

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

OCTOBER, 1928.



### General, Physical, and Inorganic Chemistry.

**Measurement of the life period of metastable mercury atoms.** T. ASADA, R. LADENBURG, and W. TIETZE (*Physikal. Z.*, 1928, **29**, 549—550).—The life period of the metastable  $^3P_0$  atom in the presence of a few millimetres of nitrogen is  $15 \times 10^{-4}$  sec. The measurements, being based on optical excitation, are free from objections such as can be made to data from electrical excitation. Absorption of the resonance line 2537 Å. excites the unstable  $^3P_1$  atom, and this state or the neighbouring metastable  $^3P_0$  and  $^3P_2$  atoms formed by collisions can be raised to the higher  $2^3P_1$  state by absorption of visible wavelengths, only to fall back spontaneously with the accompaniment of fluorescent emission of the 5461 line. By means of a rotating disc equipped with filters this line can be photographed and from the intensity the life period can be calculated. The method has possibilities for further applications.

R. A. MORTON.

**Colouring [of band spectra] and [electron] exchange.** H. LUDLOFF (*Naturwiss.*, 1928, **16**, 611—612).—The two ways in which molecules can be formed out of atoms, *i.e.*, on the basis of the space distribution of their charges and on the basis of electron exchange, can be distinguished by observing the band spectra of the compounds. Two examples are taken and examined by quantum mechanics. The first, that of the combination of two hydrogen atoms to form a molecule, would give red colouring of the band spectrum. The second is the combination of hydrogen with a metal such as calcium or zinc. This should give violet colouring.

A. J. MEE.

**Spark spectra of sulphur, selenium, and tellurium in the Schumann region.** P. LACROUTE (*J. Phys. Radium*, 1928, [vi], **9**, 180—184).—The source of light used was a discharge tube with external electrodes. A fluorite window was used and limited the measurements to the region greater than 1235 Å. A vacuum grating spectrograph was employed. Tables of wave-lengths of lines found are given.

W. E. DOWNEY.

**Width of the lines of the Balmer series.** (MLLE.) M. HANOT (*J. Phys. Radium*, 1928, [vi], **9**, 156—169).—See this vol., 209.

**Colour temperature of the magnesium flame.** W. DZIOBEK (*Z. wiss. Phot.*, 1928, **25**, 287—290).—Measurement of the colour temperature of a magnesium flame gave the value  $3700^\circ \pm 75^\circ$ . W. CLARK.

**Factors governing the appearance of the forbidden line 2656 in the optical excitation of**

**mercury.** R. W. WOOD and E. GAVIOLA (*Phil. Mag.*, 1928, [vii], **6**, 271—276).—The presence of water vapour, for enhancing the forbidden line of mercury, has the disadvantage that under illumination it liberates free hydrogen, which is known to be very efficient in shortening the life of the metastable atoms necessary for the appearance of the line, as well as decreasing the intensity of the resonance line. With water vapour it is necessary always to neutralise the effect of the hydrogen by admitting small quantities of air or oxygen. These difficulties are reduced by employing a mixture of 2—3 mm. of nitrogen and 0.1—0.4 mm. of water vapour and introducing a small quantity of mercuric oxide into the tube. This serves to remove the hydrogen as fast as it is formed.

A. E. MITCHELL.

**Active nitrogen.** A. E. RUARK (*Phil. Mag.*, 1928, [vii], **6**, 335—336).—A discussion of certain discrepancies between the results of Okubo and Hamada (this vol., 210) and those of Ruark, Foote, Rudnick, and Chenault (*A.*, 1927, 395). The differences in the spectra obtained from thallium, cadmium, and mercury in contact with active nitrogen can be attributed to the different pressures at which the observations were made. The Geissler type of discharge tube employed by Okubo and Hamada introduces possible secondary effects such as collisions of the second kind, so that their observation of the  $2^3P-2^3P'$  lines of magnesium cannot be accepted as conclusive proof that two electrons can be displaced simultaneously to higher energy levels by the primary process giving rise to metallic spectra at much lower pressure. The criticism of the observation of the second positive bands of nitrogen in the afterglow spectrum is shown to be invalid. A. E. MITCHELL.

**Power relation of the intensities of the lines in the optical excitation of mercury.** R. W. WOOD and E. GAVIOLA (*Phil. Mag.*, 1928, [vii], **6**, 352—356).—The previous work of Wood (*A.*, 1925, ii, 1015) in which it was shown that the relative intensity of the line 3650 Å. of mercury could be varied over a large range by changing the conditions of excitation has been extended to the case where the intensity of the exciting radiation has been diminished to a known extent by interposition of a wire gauze screen. The intensities of the lines that appear in fluorescence are shown to be proportional to the square of the intensity of the exciting radiation with the exception of 3650 and 3021 Å., which change with the third power, and of 2537 and 2656 Å., which

are directly proportional to the intensity of the exciting radiation. These results form the basis of an explanation of the previous observations (*loc. cit.*).

A. E. MITCHELL.

**Continuous spectrum of hydrogen.** Y. TAKAHASHI and Y. HUKUMOTO (*Sci. Rep. Tôhoku Imp. Univ.*, 1928, 17, 675—678).—The spectra emitted by a hydrogen discharge tube at the ordinary temperature and when cooled in liquid air were compared. The continuous spectrum, particularly in the region of wave-lengths greater than 2300 Å., was enhanced by cooling, whilst the intensities of the lines of the secondary spectrum and Balmer's series were reduced.

