amer. Chem. Soc., 1929, 51, 2460-2470, 2471-2486).-I. Sulphonation of phenanthrene with sulphuric acid (2 mols.) at 120-125° for 3 hrs. (cf. Werner and others, A., 1902, i, 437; Sandqvist, A., 1912, i, 843) gives optimum yields of phenanthrene-2-sulphonic acid (I) [25%; p-toluidine salt, m. p. 291° (corr.)], and -3-sulphonic acid (II) [27%; p-toluidine salt, m. p. 222° (corr.)]. Separation of I and II is best effected by conversion first into the mixed sodium salts, removal of I as the insoluble barium salt, and purification of II through the barium and potassium salts. The corresponding hydroxyphenanthrenes are readily obtained by fusion of the barium salts with potassium hydroxide at 290-325°. When sulphonation is carried out at 60° during 3 days, I (18%), II (18%), the 9-sulphonic acid (III) [13%; p-toluidine salt, m. p. 235° (corr.)], and phenanthrene-1-sulphonic acid (IV) [8%; p-toluidine salt, m. p. 267° (corr.); potassium (V), barium, and ferrous salts; methyl ester, m. p. 102°] are obtained; these are separable by a process similar to that for I and II. The non-isolation of III and IV during sulphonation at 120° is probably because of their further sulphonation. Acetylation of the product obtained by alkali fusion of a residue from the sulphonation at 60° affords the acetate (VI), m. p. 135-136°, of 1-hydroxyphenanthrene (VII), m. p. 157° (corr.) [9:10-quinone, m. p. 227° (corr.)]. Oxidation of V and VI with chromic oxide in acetic acid solution gives potassium phenanthrene-9: 10-quinone-1-sulphonate and 1-acetoxyphenanthrene-9: 10-quinone, m. p. 201°, respectively. When VII is coupled with diazotised sulphanilic acid and the reaction product reduced with sodium hyposulphite 4-amino-1-hydroxyphenanthrene (hydrochloride; triacetyl derivative, m. p. 143°) results. Oxidation of this with chromic oxide and dilute sulphuric acid gives phenanthrene-1: 4-quinone, m. p. 155° (corr.), converted by treatment with zinc dust in presence of acetic anhydride and sodium acetate into 1:4-diacetoxyphenanthrene, m. p. 137-138°. Oxidation of this with chromic oxide in acetic acid solution at 40° affords 1:4-diacetoxyphenanthrene-9: 10-quinone, m. p. 184° (corr.).

II. Treatment of potassium phenanthrene-3-sulphonate with sulphuric acid at  $125-130^{\circ}$ , subsequent neutralisation of the reaction mixture with potassium hydroxide solution, and fusion of the dry, mixed potassium salts obtained with potassium hydroxide at  $280-305^{\circ}$  affords a mixture of dihydroxyphenanthrenes. Acetylation of this mixture followed by fractional crystallisation gives 3:6-, m. p.  $124\cdot5^{\circ}$ (59%), 3:8-, m. p.  $186^{\circ}$  (corr.; 0.9%), and 2:6-diacetoxyphenanthrenes, m. p.  $122-123^{\circ}$  (10%). Similarly, potassium phenanthrene-2-sulphonate yields  $2:6 \cdot (54\%)$ , 2:7-, m. p.  $183\cdot5^{\circ}$  (corr.;  $2\cdot1\%$ ), and 2:8diacetoxyphenanthrenes, m. p.  $125^{\circ}$  (1%). In both cases substitution occurs in the 6-, 7-, and 8-positions. The following dihydroxyphenanthrenes, obtained by hydrolysis of the diacetates with alcoholic sodium hydroxide, are described : 2:6-, m. p. 239° (corr.; dimethyl ether, m. p. 87°); 2:7-, m. p. 265° (corr.; dimethyl ether, m. p. 167-168°); 2:8-, m. p. 205° (corr.); 3:6-, m. p. 225° (corr.; dimethyl ether, m. p. 105°); 3:8-, m. p. 253° (corr.; dimethyl ether, m. p. 117°). Oxidation of the diacetoxyphenanthrenes with chromic acid in acetic acid solution yields 2:6-, m. p. 220-221° (corr.); 2:7-, m. p. 244° (corr.); 2:8-, m. p. 223-224° (corr.); 3:6-, m. p. 232° (corr.), and 3: S-diacetoxyphenanthrene-9: 10-quinones, m. p. 221-222° (corr.). 2:6- and 3:6-Dihydroxyphenanthrene-9: 10-quinones are also described. Oxidation of 3: 6-dimethoxyphenanthrene-9: 10-quinone, m. p. 241° (corr.), with hydrogen peroxide in acetic acid solution at 60-90° affords a mixture of 5:5'-dimethoxydiphenic acid, m. p. 234° (corr.; obtained also from diazotised 2-amino-4-methoxybenzoic acid and cuprous hydroxide), and the lactone, m. p. 194° (corr.), of 2-hydroxy-5:5'-dimethoxydiphenyl-2'-carboxylic acid. Methylation of the lactone with methyl sulphate in alkaline solution gives 2:5:5'-trimethoxydiphenyl-2'-carboxylic acid, m. p. 147-148°, converted by treatment with cold sulphuric acid into 1:4:6-trimethoxyfluorenone, m. p. 157°. Treatment of the above diphenic acid with sulphuric acid at 50° yields 1 : 6-dimethoxyfluorenone-4-carboxylic acid, m. p. 303° (corr.), with elimination of carbon dioxide [amide, m. p. 268° (corr.)]. Application of Dimroth's boroacetic anhydride test (A., 1926, 297) to a series of mono-, di-, and tri-hydroxyanthrene-9: 10-quinones confirms the observation that a colour change is usually given only when a hydroxyl group is in the 1(8)-position. The 3:4-dihydroxy-derivative gives a colour change probably because of the formation of the C O = B O Ac grouping. Attempts to isolate the disulphonic acids formed during the monosulphonation of phenanthrene (this vol., 1171) failed. No 4- or 5-substituted derivative has been isolated during the investigations. H. BURTON.

Phenylallylthiocarbamide as a solvent. V. P. SCHISCHOKIN (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 195—224).—Phenylallylthiocarbamide forms compounds with chloroform, paraldehyde, trichloroacetic acid, and acetic anhydride, and probably with acetic acid, dibromobenzene, nitrobenzene, ethyl alcohol, methyl alcohol, allylthiocarbimide, benzene, toluene, and naphthalene, but not with aniline, o-nitroaniline, or diphenylamine. The heat of fusion of phenylallylthiocarbamide is computed to be 6400— 6960 g.-cal. per mol. The internal pressure of phenylallylthiocarbamide must be near to that of aniline, and of allylthiocarbimide to that of nitrobenzene.

### CHEMICAL ABSTRACTS.

Derivatives of 1:1'-dinaphthyl. A. CORBEL-LINI and E. DEBENEDETTI (Gazzetta, 1929, 59, 391-399).—Both the 2:2'- and 1:1'-positions have been assigned to the linking in di- $\alpha$ -naphthol (cf. Willstätter and Schuler, A., 1928, 408; Goldschmidt and Wessbecher, *ibid.*, 409; Zinke and Schöpfer, A., 1924, i, 1081). Further evidence has now been obtained for the latter view. When naphthidine is diazotised in suspension in dilute sulphuric acid and the solution decomposed by heating after the addition of carb. amide, a product is obtained which cannot be purified but yields when methylated with methyl sulphate 4:4'-dimethoxy-1:1'-dinaphthyl, m. p. 252°, identical with the methylation product of di-anaphthol obtained by other methods. By Sandmeyer's reaction 4:4'-dichloro-1:1'-dinaphthol, m. p. 215.5-216°, and 4:4'-dibromo-1:1'-dinaphthyl, m. p. 217.5° (lit. 215°), are obtained from naphthidine. The formation of naphthacarbazole by the action of acid on the diamino-compound in the preparation of 2: 2'-diamino-1: 1'-dinaphthyl from  $\beta\beta$ -azonaphthol is confirmed. By a Sandmeyer reaction 2:2'-diamino-1: 1'-dinaphthyl yields 2: 2'-dichloro-1: 1'-dinaphthyl, m. p. 151-152°. Decomposition of the diazonium sulphate yields a substance, m. p. about 250-252°, of acid properties, and not the expected dinaphthol. R. K. CALLOW.

Derivatives of 2:5-dibromonitrobenzene. L. C. RAIFORD and B. C. BREN (J. Amer. Chem. Soc., 1929, 51, 2539-2541).-Reduction of 2:5:2':5'tetrabromoazobenzene, m. p. 247° (corresponding azozyderivative, m. p. 217°), with stannous chloride and hydrochloric acid gives a 42% yield of 2: 5-dibromoaniline (I). The diazonium chloride (II), decomp. explosively above 117°, from I is reduced by stannous chloride and alcoholic hydrochloric acid to I, and when boiled with water does not yield a phenol. β-Naphthol and II yield a dye, C<sub>16</sub>H<sub>10</sub>ON<sub>2</sub>Br<sub>2</sub>, whilst with aniline the corresponding diazoaminobenzene, m. p. 185°, results. Rearrangement of this into the aminoazo-derivative is not possible. 4-Bromo-2-nitroanisole gives on alkaline reduction 5:5'-dibromo-2: 2'-dimethoxy-azoxy- and -azo-benzenes, m. p. 121° and 238°, respectively. 5:5' Dibromo-2:2' dimethoxyhydrazobenzene, m. p. 120-121°, is converted by the usual method into 5:5'-dibromo-2:2'-dimethoxybenzidine, m. p. 168° (dibenzoyl derivative, m. p. 274°; dye from  $\beta$ -naphthol). 5:5'-Dibromo-2:2'-diethoxyhydrazobenzene has m. p. 171-172°. H. BURTON.

Formation of mixed azo-derivatives corresponding with alkylacetylacetones. G. FAVREL (Compt. rend., 1929, 189, 335-337).-The interaction of diazonium hydroxides and alkylacetylacetones under slightly modified conditions yields mixed azocompounds which are the intermediate stages in the formation of monophenylhydrazones of  $\alpha$ -diketones (A., 1901, i, 167). *p*-Chloroaniline is diazotised in hydrochloric acid and the solution treated with excess of sodium acetate and with precipitated calcium carbonate until only half an equivalent of acetic acid remains free. y-Ethylacetylacetone in ethereal solution is then added.  $\gamma$ -p-Chlorobenzeneazo- $\gamma$ -ethylacetyl-acetone, m. p. 34—35°, separates. The p-bromo-compound, m. p. 73—74°, p-nitro-compound, m. p. 76°, and  $\gamma$ -p-nilrobenzeneazo- $\gamma$ -methylacetylacetone, m. p. 79°, are obtained similarly. When the azo-compounds are reduced, the aniline is obtained, and when warmed with water, acetic acid and the monophenylhydrazone of the diketone are formed. R. K. CALLOW.

Addition reactions of azodicarboxylic esters. R. STOLLÉ and W. REICHERT (J. pr. Chem., 1929,

[ii], 123, 74-81; cf. A., 1924, i, 1002; 1925, i, 1469). -p-Cymene and methyl azodicarboxylate condense in the presence of concentrated sulphuric acid or of dry hydrogen chloride and a trace of iodine to yield methyl 2: 5-dihydrazino-p-cymene-NN'N''N''-tetracarboxylate, m. p. 220°, reduced by acetic and hydriodic acids to 2:5-diamino-p-cymene; ethyl azodicarboxylate similarly affords the corresponding ethyl ester, m. p. 192°. Phenetole and methyl or ethyl azodicarboxylate furnish methyl and ethyl p-hydrazino-phenetole-NN'-dicarboxylate, m. p. 135° and 81°, respectively, reduced by acetic and hydriodic acids to p-aminophenol; anisole yields methyl p-hydrazino-anisole-NN'-dicarboxylate, m. p. 99°. Indene condenses with methyl or ethyl azodicarboxylate in the presence of dry hydrogen chloride; the condensing agent also reacts with the indene, affording derivatives of 1-chlorohydrindene, which, since addition of azodicarboxylic esters to saturated compounds has not yet been observed, are considered to be methyl and ethyl 1-chloro-6- or -7-hydrazinohydrindene-NN'-dicarboxylate, m. p. 138° and 111°, respectively. Tetrahydronaphthalene condenses with methyl or ethyl azodicarboxylate when heated in a sealed tube, giving products which, by analogy with those obtained from toluene and bromobenzene (A., 1924, i, 881), are formulated as methyl and ethyl 3-hydrazino-5:6:7:8tetrahydronaphthalene-NN'-dicarboxylate, m. p. 136° and 106°, respectively. C. W. SHOPPEE.

Thermal decomposition of azodibenzoyl and methyl azodicarboxylate. R. STOLLÉ and W. REICHERT (J. pr. Chem., 1929, [ii], **123**, 82—84; cf. A., 1912, i, 225).—The thermal decomposition of azodibenzoyl in high-boiling media such as deca- and tetra-hydronaphthalene and naphthalene has been investigated; 50% of the theoretical amount of nitrogen is evolved, with the production of diphenylfurodiazole and benzoic anhydride. The formation of these products is considered to be due to the intermediate production of "tetrabenzoylhydrazine," CPhBz:N·N:CPhBz, which has been shown by Stollé and Benrath (A., 1904, i, 935) to yield them by thermal decomposition. A scheme to explain the formation of di- and tri-benzoylhydrazine, which have been found in small quantity by Stollé and Benrath (*loc. cit.*), by the action of water, is suggested.

Methyl azodicarboxylate is more stable than azodibenzoyl, and exhibits no decomposition when heated in decahydronaphthalene  $(188^{\circ})$ ; in tetrahydronaphthalene no decomposition occurs, but addition of the ester to the medium affords a compound of m. p. 136° (cf. preceding abstract). When heated in naphthalene  $(218^{\circ})$  for a long period, methyl azodicarboxylate evolves 65—70% of its nitrogen, giving, as the main decomposition products, carbon monoxide, and methyl carbonate and oxalate. C. W. SHOPPEE.

Amino-oxidation. XII. Hydrazyls.  $\beta$ -Benzoyl- $\alpha\alpha$ -diarylhydrazyls. S. GOLDSCHMIDT and J. BADER (Annalen, 1929, 473, 137—162).—Treatment of benzoylazo-*p*-bromobenzene with copper chloride in alcoholic solution affords benzoic acid, *p*-chlorobromobenzene, and  $\beta$ -benzoyl- $\alpha\alpha$ -di-p-bromophenylhydrazine, m. p. 235°, formed also by the action of copper acetate on  $\beta$ -benzoyl-*p*-bromophenylhydrazine in boiling alcoholie solution. Similar treatment of  $\beta$ -benzoyl-p-anisylhydrazine, m. p. 139—140°, gives  $\beta$ -benzoyl- $\alpha\alpha$ -di-p-anisylhydrazine, m. p. 228°.  $\beta$ -Benzoyl- $\alpha\alpha$ -di-p-anisylhydrazine has m. p. 276°.  $\beta$ -Benzoyl- $\alpha\alpha$ -diphenylhydrazine is obtained by the action of copper acetate on benzoylphenylhydrazine in alcoholic solution; in presence of benzenediazonium chloride or phenylhydrazine hydrochloride the yield is improved. The mechanism of the formation of  $\beta$ -benzoyl- $\alpha\alpha$ -diarylhydrazines from benzoylarylhydrazines is: NHR·NHBz Caulton NR:NBz H<sub>0</sub>O Bz·OH+NR:NH <sup>oxidation</sup> [NR:N|X <sup>NHR-NHBz</sup>

 $NR:N\cdot NR\cdot NHBz \longrightarrow N_2 + NR_2 \cdot NHBz$  (cf. Tafel. A., 1892, i, 710; Gattermann, ibid., 843). Mixed  $\beta$ -benzoyldiarylhydrazines are prepared by the action of copper acetate on an alcoholic solution of a benzoylarylhydrazine and arylhydrazine hydrochloride. Using phenylhydrazine hydrochloride and the appropriate β-benzoylarylhydrazine the following were prepared : β-benzoyl-a-phenyl-a-p-bromophenyl-, m. p. 198—199°; β-benzoyl-α-phenyl-α-p-anisyl- (readily oxidised in solution);  $\beta$ -benzoyl- $\alpha$ -phenyl- $\alpha$ -p-tolyl-, m. p. 171–172°, and  $\beta$ -benzoyl- $\alpha$ -phenyl- $\alpha$ -p-nitro-phenyl-hydrazines, m. p. 172–173°. Oxidation of the above diarylhydrazines with potassium ferricyanide in presence of alcoholic sodium methoxide or occasionally with lead dioxide affords solutions of the corresponding tetrazans, which after purification are used to determine the equilibrium tetrazan-hydrazyl. At  $-80^{\circ}$  to  $-50^{\circ}$  the equilibrium point is reached much more slowly than at  $-18^{\circ}$ . The equilibrium constant is smallest for the di-p-nitrophenyl derivative, and increases in the following order : di-p-nitrophenyl, phenyl-p-nitrophenyl, di-p-bromophenyl, phenyl-pbromophenyl, diphenyl, phenyl-p-tolyl, di-p-tolyl, phenyl-p-anisyl, di-p-anisyl (wholly dissociated in acetone). The introduction of positive groups in the para positions causes an increase in the dissociation; negative groups cause a decrease. The heat of dissociation of the tetrazan N·N linking varies from 5500 to 10,500 g.-cal. for dibenzoyltetraphenyltetrazan in chloroform or toluene. For the series studied the values vary from 5200 to 18,100 g.-cal. (extreme limits), and an increased degree of dissociation corresponds with a decrease in the heat of dissociation.

#### H. BURTON.

Vapour-phase hydrolysis of chloro- and bromobenzene. L. CHALKLEY, jun. (J. Amer. Chem. Soc., 1929, 51, 2489-2495).—When chloro- or bromobenzene vapour mixed with steam is passed over silica gel at 500-600° under ordinary pressure varying amounts of phenol, hydrogen chloride, and diphenyl ether are produced. The amount of hydrolysis increases with decrease in the rate of flow of the reaction mixture. Poisoning of the catalyst occurs, but reactivation takes place when it is heated in air or oxygen. Other catalysts are titanium, zirconium, aluminium, thorium, and tungsten (blue) oxides. Kaolin has practically no action. Silica gel and titanium oxide are the most active catalysts used.

H. BURTON. Trichloro- and higher chloro-phenols and their electrical conductivity in water. G. J. TIESSENS

(Rec. trav. chim., 1929, 48, 1066-1068).-2:3:6-Trichlorophenol, m. p. 58°, is obtained in about 15% yield when the corresponding diazonium salt is decomposed with a boiling solution of copper and sodium sulphates. The relative conductivities  $(k \times 10^{10})$  of dilute aqueous solutions of the various chlorophenols used, at 25°, are: 2:4-dichloro-, 310; 2:3:4-trichloro-, m. p. 83.5°, 252; 3:4:5-trichloro-, m. p. 101°, 45; 2:3:6-trichloro-, 7360; 2:3:5-trichloro-, m. p. 62°, 500; 2:4:5-trichloro-, m. p. 68°, 430; 2:4:6-trichloro-, m. p. 69°, 3900; 2:3:4:5-tetrachloro-, m. p. 116°, 1100; 2:3:4:6tetrachloro-, m. p. 70°, 42,000; 2:3:5:6-tetrachloro-, m. p. 115°, 33,000; pentachloro-, m. p. 144°, 55,000. The presence of chlorine atoms in the two ortho positions causes a marked increase in the acidity. The conversion of an amine into a phenol does not appear to depend on the basicity of the amine. Many of the above chlorophenols are new and details of their preparation are to be published later.

H. BURTON. Synthesis in diphenyl ether series. I. Simple derivatives. C. M. SUTER (J. Amer. Chem. Soc., 1929, 51, 2581-2585).-Nitration of diphenyl ether with a mixture of nitric  $(d \ 1.52)$  and acetic acids in acetic anhydride solution at 25-30° gives an 86% yield of a mixture of the 2- and 4-nitro-derivatives. Separation of the 4-nitro-derivative by keeping the mixture at 0° is incomplete, but when the remaining mixture is reduced by zinc and calcium chloride in aqueous-alcoholic solution the resulting amines are readily separated owing to the insolubility of the 4-amino-sulphate in water. The original mixture of ·nitro-compounds contains 54% of the 4-derivative. 2-Acetamidodiphenyl ether has m. p. 81.° Bromination of 4-nitrodiphenyl ether in carbon tetrachloride solution affords the 4'-bromo-derivative, reduced by iron powder and alcoholic hydrochloric acid to 4-bromo-4'-aminodiphenyl ether, m. p. 109° (cf. Le Fèvre, Saunders, and Turner, A., 1927, 660) [acetyl derivative, m. p. 162-163° (corr.), obtained also by bromination of 4-acetamidodiphenyl ether]. Bromination of diphenyl ether in carbon tetrachloride solution with an equimolecular quantity of bromine gives 47% of the 4-bromo-derivative, together with unchanged material, dibromo- and polybromo-(traces) compounds. 2-Cyano-, b. p. 188° (corr.)/14 mm., and 4-cyano-diphenyl ethers, b. p. 187-188° (corr.)/14 mm., m. p. 47°, are hydrolysed to the corresponding carboxylic acids. H. BURTON.

Influence of structure on the breaking by heat of the carbon-oxygen linking in certain ethers. R.C. YOUNG (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 60—64).—By the action of ether on the molecular compound of triphenylmethyl chloride and aluminium chloride an 80-90% yield of triphenylmethane is obtained : CPh<sub>3</sub>Cl+Et<sub>2</sub>O  $\longrightarrow$  EtCl+CPh<sub>3</sub>·OEt  $\longrightarrow$ CHPh<sub>3</sub>+Me·CHO, since the intermediate triphenylmethyl ethyl cther reacts with aluminium chloride in ether solution to yield triphenylmethane and in carbon disulphide to yield triphenylmethyl chloride. The latter reaction is proved to be represented by 2CPh<sub>3</sub>·OEt + 2AlCl<sub>3</sub>  $\longrightarrow$  CPh<sub>3</sub>Cl + CPh<sub>3</sub>Cl,AlCl<sub>3</sub> + Al(OEt)<sub>2</sub>Cl, decomposition of the product with ice

giving a quantitative yield of triphenylmethyl chloride. Similarly, the action of ether on the molecular compound of dichlorodiphenylmethane and aluminium chloride gives an 80% yield of benzophenone. By the action of the sodium derivatives of various alcohols on triphenylmethyl chloride a series of triphenylmethyl ethers has been prepared and their relative thermal stabilities have been compared, the temperatures of decomposition into triphenylmethane and an aldehyde or ketone being as follows : triphenylmethyl methyl ether, m. p. 81-81.8°, 262°; ethyl, m. p. 80·3—81·1°, 242°; n-propyl, m. p. 103·0– 104·0°, 230°; isopropyl, m. p. 112·1—113·1°, 220°; n-butyl, 239°; sec.-butyl, 216°; isobutyl, 228°; isoamyl, 237°; benzyl, 226°; β-phenylethyl, m. p. 87·1-87·8°, 236°. The corresponding velocity coefficients for the reaction between the corresponding alcohol and p-nitrobenzoyl chloride are, respectively, 0.184, 0.085, 0.066, 0.074, 0.010, 0.0074, 0.031, 0.073, 0.017, and 0.040. Thus, in general, the greater is the reaction velocity the greater is the stability of the corresponding triphenylmethyl ether. Substitution of a methyl group in the p-position of the phenyl radicals decreases the thermal stability of the ether, tritolylmethyl ethyl ether decomposing at 224°. The lowering in the m. p. of these ethers caused by heating at 193° and 215° for 1 hr. is smaller the greater is the stability of the ether. Catalysts such as ferric chloride or aluminium oxide lower the decomposition temperature considerably. Interaction of sodium acetate or benzoate with triphenylmethyl chloride in acetic anhydride yields the corresponding acetate or benzoate, both of which are decomposed with ferric chloride to yield triphenylcarbinol. Thermal decomposition of the acetate (228°) yields triphenylmethylcarbinol, triphenyl-J. W. BAKER. methane, and acetic acid.

Ketones and acids containing the alkoxy-group. S. SABETAY (Bull. Soc. chim., 1929, [iv], 45, 534-540). -Improved yields of tetrahydro-β-naphthoxyacetone, b. p. 154-155°/5 mm., m. p. 37.5° (semicarbazone, m. p. 172°), are obtained from chloroacetone and artetrahydro-β-naphthol in presence of porphyrised copper and 1 mol. of potassium hydroxide (cf. Thoms and Kross, A., 1927, 659). p-tert.-Butylphenoxy-acetone, b. p. 131°/5 mm., n<sup>19</sup><sub>D</sub> 1.5085 (semicarbazone, m. p. 164°), from p-tert.-butylphenol, m. p. 96°, and p-tolyl phenoxymethyl ketone, m. p. 73°, b. p. 181-184°/4 mm., are readily obtained by the same method, but sodium  $\beta$ -phenylethoxide does not condense with chloroacetone in this way or in presence of xylene or with the chloroacetal, CMe(OEt), CH,Cl. β-Phenylethoxyacetone, b. p.  $120^{\circ}/5$  mm.,  $n_{\rm D}^{23}$  1.5035,  $d^{23}$  1.028, is obtained from magnesium methyl iodide and methyl β-phenylethoxyacetate, b. p. 133°/6 mm., n<sup>19</sup> 1.5025,  $d^{19}$  1.085, prepared by converting  $\beta$ -phenylethyl chloroformate (A., 1928, 1130) into β-phenylethoxyacetonitrile, b. p. 125-126°/5 mm., np 1.5105, d. 1.046, and hydrolysing with hydrogen chloride in cold absolute methyl alcohol. B-Phenylethoxyacetic acid has m. p. 45-46°, b. p. 171°/6 mm., nº 1.5211. n-Octyloxyacetonitrile, b. p. 106°/5 mm., n<sup>17</sup><sub>D</sub> 1.4308, d<sup>17</sup> 0.8767, n-octyloxyacetic acid, m. p. 17°, b. p. 155–156°/7 mm.,  $n_{1}^{13}$  1.4433,  $d^{13}$  0.9627 (isobutyl ester, b. p. 140°/5 mm.,  $n_{\rm p}^{19}$  1.4312), and n-octyloxyacetone, b. p. 106°/6 mm.,  $n_{\rm p}^{13}$  1·4325,  $d^{13}$  0·8791, are similarly obtained from n-octyl chloroformate, b. p. 84—85°/5 mm.,  $n_{\rm p}^{18}$  1·4418. R. BRIGHTMAN.

Oxidation of m-xylorcinol. J. F. WALKER (Abst. Theses Mass. Inst. Tech., 1929, No. 4, 58—60).— Oxidation of m-xylorcinol (I) (4:6-dihydroxy-mxylene) with ferric chloride effects combination of two nuclei in the 5-position to yield first crystalline dimetaxylorcinol (II) (2:6:2':6'-tetrahydroxy-3:5:3':5'-tetramethyldiphenyl), m. p. 242—243° (slight decomp.) (tetra-acetate, m. p. 158°), which is converted by bromine in chloroform into a substance,  $C_{16}H_{16}O_2Br_2$ , m. p. 244—247° (decomp.). Further oxidation of I converts it into a green precipitate, possibly the diphenylyl ether,

 $[C_6HMe_2(OH)_2\cdot C_6Me_2(OH)_2]_2O$ , charring above 250°. Bromination of I in chloroform solution converts it into the 5(?)-bromo-derivative, m. p. 119—120°, which readily loses hydrogen bromide when gently heated with a trace of sulphuric acid, forming a brilliant red melt, and is oxidised by ferric chloride in aqueous solution to give first a violet coloration and then a white precipitate from which a crystalline substance, charring above 265°, is isolated.

J. W. BAKER.  $\beta$ -2:4:5-Trimethoxyphenylethylamine. M. JANSEN (Chem. Weekblad, 1929, 26, 421-422).---This compound, isomeric with mescaline, the 3:4:5derivative, which has powerful physiological properties, has been prepared by condensing nitromethane and 2:4:5-trimethoxybenzaldehyde, and reducing the nitrostyrene. Its chemical behaviour is similar to that of mescaline. S. I. LEVY.