C. J. SMITHELLS.

**Stark effect of the second order in hydrogen.** H. R. VON TRAUBENBERG (*Naturwiss.*, 1928, 16, 655—656).—An apparatus is described with which it was found possible to investigate the Stark effect of the second order (displacement towards the red of the resolved components) in hydrogen in a field of 420,000 volts/cm. The results obtained agree well with the values calculated by Schrödinger's theory, but not so well with those obtained by Epstein. The displacement is proportional to the square of the field strength, as theory indicates.

A. J. MEE.

**Fine structure of the sodium *D* lines.** L. DOBREVZOV and A. TEREIN (*Naturwiss.*, 1928, 16, 656).—The structure of the sodium *D* lines was investigated using a Lummer-Gehrcke plate perpendicular to the rays. Without resolution of the *D*<sub>1</sub> and *D*<sub>2</sub> lines, the interference pattern appeared as a series of fine triplets, which on resolution of the *D* lines were resolved into two series of fine doublets, the separation of the components being of the order of 0.01 Å.

A. J. MEE.

**A fine quantum analysis of certain terms of thallium I.** M. KIMURA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, 9, 51—56).—Using the data of Mohammad and Mathur (this vol., 677), the term separations and the fine quantum numbers of each of the sub-terms of *2p*<sub>1</sub>, *2p*<sub>2</sub>, *3d*<sub>1</sub>, *3d*<sub>2</sub>, and *2s* terms of the thallium I spectrum have been calculated.

R. A. MORTON.

**Series relations of the neon spectrum.** Y. ISHIDA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, 9, 1—3).—Stark effect patterns of the neon spectrum are not in complete agreement with Paschen's series classification. In *p-d* combinations the predominating patterns are (1) an unsymmetrical type, consisting of three lines, the centre component being slightly bent to the positive side; the right component is an ordinary line, whereas the other two components are combination lines; (2) a symmetrical type consisting of four lines, the inner pair being deflected about one half as much as the outer pair; the two positive lines are ordinary lines, whereas the two negative lines are combination lines.

R. A. MORTON.

**Zeeman effect in the band spectrum of helium.** W. E. CURTIS and W. JEVONS (*Proc. Roy. Soc.*, 1928, A, 120, 110—127; cf. A., 1925, ii, 1103).—Observations have been made of the Zeeman effects in two regions of the helium band spectrum, in fields

up to 20,000 gauss, using (i) an Eagle spectrograph with an 8 ft. concave grating, giving a dispersion of about 2.35 Å./mm. in the third order, and (ii) a 1 cm. Fabry-Perot étalon in conjunction with a glass prism spectrograph. The ranges of wave-lengths investigated with the grating were 4758—4365 Å. and 4161—3626 Å., and with the étalon spectrograph, 5000—4300 Å. Special H-shaped discharge tubes were employed, with copper strip electrodes sealed into the upper ends of the vertical limbs, which were of circular section, the horizontal limb being of elliptical cross-section. Resolution of the magnetic components has been effected only in one case (the band near  $\lambda$  4648), but many instances of broadening have been observed, and some information as to the polarisation of the components has been obtained by means of a double-image prism. The results for the bands due to transitions between *S* and *P* electronic states are in complete accordance with theoretical predictions. The effects decrease in amount with increase of rotation, and the polarisation of the outer components is opposite in character for *Q* and *PR* type branches. A totally different behaviour has been observed in the case of the band near  $\lambda$  4472; the effects are relatively large throughout both *Q* and *R* branches (the *P* branch being too weak for observation), and they show similar polarisations. They have a common set of initial levels, and the final levels are the *B* and *A* rotational sub-levels of the *2P* electronic state of the ortho-helium molecule. It is termed *4Z*, and shows certain other unusual characteristics besides the exceptional magnetic behaviour. A table is given of unallocated lines which show well-marked broadenings in the field.

L. L. BIRCUMSHAW.

**Energy distribution in the continuous spectrum [of radiation emitted] from aluminium electrodes sparking under water.** I. WYNEKEN (*Ann. Physik*, 1928, [iv], 86, 1071—1088).—The distribution of energy was determined by comparison with that in the spectrum of the carbon arc, which is already known. A rotating-sector photometer was used in conjunction with a camera, the velocity of rotation of the sector being so arranged that the frequency of extinction was the same as the spark frequency. The photograph of the spectrum of light emitted from a copper arc was taken on the same plate for calibration purposes. The photometric comparison of intermittent and continuous light sources is discussed. The energy of radiation was calculated and plotted against the wave-length. There is a clear energy maximum at a wave-length of about 2850 Å. On the basis of Wien's law this would correspond with a temperature of 10,000° Abs. By extrapolating the curve to zero intensity it is found that the energy of radiation is zero at approximately 2000 Å. This decrease in energy is not due to absorption by the water or colloidal particles present.

A. J. MEE.

**Stark effect of Balmer series at high field.** Y. ISHIDA and S. HIYAMA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, 9, 1—14).—By employing a high electrical field, measurements have been made of the Stark effect of the Balmer series of hydrogen

up to the third order. The results obtained generally support the theoretical conclusions reached from wave mechanics, both as regards intensity and deflexion.  
J. W. SMITH.

**Zeeman resolution of the oxygen spectral line at  $\lambda 5577 \text{ \AA}$ , the auroral green line.** J. C. McLENNAN, J. H. McLEOD, and R. RUEDY (Phil. Mag., 1928, [vii], 6, 558—567; cf. A., 1927, 910).—The oxygen green line at  $\lambda 5577 \text{ \AA}$  is resolvable magnetically into a normal triplet and must originate in electronic transitions from the  $^1S_0$  to the  $^1D_2$  metastable levels of oxygen atoms.