Formation of rubrene from compounds not containing chlorine. J. ROBIN (Compt. rend., 1929, 189, 337—339).—Rubrene cannot be obtained from diphenylphenylacetylenylcarbinol by the action of heat alone or with dehydrating agents. When it is obtained by heating the carbinol in presence of hydrochloric acid, or the hydrochloride of the corresponding amine, the chloride is a possible intermediate stage. However, when the acetate, propionate, butyrate, or benzoate of the carbinol is heated, rubrene is obtained in successively less violent decompositions and in decreasing yield, accompanied by increasing amounts of a yellow hydrocarbon, m. p. 245°. The methyl or ethyl ether of the carbinol also yields rubrene when heated under carefully controlled conditions. The action of alcohol on the compound  $C_{42}H_{29}Cl$  (Moureu, Dufraisse, and Robin, this vol., 922) yields a chlorine-free compound, m. p. 214—215°, which yields rubrene when heated. R. K. CALLOW.

Production of pinacols in the reaction between a carboxylic ester and a Grignard reagent. H. H. HATT (J.C.S., 1929, 1623—1632).—Attempts have been made to improve the small yields of benzpinacol previously obtained (A., 1927, 558) by interaction of methyl benzoate and magnesium phenyl bromide, by using larger quantities of magnesium and magnesium iodide. The production of pinacols in reactions of the foregoing type is assumed to be due to the reduction of the corresponding ketone, formed as an intermediate, by magnesium and magnesium iodide through the metal ketyl, RR'CO... Mg, or the

halogenomagnesium pinacolate, [OMgI·CRR'·], (I) (cf. Gomberg and Bachmann, A., 1927, 245); when the above reaction was conducted in the presence of sufficient magnesium and magnesium iodide to give a theoretical yield of I (R and R'=Ph), no benzpinacol could be isolated. Similarly, the yield of the pinacol obtained from ethyl o-chlorobenzoatc and magnesium phenyl bromide fell from 27 to 5%. Experiments indicated the primary production of I, which might immediately be converted into II (cf. Schlenk, A., 1914, i, 396):  $2RR' \cdot C \cdot OMgI \xrightarrow{Mg}_{MgI_{*}} 2RR' C (MgI) \cdot OMgI$ (II); no evidence of the formation of II (R and R'=Ph) was obtained when benzophenone was shaken for long periods with excess of magnesium and magnesium iodide in ether-benzene solution. An ethereal solution of I (R and R'=Ph) showed no special reactivity toward methyl benzoate, magnesium phenyl bromide, or bromobenzene in the presence of magnesium and magnesium iodide. The optimum quantity of magnesium iodide is about 10% of theory, affording in the case of ethyl o-toluate and magnesium phenyl bromide a 45% yield of the corresponding pinacol. The effect of substituents in the benzene nuclei of the ester and of the Grignard reagent on the yield of pinacol has been studied under standard conditions. o-Substituted esters favour the production of pinacols; no pinacol is formed, however, if both ester and Grignard reagent contain o-substituents, although ethyl o-toluate and magnesium o-tolyl bromide in the absence of magnesium give a 66% yield of di-o-tolyl ketone, m. p. 70.5°, which reacts in ether-benzene solution with magnesium and magnesium iodide to form the iodomagnesium pinacolate, hydrolysis of which yields 25% of di-o-tolylcarbinol.

Ethyl a-naphthoate and magnesium phenyl bromide afford diphenyl- $\alpha$ -naphthylcarbinol (22%) and diphenyldi- $\alpha$ -naphthylpinacol, m. p. 199°; the latter appears to be the second form, m. p. 200°, described by Bachmann and Shankland (this vol., 316; cf. Cohen and Montagne, A., 1919, i, 210). Methyl o-anisate and magnesium phenyl bromide furnish a 52% yield of diphenyl-o-anisylcarbinol as the sole product. Ethyl o-bromobenzoate and magnesium phenyl bromideafford a 5% yield of o-bromotriphenylcarbinol. isolated as o-bromotriphenylchloromethane, and 9% of s-2: 2'-dibromobenzpinacol, m. p. 166° (cf. Koopal, A., 1915, i, 693); in another experiment both the pinacol and o-bromotriphenylcarbinol were isolated, together with o-bromotriphenylmethane. Ethyl o-chlorobenzoate and magnesium phenyl bromide yield 27% of s-2: 2'-dichlorobenzpinacol, a-form (III), m. p. 164° (decomp.), affording by rearrangement o-chlorophenyl 2:2':2''-trichlorotriphenylmethyl ketone, m. p. 139.5-140.5° [β-form (IV), m. p. 181°; cf. Koopal, loc. cit.], and 31% of o-chlorotriphenylcarbinol; treatment of III with hot alcoholic potassium hydroxide followed by reduction with zinc in the same medium gave o-chlorodiphenylcarbinol. Ethyl o-toluate and magnesium p-tolyl bromide afforded a 52% yield of di-p-tolyldi-o-tolylpinacol, m. p. 174° (decomp.), reduced by zinc and alcoholic potassium hydroxide to p-tolyl-o-tolylcarbinol, m. p. 61-61.5°, and 6% of di-p-tolyl-o-tolylcarbinol isolated as di-ptolyl-o-tolylchloromethane, m. p. 106°, together with some di-*p*-tolyl. Ethyl *o*-toluate and magnesium phenyl bromide gave a 23% yield of diphenyl-*o*-tolylcarbinol and 40% of diphenyldi-*o*-tolylpinacol; the latter by treatment with boiling glacial acetic acid and iodine afforded o-toluoyldiphenyl-o-tolylmethane, m. p. 129°, hydrolysed by 10% alcoholic potassium hydroxide to *o*-toluic acid and diphenyl-*o*-tolylmethane; in a similar experiment a substance,  $C_{28}H_{24}O$  (probably an isomeric *o*-toluoyldiphenyl-*o*tolylmethane), m. p. 93·5—94·5° (compound, +1EtOH, m. p. 93·5—94·5°), was obtained, which passed into the isomeride, m. p. 129°, on keeping.

Reduction of o-chlorobenzophenone with zine and glacial acetic acid at 50° affords both the pinacols III and IV; at 15° the yields are slightly improved. Reduction with magnesium and magnesium iodide in benzene at 15° yields III, IV, and a third substance (V), m. p. 180°, the yield of which is increased by raising the temperature of reduction. Magnesium phenyl bromide in benzene solution at 15° in an atmosphere of nitrogen partly converts IV into III; if the reaction is conducted under reflux, V is also obtained. It is suggested that the isomeric pinacols are meso- and racemic forms, and their production in the above reactions, and the transformation of one form into the other, are discussed. C. W. SHOPPEE.

Action of the halogen acids on acetylenic glycols. V. Action of hydrogen iodide on tetraphenylbutinenediol. J. SALKIND and A. KRUGLOV (J. Russ. Phys. Chem Soe., 1929, 61, 803— 814).—The products of reaction of hydrogen iodide and tetraphenylbutinenediol are not analogous to those with other aromatic glycols, since the cyclic iodo-oxide is obtained only with difficulty, and only hydrocarbons can be isolated, instead of di-iododerivatives. Dilute aqueous hydriodic acid and the glycol yield 3-iodo-2:2':5:5'-tetraphenyldihydrofuran, m. p. 139—140°, together with small quantities of  $\alpha\alpha\delta\delta$ -tetraphenylbutatriene, m. p. 235°. If the hydriodic acid is more concentrated, this hydrocarbon is the main product, although a certain quantity of 1:10:10-triphenylbenzofulvene, m. p. 205—206°, is also obtained. With saturated solutions of hydrogen iodide in water or glacial acetic acid, the yield of 1:10:10-triphenylbenzofulvene is greatly increased, and traces of  $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m. p. 201—202°, are also obtained. M. ZVEGINTZOV.

Zymosterol. H. PÉNEAU and G. TANRET (J. Pharm. Chim., 1929, [viii], 10, 193-195).—See this vol., 809.

Mechanism of the azide rearrangement. G. POWELL (J. Amer. Chem. Soc., 1929, 51, 2436—2439). —An attempt has been made to obtain evidence of the intermediate formation of the univalent nitrogen postulate,  $R \cdot CO \cdot N < (I)$ , in the change  $R \cdot CO \cdot N_3 \longrightarrow I \longrightarrow R \cdot NCO$ . Benzoyl azide decomposes in boiling benzene solution in presence of triphenylmethyl to nitrogen and phenylcarbimide. No compound of the type  $R \cdot CO \cdot NR'_2$  is formed, indicating the nonreactivity of I. Acid chlorides and potassium azide react in aqueous acetone, giving almost theoretical yields of the acid azides. Dibenzylacetyl azide, m. p.  $52-53^\circ$ , decomposes on keeping into dibenzylmethylcarbimide (ethyl dibenzylmethylaminoformate, m. p. 106—107°, and phenyldibenzylmethylcarbamide, m. p. 153—154°, are prepared by the action of alcohol and aniline, respectively). When methyl 2-phenylquinoline-4-carboxylate is treated with hydroxylamine in presence of methyl-alcoholic sodium methoxide 2-phenylquinolyl-4-formhydroxamic acid, m. p. 155— 156° (decomp.) (copper and silver salts; benzoyl derivative, m. p. 150—151°, obtained by the action of benzoyl chloride on the sodium salt), results.

H. BURTON.

Structure of benzene. N. M. MAXIM (Bul. Soc. Chim. România, 1929, **11**, 29—36).—The action of diethylamine on the three isomeric toluoyl chlorides gave o-toludiethylamide, b. p.  $160^{\circ}/24 \text{ mm. } d_1^{30} 0.998$ ,  $n_D^{30}$  1.51951; m-toludiethylamide, b. p.  $160^{\circ}/19 \text{ mm.}$ ,  $d_1^{30} 0.996$ ,  $n_D^{30}$  1.52175; and p-toludiethylamide, b. p.  $163^{\circ}/17 \text{ mm.}$ ,  $d_1^{30} 0.999$ ,  $n_D^{30} 1.52515$ . The exaltations of refraction and dispersion increase progressively in the order o, m, p, as observed by Auwers with other derivatives of the toluic acids, and a similar explanation to that of Auwers, based on the Kekulé benzene formula and conjugation, is accepted.

A. A. GOLDBERG.

cycloHexanone-2: 6-dicarboxylic ester and the mechanism of the reducing action of zinc on halogen derivatives. M. I. USCHAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 794-802).-The conditions of the formation of three-membered ring systems by the action of zine dust on  $\alpha\gamma$ -dihalogen derivatives are investigated. Ethyl pentane-aazztetracarboxylate is condensed by sodium in ethylalcoholic solution, giving, after hydrolysis, ethyl cyclohexanone-2: 6-dicarboxylate, b. p. 165-165.5°/ 12 mm., m. p. 87.5-88°, d4 1.1239, n18.5 1.4692. Treatment of this with bromine yielded a yellow liquid 2:6-dibromo-derivative, which reacted vigorously when heated with zinc dust in toluene solution. On addition of water to the reaction mixture, zine hydroxide was precipitated (indicating the presence of an organometallic zinc compound) and a 70% yield of ethyl cyclohexanone-2: 6-dicarboxylate obtained, no ring closure in the 2:6-position having taken place. The mechanism of the reaction is discussed.

M. ZVEGINTZOV.

Action of phenylhydrazine on aromatic dithioacids. H. WUYTS [with T. JANSSENS] (Bull. Soc. chim. Belg., 1929, 38, 195—204).—The interaction of phenylhydrazine with aromatic dithio-acids yields ultimately the phenylhydrazone of the corresponding aldehyde, the probable course of the reaction being:  $R \cdot CS \cdot SH, NH_2 \cdot NHPh \longrightarrow R \cdot CS \cdot NH \cdot NHPh \longrightarrow$  $R \cdot CH \cdot N \cdot NHPh$ . The intermediate stages may be isolated in some cases under appropriate conditions.

Dithio-acids are prepared by the interaction of carbon disulphide with magnesium aryl halides. Dithiobenzoic acid and phenylhydrazine in ethercal solution yield a precipitate of the salt at  $-40^{\circ}$ . When the solvent is removed and the residue heated to  $100^{\circ}$  the reaction goes to completion with the formation of hydrogen sulphide, sulphur, and benzaldehydephenylhydrazone. Similarly, dithio-o-toluic acid yields the salt, and then a mixture of o-toluthiophenylhydrazide, m. p. 116-118°, and o-tolualdehydephenylhydrazone, m. p. 105-106°. Dithio-p-toluic acid yields p-tolualdehydephenylhydrazone, m. p. 110-112°; the salt or thiophenylhydrazide cannot be isolated. Dithio- $\alpha$ -naphthoic acid yields the salt, decomp. below 100°, the thiophenylhydrazide, m. p. 150—152°, and  $\alpha$ -naphthaldehydephenylhydrazone, m. p. 79·5—80°. R. K. CALLOW.

Reduction of cinnamaldehyde to  $\beta$ -phenylpropaldehyde with alcohols. P. E. WESTON and H. ADKINS (J. Amer. Chem. Soc., 1929, 51, 2589).— When a solution of cinnamaldehyde in methyl, ethyl, or propyl alcohol is passed over aluminium oxide at 330°  $\beta$ -phenylpropaldehyde is obtained (from about 60% of the cinnamaldehyde reacting), the alcohol being dehydrogenated to aldehyde (cf. A., 1928, 968, 991). H. BURTON.

Reimer-Tiemann reaction with m-fluorophenol and the nitration of 4-fluoro-2-hydroxyand 2-fluoro-4-hydroxy-benzaldehydes. H. H. HODGSON and J. NIXON (J.C.S., 1929, 1632-1639; cf. this vol., 559) .- The influence of fluorine in the *m*-position on the Reimer-Tiemann reaction is similar to that of the other halogens; the ratio, o-/p-hydroxyaldehyde is 0.87 and shows that the deactivation of the *p*-hydrogen atom is much greater than that produced by *m*-chlorine (o/p ratio 0.71); this is supported by the fact that, for nitration, 4-fluoro-3-bromo- and 4-fluoro-5-bromo-2-hydroxybenzaldehydes require more drastic treatment than the chloro-analogues. By the Reimer-Tiemann reaction, m-fluorophenol affords 4-fluoro-2-hydroxybenzaldehyde (I), m. p. 69° [sodium (bright yellow), iron, copper, and chromium derivatives; oxime, m. p. 125°; semicarbazone, m. p. 236°; p-nitrophenylhydrazone, m. p. 248°, cherry-red (the colours produced by alcoholic solutions of hydrazones and p-nitrophenylhydrazones with alcoholic potassium hydroxide are given immediately after the m. p.)], and 2-fluoro-4-hydroxybenzaldehyde (II), m. p. 171° [sodium (colourless), iron, copper, and chromium derivatives; benzoate, m. p. 63°; oxime, m. p. 151°; semicarbazone, m. p. 238°; p-nitrophenylhydrazone, m. p. 261°, bluish-red]. Mononitration of I yields 4-fluoro-5nitro-2-hydroxybenzaldehyde, m. p. 120° [phenyl-hydrazone, m. p. 173° (decomp.), brownish-yellow; p-nitrophenylhydrazone, m. p. 340° (decomp.), bluishred], which is volatile in steam, whilst dinitration 4-fluoro-3 : 5-dinitro-2-hydroxybenzaldehyde, affords m. p. 165° [phenylhydrazone, m. p. 221°; p-nitro-phenylhydrazone, m. p. 254° (decomp.), bluish-red]. Mononitration of II furnishes 2-fluoro-5-nitro-4hydroxybenzaldehyde, m. p. 126° [phenylhydrazone, m. p. 153°, red; p-nitrophenylhydrazone, m. p. 270° (decomp.), violet-red], readily volatile in steam, and dinitration gives 2-fluoro-3: 5-dinitro-4-hydroxybenzaldehyde, m. p. 138° [phenylhydrazone, m. p. 212°, magenta; p-nitrophenylhydrazone, m. p. 260° (violent decomp.), cherry-red].

2-Bromo-3-fluorophenol, b. p. 123°/80 mm., f. p. below -20°, obtained from *m*-fluorophenol by disulphonation, bromination, and hydrolysis, by the Reimer-Tiemann reaction affords 3-bromo-4-fluoro-2-hydroxybenzaldehyde (III), f. p. below -20° (phenylhydrazone, m. p. 138°; p-nitrophenylhydrazone, m. p. 215°, ruby-red), and 3-bromo-2-fluoro-4-hydroxybenzaldehyde (IV), m. p. 106° [phenylhydrazone, m. p. 85°,

golden-yellow; p-nitrophenylhydrazone, m. p. 258° (decomp.), violet; oxime, m. p. 148°; semicarbazone, m. p. 210°]. Nitration of III in glacial acetic acid at 100° with nitric acid of d 1.5 furnishes 3-bromo-4-fluoro-5-nitro-2-hydroxybenzaldchyde, m. p. 151° [phenylhydrazone, m. p. 193°, brown; p-nitrophenylhydrazone, m. p. 270° (decomp.), ruby-red], also obtained by bromination of 4-fluoro-5-nitro-2-hydroxybenzaldehyde. By nitration of 5-bromo-4-fluoro-2-hydroxybenzaldehyde, m. p. 81° (phenylhydrazone, m. p. 166°; p-nitrophenylhydrazone, m. p. 242°, bluish-red), 5-bromo-4-fluoro-3-nitro-2-hydroxybenzaldehyde, m. p. 115° [sodium derivative (red); phenylhydrazone, m. p. 215°, golden-brown; p-nitrophenylhydrazone, m. p. 258° (decomp.), deep reddish-violet], is obtained. Nitration of IV under similar conditions to those employed with III, but at 30-40°, affords 3-bromo-2-fluoro-5-nitro-4-hydroxybenzaldehyde, m. p. 111° [phenylhydrazone, m. p. 166°, brownish-red becoming yellow; p-nitrophenylhydrazone, m. p. 256° (decomp.), purplish-red; semicarbazone, m. p. 230°], also obtained by bromination of the mononitration product of 2-fluoro-4-hydroxybenzaldehyde.

4-Fluoro-2-methoxybenzaldéhyde, m. p. 53° (p-nitrophenylhydrazone, m. p. 213°, magneta; oxime, m. p. 128°; semicarbazone, m. p. 162°), from 4-fluoro-2hydroxybenzaldehyde with methyl sulphate in the presence of anhydrous sodium carbonate in boiling xylene, by oxidation with alkaline potassium permanganate yields 4-fluoro-2-methoxybenzoic acid, m. p. 136°, readily demethylated by hydriodic acid, d 1.7, to 4-fluoro-2-hydroxybenzoic acid, m. p. 186°. The isomeric 2-fluoro-4-methoxybenzaldehyde, m. p. 47° (phenylhydrazone, m. p. 101°; p-nitrophenylhydrazone, m. p. 217°, ruby-red; oxime, m. p. 95°; semicarbazone, m. p. 228°), is obtained similarly and by oxidation affords 2-fluoro-4-methoxybenzoic acid, m. p. 192°, which could not be demethylated by hydriodic acid.

The bright yellow colour of the sodium derivatives of 4-halogeno-2-hydroxybenzaldehydes, the contrasting colourless sodium derivatives of 2-halogeno-4-hydroxybenzaldehydes, and the deeper colour of the copper and chromium derivatives of the former, are attributed to co-ordination, which may also account for the unexpected volatility in steam of 4-fluoro-5nitro-2-hydroxybenzaldehyde, and for the liquid nature of 2-bromo-3-fluorophenol and of 3-bromo-4-fluoro-2-hydroxybenzaldehyde. The non-demethylation of 2-halogeno-4-methoxybenzoic acids and the greater reactivity of the isomeric 4-halogeno-2methoxybenzoic acids are discussed and an explanation is suggested. C. W. SHOPPEE.

Influence of substituents on the Reimer-Tiemann reaction. II. H. H. HODGSON and T. A. JENKINSON (J.C.S., 1929, 1639—1642; cf. this vol., 559).—The standardised reaction previously described has been conducted with other phenols and also with bromoform and iodoform. The following results for the o/p ratio are given : (a) with chloroform : phenol 0.6, o-cresol 0.48, o-chlorophenol 1.6, o-bromophenol 1.25, o-iodophenol 1.07; salicylic acid 0.06, m-cresol 0.46, m-chlorophenol 0.71, m-bromophenol 0.72, m-iodophenol 0.78; (b) with bromoform : phenol 0.44, o-cresol 0.37, o-chlorophenol 0.71, o-bromophenol 0.65, o-iodophenol 0.65; salicylic acid 0.05, m-cresol 0.85, m-chlorophenol 0.84, m-bromophenol 0.77, m-iodophenol 0.84. With iodoform, the o/p ratio for phenol and its o-halogeno-derivatives ranged from 0.2 to 0.3. These results are discussed on the basis of current electronic theories, and it is suggested that the variation observed by substitution of bromoform for chloroform may be explained by assuming that the cationoid reagent derived from the former has a greater specific volume than that derived from the latter. In general the presence of halogen leads to deactivation; thus 4-chloro- and 2:6-dichlorophenol give very small yields of aldehydes. Resorcinol monomethyl ether reacts very vigorously with production of much resin, and gives a much greater yield of 4-hydroxy-2-methoxybenzaldehyde than of 2-hydroxy-4-methoxybenzaldehyde (cf. Tiemann and Parrisius, A., 1881, i, 270). C. W. SHOPPEE.

Schiff bases from 5-chlorovanillin. R. M. HANN. G. S. JAMIESON, and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 2586-2588).-The following Schiff's bases are described : 5-chloro-4-hydroxy-3-methoxybenzylidene-o-toluidine, m. p. 115° (all m. p. are corr.); -m-toluidine (picrate, m. p. 224°); -p-toluidine, m. p. 142° (picrate, m. p. 230°); -m-nitroaniline, m. p. 160° (picrate, m. p. 190°); -p-chloroaniline, m. p. 128° (picrate, m. p. 215°); -cymidine, m. p. 146—147°; -p-anisidine, m. p. 131° (picrate, m. p. 229—230°); -benzidine, m. p. 251—252° [picrate, m. p. 250—260° (decomp.)]; -m-aminobenzoic acid, m. p. 207° (picrate, m. p. 236°, +EtOH, m. p. 241°); -p-aminophenol, m. p. 150° [picrate, m. p. 224–225° (decomp.)]; -o-dianisidine, m. p. 188° (picrate, decomp. 225° with darkening). Condensation products are not obtained with o- and p-nitro-, 2:4-dichloro-, and trinitro-3-Nitro-p-toluidine and 5-chlorovanillin anilines. afford 5-chlorovanillylidenebis-3-nitro-p-toluidine, m. p. 125° (picrate, m. p. 148° not sharp). H. BURTON.

Nitrogen derivatives of 2-hydroxy-3-methoxybenzaldehyde and their metallic compounds. M. PICHON (Bull. Soc. chim., 1929, [iv], 45, 528-534). -2-Hydroxy-3-methoxybenzaldehyde (o-vanillin) in alcoholic solution with ammonia yields the hydramide (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>)<sub>3</sub>N<sub>2</sub>, citron-yellow, m. p. 158°, hydrolysed by N-hydrochloric acid, and yielding in benzene solution a hydrochloride, [C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>]<sub>3</sub>N<sub>2</sub>, HCl, and a picrate, m. p. 188°. The following metallic salts of 2-hydroxy-3methoxybenzylideneimine, [NH:CH·C<sub>6</sub>H<sub>3</sub>(OMe)·O]<sub>2</sub>M, are obtained on adding the saturated metallic salt solution to an alcoholic solution of the aldehyde in presence of ammonia (1 mol.): cupric, m. p. 192°, nickel, m. p. 327°, cobaltous, m. p. 278°, and cobaltic, black, non-crystalline, [NH:CH·CgH3(OMe)·O]3Co, m. p. 177°. Neither the ferrous nor ferric salts could be obtained in this way, or by the action of ammonia on the corresponding o-vanillin salt (Noelting, A., 1910, i, 176) as in the case of the cupric salt. 2-Hydroxy-3-methoxybenzylidenemethylimine, m. p. 77° (cupric salt, m. p. 207°; sodium salt), the cupric salt of 2-hydroxy-3-methoxybenzylidenedimethyldi-imide,

 $[(\mathrm{NMe}_2)_2\mathrm{CH}\cdot\mathrm{C_6H_3}(\mathrm{OMe})\cdot\mathrm{O}]_2\mathrm{Cu}$ , m. p. 236°, and 2-hydroxy-3-methoxybenzylidenebenzylimine, m. p. 61.5° (cupric salt, m. p. 211°), are similarly obtained. Analogous copper salts with aniline could not be obtained. o-Veratraldehyde similarly yields a white hydramide,  $[C_6H_3(OMe)_2 \cdot CH \cdot ]_3N_2$ , m. p. 115° (hydrochloride). R. BRIGHTMAN.

Action of nitrosodimethylaniline on apiole. A. QUILICO and M. FRERI (Gazzetta, 1929, 59, 273-279; cf. A., 1928, 880).—Nitrosodimethylaniline acts slowly on parsley apiole at 90-100°, giving a mixture of azo- and azoxy-dimethylaniline with a *substance*, m. p. 90-100°, which has the properties of a Schiff's base, and probably has the structure

 $CH_2O_2:C_6H(OMe)_2\cdot CH:CH\cdot CH:N\cdot C_6H_4\cdot NMe_2$ . This substance is hydrolysed by acids to dimethyl-*p*phenylenediamine and apioleacraldehyde, m. p. 140° (cf. Alessandri, A., 1915, i, 555), of which the p-*nitrophenylhydrazone*, m. p. 268°, and the oxime, m. p. 166° (cf. *loc. cit.*), are prepared. When dimethyl*p*-phenylenediamine acts on apioleacraldehyde in alcohol, the Schiff's base is regenerated.

The identification (A., 1928, 997) of the product from isoapiole with m. p. 228—229° as apiolealdehydep-nitrophenylhydrazone is confirmed by synthesis. E. W. WIGNALL.

Anæsthetics. Acylaniline derivatives. W. H. HARTUNG and J. C. MUNCH (J. Amer. Chem. Soc., 1929, 51, 2570—2574).—Nitration of a series of aryl alkyl ketones and subsequent reduction of the m-nitro-derivatives obtained gives amino-ketones, NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>R·CO·Alk, the anæsthetic actions of which have been determined. For anæsthetic action Alk must be at least Pr<sup>a</sup>; the isopropyl derivative is less active than the n-derivative. The following ketones are new: m-nitrovalerophenone, b. p. 145—150°/ 3 mm.; 3-nitro-p-tolyl propyl, m. p. 77·5° (semicarbazone, m. p. 215—216°); 3-nitro-p-tolyl isopropyl, m. p. 41°; 3-nitro-p-tolyl n-butyl, m. p. 48° (semicarbazone, m. p. 210°); 3-nitro-p-tolyl isobutyl, m. p. 54·5° (semicarbazone, m. p. 214°); m-aminovalerophenone, b. p. 160—163°/3 mm. (hydrochloride, m. p. 155·55—156°); 3-amino-p-tolyl derivative, m. p. 131·5°; hydrochloride, m. p. 204° (decomp.)]; 3-aminop-tolyl propyl, m. p. 69° (acetyl derivative, m. p. 130·5°; hydrochloride, m. p. 168°); 3-amino-p-tolyl isopropyl, b. p. 150—153°/3 mm. (hydrochloride, m. p. 167·5°); 3-amino-p-tolyl n-butyl, m. p. 61° (acetyl derivative, m. p. 93—94°; hydrochloride, m. p. 91·5—93°); 3-amino-p-tolyl isobutyl, b. p. 165—170°/3 mm. (acetyl derivative, m. p. 117·5°; hydrochloride, m. p. 142·5°). H. BURTON.

β-Phenylisobutyl methyl ketone and derivatives. Synthesis of α- and β-phenylisovaleric acids. A. HOFFMAN (J. Amer. Chem. Soc., 1929, 51, 2542-2547).—Mesityl oxide and benzene react in presence of anhydrous aluminium chloride, forming β-phenylisobutyl methyl ketone (I), b. p. 134°/22 mm., 252° (corr.)/760 mm., d= 0.972 (semicarbazone, m. p. 163-164°; oxime, b. p. 181°/27 mm., m. p. 52-54°; tetrabromo-derivative, m. p. 96-98°), which when heated with anhydrous zinc chloride gives, in addition to other products, a hydrocarbon (II), C<sub>24</sub>H<sub>28</sub>, b. p. 195°/18 mm., m. p. 130·5-131° (corr.). Nitration of II with boiling nitric acid (d 1.42) affords a trinitroderivative, m. p. 180-184°; II is stable towards oxidising agents. Reduction of I with sodium and alcohol yields  $\beta$ -phenylisobutylmethylcarbinol, b. p. 132—133°/17 mm.,  $d_{23}^{23}$  0.960, dehydrated by heating with zinc chloride to a hydrocarbon (probably  $\delta$ -phenyl- $\delta$ -methyl- $\Delta^{\beta}$ -pentene), b. p. 96—98°/17 mm.,  $d_{23}^{23}$  0.889. Oxidation of I with sodium hypobromite gives  $\beta$ -phenylisovaleric acid (III), m. p. 58—58.5° (methyl ester, b. p. 120°/11 mm.; anilide, m. p. 122—123°; nitro-derivative, m. p. 169—172°), identical with the  $\alpha$ -phenylisovaleric acid of Eykman (A., 1908, i, 794). Ethyl sodiophenylmalonate and isopropyl iodide react, yielding a mixture of ethyl phenylacetate and ethyl phenylisopropylmalonate. Hydrolysis of the mixture, distillation of the acids obtained, and removal of phenylacetic acid as the soluble silver salt afford  $\alpha$ -phenylisovaleric acid, b. p. 159—160°/14 mm., m. p. 60° (anilide, m. p. 132—133°; silver salt).  $\beta$ -Phenylisopropyl chloride and ethyl sodiomalonate give mainly  $\alpha$ -methylstyrene; a small amount of ethyl  $\beta$ -phenylisopropylmalonate is also formed. Hydrolysis of this and thermal decomposition of the resulting acid yields III. H. BURTON.

Truxillic and truxinic ketones. II. Photochemistry of cinnamic acids, chalkones, and their derivatives. H. STOBBE and K. BREMER (J. pr. Chem., 1929, [ii], **123**, 1—60).—The two dimerides previously obtained by Stobbe and Hensel (A., 1926, 1248) by irradiation of chalkone have been examined further, and the work has been extended to include p-methyl-, p'-methyl-, pp'-dimethyl-, p-methoxyp'-methyl-, pp'-dimethoxy-, methylene-3: 4-dioxy-,  $\beta$ -methyl-, and p'-methoxy- $\alpha$ -methyl-chalkone.

Bischalkone A (I), m. p. 124° (truxinic ketone type), is non-volatile in steam, and affords a *dioxime*, m. p. 227°, and a *disemicarbazone*, m. p. 235-237°; it

(L) Ph·CH—CH·COPh Ph·CH—CH·COPh (II) Ph·CH—CH·COPh Ph·CO·CH—CHPh (II)

is stable to hydrogen peroxide in glacial acetic acid solution and to cold alkaline permanganate, but with concentrated nitric acid yields benzoic acid and resinous products; it is unaffected by bromine. Rapid distillation furnishes traces of benzoic acid and chalkone, together with 4% of stilbene, the amount of the latter rising to 20% when the distillation is prolonged. By irradiation with sunlight or with a quartzmercury lamp, either in the solid state or in solution, decomposition (probably depolymerisation) is caused with the production of brown resins; heating with sodium acetate and acetic anhydride effects no conversion into a furan derivative, whilst alcoholic potassium hydroxide, pyridine, and acetic acid are without action. Bischalkone B (II), m. p. 225-226° (truxillic ketone type), is also non-volatile in steam and stable to cold alkaline permanganate, but gives no oxime, and by heating with sodium acetate and acetic anhydride, or with a dilute acetic acid solution of semicarbazide hydrochloride containing potassium acetate, passes into bischalkone D, m. p. 195°. The dimeride B is not identical with the reduction product,  $C_{20}H_{21}O_2$ , m. p. 220–222°, of dibenzoyldiphenyl-butadiene, described by Wislicenus and Lehmann (A., 1899, i, 59), which affords a dioxime, m. p. 230°, and by treatment with acetic anhydrido and potassium

acetate yields a substance, C30H22O, m. p. 180-181°. The dimeride B is decomposed (probably depolymerised) to a small extent only by irradiation in the solid state or in chloroform solution; by distillation it gives 60% of chalkone and traces of stilbene, the latter resulting by decomposition, not of the dimeride B, but of monomeric chalkone, which has been shown to yield 8% of stilbene by distillation (cf. Stobbe and Hensel, loc. cit.), in addition to benzoic acid and resin. The dimeride B is unaffected by treatment with trichloroacetic acid in acetic acid solution, but by heating with sodium acetate and acetic anhydride it is converted into the stereoisomeride, bischalkone D, m. p. 195°. Irradiation of chalkone in solution affords the dimeride A only, irrespective of the wave-length of the light used; the yields obtained using acetic acid, chloroform, and ethyl alcohol are similar (30-35%), but are smaller in benzene. The atmospheric conditions (air, carbon dioxide, vacuum), and likewise the presence of hydrochloric acid or erythrosin, are without influence on the yield of dimeride A; the presence of chlorophyll, however, reduces the yield to about one third of the former value, and affords 1-1.5% of the dimeride *B*. In benzene solution containing a trace of iodine, chalkone, by irradiation with ultra-violet light from a quartz-mercury lamp, furnishes solely 7.5% of a third dimeride, bischalkone C, m. p. 178–179°, which was obtained only in one experiment; the dimeride C is stable to cold alkaline permanganate and to bromine. In all experiments, using solutions of phenyl styryl ketone, polymerisation occurs, whereas the analogously constituted cinnamic acids in solution always isomerise and never polymerise. Irradiation in the solid state or in suspension affords both the dimerides A and B, the relative yields depending on the wave-length of the light used. In general, the yield of the dimeride B decreases with decreasing wave-length, but the presence of hydrochloric acid or mercuric chloride, or the atmospheric condition, has no apparent effect. The production of the lower-melting truxinic ketone type (I) by irradiation in solution, and of the higher-melting truxillic ketone type (II) by irradiation in the solid state, are in agreement with the results obtained by Reimer (A., 1924, i, 642) on methyl benzylidenepyruvate. All attempts to obtain the dimeric ketone, m. p. 134°, prepared by Wieland (A., 1904, i, 432) by treatment of chalkone with acetic anhydride and concentrated sulphuric acid, were unsuccessful. The absorption spectra of chalkone, dihydrochalkone (which is stable to ultra-violet radiation), the three photo-dimerides A, B, C, and the dimeride D conform to the rule of Stobbe (Z. angew. Chem., 1926, 39, 673); the absorption curves of the dimerides lie between those of the monomeride and the saturated dihydro-compound, and exhibit a close formal resemblance to that of the latter.

In order to compare chalkones in which the ketogroup is substituted with cinnamic acid derivatives in which the carboxyl group is modified (salts, esters, amide), *anti*-chalkoneoxime and the chalkonesemicarbazones have been examined. Exposure of *anti*-chalkoneoxime, m. p. 75°, obtained by Henrich's method (A., 1907, i, 324), to a quartz-mercury lamp produced a certain amount of discoloration but no polymerisation. Chalkone- $\alpha$ -semicarbazone, m. p. 168° (cf. Heilbron and Wilson, J.C.S., 1912, **101**, 1482; 1913, **103**, 1504), by similar treatment yielded equal quantities of resin and unchanged product, but chalkone- $\gamma$ -semicarbazone, m. p. 179–180° (cf. Heilbron and Wilson, *loc. cit.*), readily underwent a peculiar transformation to a yellow isomeride.

p'-Methylchalkone ( $\alpha$ -form), m. p. 74-75° [oxime, m. p. 130-132°; hydroxylamino-oxime(?), m. p. 150-160°], was obtained by condensing benzaldehyde and p-methylacetophenone in alcoholic solution with 10% sodium hydroxide (cf. Wcygand and Matthes, A., 1926, 1041) Irradiation of p'-methylchalkone in ethyl-alcoholic solution with sunlight affords a 45% yield of bis-p'-methylchalkone A, m. p. 114°, together with traces of bis-p'-methylchalkone B, m. p. 218°; use of the solid substance furnishes two other dimerides in equal proportion, bis-p'-methylchalkone C, m. p. 205°, and bis-p'-methylchalkone D, m. p. 243°. Ultra-violet light transforms the dimeride A into the dimeride B, and the yield of the latter increases with the use of shorter waves. By slow distillation, A yields traces of p'-methylchalkone and 10% of stilbene; since under the same conditions p'-methyl-chalkone affords but 2% of stilbene, the truxinic ketone structure (I) is assigned to the dimeride A. All four dimerides are stable to cold alkaline per-manganate and to bromine; they yield no semicarbazones when heated with semicarbazide hydrochloride and potassium acetate in alcoholic solution, but under these conditions the dimeride A is partly converted into B, whilst D affords a fifth isomeride, bis-p'-methylchalkone E, m. p. 216°, a transformation also brought about by hot acctic anhydride. The five dimerides fall into two groups according to the colour produced with concentrated sulphuric acid; A and  $\hat{B}$  yield a carmine-red, whilst C,  $\hat{D}$ , and E give a yellow colour. Since B can be reconverted into Aby acetic anhydride, it is considered to be a stereoisomeride of the dimeride A, whilst C, D, and E are stereoisomerides of the truxillic ketone type (II). The absorption spectra of the dimerides B, C, D, and E are identical and closely similar to those of A and dihydro-p'-methylchalkone; the absorption curves of all five dimerides lie between those of p'-methylchalkone and its dihydro-compound. The latter, m. p. 69°, was prepared by reduction of p'-methylchalkone with hydrogen and colloidal palladium in alcoholic solution; it is stable to light.

p-Methylchalkone (\beta-form), m. p. 96.5° (cf. Weygand, A., 1928, 180), was prepared by a slight modification of the method of Hanzlik and Bianchi (A., 1899, i, 890); by irradiation with sunlight the solid substance gives a 14% yield of a single dimeride, bisp-methylchalkone, m. p. 198-200°; the yield falls to 2% with ultra-violet light, and no dimerisation occurs in solution with radiation of any wave-length. The dimeride is stable to cold alkaline permanganate and to bromine, and affords no semicarbazone; it is slowly depolymerised by ultra-violet rays of short wavelength. p-Methylchalkone yields an oxime, m. p. 134° (cf. Hanzlik and Bianchi, loc. cit.), which when irradiated with ultra-violet light in the solid state or in solution becomes greenish-yellow, the production of colour indicating fission to the monomeric ketone.

pp'-Dimethylchalkone, m. p. 127.5°, obtained from p-tolualdehyde and p-methylacetophenone by condensation with 10% sodium hydroxide in alcoholic solution (cf. Weygand and Matthes, *loc. cit.*), exhibited so great a tendency to resinification on irradiation, either in the solid state or in solution, that no polymeride could be isolated. This behaviour, anomalous compared with that of the foregoing monomethylchalkones, is not due to greater light absorption, since the absorption curves of chalkone, p'-methyl-, p-methyl-, and pp'-dimethyl-chalkone all lie close together and exhibit a close formal resemblance.

p-Methoxy-p'-methylchalkone, m. p. 94°, obtained in 45% yield by condensation of p-anisaldehyde and p-methylacetophenone, is rapidly and completely resinified by irradiation with sunlight or ultra-violet light in the solid state, but in ethyl-alcoholic solution a 2.5% yield of a *substance*, probably bis-*p*-methoxy-*p'*-methylchalkone, m. p. 208°, was isolated. *pp'*-Di-methoxychalkone, m. p. 101°, is rapidly and completely resinified by irradiation with ultra-violet light both in the solid state and in solution. The absorption curves of the foregoing disubstituted monomeric chalkones and of p-methoxychalkone (m. p. 76°) are extremely similar and in part coincident. Dihydro-pmethoxychalkone, m. p. 59°, could not be obtained by the method of Bargellini and Bini (A., 1911, i, 211), and was prepared using hydrogen with colloidal palladium and sodium protoalbinate in aqueousalcoholic solution. Solid 3:4-methylenedioxy-chalkone, m. p. 122°, is largely unaffected by irradiation with sunlight or ultra-violet light, only traces of resin being produced; no polymerisation occurs in chloroform solution, but resinification increases (cf. Stobbe and Wilson, J.C.S., 1910, 97, 1724).

In contrast with *p*-methoxy-*p'*-methylchalkone.  $\alpha$ -methyl-*p'*-methoxychalkone *A* (yellowish-green), m. p. about 30°, by irradiation with the quartzmercury lamp as the solid or in solution affords a colourless isomeride,  $\alpha$ -methyl-p'-methoxychalkone B, m. p. 64.5°, which decolorises permanganate and reacts with bromine.

The results are discussed in relation to other examples, previously reported; it appears that unsubstituted chalkone and all p- or p'-monosubstituted chalkones tend to photopolymerise, whilst pp'-disubstituted chalkones resist this process. The polymerisability of various arylideneacetophenones (chalkones) is compared with that of the corresponding arylideneacetic acids (cinnamic acids), but no general relation between light-sensitivity and constitution in the two series can be found. A comparison of existing data with results given above shows that chalkones with an a-substituted ethylene group, Ar·CH:CR·COAr, readily photo-isomerise when R=Mc or Ph, but that reaction is inhibited when R=Ac or  $CO_2Et$ ; photopolymerisation never takes place. One example only of the effect of  $\beta$ -substitution has been investigated;  $\beta$ -methylchalkone (dypnone) alone, or in chloroform solution, is unaffected by ultra-violet light. A comparison with similarly constituted arylideneacetic acids shows that  $\alpha$ - and  $\beta$ -substituents generally impede photopolymerisation, but certain C. W. SHOPPEE. exceptions are quoted.

Halogenated 3:9-dibenzoyl derivatives of perylene. Synthesis of isoviolanthrone. V. V. SCHARVIN and L. Z. SOBOROVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 789-794).-Perylene, m. p. 265°, was obtained in 25% yield by the action of anhydrous phosphoric acid and phosphorus trichloride at 500° on β-dinaphthol. With o-chlorobenzoyl chloride in carbon disulphide solution, perylene gives, by the Friedel-Krafts reaction, 3: 9-di-o-chloro-benzoylperylene (I) in 85% yield. By using the bromo- or iodo-benzoyl compounds, the corresponding bromo- and iodo-derivatives are obtained. All three compounds are deep red in colour, and do not melt at 320°. The internal condensation of I to isoviolanthrone is carried out either by heating at 170° with anhydrous aluminium chloride, or by boiling a mixture of the chloro-derivative with potassium hydroxide in quinoline. In both cases, on extraction with a solution of an alkaline hyposulphite, a deep violet precipitate of the vat dye is obtained, and on neutralising the alkaline mother-liquor, a precipitate of 3:9-di-o-hydroxybenzoylperylene is obtained as a M. ZVEGINTZOV. by-product.

Rotenone. I. Reduction products. F. B. LAFORGE and L. E. SMITH (J. Amer. Chem. Soc., 1929, 51, 2574-2581).-Reduction of rotenone with hydrogen (1 mol.) in presence of palladised barium sulphate and acetone or platinum oxide and ethyl acetate (cf. Kariyone, A., 1924, i, 251; Butenandt, A., 1928, 1017) gives a mixture of dihydrorotenone (I), m. p. 164° (lit. 216°),  $[\alpha]_{17}^{m}$  -225.2° in benzene [the oxime, m. p. 256-257° (decomp.), obtained also by catalytic reduction of rotenoneoxime (Takei, A., 1928, 765) (benzenesulphonyl derivative, m. p. 143°), is converted by prolonged treatment with hydrochloric acid at the ordinary temperature into the isooxime, m. p. 270–273° (decomp.)], and an acid (II),  $C_{23}H_{24}O_6$ , m. p. 209°,  $[\alpha]_{10}^{20}$  +36.2° in chloroform. Further reduction of I or II with hydrogen in presence of platinum oxide and ethyl acetate affords an acid, C23H26O6, m. p. 215° (only in small amount from I). Reduction of rotenone with zinc dust and alcoholic potassium hydroxide yields a mixture of rotenol (III), m. p. 120° (lit. 115°), and derritol (IV), m. p. 164° (lit. 161°),  $[\alpha]_{b}^{\circ}$  -62.2° in chloroform (cf. Butenandt, loc. cit.); the use of 5% alkali gives mainly 111, 20% alkali mainly IV. At the same time small amounts of a substance, m. p. 161°, are produced. Contrary to the statement of Butenandt, similar zinc dust reduction of I affords dihydrorotenol and dihydroderritol, m. p. 122°. isoRotenone (Takei, loc. cit.) is converted by zinc dust and 15% alcoholic potassium hydroxide into a mixture of isorotenol, C23H24O6, m. p. 133°, and isoderritol, m. p. 150°. Initial reduction of rotenone probably occurs at two centres and the production of derritol derivatives appears to be independent of the presence of a double linking, since isorotenone is probably a saturated H. BURTON. (ring) compound.

[A constituent of] Lactucarium germanicum. K. H. BAUER and E. SCHUB (Arch. Pharm., 1929, 267, 413—424).—Lactucerin was isolated from the petroleum extract of the dried drug and attempts were made to purify it by crystallisation alternately from alcohol and light petroleum, but it was impossible to effect complete purification. The product had m. p. 232°,  $[\alpha]_{\rm b}$  +39.08° after nine crystallisations, M 460 (Rast).  $\alpha$ -Lactucerol,  $C_{30}H_{49}$ ·OH, was recrystallised eight times, when the m. p. and  $[\alpha]_{\rm p}$ gradually increased to 203° and  $[\alpha]_{\rm p}$  +78.44°, respectively (benzoate, m. p. 257°).  $\beta$ -Lactucerol, m. p. 162°,  $[\alpha]_{\rm p}$  +53.81°, was isolated from the motherliquor from  $\alpha$ -lactucerol (benzoate, m. p. 260°). Attempts to break down  $\alpha$ -lactucerol with nitric acid, chromic acid, hydrogen peroxide, mercuric acetate, hypochlorite, and copper oxide were abortive. Both lactucerols afford lactucene,  $C_{30}H_{48}$ , m. p. 207°, when treated with phosphorus pentachloride, which gives propionic and other acids on ozonisation. The corresponding saturated hydrocarbon lactucane is obtained when lactucene is hydrogenated or when lactucerol is reduced with hydriodic acid.

S. COFFEY.

Synthesis of some phenyl styryl ketones and related compounds. N. M. CULLINANE and D. PHILPOTT (J.C.S., 1929, 1761-1765).—Phloroaceto-phenone 4:6-dimethyl ether and 2:4-dimethoxy-benzaldehyde (improved method of preparation described) condense in the presence of aqueousalcoholic potassium hydroxide at 60° to give 2-hydroxy - 4:6 - dimethoxyphenyl 2:4 - dimethoxystyrvl ketone, m. p. 128° (cf. Kostanecki and Tambor, A., 1899, i, 891, who give m. p. 152°), which by bromin-ation in chloroform solution at 0° and treatment of the crude bromination product (m. p. 230°) with hot 50% sodium hydroxide yields a compound,  $C_{13}H_{17}O_6Br$ , m. p. above 300°, which is probably 3:5:2':4'-tetramethoxy-4-bromobenzylidenecoumaran-2-one. The production of a coumaranone as opposed to a flavorie (cf. von Auwers and Anschütz, A., 1921, i, 682) and its behaviour on bromination are analogous to the results previously described by Kostanecki and Tambor (loc. cit.) and by Tambor (A., 1912, i, 43).

Phloroacetophenone trimethyl ether combines with salicylaldehyde under the conditions given above to yield 2:4:6-trimethoxyphenyl 2-hydroxystyryl ketone, m. p. 205.5°, converted by dry hydrogen chloride in glacial acetic acid solution into 2':4':6'-trimethoxyflavylium chloride, m. p. 162° (ferrichloride, m. p. 198°). C. W. SHOPPEE.

Condensations of ketones with phenols. III. Condensation products of mesityl oxide and monohydroxybenzenes. J. B. NIEDERL [with N. AMBINDER, R. CASTY, D. W. C. KNOWLES, I. RAPPA-PORT, and W. SASCHEK] (J. Amer. Chem. Soc., 1929, 51, 2426—2430).—When a mixture of mesityl oxide (1 mol.) and a phenol (1 mol.) is treated with sulphuric acid (1 mol.) at 0° and kept at 15—20° for 1 week, substituted 2:4:4-trimethyl-2-chromanols or di-2:4:4-trimethyl-2-chromanyl ethers are obtained. Formation of the chromanol occurs either by direct addition of the oxide to the phenol, or by re-arrangement of an intermediate  $\beta$ -hydroxyphenylisobutyl methyl ketone, formed by interaction of the phenol with the additive compound from the oxide and sulphuric acid. The following substituted 2-chromanols are obtained from the appropriate phenol: 2:4:4-trimethyl-, m. p. 89° (dinitro-derivative, m. p. 155°); 7-nitro-2:4:4-trimethyl-, m. p. 148°; 6-nitro-

2:4:4-trimethyl-, m. p. 132°; 2:4:4:8-tetramethyl-, m. p. 120°, and 2:4:4:7-tetramethyl-, m. p. 120° (from trinitro-m-cresol). Di-2:4:4:7-tetramethyl-, m. p. 58° (tetranitro-derivative, m. p. 145°); di-11. p. 65 (tetranethyl-, m. p. 57° (tetranitro-derivative, m. p. 167°); di-5-chloro-2:4:4:7-tetramethyl-, m. p. 71°; di-2:4:4:6:8-pentamethyl- (tetranitro-derivative, m. p.  $155^{\circ}$ );  $di \cdot \hat{2} : 4 : 4 : 8$ -tetramethylisopropyl-(from carvacrol) (dinitro-derivative, m. p.  $185^{\circ}$ ), and di-2:4:4:5 - tetramethyl - 8 - isopropyl - 2 - chromanyl ethers, m. p. 136° (dinitro-derivative, m. p. 201°), are also described. Oxidation of the chromanols with chromic oxide in acetic acid solution affords substituted  $\beta$ -hydroxyphenylisovaleric acids.

H. BURTON.

compounds containing Cyclic aldehydic groups. I. G. FARBENIND. A.-G. -See B., 1929, 747.

Condensation products of the benzanthrone series [cyclic sulphur derivatives]. I. G. FARBENIND. A.-G.-See B., 1929, 748.

Anhydro-compounds derived from 2-nitro-3:4-dimethoxyphenylacetonitrile and certain pseudo-bases. J. M. GULLAND and C. J. VIRDEN amine, obtained from 3-methoxycinnamic acid (Chakravarti, Haworth, and Perkin, A., 1927, 1096) as described by Helfer (A., 1924, i, 1341), by treatment with anhydrous formic acid at 175° yields formyl- $\beta$ -3-methoxyphenylethylamine, b. p. 216°/17 mm., converted by phosphorus oxychloride into 6-methoxy-3: 4-dihydroisoquinoline, b. p. 155°/16 mm. [methiodide, (I), m. p. 199° (decomp.); periodide,

 $C_{11}H_{14}ONI_3$ , m. p. 82° (decomp.); periodide,  $C_{11}H_{14}ONI_5$ , m. p. 82° (decomp.)]; treatment of I with potassium hydroxide affords 1-hydroxy-6-methoxy-2-methyltetrahydroisoquinoline (II), m. p. 102°. By reduction of I with zinc and hydrochloric acid is obtained 6-methoxy-2-methyltetrahydroisoquinoline (hydriodide, m. p. 173-174; picrate, m. p. 130-131°). and oxidation of the methochloride corresponding with I with alkaline potassium permanganate affords 6-methoxy-1-keto-2-methyltetrahydroisoquinoline, m. p. 50°. The preparation of  $\beta$ -3-methoxyphenylethylamine was also attempted as follows: condensation of 3-methoxybenzaldehyde and nitromethane using alcoholic sodium ethoxide at 0° gives the sodium salt of the aci-form of 3-methoxy-a-hydroxy-B-nitroethylbenzene (cf. A., 1902, i, 682), dehydrated by fused zinc chloride in hot glacial acetic acid to w-nitro-3-methoxystyrene, dimorphic (a-form, needles, m. p. 91-92°; β-form, plates, m. p. 91-92°), also obtained directly from 3-methoxybenzaldehyde and nitromethane in the presence of methylamine hydrochloride and anhydrous sodium carbonate in alcoholic solution at 15°. Reduction of the nitro-compound with zinc and dilute acetic acid yields 3-methoxyphenylacet-aldoxime, m. p. 91°; the method was abandoned on account of the poor yield (11%) obtained.

2-Nitrohomoveratrole, prepared by the method of Oberlin (A., 1926, 283) and also by methylation of 2-nitro-3-hydroxy-p-tolyl methyl ether, does not appear to condense with suitable pseudo-bases of the isoquinoline series, but by use of 2-nitro-3: 4-di-methoxyphenylacetonitrile, obtained by the inter-

action of 2-nitro-3: 4-dimethoxybenzyl chloride and alcoholic potassium cyanide (cf. Kay and Pictet, J.C.S., 1913, 103, 953) along with 2-nitro-3: 4-dimethoxyphenylacetamide, m. p.  $151-153^{\circ}$ , the following anhydro-compounds are obtained : II affords  $1-\alpha$ cyano-2'-nitro - 3': 4' - dimethoxybenzyl - 6 - methoxy - 2methyltetrahydroisoquinoline (III), m p. 95-96°; cotarnine yields anhydrocotarnine-2-nitro-3:4-dimethoxyphenylacetonitrile (IV), m. p. 153° (decomp., gradually becoming red from 120°); and laudaline furnishes anhydrolaudaline - 2 - nitro - 3 : 4 - dimethoxyphenylacetonitrile (V), m. p.  $125-127^{\circ}$ . Subsequent attempts to convert the anhydro-compounds III and V into aporphine bases were unsuccessful owing to ready hydrolysis by dilute acids to the components, a property shared by the base IV. It was also found impossible to effect reduction in alkaline media without causing fission of the molecule; thus with ammoniacal ferrous hydroxide, III yielded 2-amino-3:4-dimethoxyphenylacetonitrile, m. p. 108° (acelyl derivative, m. p. 184°), also obtained by reducing 2-nitro-3: 4-dimethoxyphenylacetonitrile, similarly whilst this nitrile was obtained from III with hot alcoholic ammonium sulphide. In view of the synthesis of apomorphine dimethyl ether recently described by Avenarius and Pschorr (this vol., 457) the action of hydrochloric acid on III has been studied under a variety of conditions, but in every case fission of the molecule occurred. By combining hydrolysis and reduction in one reaction, the procedure adopted by Avenarius and Pschorr, a small quantity only of a base (probably 6-methoxy-2-methyltetrahydroisoquinoline), which could not be diazotised, was obtained.

The work of Avenarius and Pschorr has been repeated, but without success; formyl-ß-phenylethylmethylamine, b. p. 183.5°/30 mm., now obtained in a state of purity, could not be isomerised by thionyl chloride to 1-hydroxy-2-methyltetrahydroisoquinoline, and isoquinoline methiodide was therefore used as starting material. As the results of a large number of condensations, following the method described by Avenarius and Pschorr, only 2-methyltetrahydroisoquinoline methiodide, m. p. 192° (corr.), was obtained. The assumed identity of the substance, m. p. 195°, described by Avenarius and Pschorr as dl-apomorphine dimethyl ether methiodide, with natural (lævorotatory) apomorphine dimethyl ether methiodide, m. p. 195° (corr.),  $[\alpha]_{\rm D} = 42.03^{\circ}$  (Pschorr, Jaeckel, and Fecht, A., 1903, i, 193), is criticised.