S. K. TWEEDY.

**New bands in the secondary spectrum of hydrogen.** D. B. DEODHAR (Phil. Mag., 1928, [vii], 6, 466—479).—Data relating to seven new bands in the secondary spectrum of hydrogen, situated in the yellow region, are recorded. These bands, which are not of the half quantum type, are emitted by an excited hydrogen molecule.

S. K. TWEEDY.

**Ultra-violet radiations emitted by point discharges.** J. THOMSON (Phil. Mag., 1928, [vii], 6, 526—546).—A preliminary investigation is recorded of the variation with pressure (up to 1 atm.) of the ionising and photo-electric radiations from hydrogen and nitrogen excited by spark discharge, and of the intensity variations of these radiations when the discharge current is varied at constant gas pressure. The radiations are probably molecular in origin and the observed variations are made up of both absorption and emission variations. The effects in carbon dioxide are exceedingly small, whilst oxygen exhibits a spontaneous ionisation probably due to the gradual change of ozone molecules formed during discharge into normal oxygen molecules (cf. Wynn-Williams, A., 1926, 331).

S. K. TWEEDY.

**Transition probabilities in the lithium atom II.** B. TRUMPY (Z. Physik, 1928, 50, 228—233).—The transition probabilities of the  $2_2-2_1$  and  $3_2-2_1$  energy changes in the lithium atom have been calculated according to the method of Schrödinger and Sugiura as  $f=0.7230$  and  $0.0642$ , respectively. Combining these values with those previously deduced (A., 1927, 998) the value of  $\Sigma f$  for the region of continuous absorption is calculated to be 0.171.

J. W. SMITH.

**Interpretation of band spectra. II.** R. DE L. KRONIG (Z. Physik, 1928, 50, 347—362; cf. this vol., 456).—Using an approximate method, the two-atom molecule is examined by means of wave mechanics. An expression is obtained for the dependence of the doublet separation on the rotation quantum number in terms of the direction of the impulse of rotation of the electrons; also, an explanation of "disturbances" or variations of some terms from the calculated values. Henri's concept of pre-dissociation is used to obtain an estimate of the life of the "pre-dissociated" molecule.

W. E. DOWNEY.

**Widening of spectral lines by the thickness of the vapour of the absorbing atoms.** E. VOGT (Z. Physik, 1928, 50, 395—396).—The measurements of Schütz (A., 1927, 1117) and of Trumpy (*ibid.*,

179) yield results which differ from one another in their order of magnitude.  
W. E. DOWNEY.

**Magneto-optical determination of the intensity of the first two members of the principal series of potassium and the vapour pressure of potassium.** J. WEILER (Z. Physik, 1928, 50, 436—439).—The intensity ratio of the doublets of the first member of the principal series of potassium for temperatures between  $155^\circ$  and  $265^\circ$  is  $1.96 \pm 0.07$ . Similarly, the ratio for the second member between  $240^\circ$  and  $353^\circ$  is  $1.94 \pm 0.09$ . The ratio of the first to the second member, in the temperature interval  $253-265^\circ$ , is  $96 \pm 4$ . The vapour pressure of potassium should obey the formula  $\log pT' = 20,000/4.571T' + 9.866$ , giving as the heat of vaporisation of potassium 20,000 g.-cal.

W. E. DOWNEY.

**Series spectra of Hg-like atoms—Tl II and Pb III.** K. R. RAO, A. L. NARAYAN, and A. S. RAO (Indian J. Physics, 1928, 2, 467—476).—A preliminary report of series regularities discovered in the spectra of singly-ionised thallium and doubly-ionised lead, which are homologous with the neutral mercury atom. The first members in each of the triplet series of these spectra have been identified. The resonance potential of thallium is 6.47 volts and the ionisation potential about 20.3 volts. In the case of lead these are 7.95 and 31.5 volts, respectively.

J. W. SMITH.

**Series spectra of Sn IV and In III.** K. R. RAO, A. L. NARAYAN, and A. S. RAO (Indian J. Physics, 1928, 2, 477—483; cf. A., 1927, 911).—Further experiments support the observations of Rao in the identification of the  $1^2D-1^2F$  member of the first fundamental series of Sn IV. It is suggested that the large  $2^2F$  term obtained by Lang (A., 1927, 911) has its origin in the  $N_4$  orbit, whilst the smaller term found by Rao arises from the  $O_4$  orbit. The results of Lang on the In III spectrum have also been extended. The ionisation potential of indium is 27.91 volts.

J. W. SMITH.

**Extreme ultra-violet spectrum of argon excited by controlled electron impacts.** K. T. COMPTON, J. C. BOYCE, and H. N. RUSSELL (Physical Rev., 1928, [ii], 32, 179—185).—In the wave-length region 1066—461  $\text{\AA}$ . 20 arc lines and 68 spark lines (attributed to A II) are recorded; 37 of the spark lines have been classified. The ionisation potential is  $27.82 \pm 0.05$  volts, whence 43.51 volts is the minimum potential for double ionisation with reference to the  $^3P_2$  limit.