C. W. SHOPPEE.

5-hydroxy-2-methylindole. Derivatives of C. D. NENITZESCU (Bul. Soc. Chim. România, 1929, 11, 37-43).-Condensation of benzoquinone with ethyl  $\beta$ -aminocrotonate, ethyl  $\beta$ -anilinocrotonate, and ethyl glycineacetoacetate gave ethyl 5-hydroxy-2methylindole-3-carboxylate, m. p. 205°, ethyl 5-hydroxy-1-phenyl-2-methylindole-3-carboxylate, m. p. 206°, and ethyl 5-hydroxy-2-methyl-1-carbethoxymethylindole-3carboxylate, m. p. 148°, respectively. Methylation of ethyl 5-hydroxy - 2 - methylindole - 3 - carboxylate yielded ethyl 5-methoxy-2-methylindole-3-carboxylate, m. p. 161°, which, on alkaline hydrolysis, gave 5-methoxy-2-methylindole-3-carboxylic acid, melting at 208° to give 5-hydroxy-2-methylindole and carbon

dioxide. Condensation of 5-hydroxy-2-methylindole with ethyl orthoformate and with formic acid gave tri-(5-methoxy-2-methyl-3-indolyl)methane, m. p. 227°, and (5-methoxy-2-methyl-3-indolyl)-(5-methoxy-2methyl-3-indolylidene)methene hydrochloride, m. p. 230° (decomp.), respectively. A. A. GOLDBERG.

3-Nitro-2-aminopyridine-5-sulphonic acid. DEUTS. GOLD- & SILBER-SCHEIDEANST.—See B., 1929, 737.

Hexamethylenetetramine phenylquinolinecarboxylate (atophanurotropin). L. VANINO and F. MUSSGNUG (Arch. Pharm., 1929, 267, 487–488).— The pure salt is obtained by allowing hexamethylenetetramine and phenylquinoline-4-carboxylic acid to react in warm alcoholic solution. Hexamethylenetetramine and thiocarbamide afford a well-defined *compound*,  $2CS(NH_2)_2,(CH_2)_6N_4$ , m. p. 176–177°, when concentrated solutions of the two components are mixed. S. COFFEY.

Organic [quinoline] bases from arylamines and acetylene. I. G. FARBENIND. A.-G.—See B., 1929, 747.

Tautomerism of 2:5-dithionpiperazine. S. ISHIKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 119–129).—2: 5-Dithionpiperazine, darkening at 220–280°, may be prepared by a modification of the method of Gatewood and Johnson (A., 1927, 62) and also by heating 2:5-diketopiperazine with phosphorus pentasulphide. It dissolves in alkalis approximately as a dibasic acid. Colour reactions, e.g., with nitroprusside, indicate that it behaves as an enolic compound only in alkaline solution. The absorption spectrum of the solution in excess of dilute sodium hydroxide solution differs from those of solutions in ether, water, one equivalent of sodium hydroxide solution, or dilute acid. An attempt to isolate the enolic form by treatment with aniline was unsuccessful. 2:5-Dithion-1:4-dimethylpiperazine, darkening at 180°, m. p. 218°, is prepared by heating sarcosine anhydride with phosphorus pentasulphide. The action of hydrogen sulphide on a-aminoisobutyronitrile yields a substance, m. p. 156° (cf. Gatewood and Johnson, A., 1928, 745), but 2:5-dithion-3:3:6:6tetramethylpiperazine, sintering at 160°, m. p. 188°, is formed by heating 2:5-diketo-3:3:6:6-tetramethylpiperazine with phosphorus pentasulphide. The fact that the 1:4-dimethyl and 3:3:6:6-tetramethyl derivatives are, respectively, sparingly and readily soluble in alkalis indicates that the mobile hydrogen atom is that of the imino-group, contrary to the assumption of Abderhalden and Schwab (A., 1926, 740). Absorption spectra of the two derivatives are R. K. CALLOW. given.

**Pyrazolines.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 541—545).—Yields of pyrazolines amounting to 80% are obtained when the condensation of the  $\alpha\beta$ -ethylenic ketone with hydrazine hydrate is effected in methyl alcohol and the distillation is carried out in an atmosphere of nitrogen (cf. Auwers and Heimke, A., 1927, 1203). Hydrolysis of the distillation residues with 20% sulphuric acid yields a further small amount of pyrazoline and ketones not always identical with the original  $\Delta^{\alpha\beta}$ -ketone. The luminescence reported by Straus, Muffat, and Heitz (A., 1919, i, 41) has not been observed in pyrazolines prepared by the authors. The latter pyrazolines are stable to dilute mineral acids and on boiling afford only the salt of the original base, and the fission observed by Curtius and Wirsing (A., 1895, i, 248) appears to be peculiar to the first member of the series. No formation of gas was observed when the pyrazolines were heated in a sealed tube at 130° with 10% sodium hydroxide solution. Crystalline derivatives are obtained with benzenesulphonyl and p-bromobenzenesulphonyl chloride in pyridine, pyrazolines derived from alkylideneacetones, CHR:CHAc, giving one, those from alkyl-alkylideneacetones, CHR:CAc·CH<sub>2</sub>R', giving two isomeric derivatives (cf. this vol., 330). R. BRIGHTMAN.

Pyrazolines and their derivatives. R. HEIL-MANN (Bull. Soc. chim., 1929, [iv], 45, 545—548).— 3:5:5-Trimethylpyrazoline, b. p. 51— $52^{\circ}/11$  mm., (benzenesulphonate, C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>·SO<sub>3</sub>Ph, m. p. 140—141°; p-bromobenzenesulphonate, m. p. 122°), 3-methyl-5-isopropylpyrazoline, b. p. 76—78°/11 mm. (benzenesulphonate, m. p. 114°; p-bromobenzenesulphonate, m. p. 134—135°), and 3-methyl-5-isobutylpyrazoline, b. p. 91—92°/10 mm. (benzenesulphonate, m. p. 115°; p-bromobenzenesulphonate, m. p. 148°), are described. The isobutylidene- and isoamylidene-acctone required were obtained from the corresponding ketols, methyl β-hydroxy-γ-methylbutyl ketone, b. p. 90°/16 mm. semicarbazone, m. p. 146—147°), and methyl β-hydroxy-δ-methylamyl ketone, b. p. 104°/17 mm. (semicarbazone, m. p. 141—142°), prepared by Grignard and Dubien's method (A., 1925, i, 111; cf. Pastureau and Zamenhoff, A., 1926, i, 272). R. BRIGHTMAN.

Action of potassium cyanate in acid medium pyrazolines. Pyrazolinecarbamides. on R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 549-552).-3:5-Dialkylpyrazolines are converted by potassium cyanate in dilute hydrochloric acid or glacial acetic acid into 1-carbamyl derivatives,  $CHR:N > N \cdot CO \cdot NH_2$ , for which the name pyrazolinecarbamides is proposed. These compounds are isomeric with the normal semicarbazones of the corresponding  $\alpha\beta$ -unsaturated ketones and aldehydes. They yield crystalline picrates, are hydrolysed by hydrochloric acid  $(d \ 1 \cdot 1)$  to the pyrazolines, and are converted by nitrous acid into the original ketone. 1-Carbamyl-3:5:5-trimethylpyrazoline, m. p. 129°, b. p. 140-141°/10 mm. (dibenzoyl derivative, m. p. 176°), 1-carbamyl 3-methyl-5-isopropylpyrazoline, m. p. 116—117°, b. p. 155—157°/11 mm. (dibenzoyl derivative, m. p. 141°), 1-carbamyl-3-methyl-5-isobutyl-

pyrazoline, m. p. 110—111°, b. p. 162—168°/10 mm. (dibenzoyl derivative, m. p. 128—129°), and 1-carbamyl-4-methyl-5-ethylpyrazoline, m. p. 109—110°, b. p. 155—160°/11 mm., from 4-methyl-5-ethylpyrazoline, b. p. 65—70° (benzenesulphonate, m. p. 118°), are described (cf. A., 1925, i, 1185; Auwers and Heimke, A., 1927, 1203). R. BRIGHTMAN.

Constitution of "Scholtz' base." R. Locquin and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 553-555).—The base, m. p. 129°, b. p. 212-213° (decomp.), obtained by Scholtz (A., 1896, i, 343; cf. Harries and Kaiser, A., 1899, i, 637) on heating the normal semicarbazone of mesityl oxide is 1-earbamyl-3:5:5-trimethylpyrazoline (picrate, m. p. 136-137°) (cf. preceding abstract). R. BRIGHTMAN.

1-Furyl-2-methylcyclopropane. N. KISHNER (J. Russ. Phys. Chem. Soc., 1929, 61, 781–788).— 5. Furyl-3-methylpyrazoline, b. p. 127–128°/22 mm.,  $d_{*}^{2n}$  1·1507, was prepared by the interaction of furfurylideneacetone, m. p. 37°, b. p. 105–106°/10 mm., and hydrazine in alcoholic solution. It was converted by phenylthiocarbimide into phenyl-(5-furyl-3-methylpyrazolinyl)thiocarbamide, which exists in two crystalline forms both having m. p. 135°, viz., unstable needles, and stable cubes or rhombohedra.

When 5-furyl-3-methylpyrazoline was gently warmed with potassium hydroxide and fragments of platinised porcelain, heat and nitrogen were evolved, 1-furyl-2-methylcyclopropane, b. p. 144·2°/743 mm. and 145·2°/758 mm.,  $d_4^{30}$  0·9522,  $n_{10}^{30}$  1·4758, being formed. This is readily oxidised in air, responds to the furan pine-shaving test, and gives a crimson coloration with concentrated sulphuric acid in acetic anhydride solution. Bromine converts it into a tetrabromide, and potaşsium permanganate oxidises it to 2-methylcyclopropanecarboxylic acid, b. p. 98—99°/18 mm., 194°/ 742 mm. and 197—198°/768 mm.,  $d_4^{15}$  1·0480,  $n_1^{15}$ 1·4441 (calcium salt, +1·5H<sub>2</sub>O; silver salt; amide, m. p. 99\*5—100°). (See Marburg, A., 1897, i, 141.) M. ZVEGINTZOV.

Condensation products of the benzodiazine [quinazoline] series. I. G. FARBENIND. A.-G.— See B., 1929, 747.

Dyes of the phenonaphthasafranine series. J. R. GEIGY.—See B., 1929, 674.

2-Phenyl- $\alpha\beta$ -naphth-1 : 2 : 3-triazolemonosulphonic acids. A. NERI (Gazzetta, 1929, 59, 384—391).—Sulphonation of 2-phenylnaphthtriazole (5 parts) by heating at 180° with concentrated sulphuric acid (1 part) yields the 4-sulphonic acid (annexed formula) [sodium (+1.5H<sub>2</sub>O), potassium



 $(+1.5H_2O)$ , and barium  $(+5H_2O)$ salts]. The constitution of the acid is proved by the formation of 2-phenylnaphthtriazolequinone by oxidation with chromic acid and by its non-identity with the 5-sulphonic

acid [sodium salt  $(+3H_2O)$ ]. The latter is obtained from 1-aminonaphthalene-2-azobenzene-5-sulphonic acid [sodium salt  $(+1\cdot5H_2O)$ ] by dehydrogenation by the action of sodium dichromate and acetic acid in nitrobenzene. Sodium 2-aminonaphthalene-1-azobenzene-4'sulphonate  $(+H_2O)$  is similarly converted into 2-phenylnaphthtriazole-4'-sulphonic acid (sodium salt, anhydrous), which is oxidised by chromic acid in acetic acid to yield 2-phenylnaphthtriazolequinone-4'sulphonic acid [sodium salt  $(+2\cdot5H_2O)$ ]; this yields with phenylhydrazine the 5-hydroxy-4-azobenzene derivative [sodium salt  $(+3H_2O)$ ].

R. K. CALLOW. Porphyrin syntheses. XXIV. Syntheses of three pyrroporphyrins, a rhodoporphyrin, a pyrroætioporphyrin, and a deuteroporphyrin. H. FISCHER and A. SCHORMÜLLER (Annalen, 1929,

473. 211-249).-Eight pyrroætioporphyrins (tetramethyltriethylporphins) are theoretically capable of existence and these can give rise to twenty-four pyrroporphyrins (tetramethyldiethyl-\beta-carboxyethylporphins). Three of the last-named compounds have been synthesised by methods similar to those previously described (cf. A., 1928, 1384). Cryptopyrrolecarb-oxylic acid condenses with 2:4-dimethylpyrrolealdehyde in presence of alcoholic hydrobromic acid, forming (3:5-dimethylpyrryl)-(3:5-dimethyl-4-B-carboxyethylpyrrolenyl)methene hydrobromide (I), m. p. 223° (decomp.) (free base, m. p. 172° after darkening at 145°). When I is heated with (5-bromo-3-methyl-4-ethylpyrryl)-(5-bromo-3-methyl-4-ethylpyrrolenyl)methene hydrobromide in presence of succinic acid about 15% of 1:4:5:8-tetramethyl-3:6-diethyl-7-3-carboxyethylporphin [termed pyrroporphyrin 6] (II) [methyl ester, m. p. 228° (phyllin derivative); copper salt, m. p. above 300°; hæmin derivative] is obtained. Treatment of II with sulphuric acid at 100° affords the corresponding *rhodin* (copper salt), whilst treatment with pyridine and 10% sodium ethoxide solution at  $180-190^\circ$  and subsequent acidification gives the corresponding chlorin. Bromination of I with 1 mol. of bromine in hot acetic acid solution yields a monobromo-derivative, C16H2002N2Br2, m. p. 228-230°, which on esterification and subsequent treatment with ammonia furnishes the brominated methene ester,

C<sub>19</sub>H<sub>25</sub>O<sub>2</sub>N<sub>2</sub>Br(?), m. p. 106°; with 3 mols. of bromine I gives the compound C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>3</sub>, not melted at 245°. When equimolecular quantities of I and (5-bromo-4-methyl-3-ethylpyrryl)-(5-bromo-4-methyl-3-ethylpyrrolenyl)methene are heated with methylsuccinic acid at 180-200°, 15% of 1:4:6:7-tetramethyl-2: 3-diethyl-8-β-carboxyethylporphin [pyrroporphyrin 21] (III) [methyl ester, m. p. 218-219° hæmin derivative (IV); copper salt, m. p. about  $300^{\circ}$  after sintering at  $270^{\circ}$ ; *rhodin*] results. Treatment of IV with acetic anhydride and stannic chloride, and subsequent removal of iron by treatment with acetic acid and hydrogen bromide at 40°, afford an acetyl derivative of III. 1:3:5:8-Tetramethyl-4:6-diethyl-7-\beta-carboxyethylporphin [pyrroporphyrin 18] (methyl ester, m. p. 248°) is prepared by heating (5-bromo-4-methyl-3-ethylpyrryl)-(5-bromo-3-methyl-4-ethylpyrrolenyl)methene hydrobromide with the methene from 2:4-dimethylpyrrolealdehyde and opsopyrrolecarboxylic acid and succinic acid at 180-200°. The three pyrroporphyrins described are designated iso-compounds, since the m. p. of the methyl esters differ from the m. p. of "analytical" pyrroporphyrin methyl ester; the absorption spectra of the porphyrins are identical.

Cryptopyrrolecarboxylic acid and 2:4-dimethyl-3carbethoxypyrrole-5-aldehyde condense in presence of alcoholic hydrobromic acid, yielding (3:5-dimethyl-4carbethoxypyrryl)-(3:5-dimethyl-4- $\beta$ -carboxyethylpyrrolenyl)methene hydrobromide (V), m. p. 205°, esterified by alcoholic hydrogen bromide to the hydrobromide, m. p. 169°, of the methene diester, m. p. 100°, and brominated first to a perbromide, C<sub>19</sub>H<sub>24</sub>O<sub>4</sub>N<sub>2</sub>Br<sub>2</sub>, m. p. 203—206°, and subsequently to a compound, m. p. 219°. When a mixture of V, (5-hromo-4-methyl-3ethylpyrryl)-(5-bromo-4-methyl-3-ethylpyrrolenyl)methene hydrobromide (VI), and succinic acid is heated rapidly over a free flame a small amount of the monoethyl ester, m. p. 290°, of rhodoporphyrin 21 (VII) (cf. this vol., 940) [dimethyl ester, m. p. 218° (copper salt, m. p. 239°; heemin, m. p. 306°, and phyllin derivatives)] is obtained. Thermal decomposition of VII or decarboxylation by heating with methylalcoholic potassium hydroxide and pyridine at 180— 190° in a sealed tube affords III.

Hydrobromic acid condensation of cryptopyrrolealdehyde and 3-acetyl-2:4-dimethylpyrrole affords (3: 5-dimethyl-4-ethylpyrryl)-(4-acetyl-3: 5-dimethylpyrrolenyl)methene hydrobromide (VIII), m. p. 237° (decomp.) (free base, m. p. 159°), which on treatment with bromine in acetic acid solution at 40—50° gives a perbromide,  $C_{17}H_{23}ON_2Br_3$ , m. p. 202° (decomp.). Succinic acid fusion of VI and VIII yields 2—3% of 2-acetyl-1:4:6:7-tetramethyl-3:5:8-triethylporphin [acetylpyrroætioporphyrin], not melted at 290°. Ethyl 1:4:6:7-tetramethyl-3:5:8-triethylporphin-2-carboxylate, m. p. 264° (methyl ester, m. p. 262°), is obtained similarly from VI and (3:5-dimethyl-4-ethylpyrryl)-(3:5-dimethyl-4-carbethoxypyrrolenyl)methene hydrobromide, m. p. 203° (decomp.).

Succinic acid fusion of a mixture of VI and (3-methyl-5-bromomethylpyrryl)-(3-methyl-4-ethyl-5bromomethylpyrrolenyl)methene hydrobromide gives 1:4:6:7-tetramethyl-2:3:8-triethylporphin [pyrroætioporphyrin 7] (bromo-derivative; chlorin, prepared by reduction of the hæmin derivative with sodium and amyl alcohol).

Opsopyrrolecarboxylic acid and dimethylpyrrolealdehyde condense in presence of alcoholic hydrobromic acid, forming  $(3-methyl-4-\beta-carboxyethylpyrryl)$ -(3:5-dimethylpyrrolenyl)methene hydrobromide, m. p. $220-221^{\circ}$  (decomp.), which when heated with (5bromo-3-methyl-4- $\beta$ -carboxyethylpyrryl)-(3-methyl-5bromomethylpyrrolenyl)methene hydrobromide and succinic acid at 240° yields 1:4:5:8-tetramethyl-2:6-di- $\beta$ -carboxydiethylporphin [deuteroporphyrin 5] [dimethyl ester, m. p. 300° (copper salt, m. p. 281°; hæmin derivative)]. Absorption spectra of most of the above porphyrins and their derivatives are given.

The absorption maxima of solutions of ætioporphyrin, meso- and proto-porphyrin esters in ethyl phthalate are displaced towards the red when the solution is warmed. At 200° the ætioporphyrin spectrum has the appearance of a rhodin spectrum; on cooling, it becomes normal again.

#### H. BURTON.

Chlorophyll. VII. Phæo- and phylloerythroporphyrins. H. FISCHER and R. BÄUMLER (Annalen, 1929, 474, 65—120).—Phæophorbide a (I),  $C_{35}H_{36}O_6N_4$  (cf. Willstätter and Stoll, "Chlorophyllbuch," 282), decomp. 190—200° (block), phæophorbide b (II), decomp. 215—225° (block), and phæophytin do not contain an acetyl group. When II is heated with 70% sulphuric acid carbon dioxide (approximately 2 mols.) is eliminated; 1 mol. of carbon dioxide is eliminated when I or II is heated alone at 100— 110°/vac. Esterification of I with diazomethane affords methylphæophorbide a,  $C_{36}H_{38}O_6N_4$ , decomp. 208° (block), whilst treatment of I with ferric acetate and sodium chloride or ferric chloride and sodium acetate in acetic acid gives an *iron* salt,

C35H38O7N4ClFe+AcOH. When I is heated with pyridine and methyl-alcoholic potassium hydroxide at 135-220° pyrroporphyrin is obtained; II is decomposed completely under these conditions, but at 155° small amounts of phyllo-, pyrro-, and verdoporphyrins result. In absence of pyridine at 150° I furnishes phyllo-, pyrro-, and rhodo-porphyrins (these and verdoporphyrin are obtained similarly from II), whilst at 200° rhodoporphyrin is the chief product. At 105° the hydrolysis products are chlorin (main) and rhodoporphyrin (small). Fission of I and II by boiling with methyl-alcoholic potassium hydroxide for a short time affords chlorin e and rhodin g, respectively. Both these last-named substances are formed in small amount by similar treatment of phæophytin (cf. Treibs and Wiedemann, A., 1928, 1383). Treatment of I with hydriodic acid in acetic acid at 100° gives pheoporphyrin a<sub>6</sub> (III), C<sub>33 or 34</sub>H<sub>36</sub>O<sub>6</sub>N<sub>4</sub> (iron, copper, and magnesium complex salts), esterified by methyl-alcoholic hydrogen chloride to a methyl ester (IV), probably C35H37O5N4, m. p. 259° [copper salt, m. p. 228° (block) after sintering at 220°]. When esterification is carried out with diazomethane a methyl ester,  $C_{31}H_{36}O_3N_4$ , m. p. 243°, results. Hydrolysis of IV first with 15% and then with 3% hydrochloric acid yields β-phæoporphyrin a4 (V), C33H35O4N4, whilst similar treatment of III gives  $\beta$ -phæoporphyrin a<sub>3</sub>, C<sub>30</sub>H<sub>31</sub>O<sub>3</sub>N<sub>4</sub>. Fission of III with pyridine and methyl-alcoholic potassium hydroxide at 155° affords pyrro- and rhodo-porphyrins only. When phæophytin and ethyl chlorophyllide are treated with hydriodic and acetic acids III is also produced, but from the chlorophyllide two other substances (methyl esters, m. p. 228 and 239°, respectively) are also obtained. Treatment of III with acetic acid and pyridine gives phæoporphyrin a4 (VI), C32H36O4N4 [copper and iron salts; dimethyl ester, m. p. 228° (not depressed by phylloerythrin ester)]. Alkaline fission of V and VI affords phyllo- in addition to pyrro- and rhodo-porphyrins. When phyllo- or rhodo-porphyrin is treated with hydriodic acid (d 1.96) in hot acetic acid solution pyrroporphyrin results (cf. Treibs and Wiedemann, loc. cit.).

Phylloerythrin (VII) (cf. Noack, this vol., 727) (iron salt) is esterified by methyl-alcoholic hydrogen chloride to a methyl ester,  $C_{32}H_{36}O_3N_4$ , m. p. 263°, and by diazomethane to a methyl ester,  $C_{33}H_{36}O_6N_4$ , m. p. 261°. The copper salt of VII is freed from metal by treatment with sulphuric acid, whereby a porphyrin,  $C_{30}H_{36}O_3N_4$ , results. Treatment of VII first with 15% and then with 3% hydrochloric acid furnishes  $\beta$ -phylloerythroporphyrin, (?)  $C_{31}H_{30}O_3N_4$ , esterified by methyl-alcoholic hydrogen chloride to a methyl ester,  $C_{32}H_{36}O_3N_4$ , m. p. 246°. Treatment of VII with acetic acid and pyridine gives phylloerythroporphyrin (VIII),  $C_{34}H_{36}O_3N_4$ . Alkaline fission of VII yields pyrro- and rhodo-porphyrins, whilst VIII affords phyllo- and rhodo-porphyrins. Crystallographic data (by STEINMETZ) and absorption spectra of a large number of the above compounds are recorded.

H. BUBTON.

Ring formation from acetyloximes of aromatic o-hydroxyketones. H. LINDEMANN and S. ROMANOFF (J. pr. Chem., 1929, [ii], 122, 214-231).--Nitration of 2-hydroxyacetophenoneoxime by nitric acid (d 1.4) in acetic acid solution gave 5-nitro-2hydroxyacetophenoneoxime, m. p. 231° (also obtained by oximation of the corresponding ketone), accompanied by (less) 3-nitro-2-hydroxyacetophenoneoxime, m. p. 182°. Nitration under similar conditions of 2-hydroxyacetophenoneacetyloxime afforded both 5-nitro-2-hydroxyacetophenoneacetyloxime, m. p. 167° (which passed, when heated at 175-185° in a vacuum, or when warmed with sodium carbonate solution, into 4-nitro-2-methylbenzisooxazole, m. p. 134°, b. p. 168-169°/13 mm.), and 3-nitro-2-hydroxyacetophenoneacetyloxime, m. p. 136-137° (also obtained by acetylation of the appropriate oxime, m. p. 182°, above).

Hydrolysis with hydrochloric acid of the oximes of m. p. 231° and 182° (above) gave, respectively, 5-nitro-2-hydroxyacetophenone, m. p. 111—112°, and 3-nitro-2-hydroxyacetophenone, m. p. 89—90°. The 5-nitro-ketone was reduced by stannous chloride and hydrochloric acid to the corresponding *amine*, m. p. 121—122°, which gave by oximation 5-amino-2hydroxyacetophenoneoxime, m. p. 201—202°. The diacetyl derivative, m. p. 173—174°, of this compound, when heated in a vacuum at 180—190°, passed into 5-acetamido-3-methylisooxazole, m. p. 163°, b. p. 215°/13 mm.

Nitration of 3-methylbenzisooxazole by sulphuric acid and potassium nitrate yielded 5-nitro-3-methylbenzisooxazole along with some 4-nitro-3-acetamidophenol (from which ON-diacetyl-4-nitro-2-aminophenol, m. p. 196°, was prepared); similarly during the nitration of 3:5-dimethylbenzisooxazole to 7-nitro-3:5-dimethylbenzisooxazole, some 2-nitro-3-acetamido-p-cresol, m. p. 250° (decomp.) (ON-diacetyl derivative, m. p. 183°), was isolated. The production of these nitroaminophenols is taken as indicating the presence of alkylbenzoxazoles in the *iso*-compounds.

The following compounds are also described: 5-nitro-3-acetamido-p-cresol, m. p. 143°, 3:5-dimethyl-4-aminobenzisooxazole (obtained by reduction of the nitro-derivative by sodium hyposulphite), m. p. 110°, 7-hydroxy-3: 5-dimethylbenzisooxazole (by diazotisation of previous compound), m. p. 247°.

# R. J. W. LE FEVRE.

Monoarylguanidines. II. Benzoxazolylguanidine. G. B. L. SMITH, J. H. KANE, and C. W. MASON (J. Amer. Chem. Soc., 1929, 51, 2522-2527).o-Aminophenol and dicyanodiamidine react in presence of boiling alcoholic hydrochloric acid, forming the hydrochloride, m. p. 254-255°, of 2-guanidinobenzoxazole +H<sub>2</sub>O, m. p. 182-184° [sulphate, m. p. 280-281°; *nitrate*, m. p. 219-220°; *picrate*, m. p. 247-248°; *diacelyl* derivative, m. p. 209-210°; *methiodide* (?), m. p. 192-194°]. Descriptions of the crystalline forms of the salts are given. Dicyanodiamidine is probably tautomeric :

 $\mathbf{NH:} \mathbf{C}(\mathbf{NH}_2) \cdot \mathbf{NH} \cdot \mathbf{CN} \Longrightarrow \mathbf{CN} \cdot \mathbf{N:} \mathbf{C}(\mathbf{NH}_2)_2.$ 

## H. BURTON.

Dyes derived from cinchomeronic acid. J. D. TEWARI (J.C.S., 1929, 1642-1644).—The following compounds were obtained by heating cinchomeronic acid with the appropriate amine or hydroxy-com-



pound in the presence of stannic chloride or of concentrated sulphuric acid : *phenol*-, unmelted at 275°; *resorcinol*-, m. p. 200°; *phloroglucinol*-, m. p. 270°; *m-diethylaminophenol*-, m. p. 127°, and m-*phenylenediamine*-*cinchomerein*, m. p. 275°. The resulting dyes have the general formula I and resemble the corresponding dyes

from quinolinic acid (Ghosh, J.C.S., 1919, 115, 1102) very closely in chemical and physical properties. A. I. VOGEL.