A. A. ELDRIDGE.

**Assignment of quantum numbers for electrons in molecules. I.** R. S. MULLIKEN (Physical Rev., 1928, [ii], 32, 186—222).—Tentative formal assignments (based on band spectra, ionisation potentials, and positive ray data) of quantum numbers for most of the known electronic states of diatomic molecules composed of elements of the first short period of the periodic classification have been made and tabulated. A notation for designation of the state of each electron and the molecule as a whole is proposed. The possible molecular states corresponding with various electron configurations are deduced. The electrons in a molecule may be classified accord-

ing to their "bonding power." Rules expressing the relations of the electronic states of a molecule to those of its dissociation products are discussed, together with selection rules for electronic transitions and certain of Hund's rules. Nearly all the observed ionisation potentials of the molecules discussed can be accounted for by the removal of a single electron from one or other of the various closed shells supposed to be present.  
A. A. ELDRIDGE.

**Spectrum of sulphur, S II.** S. B. INGRAM (Physical Rev., 1928, [ii], 32, 172—178).—In the spectrum of S II 183 lines have been classified. The ionisation potential of the S II ion is  $23.3 \pm 0.1$  volts.  
A. A. ELDRIDGE.

**Rotational structure of the blue-green bands of Na<sub>2</sub>.** F. W. LOOMIS and R. W. WOOD (Physical Rev., 1928, [ii], 32, 223—236).—Measurement of the bands in absorption shows that they consist of only one *P*, one *Q*, and one *R* branch. The combination relations hold rigorously except for a small *PQR* defect. Constants of the band system are recorded; the large internuclear distances correspond with weak molecular binding, which accords with the low heat of dissociation. No alternation in intensity of the absorption lines was observed.  
A. A. ELDRIDGE.

**Spark potential curve of a pure gas at low pressures.** K. ZUBER (Naturwiss., 1928, 16, 615—616).—An expression for the spark potential is calculated which gives, within certain limits, values in agreement with experiment.  
A. J. MEE.

**New photo-electric phenomenon with thin sheets of alkali metals.** R. SUHRMANN (Naturwiss., 1928, 16, 616—617; cf. this vol., 680).—Gudden's explanation of the phenomenon (this vol., 808), viz. that there are local differences of potential of the order of 0.1 volt on the metal film, is in contrast with the hypothesis of surface ionisation. It should be possible to decide between the two by investigating the influence of temperature on the effect.  
A. J. MEE.

**Multiple valency.** A. F. RICHTER (Z. physikal. Chem., 1928, 135, 444—460).—The effect of the ratio of the stabilities of opposing configurations of electrons on the work necessary to detach electrons is examined.  
W. E. DOWNEY.

**Photo-electric thresholds of potassium.** (Miss) J. BUTTERWORTH (Phil. Mag., 1928, [vii], 6, 352).—A correction to the previous paper (this vol., 931) in which centigrade temperatures were inadvertently used instead of absolute temperatures. The corrected calculations show that potassium has photo-electric thresholds at 7100 and 21,000 Å., with a possible threshold at 10,000 Å. Previous observations have been confirmed by modification of the method.  
A. E. MITCHELL.

**Photo-electric effect of soft X-rays.** G. B. BANDOPADHYAYA (Proc. Roy. Soc., 1928, A, 120, 46—58).—An investigation of the yield of photo-electrons, due to the same beam of soft X-rays, from different elements under similar conditions. Twelve elements (carbon, aluminium, iron, cobalt, nickel, copper, molybdenum, silver, tantalum, tungsten,

platinum, and gold) were used, and the photo-electric currents were measured with an electrometer by the ordinary timing method, all the readings being taken at a pressure of the order of  $10^{-7}$  mm. Values of the photo-electric efficiency  $i_p/i_t$  (photo-electric current/thermionic current) observed with different elements by the action of X-rays from a copper anticathode at voltages from 200 to 500 are tabulated, readings for both thoroughly degassed and undegassed photo-electric plates being recorded. The latter values are in general higher, except for aluminium, and it is found that degassing affects the relative values. On plotting  $i_p/i_t$  against atomic number for the different elements, it appears that there is no simple relation between the two properties. The sensitiveness of different elements under soft X-rays is very similar to that under ultra-violet light. Assuming that the law governing the ejection of photo-electrons under soft X-rays is similar to that for ejection under ultra-violet light, a formula is deduced indicating that the number of photo-electrons liberated should be proportional to the voltage. This is found to be approximately true.  
L. L. BIRCUMSHAW.

**Critical potentials of metallic vapours. I. Copper.** H. B. WAHLIN (Physical Rev., 1928, [ii], 32, 277—286).—A number of critical potentials in copper vapour in the region 0—20 volts have been found, and their significance is discussed.  
A. A. ELDRIDGE.

**Thermionic emission.** L. TONKS (Physical Rev., 1928, [ii], 32, 284—286).—It is proved thermodynamically that the work function in the exponent of the Richardson equation is the same whether emission takes place at constant total charge or constant surface charge.  
A. A. ELDRIDGE.

**Diffraction of electrons at an optical grating.** E. RUPP (Naturwiss., 1928, 16, 656).—It was found possible to diffract electrons at an optical grating by using the method of grazing reflexion. For the success of the experiment it is necessary to use a metal grating, to focus the electron beam by means of a magnetic field, and to bombard the grating repeatedly with rapid electrons during an exposure. Estimation of the "wave-length" of electrons by this method can be carried out with an accuracy of  $\pm 5\%$ .  
A. J. MEE.

**Cathodic sputtering. IV. Effect of material and state of cathode on sputtering.** E. BLECHSCHMIDT and A. VON HIPPEL (Ann. Physik, 1928, [iv], 86, 1006—1024; cf. A., 1926, 1013; 1927, 118).—The simple theory to explain cathodic sputtering put forward in previous papers is extended, and the influence of surface layers of adsorbed gas on the cathode is discussed. A new and better method is described by means of which the extent of sputtering of pure metallic surfaces can be measured. Experiments carried out with cadmium, antimony, bismuth, lead, zinc, silver, copper, magnesium, and aluminium gave results in agreement with theory.  
A. J. MEE.