Nicotine and its derivatives. II. Optical rotatory power and rotatory dispersion. T. M. LOWRY and W. V. LLOYD (J.C.S., 1929, 1771-1791). -Measurements at 20° of the optical rotatory power and also of the rotatory dispersion, over a wide range of wave-lengths, of nicotine, of nicotine in acctone, water, acetic and butyric acids, of nicotine butyrate and crotonate in acetone, and of the last-named in acetone, of the nicotine-zine chloride double compound in water, and of nicotine dimethiodide in water have been made and the data employed to test the applicability of the one-term Drude equation. The characteristic frequencies deduced from the rotatory dispersions are compared with the observed maxima of selective absorption. It is suggested that nicotine forms a pseudo-base, and that the reversal in sign on salt formation is associated in nicotine with the saturation of a lone pair of electrons in the pyrrolidine nitrogen, and is dependent on the elimination of an incipient dative linking between the two rings.

The best values for the specific rotations of nicotine are  $[\alpha]_{10}^{20} + 169.3^{\circ}, [\alpha]_{3461}^{20} + 204.1^{\circ}$ . A. I. VOGEL.

Sparteine. K. WINTERFELD (Arch. Pharm., 1929, 267, 433-455).-[With F. W. HOLSCHNEIDER.] Dibromosparteine dicyanamide (chloroaurate, m. p. 144-145°) and two isomeric monobromosparteine cyanamides, one monobasic, m. p. 89° (chloroaurate, m. p. 178°; picrate, m. p. 165°; mercurichloride, m. p. 117°), the other a dibasic oil (chloroaurate, m. p. 181° (decomp.); picrate, m. p. 176°], are produced when evanogen bromide is allowed to react on sparteine directly. These compounds are also obtained along with sparteine hydrobromide when the reagents are mixed in moist ethercal solution, but in absolute ether a double *compound* of sparteine and cyanogen bromide is obtained. The two isomeric monobromosparteine cyanamides are obtained in varying amounts according to the conditions of experiment, the proportions of crystalline isomeride to liquid isomeride being 1:2 in ether, 2:1 in boiling benzene, whilst only the crystalline modification is produced in boiling cyclohexanol. Reduction of the crystalline form with tin and hydrochloric acid affords sparteine cyanamide (chloroaurate, m. p. 186-187°; chlorostannate), which gives a secondary base,  $[\alpha]_{D} = -16.3^{\circ}$ in chloroform, very stable towards alkaline permanganate solution, on treatment with 60-65% sulphuric acid (complex chloroaurate, m. p. 130-131°; picrate, m. p. 179°). This base affords an oily monobenzoyl derivative [chloroplatinate, decomp. 195°;
chloroaurate, m. p. 145° (decomp.)], which on degradation by means of phosphorus pentabromide produces a base (chloroplatinate, m. p. 248-249°; chloroaurate, m. p. 178-179°) giving a pyrrole reaction. Under similar conditions, the liquid bromosparteine cyanamide affords a sparteine cyanamide,  $[\alpha]_{\rm D} = -11.84^{\circ}$  in chloroform [chloroaurate, m. p. 172° (decomp.); picrate, m. p. 172-173° (decomp.); chlorostannate. m. p. 128°], and a liquid secondary base,  $[\alpha]_p - 16.5^{\circ}$ in chloroform [chloroaurate, m. p. 181-182° (decomp.); picrate, m. p. 178°; chloroplatinate; m. p. 257° (decomp.)], which gives a benzoyl derivative, [a] -13.6° in chloroform [chloroaurate, m. p. 185° (decomp.); chloroplatinate, m. p. 248-249° (decomp.)]. Degradation of the latter with phosphorus pentabromide affords a bromo-compound (chloroaurate) produced by the partial fission of the ring and subsequent hydrolysis of a bromoimide, to which the formula NHBz·CH<sub>2</sub>·CH<sub>2</sub>·CHEt·CH(CH<sub>2</sub>Br)·CH<sub>2</sub>·C<sub>7</sub>H<sub>12</sub>N is ascribed. The latter gives a base, b. p. 160°, [a]<sub>p</sub> -11.5° in chloroform [chlorostannate, m. p. 160°; chloroaurate, m. p. 196-197° (decomp.); chloroplatinate, m. p. 255° (decomp.); hydriodide, m. p. 227°; picrate, m. p. 180°; mercurichloride; methiodide, m. p. 205°], which does not give the pyrrole reaction, on reduction with tin and hydrochloric acid. From these results it is concluded that sparteine is an alkylated  $\alpha$ - or  $\beta$ -quinuclidine, which is confirmed by study of the degradation of  $\alpha$ -methylquinuclidine.

[With C. VON RAUSCH.] Dehydrosparteine may be oxidised with potassium permanganate to an acid, which is readily esterified and the methyl(?) ester (cf. A., 1928, 906) affords a *benzoyl* derivative, m. p. 142— 143° (decomp.). The latter is broken down by phosphorus pentabromide to the corresponding secondary cyclic amine, which gives a hydrocarbon and 2-methylpyrrolidine on oxidation with permanganate. Thus the second tertiary nitrogen atom in sparteine is situated in a pyrrolidine ring.

S. COFFEY.

Synthetical experiments on the aporphine alkaloids. VII. Attempted syntheses of apomorphine dimethyl ether. J. M. GULLAND, R. D. HAWORTH, C. J. VIRDEN, and (in part) R. K. CALLOW (J.C.S., 1929, 1666-1676).-Condensation of m-nitro-benzyl chloride and ethyl sodiomalonate in alcohol afforded a mixture of ethyl di-(3-nitrobenzyl)malonate, m. p. 112°, and ethyl 3-nitrobenzylmalonate, from which 3-nitrobenzylmalonic acid, m. p. 171°, was obtained by partial hydrolysis with 30% potassium hydroxide solution. The latter on heating gave 3-3-nitrophenylpropionic acid, m. p. 117-118°, converted by thionyl chloride and aqueous ammonia into the amide, m. p. 99°, then by sodium hypochlorite into β-3-nitrophenylethylamine hydrochloride, m. p. 207-209°, and finally by stannous chloride and hydrochloric acid into \$-3-aminophenylethylamine dihydrochloride (I), m. p. 310° (decomp.). Condensation of the free base of I with 2-nitro-3: 4-dimethoxyphenylacetyl chloride in benzene furnished 2'-nitro-3': 4'dimethoxyphenylaceto-\$\beta-3-(2"-nitro-3" : 4"-dimethoxyphenylacetamido)phenylethylamide, from which no basic material could be isolated after prolonged treatment with phosphorus pentachloride in chloroform.

B-Phenylethylamine 2-benzamidophenylglyoxylate,

m. p. 177-179° (decomp.) (from 2-benzamidophenylglyoxylic acid and  $\beta$ -phenylethylamine in ether), could not be converted into the amide by phosphorus pentachloride or phosphoric oxide; 2-benzamidophenylglyoxylo-\$-phenylethylamide, m. p. 136.5-138°, was produced by interaction of the acid chloride of 2-benzamidophenylglyoxylic acid and β-phenylethylamine in benzene, but was unaffected by treatment with phosphorus pentachloride in chloroform for 1 month. a-Cyano-2-nitro-3: 4-dimethoxystilbene, m. p. 125.5°, is obtained by condensation of 2-nitro-3: 4dimethoxyphenylacetonitrile and benzaldehyde in alcohol in the presence of sodium ethoxide or piperidine at 40-50°. a-Cyano-2-nitro-3: 4-dimethoxy-2'aldehydostilbene, m. p. 153° (phenylhydrazone, m. p. 179—180°), is similarly prepared (80% yield) from the nitrile and phthalaldehyde at  $45^\circ$ : it is unaffected by boiling with concentrated hydrochloric acid for 24 hrs., by stannous chloride or tin in a cold mixture of glacial acetic and hydrochloric acids, and by aqueous ammonia, is destroyed by zine dust in hot dilute hydrochloric or acetic acid, and no crystalline product is obtained on heating with malonic acid and piperidine in pyridine solution.

When a mixture of *m*-aminobenzoic acid (1 mol.) and  $\alpha$ -cyano-2-nitro-3: 4-dimethoxy-2'-aldehydostilbene (1 mol.) is heated at 135° for 30 min.  $\alpha$ -cyano-2-nitro-3: 4-dimethoxy-2'-m-carboxyphenyliminomethylstilbene, m. p. 237° (decomp.), is obtained, and is converted by reduction with ferrous sulphate and ammonia in a hydrogen atmosphere into 2-(2'-m-carboxyanilinomethylphenyl)-3-cyano-6 : 7-dimethoxyindole (II) or the dihydro-derivative [hydrochloride, m. p. 307° (decomp.)], unaffected by concentrated hydro-

OMe 
$$C C CN$$
  
 $C C_6 H_4 CH_2 NH C_6 H_4 CO_2 H$  (II.)  
OMe NH

chloric acid and yielding the *tri-* and *hexa-hydrates*, m. p. 322°, of II on decomposition with aqueous sodium acetate. This substance is unsuitable for the synthesis of *apo*morphine dimethyl ether.

Piperonylidene-m. and -p-aminobenzoic acids, m. p. 244-245° and 243°, respectively, are formed by heating piperonal with the acids at 160° for 30 min.

A. I. VOGEL.

Sinomenine and disinomenine. X. Synthesis of dimethylsinomenol. Sinomenolquinone. K. Goto and H. SADZUKI (Bull. Chem. Soc. Japan, 1929, 4, 163—169).—The synthesis of 3:4:6:7-tetramethylphenanthrene and its identity with dimethylsinomenol (Kondo and Ochiai, this vol., 1088) has been confirmed. Sinomenol is considered to be 4:6-dihydroxy-3:7-dimethoxyphen-

OMe OH H2 OMe anthrene. The reactions of sinomenine are reviewed and to it is assigned the annexed revised formula (cf. Goto, A., 1920, 1160).

When diacetylsinomenol is oxid-NMe ised by chromic anhydride in acetic acid there is formed diacetylsinomenolquinone, m. p. 217-219° (phenazine compound, m. p.

256°), which on hydrolysis yields sinomenol-

quinone, m. p. 259-263° (phenazine, m. p. 272°). When dibenzoylsinomenolquinone (Goto, loc. cit.) is treated with alkyl sulphates in alkaline solution there are formed sinomenolquinone diethyl ether, m. p. 174° (phenazine, m. p. 188°), and sinomenolquinone dimethyl ether, m. p. 266° (phenazine, m. p. 184°).

T. H. MORTON. Organic antimony compounds [arylstibinic acids]. I. G. FARBENIND. A.-G.—Sce B., 1929, 699.

Tin methyl derivatives. Action of zinc on tin trimethyl bromide. Tin trimethyl phenoxide. Decamethylstannobutane. C. A. KRAUS and A. M. NEAL (J. Amer. Chem. Soc., 1929, 51, 2403— 2407).—Zinc and tin trimethyl bromide react in aqueous solution, giving mainly tin tetramethyl accompanied by tin trimethyl hydroxide and metallic tin. Sodium phenoxide in liquid ammonia solution converts tin trimethyl bromide into phenoxytrimethylstannane, SnMe<sub>3</sub>·OPh, b. p. 223—224°, which is stable in air but colours in sunlight, and reacts with the appropriate quantity of sodium as follows : SnMe<sub>3</sub>·OPh+2Na=SnMe<sub>3</sub>Na+NaOPh; 2SnMe<sub>3</sub>·OPh +2Na=(Me<sub>3</sub>Sn)<sub>2</sub>+2NaOPh. Decamethylstannobutane, Me<sub>10</sub>Sn<sub>4</sub>, obtained by the interaction in liquid ammonia of disodium tetramethylstannoethane and tin trimethyl bromide, is a somewhat viscous, colourless liquid which readily oxidises to a white solid. S. K. TWEEDY.

Deaminocaseinogen. H. STEUDEL and R. SCHUMANN (Z. physiol. Chem., 1929, 183, 168—176).— Caseinogen was subjected to deamination by nitrous acid and the nitrogen loss in the various fractions obtained on hydrolysis investigated. Nitrous acid causes no considerable changes in the caseinogen molecule. The lysine fraction is attacked, the arginine in part, and the histidine more strongly. Tyrosine and tryptophan are unchanged. The cystine content by Folin's method of the deaminated molecule was about six times that of the original material. J. H. BIRKINSHAW.

Proteins. V. Benzoylproteins : benzoylovalbumin and its hydrolysis. S. GOLDSCHMIDT and A. KINSKY (Z. physiol. Chem., 1929, 183, 244-260; cf. A., 1927, 581).-The hydrolysis of benzoylalbumin with alkali and acid was studied. Definite breaks in the time curve appear with N-sodium hydroxide (at 100°) at 6.5% and 12.5-13% hydrolysis. With sulphuric acid at 34° the benzoyl groups hydrolysed reach a steady maximum at 6.5%. At 100° the hydrolysis again reaches a maximum in a few hrs. and about 90% of the total nitrogen is present as amino-nitrogen. About 7% of the benzoyl complex remains unhydrolysed. c-Benzoyllysine was isolated from this portion, showing that the *e*-amino-group of lysine accounts for about half of the free amino-groups of egg-albumin.

### J. H. BIRKINSHAW.

Degradation of gelatin with acetic anhydride. Isolation of acetylated associates of partly dehydrated polypeptides. IV. Degradation of proteins and their derivatives. A. FODOR and C. EPSTEIN (Biochem. Z., 1929, 210, 24-41; cf. A., 1928, 1387).—Degradation of gelatin with acetic anhydride under conditions in which hydrolysis is excluded gives a value of 0.66 for the ratio amino-nitrogen/total nitrogen (v), but if the treatment with the reagent is repeated several times v approaches 0.5. This suggests a degradation of a tri- to a di-peptide of proline or hydroxyproline. From other considerations the proline group must occupy the central position in the chain between a glycine and an alanine group. The acetylated gelatin complexes represent associations of three tripeptide groups. Possible constitutions for these are considered.

J. H. BIRKINSHAW.

Denaturing of proteins. I. T. TADOKORO and K. YOSHIMURA. II. T. TADOKORO and S. WATANABE (J. Fac. Agric. Hokkaido, 1928, 25, 117—132, 133—149).—Rice oryzenin was denatured in solution by boiling and by freezing; soya-bean glycinin by boiling, freezing, superheated steam, gasoline, or benzine; soya beans by heating, boiling, freezing, and soaking in gasoline; salmon proteins by cooling, freezing, salting, and smoking. The resulting chemical and optical changes were followed.

CHEMICAL ABSTRACTS.

Nitrogen distribution of gelatin. F. S. DAFT (Compt. rend. Trav. Lab. Carlsberg, 1929, 17, No. 12, 1—17).—Contrary to the statements of other workers (Knaggs, A., 1923, i, 1143; Knaggs and Schryver, A., 1925, i, 90; Thornley, A., 1928, 81), preliminary treatment of gelatin with acid or alkali has no effect on the percentages of non-amino- and of diaminonitrogen. The methods of determination of the different forms of nitrogen in proteins are discussed and certain modifications are described which, it is claimed, give comparable figures for nitrogen distribution. In particular, separation of amino-acids with phosphotungstic acid is carried out under strictly defined conditions of concentration and temperature, and the treatment of the fractions before determination by the nitrous acid or formaldehyde methods is described. R. K. CALLOW.

Determination of carboxyl groups in digestion products of proteins. I. A. SMORODINCEV, A. N. ADOVA, and S. S. TSCHULKOVA (Fermentforsch., 1929, **11**, 37–44).—The method described by Felix and Müller (A., 1928, 535) gives best results when a 0.01% solution of alizarin-yellow is used as indicator and 0.5 c.c. of this is mixed with the alkali (10 c.c.). The total amount of carboxyl groups present is determined, whereas Willstätter and Waldschmidt-Leitz' method (A., 1922, ii, 169) gives values both for amino-acids and peptides. H. BURTON.

Determination of antimony in organic antimony compounds. S. GHOSH (Indian J. Med. Res., 1929, 16, 457–460).—The substance (0.05-0.07 g)is digested with 2 g. of potassium sulphate and 3 c.c. of arsenic-free, concentrated sulphuric acid in a loosely-stoppered conical flask until colourless, diluted with 25 c.c. of distilled water, and boiled for 3–5 min. To the warm solution 3–4 c.c. of concentrated hydrochloric acid are added and the solution is rapidly cooled and diluted to 100 c.c.; 25 c.e. of this solution are made faintly alkaline to litmus by a 40% solution of sodium hydroxide, acidified with 5 c.c. of a 1% solution of tartaric acid, and again made alkaline with 10 c.e. of a 4% solution of sodium hydrogen carbonate.

After addition of 25-30 drops of a 1% starch solution, the antimony is determined by titration with 0.01Niodine solution previously standardised against sodium antimony tartrate. By titration of the whole of the solution instead of an aliquot part, accurate results may be obtained with only 0.02 g. of substance.

J. W. BAKER. Rapid determination of alcohol. W. L. O. WHALEY (Planter and Sugar Mfr., 1928, 81, 321-323).-Alcohol is satisfactorily determined by measurement, with the Juerst ebulliometer, of the lowering of h. p. of its aqueous solution.

CHEMICAL ABSTRACTS.

Influence of boric acid on oxidation of organic substances with which it forms complexes. I. General investigations based on methods used in sugar analysis. J. VOICU and (MLLE.) V. DUMITRESCU (Bul. Soc. Chim. România, 1929, 11, 15-24).-Low results are obtained in the determination of reducing sugars by the usual methods when boric acid is present, the deficit increasing with increasing boric acid content. The formation of boric acid-tartrate complexes etc. as well as that of boric acid-sugar complexes is possible. Priority is claimed over Levy and Doisy (A., 1928, 741). J. S. CARTER.

## Biochemistry.

Storage of manganese and copper in the animal body; influence on hæmoglobin formation. R. W. TITUS and J. S. HUGHES (J. Biol. Chem., 1929, 83, 463-467).-Addition of small amounts of copper or manganese to a whole wheat-milk powder diet did not prevent the development of nutritional anæmia, but enabled the animals to utilise inorganic iron for the synthesis of hæmoglobin. C. R. HARINGTON.

Physico-chemical properties of natural globin. G. ROCHE (Compt. rend., 1929, 189, 378-380).-The isoelectric point of globin, obtained from hæmoglobin by the method of Hill and Holden, has been determined by cataphoresis and by means of neutralisation curves, both methods giving a single value of  $p_{\rm H}$  7.5, whereas that of hæmoglobin is at  $p_{\rm H}$  6.8. It is suggested that this lowering of  $p_{\rm H}$  is the natural result of combination with the acid hæmatin.

#### P. G. MARSHALL.

Change in oxyhæmin on drying. A. HAMSÍK (Z. physiol. Chem., 1929, 183, 269-272).-The reactivity of a-oxyhæmin preparations is lessened on drying, owing to anhydride formation. Probably a-oxyhæmin exists pure only in the moist state, but hæmins (especially formylhæmin) retain their J. H. BIRKINSHAW. reactivity on drying.

Peroxidase reaction. XXIV. Simultaneous application of the oxidase and peroxidase reactions on leucocytes. K. Tokuź (Tohoku J. Exp. Med., 1929, 12, 295-300).-Saturated aqueous benzidine (containing 2 drops of 3% hydrogen peroxide per 100 c.c.) is applied to an air-dried fresh blood smear for 2 min., followed by 1% aqueous eosin for 5-10 sec. After washing and examining, Winkler-Schultze oxidase reagent is added, the slide being washed and re-examined after 2 min.

CHEMICAL ABSTRACTS.

Immediate acid change in shed blood. R. E. HAVARD and P. T. KERRIDGE (Biochem. J., 1929, 23, 600-607).-There is a change in the hydrogen-ion concentration of blood, soon after being shed, of  $-0.05 p_{\rm H}$  at 38° and at 28°. It takes place within about 6 min. at 38° and 11 min. at 28°. It does not occur until after 1.5-2 hrs. at the ordinary temperature. The change is unaffected by sodium fluoride, anticoagulants, potassium cyanide, or thymol. It takes place in laked blood and centrifuged laked blood, but not in plasma. S. S. ZILVA.

in increase in the apparent amount

Blood-fat. I. Preparation and general characteristics. H. J. CHANNON and G. A. COLLINSON( Biochem. J., 1929, 23, 663-675).-Fat has been prepared from 12 samples of ox-blood at fasting level by precipitating the blood with 3 vols. of alcohol and by extracting with ether the protein residue and the residue obtained by evaporating the alcoholic filtrate. Of the fat present in blood 80% may be extracted in this way. The fat constants, phosphorus, and nitrogen of the samples have been determined. The amount of fatty acid present varies little from that required if the phosphorus of the fat be calculated as leeithin and the cholesteryl ester as cholesteryl stearate, which suggests that glycerides are not present in appreciable quantity.

S. S. ZILVA.

Water content of blood-serum. H. SPENCER (Amer. J. Dis. Children, 1929, 37, 546-552).-Of methods for determining sp. gr. of blood-serum, the falling-drop method is preferred.

CHEMICAL ABSTRACTS.

Tungstomolybdic acid as a precipitant for blood-proteins. S. R. BENEDICT and E. B. NEWTON (J. Biol. Chem., 1929, 83, 357-360) .-- A mixture of sodium molybdate and sodium tungstate is recommended as a substitute for the sodium tungstate employed in the Folin-Wu method for the precipitation of blood-proteins. Filtrates obtained with the aid of the new reagent show higher values for uric acid and ergothioneine. C. R. HARINGTON.

Non-sugar reducing substances of blood and urine. I. Glutathione and ergothioneine in blood. S. R. BENEDICT and E. B. NEWTON (J. Biol. Chem., 1929, 83, 361-365).-Sheep blood was freed from proteins with tungstic acid, the filtrate was treated with silver lactate, and the precipitate separated and extracted with hydrochloric acidsodium chloride solution; the residue was boiled with dilute hydrochloric acid and the filtrate, after treatment with zinc and platinum to remove traces of tungsten and silver, was treated with mercuric acetate. The solution obtained on recovery from the mercury precipitate was treated with mercuric sulphate, the

preparation of solutions and the application of the method to the determination of sugar in blood deproteinised with tungstic acid are also described. CHEMICAL ABSTRACTS.

Determination of blood-sugar. P. HORKHEIMER (Pharm. Ztg., 1929, 74, 546).—Micro-methods should replace macro-methods. That of Hagedorn and Jensen is better than the method of Kaufmann (Klin. Woch., 1927, No. 14; 1928, No. 5), which gives only approximate results, and more rapid than that of Glassmann and Zwilling (cf. this vol., 207). The blood sample is best taken by absorption in prepared filter-papers which are weighed on a torsion microbalance.

W. McCARTNEY. Carbohydrate metabolism. I. Micro-determination of dextrose. R. MIYAMA (Bull. Sci. Fak. Terkultura, Kjusu, 3, 122—131).—For the determination of blood-sugar Hagedorn's method is the most accurate. The results diminished in the order: Benedict, Folin–Wu, Hagedorn, Folin, Schaffer-Hartmann, Bang. All the results were affected by the addition of cystine; the addition of sodium sulphite gave high results in Folin and Wu's method and low results in Bang's method.

CHEMICAL ABSTRACTS. Blood-sugar. J. C. BOCK (Wien. med. Woch., 1929, 79, 43-47; Chem. Zentr., 1929, i, 1364).-A study of the speed of reaction of the fasting human organism to administration of dextrose.

A. A. ELDRIDGE. Influence of various substances on the sugar and ammonia content of blood. H. WANTOCH (Arch. exp. Path. Pharm., 1929, 143, 337-357).-The influence of administration of various acids, alkalis, salts, sugars, and of urea, "oxantin" (di-hydroxyacetone), insulin, "synthalin," and liver as well as the effects of X-ray irradiation on the sugar and ammonia content of the blood in rabbits have been studied. Of the acids hydrochloric, sulphuric, and phosphoric, orally administered, the first produces no increase, the others, sometimes a slight increase in the ammonia content : all three always raise the bloodsugar. Oral administration of malic, citric, or β-hydroxybutyric acid causes sometimes very great increase in the ammonia content, sometimes, for reasons unknown, no increase, whilst oral or subcutaneous administration of the sodium salts of these acids produces no change. The organic acids also regularly cause hyperglycæmia. N-Sodium hydroxide solution or aqueous sodium carbonate solution, given orally, always causes the ammonia content to rise. Oral or subcutaneous administration of ammonium chloride or carbonate greatly increases both the ammonia and the sugar content and the administration of urea likewise causes distinct, and often great, increase in the ammonia content and distinct hyperglycæmia. Dextrose or oxantin when administered alone, orally or subcutaneously, has no effect on the ammonia content, but dextrose distinctly reduces the increase which follows administration of ammonium salts or urea. Lævulose acts like dextrose in this respect, but less powerfully. Insulin, subcutaneously injected, sometimes raises the ammonia content, but it has no definite effect on the increase occurring after the giving of urea. "Synth-

precipitate was decomposed, and the filtrate, after exact removal of sulphuric acid, concentrated and poured into excess of alcohol, yielding a precipitate of glutathione. The yield was 0.1 g. per litre of blood, and the product showed the high nitrogen and low sulphur content observed by Hunter and Eagles (A., 1927, 477, 478); it possessed a reducing action towards the Folin-Wu sugar reagent equivalent to one fifth of its weight of dextrose. Ergothioneine also shows a slight reducing action with this reagent.

C. R. HARINGTON. New constituent of blood. E. W. ROCKWOOD, R. G. TURNER, and J. J. PFIFFNER (J. Biol. Chem., 1929, 83, 289—297).—Hydrolysis with sulphuric acid of a protein-free blood filtrate or muscle extract causes an increase in the apparent amount of ergothioneine as determined by the method of Benedict (this vol., 714); this increase is ascribed to the liberation of a new substance Z, figures for the concentration of

Determination of carbamide in blood. S. L. LEIBOFF and B. S. KAHN (J. Biol. Chem., 1929, 83, 347—352).—The protein-free blood filtrate is heated at 150° for 10 min. in a special pressure tube with dilute sulphuric acid. Ammonia is determined directly in the resulting solution by Nessler's method. C. R. HARINGTON.

which in various samples of blood and tissues are

Manometric determination of carbamide in blood and urine. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 449—461).—Carbamide can be determined in diluted urine or in a protein-free blood filtrate by the use of the author's manometric apparatus (A., 1924, ii, 872), the reaction with hypobromite being employed. The error is about  $\pm 4\%$  in the case of urine, and  $\pm 2$  mg. of nitrogen per 100 c.c. in blood.

C. R. HARINGTON.

C. R. HARINGTON.

Determination of acetone substances in blood and urine. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 415–423).—The validity of the author's method (A., 1918, ii, 86) is confirmed, the criticisms of Smith (A., 1926, 1283) being answered on the ground that the latter author failed to make control determinations with pure  $\beta$ -hydroxybutyric acid.

## C. R. HARINGTON.

Determination of sugar in blood and urine. P. J. CAMMIDGE and H. A. H. HOWARD (Brit. J. Urol., 1929, 1, 17-32).-A solution (I) is prepared by boiling arsenious oxide (4.948 g.) and sodium hydrogen carbonate (25 g.) with water (300 c.c.), and diluting the cold solution to 1 litre; a solution (II) is prepared by dissolving potassium citrate (81 g.), carbonate (70 g.), and oxalate (92 g.) in hot water (600 c.c.), adding a solution of copper sulphate pentahydrate (25 g.), in warm water (150 c.c.), and a solution of potassium iodate (3.2496 g.) in water (150 c.c.) which has been made alkaline with potassium carbonate and treated with potassium iodide (50 g.), the mixed solutions being diluted to 1000 c.c. For the deter-mination of sugar in urine, 50 c.c. of II and 50 c.c. of water are boiled and treated with 5 c.c. of urine, 7.5 c.c. of 30% sulphuric acid are added to the cooled solution, and the mixture is immediately titrated with I, a blank determination being performed. The

given.

alin," given orally, does not increase the ammonia content, but appears to minimise the influence of previously-administered ammonium carbonate or urea. Raw or boiled liver has no effect on the ammonia content, but it likewise appears to have this minimising influence. Intense X-ray irradiation causes increase of the ammonia content. W. MCCARTNEY.

Hæmatoporphyrin hæmolysis. H. KAWAI (J. Biochem. Japan, 1929, **10**, 325—350).—When red corpuscles are hæmolysed by exposure to light in presence of hæmatoporphyrin no substance capable of producing hæmolysis is found. Hæmatoporphyrin hæmolysis is often observed in corpuscles with a high content of acid-soluble phosphoric acid, and is accompanied by decomposition of organic phosphoric acid. This, however, does not occur in the disintegration of the stroma. CHEMICAL ABSTRACTS.

Relationship between hæmolytic complement of guinea-pig serum and lipase. J. GORDON and A. WORMALL (Biochem. J., 1929, 23, 730-737).--The complement activities of various guinea-pig sera tend to run parallel with the esterase activities of these sera, although discrepancies occur. The destruction or inactivation of either of the two relatively heatstable components of complement does not appreciably diminish the esterase or lipase activity of guineapig serum. The serum retains a distinct esterase power after the inactivation of the complement by heating it at 56% for 30 min. Protein preparations obtained by treating the serum with alcohol and other at low temperatures possess no complete complement power, but retain a large part of the original esterase of the serum. The immune body essential for complement action has no influence on the esterase or lipase activity of guinea-pig serum when used in amounts sufficient to promote hæmolysis of ox redcells. The esterase or lipase of guinea-pig serum does not take part in specific hæmolysis, nor can the action of hæmolytic complement be ascribed to a hydrolysis of the fatty substances of the red-cell envelope by S. S. ZILVA. lipolytic enzymes.

Electrometric determination of chlorides in whole blood and tissues. J. C. FORBES and H. IRV-ING (J. Biol. Chem., 1929, 83, 337-344).—Diluted blood or tissue extract is heated with dilute sulphuric acid and silver nitrate; after partial neutralisation with ammonia the excess of silver is titrated electrometrically with standard sodium chloride solution. C. R. HARINGTON.

Determination of chloride in animal tissues. E. H. CALLOW (Biochem. J., 1929, 23, 648-653).— The chloride is completely extracted from the tissues by boiling with distilled water and is determined in the extract by a modification of Volhard's method. Christy and Robson's method for the determination of chloride in biological fluids (A., 1928, 564) is criticised. S. S. ZILVA.

Relation between cystine yield and total sulphur in various animal hairs. C. RIMINGTON (Biochem. J., 1929, 23, 726-729).—In all varieties except camel hair, the entire sulphur of the purified hair could be accounted for as cystine. Camel hair yields 94% of the total sulphur as cystine.

S. S. ZILVA.

Quantity of cysteine in living tissue proteins and its biological significance. Y. OKUDA (Proc. Imp. Acad. Tokyo, 1929, 5, 246-248).-An iodometric method has been devised for the determination of cysteine and cystine in proteins, and the distribution of these two substances in various proteins contained in fresh muscle, liver, and egg has been studied. The proteins of physiologically active tissue contain most of their sulphur-containing amino-acids in the form of cysteine and very little in the form of cystine; with egg-protein and the keratins, the reverse is the case. The oxygen uptake of proteins containing either cysteine or cystine alone is very small; the presence of both cysteine and either cystine or glutathione is necessary for the rapid absorption of oxygen. A. A. GOLDBERG.

Chemical change in the drying by heat of fish muscle. I. S. YAMAMOTO and S. MASUDA (J. Imp. Fish Inst., Tokyo, 1926, 22, 53-55, 188-197).—During desiccation of fish muscle by heat the monoamino-acid nitrogen is generally gradually diminished, whilst the diamino-acid nitrogen tends to increase. Optimal conditions for drying are described. CHEMICAL ABSTRACTS.

Isolation of di-iodotyrosine from the thyroid. G. L. FOSTER (J. Biol. Chem., 1929, 83, 345-346).— The isolation of di-iodotyrosine and of thyroxine from the thyroid described by Harington and Randall (this vol., 839) has been repeated by a simplified procedure; 33% of the total iodine was obtained as di-iodotyrosine and 16% as thyroxine.

C. R. HARINGTON.

Distribution of various phosphoric acid fractions in different portions of the heart. A. C. WHITE (Z. physiol. Chem., 1929, **183**, 184–190).--The various portions of ox-heart show differing water content; the left auricle has more dry matter than the right, and still higher values are found in the ventricle. The total phosphorus increases in the order right auricle, left auricle, right ventricle, left ventricle. The acid-soluble phosphoric acid is greater in the left auricle than in the right and still greater in the ventricles. The phosphatide-phosphorus is much lower in the auricle than in the ventricle, in the right auricle lower than in the left. J. H. BIRKINSHAW.

Choline in the placenta and its relation to labour. F. WREDE, E. STRACK, and E. BORN-HOFEN (Z. physiol. Chem., 1929, 183, 123-132).--Normally and abnormally born human placentas contained about 180 mg. of choline per kg. of fresh organ, the placenta of the cow 114 mg. per kg.

J. H. BIRKINSHAW.

**Protamine.** I. R. HIROHATA (J. Biochem. Japan, 1929, 10, 251–258).—A protamine ("mugiline- $\beta$ ") isolated from the sperm of *Mugil japonicus* probably contains no aromatic amino-acids, nor any basic amino-acids except arginine; large quantities of monoamino-acids soluble in ethyl or methyl alcohol are present. CHEMICAL ABSTRACTS.

Oxytocic substance of cerebrospinal fluid. H. B. VAN DYRE, P. BAILEY, and P. C. BUCY (J. Pharm. Exp. Ther., 1929, 36, 595-610).—The oxytocic action of the cerebrospinal fluid, as shown by experiments on the isolated guinea-pig uterus is related to its calcium content. It is suggested that calcium may be responsible for the oxytocic action of normal cerebrospinal fluid and also for the melanophore-expanding action exhibited by normal cerebrospinal fluid and serum. W. O. KERMACK.

**Excretion of lead.** R. A. KEKHOE and F. THAMANN (J. Amer. Med. Assoc., 1929, **92**, 1418— 1421).—Lead in the fæces (mg. per g. of ash) and urine (mg. per litre) was found as follows : students 0.08, 0.08; workmen with slight, if any, exposure to lead, 0.10, 0.13; workmen with moderate or severe exposure, 0.65, 0.22. CHEMICAL ABSTRACTS.

Excretion of lead in urine. H. MILLET (J. Biol. Chem., 1929, 83, 265-268).—Figures are given for the urinary exerction of lead, the determinations being made electrometrically. Normal individuals and untreated cancer patients excrete daily about 0.09 mg. of lead; this amount is not increased by injections of colloidal lead phosphate.

### C. R. HARINGTON.

Detection of ketonic substances in urine. B. SCHWENKE (Pharm. Ztg., 1929, 74, 992–994).— The iodoform reaction is more sensitive towards acetone than the nitroprusside reactions of Legal or Lange. The substance which gives the nitroprusside reaction is ethyl acetoacetate and not acetone, since urine, which gives the nitroprusside reaction and not the iodoform reaction in the cold, gives a positive iodoform reaction and a negative nitroprusside reaction after heating to  $100^{\circ}$  for  $\frac{1}{2}$  hr. The *p*-aminoacetophenone test is most sensitive for ethyl acetoacetate. S. COFFEY.

Determination of sugar in urine. W. G. EXTON, A. R. ROSE, and P. V. WELLS (Proc. 38th Ann. Mtg. Assoc. Life Ins. Med. Dir. Amer., 1928, 14, 436— 441).—The urine (0.2 c.c.) is diluted to 10 c.c. with a reagent prepared by adding phenol (6 g.) and then sodium sulphite (5 g.) to 200 c.c. of 4% sodium hydroxide solution, diluting with water to about 500 c.c., adding sodium potassium tartrate (100 g.), and then a solution of 3 : 5-dinitro-2-hydroxybenzoic acid (7 g.) in water (300 c.c.), and diluting to 1000 c.c. The tube containing the mixture is immersed in boiling water for 5 min., cooled, placed in a scopometer with the green light filter in place, and the wedge reading at the extinction point is noted. The dextrose content is determined by reference to a chart.

CHEMICAL ABSTRACTS. Bergeim test for intestinal putrefaction. F. HOELZEL (J. Biol. Chem., 1929, 83, 331-332).—The presence of reducing substances in normal fæces renders the test of Bergeim (A., 1925, i, 99) for intestinal putrefaction valueless.

### C. R. HARINGTON.

Sugar tolerance in arthritis. II. Arthritis of the menopause. B. H. ARCHER (Arch. Int. Med., 1929, 44, 238—243).—Of twenty typical cases of arthritis of the menopause 70% showed diminished sugar tolerance, whereas it had previously been shown that, in a parallel series of infectious cases, only 15% exhibited this phenomenon. The lowering of the sugar tolerance may be due either to the disease of the joints or to associated conditions. W. MCCARTNEY.

Acute yellow atrophy of the liver. Origin of carbamide in the body. I. M. RABINOWITCH (J. Biol. Chem., 1929, 83, 333—335).—A case of acute yellow atrophy showed great dilution of the (small amount of) urine, combined with complete absence of carbamide from the blood. The hypothesis that carbamide is formed exclusively in the liver is therefore supported. C. R. HARINGTON.

Effect of muscular exercise in beri-beri. I. Gas and carbohydrate metabolism. R. INAWA-SHIRO and E. HAYASAKA. II. Circulatory apparatus. E. HAYASAKA and R. INAWASHIRO (Tohoku J. Exp. Med., 1928, **12**, 1–28, 29–61).— The resynthesis of lactic acid is retarded; the decrease of oxygen consumption and respiratory volume to initial values is prolonged; acidosis and blood-sugar are increased. CHEMICAL ABSTRACTS.

**Excretion of oxalic acid in phloridzin diabetes.** G. VIALE, L. NAPOLEONI, and D. ROSSELLI (Compt. rend. Soc. Biol., 1929, **99**, 2005–2006; Chem. Zentr., 1929, i, 1708).—Although oxalic acid is sometimes excreted by the phloridzinised dog in larger amounts than by the normal animal, no relation between oxaluria and glycosuria was detected.

A. A. ELDRIDGE. Effect of dextrose on alimentary galactosuria. O. WELTMANN (Wien. klin. Woch., 1929, 42, 8–10; Chem. Zentr., 1929, i, 1365).—On ingestion of 40 g. of galactose and 50—100 g. of dextrose the elimination of galactose is reduced (especially in disease of the liver) to a smaller extent than by ingestion of the galactose alone. A. A. ELDRIDGE.

Arterial hypertension. R. H. MAJOR (Amer. J. Med. Sci., 1929, 177, 188—194).—Few cases of hypertension (without diabetes) showed blood-sugar values greater than 120 mg. per 100 c.c., but 61% of cases of essential hypertension, and all cases of chronic nephritis with hypertension, showed abnormally high blood-guanidine values, the normal being 0·1 mg. (average), 0·2 mg. (max.) per 100 c.c. "Bloodguanidine" resembles guanidine, but the identity was not conclusively established.

CHEMICAL ABSTRACTS. Inflammation. III. Carbohydrate metabolism in inflamed tissue during the initial stage. F. BRIKKER and F. SUPONITZKI. IV. Nitrogen exchange in the initial stage. F. BRIKKER and I. LAZARIN. V. Acetone substances in the blood of inflamed tissue. F. BRIKKER (Zhur. exp. Biol. Med., 1928, 9, 285—290, 291—299, 300— 403).—The venous blood of the inflamed (rabbit's) ear has an abnormally high dextrose and acetone-substance content and amylolytic index. The protein of the inflamed region undergoes increased catabolism.

CHEMICAL ABSTRACTS. Chemistry of increase of blood-pressure in nephritis. W. HÜLSE and K. FRANKE (Arch. exp. Path. Pharm., 1929, 143, 257–268).—In ordinary cases of hypertonic nephritis as well as in those in which there is no insufficiency in the action of the kidneys, the deproteinised blood-plasma contains considerably more amino-nitrogen after acid hydrolysis than does normal plasma. The material which gives rise to this extra amino-nitrogen is responsible for the increase in blood-pressure in nephritis. Animal charcoal easily adsorbs the material and it is soluble in alcohol, ether, chloroform, acetone, and water. It gives positive ninhydrin, carbylamine, and iodoform reactions and negative phenyl reaction. It possibly belongs to the phosphatide group or to the group of compounds containing amino-nitrogen from which phosphatides are built up. W. MCCARTNEY.

Effect of administration of amino-acids on the structure of plasma-protein. A. NITSCHKE (Z. exp. Med., 1929, 64, 111—119; Chem. Zentr., 1929, i, 1363—1364).—In pathological conditions of the kidneys administration of amino-acids caused a diminished elimination of protein; the albumin fraction is increased, whilst the fibrinogen and globulin fractions are diminished.

A. A. ELDRIDGE.

[Retention of] inorganic serum-sulphates, urea, and creatinine in cases of renal insufficiency. Effect of diuresis [and of chronic nephrosis] on serum-sulphates. E. G. WAKE-FIELD (Arch. Int. Med., 1929, 44, 244—251).—In cases of renal insufficiency increase in the amount of urea or creatinine in the blood is usually accompanied by increase in the amount of inorganic serum-sulphate. No direct correlations can be traced, however, and patients showing no evidence of renal disease may have more inorganic sulphate in the serum than have normal healthy persons. Diuresis seems to lower the concentration of inorganic sulphates in serum. In cases of chronic nephrosis there may not be any retention of inorganic sulphates. W. MCCARTNEY.

Chemical changes occurring in the body as a result of certain diseases. IV. Primary pneumonia in children. D. C. DARROW and A. F. HARTMANN (Amer. J. Dis. Children, 1929, 37, 323— 334).—The plasma chloride, hydrogen carbonate, and total base are decreased; a low f. p. depression and a high normal  $p_{\rm H}$  value were observed.

CHEMICAL ABSTRACTS. Calcium and phosphorus concentration in the intestinal contents of rats in relation to rickets. A. M. COURTNEY, F. F. TISDALL, and A. BROWN (Can. Med. Assoc. J., 1928, **19**, 559—562).—The total calcium content of the cæcum of rats fed on McCollum's rachitogenic diet and kept inside was much higher than that of rats similarly fed and exposed to sunshine, although the calcium combined with phosphorus was practically the same in both groups.

# CHEMICAL ABSTRACTS.

Carbohydrate metabolism of tumours. III. Rate of glycolysis of tumour tissue in the living animal. C. F. CORI and G. T. CORI (J. Cancer Res., 1929, **12**, 301—313).—The tolerance limit of normal rats for intraveneously injected sodium *d*-lactate was a rate of infusion of  $95\pm5$  mg. of lactic acid per 100 g. of body-weight per hr. Rats with tumours weighing 14—21% of the body-weight showed a marked increase in the blood-lactic acid. The decrease in lactic acid tolerance was approximately proportional to the size of the tumour. It is computed that the rate of lactic acid production by the tumour tissue in the living animal is 570—800 mg. of lactic acid per 100 g. of fresh tumour per hr. The rate of glycolysis of the tumour *in vivo* depends on the blood-sugar concentration. At a normal blood-sugar level of the tumour-bearing animals the glycolysis corresponds with one half of the maximum possible glycolysis of the tumour. The intravenous dextrose tolerance of tumour-bearing rats is the same as that of normal rats. CHEMICAL ABSTRACTS.

Actual reaction of urine and its relation to fatigue. M. S. RESNITSCHENKO (Biochem. Z., 1929, 210, 393-402).—A series of curves shows the variations of urinary acidity during various periods of muscular exercise. With severe work an increased acidity is usually obtained, but in athletes there is no increase and occasionally a decrease.

#### P. W. CLUTTERBUCK.

Absolute amount of hydrogen ions in urine on the march and in running. M. S. RESNITSCHENKO (Biochem. Z., 1929, 210, 403-413).—Work of medium intensity (10 km. march with pack) causes, in persons of average physique, an increased acidity of urine and in stronger persons first a decrease and subsequently an increase to normal acidity. More intense exercise but of shorter duration (700 m. run) increases the concentration and the absolute amount of the hydrogen ions of the urine.

#### P. W. CLUTTERBUCK.

Effect of "training" of muscle on its content of phosphorus compounds. D. FERDMANN and O. FEINSCHMIDT (Z. physiol. Chem., 1929, **183**, 261— 268).—"Training" of the leg muscle of the rabbit by electrical stimulation for 3—4 min. twice daily causes a considerable increase in the creatinephosphorie acid. On cessation of the training, the normal value is again attained after 4—6 days. No change is produced by training in the pyrophosphoric acid or the hexosephosphoric acid. J. H. BIRKINSHAW.

Rôle of phosphorus in the metabolism of carbohydrate in muscle. E. AUBEL and T. CAHN (Bull. Soc. Chem. biol., 1929, **11**, 903–928).—A review. W. O. KERMACK.

Lactic acid metabolism of the surviving hindlimbs. A. BORNSTEIN and E. SCHMUTZLER (Pflüger's Archiv, 1929, 221, 395—399; Chem. Zentr., 1929, i, 1366).—The isolated hind-limbs of dogs were perfused with blood with addition of dextrose to a constant blood-dextrose content. The lactic acid remains constant or falls. Addition of insulin or alcohol to the perfusion liquid causes no change. Sodium cyanide increases the production of lactic acid, corresponding with the inhibition of oxidation. The disappearance of added lactic acid was studied.

A. A. ELDRIDGE.

Nerve metabolism. IV. Carbohydrate metabolism of resting mammalian nerve. E. G. HOLMES and R. W. GERARD (Biochem. J., 1929, 23, 738—747).—There is a rise of lactic acid and a corresponding fall in carbohydrates (*i.e.*, "free sugars" and glycogen) in rabbit's nerves in nitrogen. In oxygen there is no disappearance of lactic acid, but a definite fall in the carbohydrates. About 60% of the resting metabolism of rabbit nerve may be maintained by the oxidation of these carbohydrates. The rate of lactic acid formation under asphyxial conditions is comparable with that of frog nerve and much less than that of rabbit brain. No oxidation or resynthesis of lactic acid occurs on admitting oxygen to an asphyxiated nerve. The formation of lactic acid, even if concerned with hexosephosphate, does not involve breakdown of mono- or di-phosphate with liberation of free phosphate. A modification of the Van Slyke-Bissinger method for separation of carbohydrates from tissue extracts is described. S. S. ZILVA.

Brain metabolism. V. Rôle of phosphates in lactic acid production. C. A. ASHFORD and E. G. HOLMES (Biochem. J., 1929, 23, 748-759).-Inorganic phosphate is liberated from brain-tissue both anaërobically and aërobically and in the presence as well as in the absence of dextrose. No evidence of hexosephosphate synthesis has been found at any stage in the process of formation of lactic acid, although the tissue is capable to a small extent of performing this synthesis. Both phosphate liberation and lactic acid production from dextrose by braintissue are inhibited by sodium fluoride, but, whilst the former is affected only by a high fluoride concentration, the latter is sensitive to very high dilutions of the salt. There is no quantitative relationship between the amounts of phosphate and lactic acid which are prevented from appearing by fluoride. Lactic acid is freely formed from dextrose, even when all available phosphate is immobilised. The velocity of lactic acid formation from dextrose is not increased by the replacement of phosphate. Much less lactic acid is formed from glycogen than from dextrose. The process is inhibited by fluoride and by immobilising phosphate. It can be restored by replacing phosphate. Brain-tissue most probably forms lactic acid by one process which involves dextrose and is independent of phosphate and another which involves glycogen and is dependent on phosphate.

S. S. ZILVA. nd carbohydra

Blood-sugar regulation, fat and carbohydrate metabolism. F. DEFISCH and R. HASENÖHRL (Klin. Woch., 1929, 8, 202-204; Chem. Zentr., 1929, i, 1477).—In normal individuals, administration of fat (up to 50 g.) has no effect on the blood-sugar curve; in diabetes the curve is parallel to the hunger curve. Injection of adrenaline, however, causes in normal individuals a more marked increase of blood-sugar than in hunger-controls. Administration of fat moderates the action of administered or endogenous insulin. A. A. ELDRIDGE.

Unsaponifiable fraction of liver-oils. V. Absorption of liquid paraffin from the alimentary tract in the rat and the pig. H. J. CHANNON and G. A. COLLINSON (Biochem. J., 1929, 23, 676-688).—The iodine value of the non-sterol fraction of the unsaponifiable fraction of the livers of rats which received liquid paraffin in their diet was 31 as against 119 for that from the control animals. A similar fall in the iodine value was observed in an experiment with pigs. The hydrocarbon was isolated from the liver of these animals which received it in their diet. S. S. ZILVA.

Compounds of conjugated bile-acids with fatty acids and their importance in fat absorption. II. Solubility and diffusibility. III. Surface

tension. F. VERZÁR and A. KÚTHY (Biochem. Z., 1929, 210, 265–280, 281–285; cf. this vol., 466).— II. Quantitative investigation of the dissolution of fatty acids in solutions of bile acids shows that at first molecular and then colloidal solutions arise. This is confirmed by nephelometric investigation and by diffusion experiments and ultrafiltration. Fatty acids diffuse along with bile acid, the diffusion of the latter being retarded by the union. The solutions may be precipitated by cations and positively-charged colloids. By means of bile acids 0.25% aqueous solutions of oleic, stearic, and palmitic acids may be prepared in which the greater part of the fatty acid is diffusible even at  $p_{\rm H}$  6.25. At higher concentrations the fat is more and more in colloidal solution.

III. Surface tension measurements with mixtures of higher fatty acids and conjugated bile acids are carried out by stalagmometer and platinum-ring methods. Changes of surface tension at varying  $p_{\rm R}$  confirm the view that in neutral and faintly acid solution (up to  $p_{\rm R}$  6.25) water-soluble complexes of oleic, stearic, and palmitic acids with bile acids exist and are characterised by very low surface tension.

P. W. CLUTTERBUCK.

Production of ammonia by surviving kidneytissue. A. PATEY and B. E. HOLMES (Biochem. J., 1929, 23, 760—766).—Washed kidney-tissue produces some ammonia under anaërobic conditions and more under aërobic conditions. In the presence of dextrose the aërobic ammonia production is brought down to the anaërobic level. The anaërobic production is not affected by dextrose. In the presence of glycine extra ammonia is formed. This occurs only in air and not anaërobically. Extra atmospheric oxygen is not, however, taken up by the tissue. The production of this extra ammonia is not inhibited by dextrose. Cyanide (0.02M) diminishes but does not entirely inhibit the aërobic ammonia formation by the tissue alone; on the other hand, the production of extra ammonia in the presence of glycine is inhibited by this reagent. Apparently three systems are involved in the ammonia production by kidney-tissue, one anaërobic and two aërobic. S. S. ZILVA.

Kidney metabolism : ammonia and phosphate metabolism, sugar utilisation. P. György and W. KELLER (Biochem. Z., 1929, 210, 434–442).— The authors' previous work on the anaërobic glycolysis and respiration of cortical and medullary kidneytissue of rats (A., 1928, 1396) is repeated and extended to phosphate and ammonia formation, using the kidney of both old and young animals. Phosphate formation in both kinds of tissue is greater in an atmosphere of nitrogen than in one of oxygen and, whereas with cortical tissue it is almost the same for young and old animals, with medullary tissue it is greater for the older animals. Both types of tissue placed in Ringer's solution gave large amounts of ammonia, the tissue of young animals giving larger amounts than that of older animals, and the cortical giving more than the medullary. That anaërobic glycolysis of the cortical tissue is small and of the medullary tissue is four to five times as great, whilst the reverse is true of the respiration, is confirmed.

P. W. CLUTTERBUCK.

Endogenous uric acid and hæmatopoiesis. J. KRAFKA, jun. (J. Biol. Chom., 1929, 83, 409—414).— The uric acid excretion of a Dalmatian hound was doubled after loss of about one third of the total blood volume by hæmorrhage. The increased output of uric acid is ascribed to the breakdown of the nuclei of the erythroblasts during the period of active regeneration of red blood-corpuscles.

C. R. HARINGTON.

Creatine-creatinine excretion during fasting. S. MORGULIS (J. Biol. Chem., 1929, 83, 299–310).— Experimental evidence is offered against the supposition (Howe and others, A., 1912, ii, 369; Palladin and Epelbaum, this vol., 345) that, in a fasting animal, increase of creatine excretion over that of creatinine necessarily indicates approaching death. Until inanition reaches an advanced stage, the creatinine coefficient remains unaltered. The experiments indicate a synthesis of creatine during fasting and a retention of creatine during re-feeding after a fasting period. C. R. HARINGTON.

Indican formation. I—III. Y. KISHI (Tohoku J. Exp. Med., 1928, 11, 504—544; 12, 75—80, 81— 87).—The effect of fasting on the urinary indican of guinca-pigs and rabbits is described. Hyperindicanæmia in nephritis is attributed to increased formation, as well as retention, of indican. Indicanuria may be due partly to increased decomposition of body protein and partly to metabolic anomalies. Indican originates abacterially.

CHEMICAL ABSTRACTS.

Food value of legumes for albino rats. A. GALAMINI (Atti R. Accad. Lincei, 1929, [vi], 9, 809— 812).—The urine of rats fed solely on raw beans changes to a neutral and then to an alkaline reaction, the animals losing weight and dying sooner than when fasting. A diet of cooked beans is more readily tolerated, although the animals still lose weight.

T. H. POPE.

Acid-base metabolism. Effects of administration of salt and of restriction of water. L. SCHOENTHAL (Amer. J. Dis. Children, 1929, 37, 244-251).—Changes observed in the blood-plasma and in the urine are recorded. CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism in artificially fed infants. I. Influence of codliver oil and irradiated milk. A. L. DANIELS, G. STEARNS, and M. K. HUTTON (Amer. J. Dis. Children, 1929, **37**, 296—310).—The following calcium : phosphorus retention ratios were observed after feeding the corresponding foods : pasteurised milk 0.5, boiled milk 1.2, pasteurised milk and cod-liver oil 0.8—1, boiled milk and cod-liver oil 1.2—1.48, milk with irradiated cod-liver oil 1.48, irradiated milk 2.0. The ratio for optimal development of infants less than 1 year old should be 2. CHEMICAL ABSTRACTS.

Iodine in blood and gland secretions after administration of iodoproteins. G. BARKAN and W. LEISTNER (Arch. exp. Path. Pharm., 1929, 144, 83—104).—After the administration of an iodoprotein to rabbits, dogs, and men, the iodine present in the blood is not completely precipitable by silver ions, but is in part present as organically-bound iodine. This organic iodine differs from the inorganic iodide 4 I in being more highly concentrated by the kidneys and in being absent from the saliva and gastric juice. After administration of potassium iodide all the iodine in the blood is precipitable by silver ions. W. O. KERMACK.

Effect of secretions and vegetable poisons on the permeability of animal membranes. E. GELLHORN and H. GELLHORN (Pflüger's Archiv, 1928, 221, 247—263; Chem. Zentr., 1929, i, 1470).—The effect of *l*-adrenaline, thyroxine, insulin, pilocarpine, and atropine on the permeability of animal membranes towards dextrose was examined.

A. A. ELDRIDGE.

Influence of temperature on the permeability of animal membranes. E. GELLHORN and H. GELLHORN (Pflüger's Archiv, 1928, 221, 264-281; Chem. Zentr., 1929, i, 1470).

Permeability of animal membranes towards dyes. E. GELLHORN (Pflüger's Archiv, 1928, 221, 230-246; Chem. Zentr., 1929, i, 1469-1470).

Ionic permeability of the body surface of invertebrate sea animals as cause of the toxicity of sea-water of abnormal composition. A. BETHE (Pflüger's Archiv, 1928, 221, 344-362; Chem. Zentr., 1929, i, 1470-1471).

Effect of  $p_{\rm ff}$  on striated muscle. S. GOLDBERGER (Atti R. Accad. Lincei, 1929, [vi], 9, 812—816).— Experiments on the action of Ringer's solutions with various  $p_{\rm ff}$  values on frog's muscle by Trendelenburg's perfusion method are described. T. H. POPE.

Influence of the external temperature on the glycogen and fat content of the liver, and the relations of the external temperature to changes in the thyroid gland and suprarenal capsule. T. NOSAKA (Folia endocrinol. Japon., 1928, 3, 1558— 1580). CHEMICAL ABSTRACTS.

Chemical and biological changes induced by X-rays in body tissue. M. T. BURROWS, L. H. JORSTAD, and E. C. ERNST (Radiol., 1928, 11, 370– 377).—One effect is to remove lipoid substances which are necessary for the growth of cancer cells. CHEMICAL ABSTRACTS.