**Single scattering of hydrogen nuclei at solid bodies.** C. GERTHSEN (Ann. Physik, 1928, [iv], 86, 1025—1036; cf. this vol., 683).—Experiments were made to test the accuracy of Rutherford's

scattering formula when applied to the single scattering of hydrogen nuclei by solid bodies. In order to overcome the difficulty, hitherto experienced, of measuring the scattering at large angles of scattering, a Geiger counter was employed. By this means it was found possible to determine the number of particles scattered through an angle range of 20—135°. Within this range the number of hydrogen particles scattered is inversely proportional to the fourth power of the sine of half the angle of scattering, *i.e.*, Rutherford's formula holds. The effect of recoil of the atomic nuclei on the observed angular distribution is investigated and the ratio of scattered to incident particles is calculated. A. J. MEE.

**At. wt. of caesium.** T. W. RICHARDS and M. FRANÇON (*J. Amer. Chem. Soc.*, 1928, **50**, 2162—2166).—Analysis of caesium chloride confirms the accepted at. wt. of caesium, *viz.*, 132.81 ( $Ag=107.880$ ). This corresponds with a "packing fraction" of  $-14 \times 10^{-4}$ , greater than would be inferred from Aston's curve (*A.*, 1927, 914), indicating that caesium may be a mixture of isotopes. S. K. TWEEDY.

**Constitution of zinc.** F. W. ASTON (*Nature*, 1928, **122**, 345).—The mass spectra of zinc indicate that the following isotopes (in lettered order of intensity) are present: 64 (*a*), 65 (*e*), 66 (*b*), 67 (*d*), 68 (*c*), 69 (*g*), 70 (*f*). A. A. ELDRIDGE.

**Electron counter for the measurement of very weak activities.** H. GEIGER and W. MÜLLER (*Naturwiss.*, 1928, **16**, 617—618).—A very sensitive electron counter is described which will measure activities of the order of the  $\beta$ - and  $\gamma$ -radiations of potassium. A. J. MEE.

**Condensation of water vapour on charged atoms of actinium-A.** M. AKIYAMA (*Compt. rend.*, 1928, **187**, 341—342).—The origins of the paths of the  $\alpha$ -particles emitted by the atoms of actinon and actinium-A demonstrated by Wilson's method are often different. Since the calculated value of the ratio of the number of charged atoms removed in a given period, measured from the moment of their production, to the total number of charged atoms of actinium-A is always twice the experimental value, it seems that about 50% of the charged recoil atoms are not utilised as nuclei for condensation. The number and lives of the displaced atoms of actinium-A are in approximate agreement with radioactive data. The charged recoil atoms probably require a higher degree of saturation than the positive ions. J. GRANT.

**Purely electronic amplification method for counting corpuscular rays.** E. RAMELET (*Ann. Physik*, 1928, [iv], **86**, 871—913).—Greinacher's method for measuring ionising radiations such as  $\alpha$ - and  $\beta$ -particles (*A.*, 1926, 553) has been studied from the quantitative aspect, and details are given of an arrangement for securing accuracy. The variations in the ionising power of  $\alpha$ -particles have been studied using the following gases in the chamber: hydrogen, nitrogen, oxygen, air, hydrogen-nitrogen 1:1, carbon dioxide. The results are discussed in detail. R. A. MORTON.

**$\gamma$ -Ray spectrum of protoactinium and the energies of the  $\gamma$ -rays arising from  $\alpha$ - and  $\beta$ -ray**

**changes.** L. MEITNER (*Z. Physik*, 1928, **50**, 15—23).—By photographing the  $\beta$ -rays emitted by protoactinium in a magnetic field it has been shown that there are three  $\gamma$ -radiations of wave-length 130, 41.9, and  $38.2 \times 10^{-11}$  cm., respectively. It is pointed out that the shortest wave-length of the  $\gamma$ -rays associated with various  $\alpha$ -ray changes is of the same order in all cases so far investigated, but in the case of the  $\beta$ -ray changes variations are found of more than 1:50. Hence it is concluded that the disarrangement of the nucleus produced is of the same order for all  $\alpha$ -ray emissions but varies widely for different  $\beta$ -ray emissions. This is parallel to the relative energies of  $\alpha$ -rays and primary  $\beta$ -rays. For  $\alpha$ -ray changes in the same disintegration series, the energy associated with the  $\gamma$ -line of shortest wave-length is the greater the longer is the life period of the emitting element. The reverse is shown by  $\beta$ -ray changes. J. W. SMITH.

**Radon content of the atmosphere as measured during aeroplane ascents.** A. WIGAND and F. WENK (*Ann. Physik*, 1928, [iv], **86**, 657—686).—An apparatus for the condensation of radon at the temperature of liquid oxygen has been used during aeroplane flights for the determination of the radon content of the atmosphere at different heights. The results indicate a falling off to quite small values as the height increases. The reading obtained at a given height depends on the origin, previous history, and stratification of the air, but it seems clear that all the radon comes from the earth's surface and that the vertical distribution arises only from the normal processes of air motion. Data obtained in a tower 30 m. high show that the radon content of smoke-laden town air may be strikingly high. R. A. MORTON.