So-called water intoxication. H. MISAWA (Japan. J. Med. Sci., 1927, 1, 355-383).—Administration of water (amounting to one third of the bodyweight) to rabbits caused a decrease of the dry bloodsubstance to 15%, a decrease of 23.5% in the serumprotein, a decrease of 20% in the blood-chlorine, -phosphorus, -sodium, -potassium, -calcium, and -magnesium, a slight decrease in the residual nitrogen and hæmoglobin, and an increase in the blood-sugar. The chlorine content of the liver was increased, and of other organs decreased. The urinary chlorine, sodium, calcium, phosphorus, and nitrogen were increased, the magnesium was unchanged, and the potassium decreased. CHEMICAL ABSTRACTS.

Blood-calcium distribution in anaphylaxis in the guinea-pig. H. BROWN and S. G. RAMSDELL (J. EXP. Med., 1929, 49, 705-709).—The total calcium is unchanged; the membrane-diffusible fraction is greater than that for the animal similarly treated but not manifesting characteristic symptoms. CHEMICAL ABSTRACTS,

Formation of complex compounds in the treatment of chronic lead and mercury poisoning. H. LUDWIG (Biochem. Z., 1929, 210, 353-392).--The affinity of the mercury ion for potassium iodide, sodium thiosulphate, and for the thiol group with complex formation is greater than that of the lead ion. With protein, however, lead sulphide is formed more readily than mercury sulphide. With serum formation of lead sulphide is less ready than that of mercury sulphide. The ammonium sulphide reaction with lead is inhibited by the presence of serum, but not of egg-albumin. Serum retains its inhibiting power after extraction with ether, but loses it after deproteinisation by either ammonium sulphate or trichloroacetic acid. In serum, lead is therefore partly in the form of complex ions. The affinity of lead for the hydroxyl group is much greater than that of mercury. The potassium iodide complex salts act as anions, precipitating proteins in acid solution, and displace the precipitation optimum of caseinogen to the alkaline side more strongly than potassium thiocyanate but less strongly than potassium ferro- and ferri-cyanide. The following heavy metals are arranged in order of strength of displacement of the caseinogen optimum to the acid side : Fe Hg > Hg"=Pb>Cu>Fe>Ni>Co. In yeast fermentation experiments, mercuric nitrate is much more poisonous than lead nitrate. In cases of poisoning mercury is therefore brought into solution by potassium iodide more readily than lead, and, moreover, the mercury combined with protein amino-groups is set free by the P. W. CLUTTERBUCK. iodide.

[Influence of administration of mixtures of] and hexamethyleneammonium chloride tetramine on the urine. E. C. WISE and F. W. HEYL (Arch. Int. Med., 1929, 44, 252-262).--Ammonium chloride (which yielded its maximum acidifying effect on the second day) in daily doses of 4.87 g. had a rapid acidifying effect on the urine of normal men and maintained the reaction at about  $p_{\rm H}$  5.5. Hexamethylenetetramine (given with the ammonium chloride) was found in the urine in concentrations which were much the same whether the daily dose was 2.43 or 6.82 g. The urinary concentrations of the tetramine are very much affected by the acidity. Other factors being equal, the concentrations of formaldehyde found in the urine were the higher the greater was the dose of the tetramine, and varied according to the times at which the urine samples were taken. W. MCCARTNEY.

Hypoglycæmic action of allylisopropylbarbituric acid and adrenaline antagonism. G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. biol., 1929, 99, 1977—1978; Chem. Zentr., 1929, i, 1708).—The injection of allylisopropylbarbituric acid causes hypoglycæmia; the hyperglycæmic action of adrenaline can be suppressed. A. A. ELDRIDGE.

Action of certain alkaloids on leucocytes isolated from the organism. C. FORTI (Atti R. Accad. Lincei, 1929, [vi], 9, 800—806; cf. A., 1926, 968).—Before killing the cell, cocaine, novocaine, and tutocaine hydrochlorides cause arrest of its activity, which is, however, recoverable. T. H. POPE.

Does *l*-ephedrine act more powerfully than *dl*-ephedrine (ephetonine)? H. KREITMAIR (Arch. exp. Path. Pharm., 1929, **143**, 358—367).—Any difference in physiological activity between *l*-ephedrine and *dl*-ephedrine is so slight as to be undetectable by pharmacological methods available up to the present. The differences reported by other workers are due to differences in experimental methods and conditions and in the condition and reactions of the individual animals used. W. MCCARTNEY.

Influence of the morphine derivative "laudanon" on the metabolism following administration of various kinds of food. W. ARNOLDI (Arch. exp. Path. Pharm., 1929, 143, 283-309).-A special form of acidosis, characterised by lack of available alkali and reduced formation of ammonia, is caused by "laudanon," especially when administra-tion is long continued. The lack of alkali causes reduced formation or reduced excretion of ketocompounds and the amount of these in the urine is always lowered. " Laudanon " also causes alterations in body-weight, in protein, carbohydrate, and fat metabolism, in the magnitude and extent of oxidative processes, in acid-base relationships, and in the functions of the kidneys and intestine. These alterations are more pronounced and more lasting in rats receiving food rich in protein than in those receiving food rich in carbohydrates, and sometimes the changes with the former food are the opposite of those with the latter. With food rich in carbohydrates the decrease in diuresis, the disturbance of the activity of the intestine, and the after-effects when administration of the drug ceases are smaller than with other food and the narcotic action seems to be more easily thrown off. The administration of single large doses of sugar rapidly counterbalances for lengthy periods the changes produced by " laudanon." W. MCCARTNEY.

Mechanism of pilocarpine hyperglycæmia. G. VIALE and L. NAPOLEONI (Compt. rend. Soc. Biol., 1929, 99, 2006; Chem. Zentr., 1929, i, 1708).—The effect is adrenaline hyperglycæmia; pilocarpine itself causes hypoglycæmia. A. A. ELDRIDGE.

[Biological] evaluation of digitalis. A. STASIAB and B. ZBORAY (Arch. exp. Path. Pharm., 1929, 144, 283-296).

Active principle of camomile flowers. K. JUNKMANN and W. WIECHOWSKI (Arch. exp. Path. Pharm., 1929, **144**, 1—7).—Tinctures and infusions of camomile flowers contain an active principle, apparently a glucoside, the pharmacological actions of which are described. It has an inhibitory effect on the mobility of the intestine. W. O. KERMACK.

Adder venom. III, V, VII, VIII. C. KOBA-YASHI (Osaka J. Med., 1928, 27, 779-786, 1405-1410, 1411-1418, 1725, 1730).—Subcutaneous injection of adder venom causes a gradual decrease in the amount of that substance in rabbit's blood which reacts with iodate. Other changes in the composition of the blood and urine were also observed. The venom does not pass through a collodion membrane. Separation of the active substance was attempted. CHEMICAL ABSTRACTS.

Effect of cyanide on the respiration of animal tissues. M. DIXON and K. A. C. ELLIOTT (Biochem. J., 1929, 23, 812-830).-In most of the animal tissues studied, a cyanide concentration of 0.001M was sufficient to produce the maximum degree of inhibition, which varied in different tissues from 40% to 90%. The respiration of spleen is not affected by small amounts (0.001M) of cyanide. Negelein's statement that the respiration of yeast is almost completely inhibited by cyanide is confirmed; some samples of yeast show an incomplete (85%) inhibition. With liver small concentrations of pyrophosphate produce a slight acceleration, larger amounts an inhibition of the rate of respiration, the inhibitory effect of pyrophosphate being less than the corresponding effect of cyanide. With muscle pyrophosphate produces a greater inhibition than cyanide. It produces no effect on yeast. Whilst pyrophosphate inhibits the reduction of methylene-blue cyanide does not influence this reaction. The action of both cyanide and pyrophosphate on respiration is reversible.

# S. S. ZILVA.

Amylases of cereal grains: oats. J. L. BAKER and H. F. E. HULTON (J.C.S., 1929, 1655—1660).— Amylase precipitated by alcohol from an extract prepared from ungerminated oats converts soluble potato starch almost completely into maltose, provided a sufficient quantity is employed. This result supports the view that starch is composed of condensed maltose units. When the conversion into maltose is incomplete, an alcohol-insoluble compound is formed closely resembling  $\alpha$ -amylodextrin. Ungerminated oat amylase has a solvent action on oat starch granules, producing dextrose. When the amylase from germinated oats acts on potato-starch paste it yields a dextrin insoluble in alcohol, a maltodextrin-like substance soluble in alcohol, and a sugar, apparently maltose. Similar results are also obtained with oat starch. W. O. KERMACK.

Malt amylase. VI. Adsorption of amylase by blood-charcoal and kaolin at varying  $p_{\pi}$  with reference to its dextrinising and saccharifying powers. T. SABALITSCHKA and R. WEIDLICH (Bio-chem. Z., 1929, **210**, 414–433).—Blood-charcoal readily adsorbs amylase at  $p_{\rm H}$  6·2—6·0, but more readily at  $p_{\rm H}$  3·2. Kaolin adsorbs amylase more strongly than blood-charcoal, the adsorption increas-ing considerably from  $p_{\rm H}$  6.2 to 4.5 and decreasing again at  $p_{\rm H}$  3. Merck's diastase is completely adsorbed under the experimental conditions by four times its weight of kaolin. With an absorption  $p_{\rm H}$ between 6.2 and 4.5, no enzymic injury is apparent on subsequent buffering to the optimal  $p_{\pi}$  for amylolysis, whilst slight injury occurs with an absorption  $p_{\rm H}$  of 4 and greater injury with  $p_{\rm H}$  of 3, and with  $p_{\pi}$  2.8 both dextrinising and saccharifying powers are destroyed. So long as the  $p_{\rm H}$  of the adsorption medium does not cause injury, the two powers increase with increasing amounts of kaolin and with decreasing P. W. CLUTTERBUCK. pu.

[Biochemical factors in] heredity. II. H. VON EULER, S. STEFFENBURG, and H. HELLSTRÖM (Z. physiol. Chem., 1929, 183, 113-122; cf. this vol., 848),—The catalase content of *Brassica* runs parallel with the number of chloroplasts. An attempt was made to determine the catalase value of a chloroplast. With further mutants of barley the catalase ratio k (normal)/k (white) was 3.3 when germinated in the dark, 5.5 in the light. Two other strains gave ratios of 1.6 and 3.4, respectively.

#### J. H. BIRKINSHAW.

Kinetics of ester hydrolysis by enzymes. I. E. BAMANN and M. SCHMELLER (Z. physiol. Chem., 1929, 183, 149—167).—The action of hepatic lipases from man, ox, sheep, dog, and rabbit on methyl butyrate was studied. There were considerable variations in activity and in  $p_{\rm H}$  optimum, which varied between 7 and 9. The relationship between the concentration of the substrate and the reaction constant for linear and unimolecular reactions and the affinity of the enzyme for the substrate was traced. J. H. BIRKINSHAW.

Growth. development, and phosphatase activity of embryonic avian femora and limbbuds cultivated in vitro. H. B. FELL and R. ROBISON (Biochem. J., 1929, 23, 767-783).-The isolated femora of 51- and 6-day fowl embryos were found to have a remarkable capacity for self-differentiation. During cultivation in a watch-glass the 51-day femora increased to more than three times their original length, the gross anatomy remaining comparatively normal. During cultivation in vitro the isolated femora synthesised a phosphatase, the gross amount formed increasing with the age of the culture. The ratio of phosphatase to the dry weight of the femur increased during cultivation from zero to a maximum value and then declined. The increase corresponded with the progress of histological differentiation and the decline with degeneration. The maximum value of this ratio was higher than that found for normal embryonic femora. Undifferentiated 3-day embryonic limb-buds cultivated in vitro gave rise to small-celled cartilage only. Such explants after cultivation were completely devoid of phosphatase, thus confirming the view that the enzyme is formed by cartilage only if hypertrophic cells are S. S. ZILVA. present.

Effect of emulsification on the peptic synthesis of protein. H. WASTENEYS and H. BORSOOK (Coll. Symp. Mon., 1928, 6, 155—172).—Benzaldehyde, benzoic acid, benzene, toluene, and chloroform accelerate peptic synthesis of protein; talc powder, barium sulphate, and kieselguhr have a slight, whilst oleic acid and olive oil have no, accelerative effect. Effective substances induce some protein synthesis even in absence of pepsin. The proteins synthesised vary in their rate of hydrolysis by hydrochloric acid and in their base-combining capacity.

### CHEMICAL ABSTRACTS.

Comparison of enzymic degradation of proteins by successive alternating action of pepsin, trypsin-kinase, and erepsin. E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1929, 11, 92–103).— When caseinogen is first acted on by pepsin-hydrochloric acid at  $p_{\pi}$  1.8, then with erepsin at  $p_{\pi}$  8, and finally with trypsin-kinase, degradation occurs during each successive action. If hydrolysis is carried out successively with trypsin-kinase and erepsin, then pepsin has no further action. With fibrin, trypsinkinase has no action after pepsin and erepsin, but pepsin causes hydrolysis after trypsin-kinase and erepsin; the total amount of fission is much greater in the last case. With edestin and gelatin more hydrolysis takes place with trypsin-kinase and erepsin than with pepsin and erepsin. The significance of the results is discussed. H. BURTON.

Action of cell enzymes on proteins and protein degradation products. E. ABDERHALDEN and O. HEREMANN (Fermentforsch., 1929, **11**, 78-85).— The enzyme preparation obtained by extraction of fat-free, dry liver (or kidney) powder with 87%glycerol generally hydrolyses di- and poly-peptides. The enzyme not adsorbed on aluminium hydroxide is capable of causing hydrolysis at  $p_{\rm H}$  8.4 as is the cluted (phosphate mixture) enzyme at the same hydrogen-ion concentration. The eluted enzyme has generally a more powerful action when elution is carried out at  $p_{\rm H}$  8.4 than at  $p_{\rm H}$  7.1. The eluted enzyme exerts optimum action on the peptides studied at  $p_{\rm H}$  7.1 and for the peptide derivatives at  $p_{\rm H}$  8.4. Hippuric acid is sometimes hydrolysed, sometimes unaffected. H. BURTON.

Influence of various alcohols in various concentrations on the rate of hydrolysis of proteins and polypeptides by proteases or the trypsinkinase and erepsin complexes. E. ABDERHALDEN and F. REICH (Fermentforsch., 1929, 11, 64-77) .---The influence of a series of alcohols on the action of pepsin-hydrochloric acid on caseinogen, trypsinkinase at  $p_{\rm H}$  8.4 on *dl*-leucylglycyl-*dl*-leucine, erepsin at  $p_{\rm H}$  7.8 on dl-leucylglycine, and the gastric, pancreatic, and intestinal juices of the dog on caseinogen at 37°, has been studied. At the concentrations studied only hexyl and tert.-butyl alcohols, respectively, cause an increased action of trypsin-kinase and erepsin, respectively. The following alcohols exert only a retarding action : on erepsin, n- and iso-propyl, hexyl, isobutyl, and benzyl; on pepsin, methyl, ethyl, n-butyl, and isoamyl; on trypsinkinase, n- and tert.-butyl, n- and iso-amyl, benzyl. The following cause an acceleration in low concentration but retard at higher concentrations : on erepsin, methyl, n-butyl, isoamyl, ethyl (also on pancreatic and intestinal juices); on pepsin, n- and iso-propyl, iso- and tert.-butyl, n-amyl, hexyl, and benzyl; on trypsin-kinase, methyl, ethyl, n- and iso-propyl, and isobutyl. n-Amyl, heptyl, and octyl alcohols and nicotine have no effect with erepsin, whilst caffeine has only an accelerating action. A temporary retardation is observed with nicotine on the gastric juice. H. BURTON.

Nature of proteases. III. Parallelism between the activities of pepsin preparations determined by the disappearance of the substrate and by the increase in carboxyl groups. A. N. ADOVA and I. A. SMORODINCEV (Z. physiol. Chem., 1929, **183**, 133—148).—Determination of the activity of various pepsin preparations by the rate of disappearance of the substrate (caseinogen and gelatin) gave the same results as the alcoholic titration of the carboxyl groups by Willstätter's method. All

the pepsin preparations attacked caseinogen more energetically than gelatin; the velocity coefficient of caseinogen digestion by strong preparations is about double that for weak ones. The velocity of digestion of caseinogen by all preparations and of gelatin digestion by strong preparations follows the Schutz-Borissov rule; for weak preparations on gelatin the equation is of zero order. J. H. BIRKINSHAW.

Caseinogen-splitting action of papain. M. SATO (Separate, 1928).—The quantity of caseinogen digested by papain during unit time is directly proportional to the concentration of papain so long as the equilibrium is not approached. The unimolecular velocity coefficient increases as the reaction proceeds. The temperature coefficient falls with rise of temperature; the optimal temperature is about 80°, and the optimal  $p_{\rm II}$  6.5. The action is arrested by N/75— N/125-sodium hydroxide. Acceleration by hydrogen cyanide is attributed to the undissociated molecules. CHEMICAL ABSTRACTS.

Effect of proteolytic enzymes on benzoyl- and deamino-derivatives of polypeptides. T. KAWAI (J. Biochem. Japan, 1929, 10, 277-310).-Glycyldl-phenylalanine, dl-leucylglycine, glycyl-l-phenyl-alanine, and glycyl-l-leucine are split by erepsin but not by trypsin; benzoylglycylglycine is not hydrolysed by erepsin or trypsin, whilst the benzovl derivatives of the other dipeptides are markedly hydrolysed by crude erepsin. Trypsin hydrolyses benzoyl-glycyl-dl- and -l-phenylalanine, -dl- and -l-leucylglycine, the hydrolysis of racemic compounds proceeding asymmetrically. Fission occurs at the peptide linking. Dipeptides not affected by trypsin are hydrolysed when the free amino-group is benzoylated. Tripeptides in which the amino-acid is combined with trypsin-resistant dipeptides are hydrolysed by trypsin. Benzoyldiglycylglycine is not split by trypsin. Deaminated dipeptides are not hydrolysed by crepsin. Deaminated polypeptides are generally resistant to erepsin, whilst some are hydrolysed by trypsin. CHEMICAL ABSTRACTS.

Problem of separation of erepsin and trypsin or trypsin-kinase complexes into fractions with specific action. E. ABDERHALDEN and A. SCHMITZ (Fermentforsch., 1929, 11, 104-118).-An erepsin preparation (from fresh small intestine) hydrolyses dl-leucylglycine after 1 day, but does not after 5 days. During the same time the amount of fission with *dl*-leucylglycyl-*dl*-leucylglycine (I) increases (optimum  $p_{\pi}$  changes from 9.3 to 7.1); hydrolysis of the tetrapeptide occurs even after 17 days. The same preparation hydrolyses glycyl-dl-leucyl-dl-leucylglycine, m. p. 228° (from chloroacetyl-dl-leucyl-dl-leucylglycine), dl-dileucylglycylglycine (II), dl-leucyldiglycyldl-leucine, diglycyl-dl-leucyl-dl-leucine (III), m. p. 233° (from chloroacetylglycyl-dl-leucyl-dl-leucine, m. p. 202°), and glycyl-dl-leucylglycyl-dl-leucine (IV). Another erepsin preparation has no action on dl-leucylglycine, II, or III, but hydrolyses glycyl-dl-leucine, glycyll-tyrosine, the four tripeptides obtainable from glycine and dl-leucine, I, and IV, at  $p_{\rm H}$  7.1 (optimum). H. BURTON.

Action of trypsin on conjugated bile-acids. A. VON BEZNÁK (Biochem. Z., 1929, **210**, 261–264).— Glycocholic and taurocholic acids are not attacked by trypsin. P. W. CLUTTERBUCK.

Reaction of azine compounds with proteolytic enzymes. G. M. RICHARDSON and R. K. CANNAN (Biochem. J., 1929, 23, 624-632; cf. Marston, A., 1924, i, 350).-When pepsin solutions and gastric juice are precipitated by the addition of safranine or neutral-red the proteolytic activity is removed from solution. The supernatant liquors from trypsin precipitates, on the other hand, retain most of their activity. The addition of these dyes in very low concentrations does not retard the catalytic activity of either pepsin or trypsin. The optimum conditions of concentration and  $p_{\rm H}$  for the complete removal of pepsin from solution by this means have been determined. The degree of removal of activity and the weight of precipitate both increase as the  $p_{\rm H}$  rises above 1. These two factors are not, however, parallel, since the actual separation of insoluble matter is spread over a range of about four  $p_{\rm H}$  units, whilst the precipitation of activity is localised about  $p_{\rm ff}$  2. The precipitated enzyme can be regained from the precipitate by treatment with sodium hyposulphite and by extraction of the dye with benzene in the absence of oxygen. Trypsin can be recovered similarly at  $p_{\mu}$  9. Observations on the purification of pepsin by means of the above precipitation method have been made. Marston's view that the azine nucleus reacts specifically with a protease, with the formation of a protease-azine complex, is not supported. S. S. ZILVA.

Influence of hydrogen-ion concentration on the inactivation of urease by heavy metals. M. KITAGAWA (J. Biochem. Japan, 1929, **10**, 197–205).— Inactivation of urease by zinc occurs in alkaline solution from  $p_{\rm H}$  6.0, whilst copper and mercury inhibit the action in either acid or alkaline solution. The effect is parallel to the influence of the  $p_{\rm H}$  on the combination of protein with heavy metals. Iodine is much more injurious to urease than potassium iodide. CHEMICAL ABSTRACTS.

Dried yeast. K. MYRBÄCK and H. VON EULER (Z. physiol. Chem., 1929, **183**, 226—236).—Dried yeast under the best conditions has a fermenting power of 50—75% of that of fresh yeast. The fermentation curves of dried yeast in presence of toluene consist of two distinct portions. The fermentation proceeds normally until all the phosphate is esterified, when the rate of fermentation falls off, since the phosphatase is inactivated by toluene. The paralysing action of toluene on the living cell is quite different and reversible. The initial velocity of dried yeast fermentation is at a maximum at  $45-48^{\circ}$ ; it is zero at  $52^{\circ}$ . J. H. BIRKINSHAW.

Fermentation and growth in dry yeast-cells. II. C. BARTEL, H. VON EULER, and K. MYRBÄCK (Z. physiol. Chem., 1929, **183**, 237–243; cf. A., 1926, 1276).—The ratio of the total number of cells to the number of living cells of an active air-dried yeast which had lost only 35% of its fermenting power was 140,000 before and 11,500 after 48 hrs.' fermentation. Thus more than 99.98% of the total amount of fermentation is due to cells incapable of reproduction. J. H. BIRKINSHAW.

Sugar combination and connected synthetic processes by yeast-cells. E. WERTHEIMER (Fer-mentforsch., 1929, 11, 22-36).-When a dextrose solution is added to a suspension of baker's yeast the sugar disappears from solution before fermentation begins. The combination is not due to adsorption and depends on the temperature. Thus, at 0-15° the coefficient is 2, at 15-35° it is 4-8. Combination is selective, since lævulose and sucrose behave similarly to dextrose, whilst galactose, lactose, maltose, and dihydroxyacetone are unaffected. It is found that part of the dextrose is converted into a polysaceharide insoluble in 60% potassium hydroxide solution. This polysaccharide is not glycogen, but when it is heated with a dilute acid solution fission occurs and glycogen appears to be formed. The same product is obtained from lævulose and sucrose, but not from galactose, lactose, maltose, dihydroxyacetone, glycerol, or acetaldehyde. Sodium fluoride arrests the synthesis, but 0.002N-potassium cyanide has no effect. Synthesis is best accomplished by an active yeast; macerated yeast-juice has no synthetic action. The yeast-cells must, therefore, first assimil-H. BURTON. ate the sugar.

Fermentation of yeast at high gas pressures. R. LIESKE and E. HOFMANN (Biochem. Z., 1929, 210, 448-457).-Yeast fermentation is investigated in sealed steel vessels fitted with contrivances for measuring the pressure attained and for removing and measuring the gas produced. At the ordinary temperature, the fermentation ceases when the pressure of the carbon dioxide formed has risen to 38-40 atm., the amount of carbon dioxide formed then being 1 mol./litre and of alcohol 40 g./litre. If the vessel is initially placed under a pressure of an inert gas of 90 atm. the fermentation is not inhibited, but at 150 atm. there is considerable inhibition, and at 1000 atm. only about half of the alcohol and carbon dioxide are produced as at the ordinary P. W. CLUTTERBUCK. pressure.

Rôle of phosphorus in fermentation. M. SCHOEN (Bull. Soc. Chim. biol., 1929, 11, 819—902).— A review. W. O. KERMACK.

Salt effect on the induction period in fermentation by dried yeast. H. KATAGIRI and G. YAMA-GISHI (Biochem. J., 1929, 23, 654-662).-The following is the order of potency of salts in prolonging the period of induction in the fermentation by dried yeast in the presence of 0.04M-phosphate:  $\frac{1}{2}Ca^{++}>$ Na<sup>+</sup> > K<sup>+</sup> >  $\frac{1}{2}$ Mg<sup>++</sup> > NH<sub>4</sub><sup>+</sup> with chlorides and sulphates and 1'>Cl'> $\frac{1}{2}$ SO<sub>4</sub>" with sodium and potassium salts. The acetate, lactate, succinate, and sulphate of ammonium were nearly as potent as acetaldehyde in reducing the period of induction, although they were less potent than hexosediphosphate. Ammonium ion produced a remarkable antagonistic action to that of sodium ion, and sulphate ion a slight antagonistic action to that of nitrate ion. A hyperbolic relation may exist between the induction period and the ratio of the concentrations of the two S. S. ZILVA. ions.

Comparison of influence of various concentrations of alcohols on alcoholic fermentation. E. ABDERHALDEN (Fermentforsch., 1929, **11**, 86–91). -Fermentation of a 40% solution of dextrose in a phosphate mixture (25 c.c.) with fresh yeast (5 g.) at  $p_{\rm ff}$  6 is accelerated by the addition of 0.05 c.c. of methyl or 0.01 and 0.05 c.c. of ethyl alcohol (in one case 0.025 c.c. caused a slight retardation). Very small amounts of n- and tert. butyl alcohols also cause acceleration, whilst n- and iso-propyl, and isobutyl alcohols effect a retardation. n- and iso-Amyl, hexyl, heptyl, and benzyl alcohols do not cause an acceleration. The results using dry yeast are quali-H. BURTON. tatively the same.

Mechanism of enzyme action. III. Relation between enzyme action and adsorption. TV. Enzymic processes in germinating barley. F. F. NORD and J. WEICHHERZ (Z. physiol. Chem., 1929, on yeast-cells was found to take place in three successive phases: external narcosis, increase in permeability, internal narcosis. The adsorptives became physically attached to the lyophilic colloid elements of maceration juice and could exercise an inhibiting and also a protective action. The inhibition is independent of the precipitating action of the narcotic. Both the increase in cell permeability and the narcosis of the enzymes inside the living cell can be separated from the harmful phase of narcosis.

IV. The enzymic processes in germinating barley are influenced by ethylene and acetylene. This is shown in the increased rate of diastatic and proteolytic degradation and the increase in the yield of green malt. Ethyl acetate was formed in green malt when air was excluded. J. H. BIRKINSHAW.

Desmolytic formation of methylglyoxal by yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1929, 210, 466-488).-The formation of methylglyoxal and hexosemonophosphate and the separation of free phosphate from magnesium hexosediphosphate under the action of plasmolysis juice of fresh top yeast, the residue of plasmolysed top yeast, washed dried bottom yeast, the washings of the same dried yeast, and untreated dried yeast are investigated quantitatively. With the plasmolysis juice an 85.4% yield of methylglyoxal was obtained. The monophosphate in all cases had a high rotation and low reducing power and was probably a mixture of hexose- and trehalose-monophosphate. With untreated dried yeast small amounts of pyruvic acid and acetaldehyde were also obtained.