**Ionisation curve in pure hydrogen for the  $\alpha$ -rays of polonium.** F. JOLIOT and T. ONODA (*J. Phys. Radium*, 1928, [vi], **9**, 175—179).—The length of the path of  $\alpha$ -rays from polonium in pure hydrogen is  $17.30 \pm 0.03$  cm. at 15° and 760 mm. Hg. The ratio of the stopping power of hydrogen to that of air is 0.223. The length of path in air is found to be  $3.87 \pm 0.01$  cm. at 15° and 760 mm. Hg. W. E. DOWNEY.

**Recoil-diffusion and secondary emission of moderately rapid cathode rays from metals.** K. H. STEHBERGER (*Ann. Physik*, 1928, [iv], **86**, 825—863).—An improved experimental arrangement is described for determining the velocity distribution of electrons from a conductor bombarded with cathode particles at definite velocities. By extrapolation on the distribution curves a distinction can be made between recoil-diffusion (*R*) and secondary emission (*S*). The secondary velocity distribution for gold, lead, copper, and aluminium at different primary velocities ( $V_p$ ) between 2000 and 10,000 volts has been studied. The distribution range of secondary emission extends from 0 to 36 volts, and the results are not dependent on  $V_p$  or the radiator. The maximum velocity cannot be fixed exactly, but is certainly very small. Another arrangement permits the normal emission to be studied and here also velocities very much smaller than those of the impinging electrons are recorded. It is shown that the

recoil-diffusion can be measured in this way, and when determinations of the total effect are also made and taken in conjunction with the ratio  $S/R$ , it is concluded that over the  $V_p$  range used the incident secondary radiation arises entirely from recoiling primary electrons. It is also possible to evaluate the recoil-diffusion constant for gold and aluminium. Control experiments on gold leaf showing the variation in  $S/R$  with thickness confirm the views as to the origin of the secondary effect. The back-diffusion layer for sputtered platinum over the  $V_p$  range 4000—9000 volts is 80—120  $\mu$  thick. R. A. MORTON.

Hall-effect in the experiments of Corbino. W. W. SLEATOR (Physikal. Z., 1928, 29, 584—585; cf. *ibid.*, 1911, 12, 561).—Corbino's experimental results are theoretically examined in the light of Sommerfeld's electron theory of metallic conduction. W. E. DOWNEY.

Hall-effect in the experiments of Corbino. W. W. SLEATOR (Physikal. Z., 1928, 29, 628—629; cf. preceding abstract).—A theoretical investigation of the work of Corbino on the action on a disc carrying a current of a perpendicular magnetic field. It is shown that this arrangement with a circular plate gives the same value for the Hall constant as is obtained by the usual rectangular foil method. The question is attacked both by the classical method and by Fermi's statistics, and equations are derived which are in agreement with those of Sommerfeld (cf. this vol., 467). A. J. MEE.

Absorption in lead, secondary rays, and wave-length of penetrating radiation. L. MYSOVSKI and L. TUVIM (Z. Physik, 1928, 50, 273—292).—The absorption of penetrating radiation by lead has been investigated in a similar manner to the absorption by water (A., 1926, 221). The absorption coefficient obtained agrees with the value calculated from the water experiments. For the investigation of the upper part of the absorption curve, the electro-scope was placed in the centre of a large block of ice, the lead absorbing sheets being placed either within or outside the ice. Some secondary radiation is produced under these conditions, and the photo-electric effect resulting from their absorption in the lead is of importance. It is pointed out that this method of determining the wave-length of penetrating radiation is qualified by the assumption that the absorption coefficient is equal to the scattering coefficient. J. W. SMITH.

Negatively modified scattering. M. N. SAHA, D. S. KOTHARI, and G. R. TOSHNIWAL (Nature, 1928, 122, 398).—A discussion of the bearing of the theory of modified scattering on the phenomena of resonance spectra of the vapours of sodium, potassium, and the halogens. A. A. ELDRIDGE.

Scattering of light by free electrons according to Dirac's new relativistic dynamics. O. KLEIN and Y. NISHINA (Nature, 1928, 122, 398—399).

Atomic synthesis occurring during atomic scattering and the theory of the building up of atoms from hydrogen and helium. W. D. HARKINS and H. A. SHADDUCK (Z. Physik, 1928, 50, 97—122).—See A., 1927, 183. J. W. SMITH.

Deductions from the atomistic constitution of light energy. J. STARK (Ann. Physik, 1928, [iv], 86, 1037—1040).—The theory is applied to the time of emission of light and to the emission of light from a moving atom. A. J. MEE.

Application of the Pauli-Fermi electronic gas theory to the problem of cohesive force. J. FRENKEL (Z. Physik, 1928, 50, 234—248).—Mathematical. The kinetic repulsive force between atoms is calculated from the point of view of relativistic mechanics, and the condition of equilibrium deduced. The Thomas-Fermi atom model, the structure of atomic nuclei, and the structure of the very dense stars are also discussed from the point of view of this theory. J. W. SMITH.

General relativity quantum theory of the electron. H. TETRODE (Z. Physik, 1928, 50, 336—346; cf. this vol., 933).—Dirac's theory is extended from the point of view of the general theory of relativity. A direct derivation of the impulse-energy principle is obtained. W. E. DOWNEY.

Transmutation of an element by cathode rays. A. KOENIG and F. VON KÖRÖSY (Z. Elektrochem., 1928, 34, 305—311).—An amplification of a previous paper (this vol., 216). L. F. GILBERT.

Absorption spectra of sulphonefluorescein and some derivatives. R. C. GIBBS and C. V. SHAPIRO.—See this vol., 1019.

Valency. IX. Molecular structure of thallium salts. (a) Thallium tri-iodide; (b) alkyl derivatives. A. J. BERRY and T. M. LOWRY [with (Mrs.) R. R. GOLDSTEIN and F. L. GILBERT] (J.C.S., 1928, 1748—1768).—The evidence for regarding thallium tri-iodide as thallic iodide or thallos polyiodide is conflicting. Solutions in methyl alcohol or acetonitrile form additive compounds with pyridine and chloropyridines, and complex ions with potassium iodide, and exhibit the general reactions of a thallic salt, but the reactions of thallos ions could not be detected with certainty. The following compounds are described:  $(C_5H_5N)_2HTlI_4$ , dark red crystals from acetone;  $(C_5H_5N)_2TlI_3$ , orange, soluble in many organic solvents;  $TlI_3(C_5H_5NCl_2)_5$ , golden-yellow crystals;  $TlI_3(C_5H_5NCl_3)_5$ .

Investigation of absorption spectra obtained with solutions in methyl alcohol shows that thallium tri-iodide alone and with iodine, the complex compound,  $KTlI_4$ , and also the above-mentioned compounds with pyridine or chloropyridines, all exhibit two absorption bands near 4000 and 2550—2600 Å.,  $\log \epsilon$  being of the order 4. The fact that the two maxima are about 1400 units apart whereas the maxima given by  $KI_3$  and by  $C_6H_5Br \cdot NMe_3 \cdot I_3$  are separated only by 650 and 720 units, respectively, indicates that the iodine atoms in thallium tri-iodide are not present as a tri-iodide ion, but are joined, at least in part, by covalent linkings directly to the metal. The view that the compound is a simple aggregate of trivalent thallium and univalent iodine atoms is ruled out because these ions do not give rise to absorption bands.

The molecular conductivities of the thallium trihalides in methyl alcohol and in acetonitrile are

less than those of potassium iodide; the salts therefore behave only as binary electrolytes, in which some of the halogen is linked to the metal, even in the most dilute alcoholic solutions.

Dimethylthallonium iodide is hydrolysed in dilute aqueous solutions and is derived from a base which is much weaker than thallos hydroxide. The molecular conductivity of thallic bromide is less than that of a binary electrolyte except in dilute aqueous solutions, where it is hydrolysed progressively. Absorption spectra indicate that the tribromide is not a mere aggregate of thallium and halogen ions, nor can the bromine be present as a perbromide ion.

The hypothesis that thallium is related to mercury as nitrogen is to carbon is used as a basis for explaining peculiarities in the properties of thallium.

R. A. MORTON.

**Ultra-violet emanations of some organic phosphatides after irradiation.** C. SERONO and A. CRUTO (*Gazzetta*, 1928, 58, 402—404).—Organic phosphatides present in impure cholesterol, after ultra-violet irradiation, possess the property of affecting a photographic film. It is shown that this is due to the re-emission of ultra-violet light by the phosphatides. Similar results are obtained with pure cerebrin and with chlorophyll, but not with pure cholesterol.

F. G. TRYHORN.

**Absorption spectrum of iodine in ethyl alcohol.** A. BATLEY (*Trans. Faraday Soc.*, 1928, 24, 438—452).—The maxima at 360 and 290  $\mu\mu$  recorded by previous workers in the ultra-violet absorption spectrum of alcoholic solutions of iodine have been proved to be due to the formation of hydrogen tri-iodide. Precise measurements of the true absorption curve between 250  $\mu\mu$  and 720  $\mu\mu$  have been made in the presence of ozone, which decomposes the iodides of hydrogen as they are formed. The true curve shows one maximum only, of wave-length 477  $\mu\mu$  ( $\epsilon_{max.} = 9.45 \times 10^5$ ), with general absorption in the far ultra-violet region. The hydrogen tri-iodide was isolated as a brown film by allowing an alcoholic solution of iodine to evaporate on a gelatin film and brushing off the layer of iodine crystals. The absorption of this film showed no traces of the characteristic iodine maximum in the neighbourhood of 444  $\mu\mu$ , but gave a definite maximum at 368  $\mu\mu$  of the nature expected from the examination of the iodine solution. The mechanism of the formation of the hydrogen tri-iodide was studied spectrophotometrically, and was shown to be represented by the equations  $\text{EtOH} + \text{I}_2 = \text{Me}\cdot\text{CHO} + 2\text{HI}$ ;  $\text{I}_2 + \text{HI} \rightleftharpoons \text{HI}_3$ . The former reaction is slow and photochemical, the latter practically instantaneous and thermal. In general, there are in solutions of iodine in alcohol opposing reactions, viz., the photochemical one given above and the photochemical oxidation of hydrogen iodides by dissolved oxygen. The factors influencing the velocities of these reactions were considered, including the purity of the solvent, the light source used, and the concentration of the iodine.

F. G. TRYHORN.

**Absorption of ultra-violet light by organic compounds. IX.** L. KWIECINSKI and L. MARCHLEWSKI (*Bull. Soc. chim.*, 1928, [iv], 43, 725—743).—

See this vol., 346. Like dextrose and lactose, *d*-galactose shows no selective absorption.