P. W. CLUTTERBUCK. Sterols from yeast. H. WIELAND and M. ASANO (Annalen, 1929, 473, 300–313).—Benzoylation of a sterol mixture (greater part of ergosterol removed) from yeast with benzoyl chloride and pyridine and subsequent fractionation of the benzoates produced affords in addition to ergosteryl benzoate, m. p. 168–170° (lit. 162–168°),  $[\alpha]_{11}^{23}$ –71.5° (all rotatory powers are in chloroform) (cf. Bills and Honeywell, this vol., 104), benzoates of four other sterols, three of which are new. The sterols, obtained by hydrolysis of the benzoates with 3% alcoholic potassium hydroxide, are : zymosterol (I),  $C_{27}H_{43}$ ·OH (cf. Smedley-Maclean, A., 1928, 329), m. p. 108—110°,  $[\alpha]_D$  +47·3° [*benzoate*, m. p. 126—128° (turbid),

138° (clear), [α]<sup>23</sup><sub>D</sub>+36·4°; acetate, m. p. 104-106° (cf. loc. cit.)], which contains two double linkings; (cf. toc. ct.)], which contains two double linkings; facosterol (II),  $C_{27}H_{46}O$  (one double linking), m. p.  $161-163^{\circ}$ ,  $[\alpha]_D^{\circ} + 42\cdot1^{\circ}$  (benzoate, m. p.  $144-146^{\circ}$ ;  $[\alpha]_D^{\circ0} + 34\cdot7^{\circ}$ ; acetate, m. p.  $159-161^{\circ}$ ); ascosterol (III),  $C_{27}H_{46}O$ , m. p.  $141-142^{\circ}$ ,  $[\alpha]_D^{\circ0} + 45^{\circ}$  (benzoate, m. p.  $130-131^{\circ}$ ,  $[\alpha]_D^{\circ1} + 37^{\circ}$ ), and neosterol (IV), probably  $C_{27}H_{44}O$ , m. p.  $164-165^{\circ}$ ,  $[\alpha]_D^{\circ4} - 105^{\circ}$ (benzoate, m. p.  $173-175^{\circ}$ ,  $[\alpha]_D^{\circ1} - 50\cdot6^{\circ}$ ; acetate, m. p.  $173-174^{\circ}$ ). The colour reactions of ergosterol we have a structure of the str and IV are identical, as are those of II and III. The colour reactions of I differ from those of II and III. H. BURTON.

Determination of micro-organisms in suspension. R. J. WILLIAMS, E. D. MCALISTER, and R. R. ROEHM (J. Biol. Chem., 1929, 83, 315-320).-The density of a suspension of yeast or other microorganisms can be determined by observing the effect of interposition of a cell containing the suspension between a small electric light and a thermo-couple connected with a galvanometer. C. R. HARINGTON.

Methods of studying the surfaces of living cells, with special reference to the relation between the surface properties and the phagocytosis of bacteria. S. MUDD, M. LUCKE, M. MCCUTCHEON, and M. STRUMIA (Coll. Symp. Mon., 1928, 6, 131-138).-A study of bacteria treated with normal and immune sera leads to an expression of the mechanism of the action of opsonins and bacteriotropins in CHEMICAL ABSTRACTS. physico-chemical terms.

Butyric acid fermentation of calcium lactate. V. N. SHAPOSHNIKOV and I. P. ZAKHAROV (Trans. Sci. Chem.-Pharm. Inst. Moscow, 1927, No. 18, 7-25).-The acids produced by fermentation of calcium lactate with a mixed culture consisted of butyric, acetic, and succinic, with small amounts of formic, valeric, and hexoic acids. Only small amounts of ethyl and propyl alcohols were produced. CHEMICAL ABSTRACTS.

Metabolism of Vibrio choleræ in aërobic and anaërobic culture. J. HIRSCH (Z. Hyg. Infekt.-Krankh., 1928, 109, 387-409; Chem. Zentr., 1929, i, 1360).-The aerophilic behaviour of Vibrio choleræ in amino-acid or peptone solutions free from carbohydrate is attributed to the substrate; the bacillus grows under strictly anaërobic conditions on carbohydrates, which are preferred to amino-acids as a source of energy. The significance of amino-acid or peptone for growth in saccharine medium lies chiefly in its being a source of nitrogen. The anoxybiotic decomposition of dextrose by V. choleræ proceeds in two independent ways : C6H12O6=2CH3 CH(OH) CO2H, and  $\mathbf{C_6H_{12}O_6 + H_2O = 2H \cdot CO_2H + CH_3 \cdot CO_2H + CH_3 \cdot CH_2 \cdot OH.}$ A. A. ELDRIDGE.

Oxidation-reduction equilibria in biological systems. II. Potentials of aerobic cultures of Bacillus typhosus. C. B. COULTER and M. L. ISAACS (J. Exp. Med., 1929, 49, 711-725).

Precipitable substances of bacilli of the salmonella group. J. FÜRTH and K. LAND-STEINER (J. Exp. Med., 1929, 49, 727-743).--Specific precipitable substances rich in carbohydrates, containing very little protein and small quantities of a material apparently of fatty nature, have been prepared from the main serological types of the typhoid-paratyphoid groups. Pronounced chemical differences have not been observed.

CHEMICAL ABSTRACTS.

"Soluble specific substance" derived from gum arabic. M. HEIDELBERGER, O. T. AVERY, and W. F. GOEBEL (J. Exp. Med., 1929, 49, 847—857).— Partial acid hydrolysis of gum arabic affords a specific carbohydrate comparable in precipitating activity for types II and III antipneumococcus serum with the bacterial soluble specific substances themselves. Hydrolysis affords galactose and two or more complex sugar acids, one of which appears to be a disaccharide acid comparable with those of bacterial origin.

CHEMICAL ABSTRACTS.

**Fractionation of diphtheria antitoxic plasmas.** P. J. MOLONEY and E. M. TAYLOR (Coll. Symp. Mon., 1928, 6, 109–114).—The antitoxin was precipitated with alcohol, tannin, and Biebrich-scarlet at various  $p_{\rm H}$  values, and its stability with respect to  $p_{\rm H}$  and alcohol was determined. CHEMICAL ABSTRACTS.

Influence of boric acid on Micrococcus ureae and urease in presence of dextrose: J. Voicu (Bul. Soc. Chim. România, 1929, **11**, 25–28).—The inhibitory effect of boric acid on the hydrolysis of urea by urease and by a species of M. ureæ is considerably diminished by the presence of dextrose.

A. A. GOLDBERG.

Presence of adrenaline in the suprarenals in the human and bovine foctus. S. SAITO (Tohoku J. Exp. Med., 1929, **12**, 254-262).—The suprarenals of the bovine foctus (4-8 months) contain proportionally as much adrenaline as the adult glands. Values (mg. per g. of gland) for the human foctus are : 12 weeks, 0; 5 months, 0.82 (Folin); 0.02 (biological); full-term, 2.45 (Folin), 0 (biological). CHEMICAL ABSTRACTS.

Determination of adrenaline in organs by means of the spectrophotometer. I. Adrenaline content of the adrenals. H. HANDOVSKY and A. REUSS (Arch. exp. Path. Pharm., 1929, 144, 105—122).—Details are given of the spectrophotometric determination of adrenaline in alcoholic extracts of the adrenal medulla. The results agree well with those obtained by the biological bloodpressure method. W. O. KERMACK.

Influence of adrenaline on formation of sugar. II. Mobilisation of muscle-glycogen by adrenaline. E. GEIGER and E. SCHMUDT (Arch. exp. Path. Pharm., 1929, 143, 321-328; cf. A., 1928, 1160).—In fasting phloridzinised dogs a first injection of adrenaline leads to increase in the amount of blood-lactic acid, but there is no increase following a second injection. The administration of adrenaline leads to conversion of the muscle-glycogen into lactic acid which, passing into the blood stream and thence into the liver, is there reconverted into glycogen and immediately, as a result of phloridzin, excreted as extra sugar. The first adrenaline injection causes decomposition of all the muscle-glycogen. In animals from which the liver has been removed no reconversion of the blood-lactic acid, and consequently no excretion of extra sugar, can occur.

W. MCCARTNEY.

Carbohydrate metabolism. VI. Antagonistic action of pituitrin and adrenaline on carbohydrate metabolism with special reference to gaseous exchange, inorganic blood-phosphate, and blood-sugar. C. G. LAMBIE and F. A. REDHEAD (Biochem. J., 1929, 23, 608-623) .- In the human subject pituitrin frequently causes a transient fall in metabolism followed by a rise. Sometimes only a rise is observed. In small doses it causes a slight fall in the inorganic phosphate of the blood. It apparently inhibits the slight rise in metabolism which occurs after the administration of insulin, but the changes produced by either insulin or pituitrin are not sufficiently marked to be of much significance. Pituitrin delays and reduces the rise in metabolism and the fall in blood-sugar following the intravenous administration of dextrose or dihydroxyacetone. In small doses sufficient to prevent the fall in blood-sugar resulting from the administration of insulin it did not prevent the fall in inorganic blood-phosphate. In rabbits large doses of pituitrin cause a transitory rise in the inorganic blood-phosphate and for a short period inhibit the fall in inorganic phosphate resulting from administration of dextrose or dihydroxyacetone. A dose of pituitrin which just suffices to prevent the fall in inorganic phosphate following administration of dextrose may fail to overcome the fall due to dihydroxyacetone. In animals rendered hypoglycæmic as a result of insulin administration pituitrin causes the blood-sugar and inorganic bloodphosphate to return to the normal level or even to exceed it. Adrenaline administered alone causes a marked and rapid rise in metabolism which is not solely dependent on the rise in blood-sugar. It does not inhibit the rise in metabolism following intravenous administration of dextrose. Adrenaline administered in large doses to hypoglycæmic animals causes a rise in inorganic blood-phosphate.

S. S. ZILVA.

Hormones of the anterior pituitary lobe. L. F. HEWITT (Biochem. J., 1929, 23, 718-725).—Preparations are described of filtered alkaline extracts of this gland which promoted growth, unfiltered alkaline extracts which promoted growth and inhibited cestrus, and acid extracts treated with kaolin which produced precocious sexual maturity and caused ripening of Graafian follicles in the rat. When the animals which had been treated with the growthpromoting extracts were no longer injected a rapid fall in weight ensued. S. S. ZILVA.

Glycosuria and insulin. G. FRICKE (Z. ges. exp. Mcd., 1929, 64, 81-94; Chem. Zentr., 1929, i, 1363).—By simultaneous administration of dextrose and insulin to the normal dog the dextrose threshold of the kidneys is diminished. In the pancreasdiabetic dog the renal elimination of sugar is increased by the action of insulin with diminishing bleod-sugar. A. A. ELDRIDGE.

Study of sugar regulation by the insulin tolerance test. M. SENDRAIL (Compt. rend. Soc. Biol., 1929, 99, 1901—1903; Chem. Zentr., 1929, i, 1708).

Behaviour of liver-glycogen after oral administration of yeast. A. BICKEL and G. NIGMANN (Biochem. Z., 1929, 210, 443-447).—Administration of dried yeast to dogs which had been largely freed from liver-glycogen by starving increased the liver-glycogen considerably. This action is not due to organic nutrients in the yeast, but to thermolabile substances in the yeast which act similarly to insulin, causing decrease of blood-sugar and increase of liver-glycogen.

P. W. CLUTTERBUCK.

Secretin. II. T. NISHIKAWA (Sei-I-Kwai Med. J., 1928, 47, No. 10).—Hydrochloric acid, but not aqueous or saline, extracts of the bovine duodenum contain activated secretin. Atropine inhibits the action of choline or histamine on pancreatic secretin.

CHEMICAL ABSTRACTS.

Preparation of the female sexual hormone from urine in pregnancy. S. VESHNJAKOV and A. LIPSCHUTZ (Biochem. Z., 1929, 210, 348—352).— A method of preparation is described which gave 4800 mouse units per litre of urine, the unit after purification weighing 0.01 mg.

P. W. CLUTTERBUCK.

Absorption spectrum of vitamin-A. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1929, 23, 633).—Dehydroergosterol, which is devoid of growth-promoting properties and does not give the blue colour reaction with arsenic or antimony trichloride, shows a selective absorption in the ultraviolet region at about  $320-328 \ \mu\mu$ . The absorption is therefore not specific for vitamin-A (cf. Takahashi and others, A., 1925, i, 1365; Morton and Heilbron, A., 1928, 1058). The peroxide of dehydroergosterol is also biologically inactive. S. S. ZILVA.

Nature of the vitamin-A constituent of green leaves. D. L. Collison, E. M. HUME, I. SMEDLEY-MACLEAN, and H. H. SMITH (Biochem. J., 1929, 23, 634-647; cf. Euler and others, this vol., 358, 610; Duliere, Morton, and Drummond, Chem. and Ind., 1929, 48, 518; Moore, Lancet, 1929, i, 499).-The unsaponifiable material from green cabbage contains at least ten times as much vitamin-A as that from white cabbage. The vitamin-A of green spinach and cabbage leaves and of carrots is present in the most highly-unsaturated fraction of the unsaponifiable matter and remains associated with the carotin. It was not diminished in specimens of carotin and crystals of higher m. p. and therefore of presumably greater purity (active dose 0.002-0.005 mg.). The carotin from cabbage softened at 174° and melted at 178°, that from spinach at 163-164°, and that from carrots at 164-169°. Since the observations of Drummond and co-workers (who found carotin inactive) were made on a fat-free diet, it is suggested that either the presence of fat or of something in the unsaponifiable fraction of the fat is possibly necessary for the utilisation of carotin. S. S. ZILVA.

Vitamin-A and carotin. Association of vitamin-A activity with carotin in the carrot root. T. MOORE (Biochem. J., 1929, 23, 803-811).—By using a basal diet containing vitamin-D it was found that daily doses of 100 mg. of fresh carrot sufficed to cure xerophthalmia and restore good growth in rats deprived of vitamin-A. Carrot-fat from which much of the carotin had been removed was found active in a dose of 0.4 mg. daily. Carotin

(m. p.  $174^{\circ}$  in air) was found even after many recrystallisations to be active in doses of 0.01 mg. A possible explanation of the divergent results of others may lie in unsuspected differences in biological technique. S. S. ZILVA,

Assay of vitamin-A. J. C. DRUMMOND and R. A. MORTON (Biochem. J., 1929, 23, 785—802).—A comparative study of the assay of vitamin-A in cod-liver oils by the biological, colorimetric, and spectroscopic (intensity of absorption band at  $328 \mu\mu$ ) methods is described. Even with the use of large number of rats, quantitative differences in vitamin-A potency of less than 100% could not be detected by the biological method. The relative values of the potency of the oils obtained by the three methods were in agreement. The results of the colorimetric and spectrographic methods were very concordant. S. S. ZILVA.

Biological and colorimetric assay of vitamin-A in fish oils. E. R. NORRIS and I. S. DANIELSON (J. Biol. Chem., 1929, 83, 469—475).—The intensity of colour produced by treatment of fish oils with antimony trichloride is approximately proportional to the amount of oil employed only at very low concentrations. By working at such low concentrations, colorimetric results in good agreement with those of biological determinations are obtained.

C. R. HARINGTON. '

Analytical remarks on vitamin-A. S. H. BERTRAM (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 664-668).-A "daylight" lamp is recommended for tintometer readings with the blue colour produced by the interaction of antimony trichloride and vitamin-A. Turbidity is often caused by basic substances such as amines or by traces of soaps, and can be avoided by adding a negligibly small volume of acctic anhydride after adding the trichloride solution. The blue colour is not quite specific and is thought to arise from the condensation of vitamin-A with impurities (perhaps aldehydic) or with itself. The reaction is probably due to a definite group, which may be present in oxycholesterol. This compound does not prevent xerophthalmia. The carotinoids in general give blue colours with antimony trichloride, indicating that conjugated double linkings are necessary. Vitamin-A and carotin can be brominated in light petroleum (the products no longer giving blue colours) and debrominated with zinc dust and acetic acid, the resulting products again giving blue colours. The colour reaction with phloroglucinol in alcohol and a few drops of hydrochloric acid is given by vitamin-A preparations, but not by carotin. Of the fats studied by the author only those containing vaccenic acid contain vitamin-A. If, as there is some evidence, oleic acid is the parent substance of cholesterol, a genetic relationship between vaccenic acid and vitamin-A seems possible. All estimates of the vitamin-A content of foods, oils, etc. based on the colorimetric method must be accepted with the utmost reserve unless the presence of bixin and carotinoids has been excluded. An extract of green cabbage leaves gave the blue colour and the phloroglucinol reaction and also showed growth-promoting and antixerophthalmic properties. R. A. MORTON.

Antimony trichloride colour test for vitamin-A. N. EVERS (Quart. J. Pharm., 1929, 2, 227-237).--Solutions of antimony trichloride obtained from different sources after recrystallisation from anhydrous chloroform and not more than 1 month old give lower but more consistent results than those prepared from samples of antimony chloride which have been merely washed with chloroform or kept for more than 1 month. Since the colorimetric readings obtained are not proportional to the concentration of the oil in the reaction mixture, the quantity of oil used is an important factor, especially with highly active fats, e.g., ox-liver fat; such errors are minimised by the addition of an inactive oil (arachis oil) so that the concentration of oil in the reaction mixture is about 2%. The natural colouring matter of ox-liver fat C. C. N. VASS. affects the determinations.

Effect of  $p_{\rm H}$  on thermolability of vitamin-B of yeast. R. R. WILLIAMS, R. E. WATERMAN, and S. GURIN (J. Biol. Chem., 1929, 83, 321-330) .--- Vitamin- $B_1$  in brewer's yeast is not completely destroyed by autoclaving for 6 hrs. at 15 lb. pressure unless the yeast be first rendered alkaline; the vitamin- $B_1$  of the relatively alkaline baker's yeast is destroyed by such treatment. In no case could complete removal of vitamin- $B_1$  be achieved without considerable simultaneous loss of vitamin- $B_2$ .

C. R. HARINGTON.

Sparing action of fat on vitamin- $B_1$ . H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1929, 83, 269-287).-Growing rats on a diet of very low fat content, but receiving supposedly adequate amounts of the various vitamins, showed marked improvement if the diet were supplemented either with fat (free from vitamin- $B_1$ ) or with an extra amount of a substance rich in vitamin- $B_1$ ; it thus appears that fat exercises a sparing action on this vitamin.

C. R. HARINGTON.

Second thermolabile water-soluble accessory factor necessary for the nutrition of the rat. V. READER (Biochem. J., 1929, 23, 689-694).-Rats which grow satisfactorily on a basal diet supplemented with marmite failed to grow when this untreated yeast extract was replaced by one which had been previously subjected to alkaline hydrolysis  $(p_n 9)$  for 1 hr. at 120°, even when vitamin- $B_1$  (the treated marmite contained vitamin- $B_2$ ) was supplied in the marmite contained vitamin- $B_2$ ) was supplied in the form of Peters' extract. This failure to grow is due to the destruction of a factor  $B_3$  in the marmite in the process of hydrolysis. Vitamin- $B_3$  is more thermolabile than vitamin- $B_1$ . Extraction with ether removed the vitamin- $B_3$  activity of marmite, but no active substance could be recovered from the ethermolabile substance could be recovered from the S. S. ZILVA. ethereal extract.

Vitamin-B. R. A. PETERS (Nature, 1929, 124, 411).-The factor discovered by Reader (preceding abstract) differs from that discovered by Hunt (A., 1928, 1405) and from Williams and Waterman's (A., 1928, 1058) thermolabile factor. At least five B-factors have now been described.

A. A. ELDRIDGE.

Distribution of vitamins-B and -C in young plants. C. KUCERA (Compt. rend. Soc. Biol., 1928, 99, 971-972; Chem. Zentr., 1929, i, 1705).-Whilst 4 K

vitamin-C is present in all parts of the young plant, vitamin-B is present only in the seed.

A. A. ELDRIDGE.

Action of vitamins and surface activity. III. Parallelism between the changes of antiscorbutic action and the surface activity of cabbage juice. N. E. SCHEPILEVSKAJA (Biochem. Z., 1929, 210, 334-347).-The parallelism between changes of surface activity and vitamin action of cabbage juice as described by Hahn (A., 1925, ii, 664; 1926, 760) does not exist. P. W. CLUTTERBUCK.

Vitamin-D in ergot of rye. E. MELLANBY, E. SURIE, and D. C. HARRISON (Biochem. J., 1929, 23, 710-717) - Ergot of rye is a powerful stimulus to calcification of bone. The factor responsible for this action is soluble in alcohol and ether, is present in the unsaponifiable fraction, and possesses the properties of vitamin-D. Ryc germ, not affected by the ergot fungus, contains a small quantity of calcifying substance which can be extracted by light petroleum. The irradiation of unground ergot grains by strong sunlight produces no increase and the irradiation by the mercury-vapour lamp only a slight increase in the calcifying activity of ergot, although there is abundant ergosterol present. S. S. ZILVA.

Nature of the rickets-producing factor in cereals. L. MIRVISH (Nature, 1929, 124, 410-411). -Oatmeal contains a substance which, when injected into rabbits, lowers the blood-calcium, the character of the effect being the same as that produced by extracts of bovine ovaries. Hence rickets is not purely a condition of vitamin deficiency.

A. A. ELDRIDGE.

Existence of a further factor necessary for growth of the rat. K. H. COWARD, K. M. KEY, and B. G. E. MORGAN (Biochem. J., 1929, 23, 695-709).-Rats often cease to grow on a diet satisfactory in calorific value, salt content, digestibility, and content of recognised vitamins when "vitamin-free casein" (Glaxo) is used. Resumption of growth takes place when this case in is replaced by "light white case in " (B.D.H.) or by the addition of certain substances such as fresh milk, lettuce, fresh and dried grass, oxmuscle, liver, or wheat embryo. Less rapid growth is brought about by water-cress and milk which has been boiled for 15 min. Butter and etiolated wheat shoots show little activity in this respect. Heat impairs the power of "light white casein" to cause growth. Treatment with cold alcohol, ether, or 2% acetic acid does not damage this property of the casein. Extraction with boiling alcohol and ether gives slightly active extracts and leaves definitely impaired casein. Boiling alcohol (90%) and ether yield extracts of definite activity from wheat embryo. S. S. ZILVA.

Avitaminosis and hæmatopoietic function. I. Vitamin-A deficiency. II. Vitamin-B deficiency. III. Vitamin-E deficiency. В. SURE, M. C. KIK, and D. J. WALKER (J. Biol. Chem., 1929, 83, 375-385, 387-400, 401-408).-I. In the early stages of vitamin-A deficiency there is a slight reduction in the number of red corpuscles and in the amount of hæmoglobin in the blood; in the later stages the effect of inanition in causing a concentration of the blood is predominant.

II. The blood-picture in vitamin-B deficiency is in general similar to that observed in deficiency of vitamin-A, with, in addition, marked reduction of the serum-proteins in the anæmic stage.

III. Vitamin-E has no effect on the hæmatopoictic function. Neither ferric citrate nor the ash of lettuce was capable of relieving sterility in females on diets deficient in vitamin-E. C. R. HARINGTON.

Behaviour of nitrogenous compounds during germination. R. BONNET (Compt. rend., 1929, 189, 373—375).—Seeds of *Lupinus luteus* and *Ervum lens* were grown in the dark in distilled water at 20° for 15 days and the various nitrogen fractions determined at different stages. Before germination the bulk of the nitrogen is in the form of protein (85%), which breaks down during germination, giving rise to ammonia etc. and amino-acids (largely asparagine, the formation of which corresponds with that of urea in the animal kingdom). Urea and allantoic acid are waste materials in the plant and nitrates do not appear to play any part in nitrogen metabolism during germination. P. G. MARSHALL.

Transformation (particularly saponification) of the reserve fat of seeds during germination. J. LEMARCHANDS (Compt. rend., 1929, 189, 375— 377).—Ungerminated seeds constitute a neutral medium in which mineral salts occur in very small amount, whereas germinating seeds constitute an acid medium consisting chiefly of acid phosphates (produced by hydrolysis of an organic phosphorus compound) together with some free phosphoric acid, sulphates, and chlorides, and free fatty acids. The cytoplasm of sunflower seed has no lipolytic activity, but that of the castor seed has a powerful action which is promoted most effectively by the acid phosphates of calcium and magnesium.

The mol. wt. of the fatty acids of sunflower-seed oil remains constant at about 292 in the initial stages of germination and rises to about 353 in the final stages. Saponification of the fats therefore takes place before utilisation of the fatty acids, the latter process beginning with the unsaturated acids. Aldehydes, produced by oxidation of the fatty acids, have only a transitory existence. P. G. MARSHALL.

Formation of xanthophyll, carotin, and chlorophyll in barley germinated in light and in darkness. H. VON EULER and H. HELLSTRÖM (Z. physiol. Chem., 1929, **183**, 177–183; cf. this vol., 848).—The chlorophyll, xanthophyll, and carotin content of germinating barley shoots was determined. The germination was allowed to proceed in the dark for 9 days; some of the shoots were then exposed to light. The xanthophyll content increased at a steady rate until the 9th day; the rate then diminished in both cases but much more in the etiolated shoots. The chlorophyll and carotin corresponded closely; both were practically absent from plants germinated in the dark. J. H. BIRKINSHAW.

Quantitative changes in chloroplast pigments in the peel of bananas during ripening. H. VON LOESECKE (J. Amer. Chem. Soc., 1929, 51, 2439—

2443).—Determinations of the amounts of chlorophyll (a+b), xanthophyll, and carotin present in the green and yellow skins of a variety of *Musa sapientum* show that the chlorophyll content decreases to zero as a linear function of time during the change from green to yellow, whilst the amount of yellow pigment (xanthophyll+carotin) remains unchanged. The amount of xanthophyll is always greater than that of carotin, but the ratio changes during ripening.

H. BURTON.

Zinc content of vegetable foods. G. BERTRAND and B. BENZON (Ann. Inst. Pasteur, 1929, 43, 386-393).—See this vol., 362.

Variation of colour of plants during desiccation. Glucoside of Lathræa clandestina, L., is aucubin. M. BRIDEL (J. Pharm. Chim., 1929, [viii], 10, 97-110).—See this vol., 857.

"Minjak pelandjau," the exudation from the wood of Pentaspadon Motleyi, Hook. P. VAN ROMBURGH and A. G. VAN VEEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 692—697).—The exudation consists mainly of a crystalline acid,  $C_{24}H_{36}O_3$ , m. p. 25—26°,  $n_{15}^{*}$  1.5225,  $d_{15}^{*}$  1.005, having five ethylenic linkings, one hydroxyl group, and a ring system. Oxidation with potassium permanganate gave azelaic and suberic acids. Propaldehyde, hexoic acid or one of its isomerides, oxalic acid, and azelaic acid were obtained by the ozonisation of the methyl estor and subsequent decomposition of the ozonide. N. M. BLIGH.

Spike disease of sandal (Santalum album). IV. Chemical composition of healthy and spiked sandal stems. D. A. R. RAO and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, 11A, 241-243).—The diseased stems of Santalum album have usually a low content of ash, calcium, and potassium, and a high content of nitrogen, phosphorus, and starch as compared with healthy stems. W. O. KERMACK.

Micro-determination of calcium. P. L. KIRK and C. L. A. SCHMIDT (J. Biol. Chem., 1929, 83, 311—314).—A special filter is described for the separation of minute amounts of calcium oxalate which makes possible a simplification of the method of Kramer and Tisdall (A., 1921, ii, 595) for the determination of calcium. C. R. HARINGTON.

[Iodine determination.] G. PFEIFFER (Biochem. Z., 1929, 210, 231-233).—The modifications in the author's method proposed by Glimm and Isenbruch (this vol., 838) are unnecessary.

J. H. BIRKINSHAW.

Manometric determination of amino-nitrogen. D. D. VAN SLYKE (J. Biol. Chem., 1929, 83, 425– 447).—The solution is introduced into the apparatus of Van Slyke and Neill (A., 1924, ii, 872) and treated with sodium nitrite and acetic acid; the liberated gases are transferred to an absorption pipette containing alkaline permanganate, and the liberated nitrogen is returned to the apparatus and determined manometrically. The method is capable of determining 0.0005 mg. of amino-nitrogen and can therefore be applied directly to a protein-free blood filtrate, the carbamide being either determined separately or destroyed with urease. C. R. HARINGTON.