**Infra-red adsorption by the S-H linking.** J. W. ELLIS (*J. Amer. Chem. Soc.*, 1928, 50, 2113—2118).—The absorption spectra between 0.59  $\mu$  and 2.80  $\mu$  are investigated for ethyl, *n*-propyl, *n*-butyl, isoamyl, phenyl, and benzyl mercaptans and the corresponding sulphides. The main bands which occur in the two series are also found in the spectra of the corresponding primary, secondary, and tertiary amines (cf. this vol., 458). The spectrum of a mercaptan differs from that of the corresponding sulphide by a single band at 1.99—2.00  $\mu$ , which may be regarded as the first harmonic of the band at 3.8—3.9  $\mu$ . Both these bands probably originate with the sulphur-hydrogen linking. The spectrum of isoamyl disulphide reveals no characteristics not shown by the monosulphide. Solid and liquid benzyl sulphide show identical absorption bands, indicating that the energy associated with the carbon-hydrogen linking probably remains unchanged during crystallisation. A small systematic error may be present in Bell's work (A., 1927, 1052).

S. K. TWEEDY.

**Structure and stages of excitation of the molecules of some nitriles, determined from the ultra-violet absorption spectra of the vapours.** (FRL.) H. E. ACLY (*Z. physikal. Chem.*, 1928, 135, 251—290).—The absorption spectra of benzonitrile and *o*-, *m*-, and *p*-toluonitriles have been studied for the vapours, and the data interpreted according to the methods of Henri. In each case the absorption is of two kinds, a banded structure and a region of continuous absorption. Equations are given which cover the data with considerable accuracy and show the occurrence of doublet series throughout. Comparison of these with earlier analyses of the spectra of benzene and benzene derivatives discloses the dominance of the benzene ring, a conclusion which is confirmed by the investigation of the absorption spectrum of cyanogen. The latter is a vibration-rotation spectrum situated in the far ultra-violet, and the oscillation periods are different from those of the nitriles and from the bands shown in the emission spectrum of nitrogen and the carbon arc.

From the data on nitriles it is shown that the molecules exhibit high deformability; indeed the distances between oscillating atoms are increased by about 3% on excitation. The moment of inertia of benzonitrile is approximately  $J = 38.8 \times 10^{-40}$  from the structure of the bands. The predissociation phenomena (Henri) occur with the toluonitriles after the first excitation and with benzonitrile after the second. Two electron states of activation have been ascertained for each of the substances studied, one deduced from the banded spectrum and the other from the continuous absorption. Numerical values for the different states are calculated.

R. A. MORTON.

**Optical examination of perylene and its derivatives. I. Visible absorption spectrum of some simple derivatives.** A. DADIEU (*Z. physikal. Chem.*, 1928, 135, 347—361).—The influence of the groups Cl, Br, Ac, CO<sub>2</sub>Et, Bz, CO·C<sub>6</sub>H<sub>4</sub>Cl on the absorption spectrum, in the visible region, of perylene has been studied. Three effects were observed:

movement of the bands towards the red, broadening of the bands, and lowering of the intensity of the bands. A proportionality was observed between the broadening of the bands and the number of electrons in the outer sheath of the substituent. The lowering of intensity runs parallel with the broadening of the bands.

W. E. DOWNEY.

**Anti-Stokes radiation of fluorescent liquids.** R. W. WOOD (Phil. Mag., 1928, [vii], 6, 310—312).—It is suggested that for the phenomenon of anti-Stokes radiation the absorbing molecule may be in states of vibration and rotation higher than the zero state and after excitation may revert to the zero state, when the excess energy requisite for the anti-Stokes term or terms was stored in the molecule before it absorbed the exciting radiation. Alternatively, when the molecule is in the excited state, it may, by collision with another molecule, be carried to a higher vibrational and rotational state and thus on reversion to the lower initial state release more energy than it absorbed. Both processes should be enhanced by rise of temperature. It is found that some solutions of dyes are non-fluorescent at 100° but fluoresce strongly at the ordinary temperature, and at the same time the absorption band increases in wave-length with rise of temperature. In this case it is suggested that at the higher temperature the molecules were in a partly excited state and that consequently less energy from the radiation of longer wave-length would be necessary to carry them to a definite upper level.

A. E. MITCHELL.

**Band system in the spectrum of iodine vapour.** P. PRINGSHEIM and B. ROSEN (Z. Physik, 1928, 50, 1—14).—A new series of bands which occurs only at temperatures above 500° has been discovered in the absorption spectrum of iodine vapour. Their fine structure has been investigated and the arrangement of the band heads deduced. A number of new bands were also found in the infra-red region at high temperatures. All the known data concerning the iodine spectrum are discussed with reference to the various electronic excitation terms of the iodine molecule.

J. W. SMITH.

**Extinction of photoluminescence in uranyl salt solutions.** S. J. VAVILOV (Z. Physik, 1928, 50, 52—57).—Mathematical. Employing an approximate method of calculation and the equation derived by Leontovitsch (cf. following abstract), an expression is deduced for the mean time between the activation of a uranyl salt molecule and its collision with another solute molecule. The calculated values, however, are about fifty times as great as those found experimentally (Vavilov and Levschin, this vol., 814). This discrepancy is attributed to either the solvation of the molecule or the possibility that every collision may not cause extinction.

J. W. SMITH.

**Theory of extinguishing collisions between dissolved molecules in viscous liquids.** M. LEONTOVITSCH (Z. Physik, 1928, 50, 58—63).—Mathematical. An expression is developed for the mean time between the activation and first collision of an active molecule with another molecule. This is equally applicable to liquids or gases.

J. W. SMITH.

**Change of colour of crystals at low temperature.** I. OBREIMOW and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 353—356).—A preliminary investigation of the absorption spectra of crystals of potassium dichromate, iodine, and azobenzene in sheets 0.1—0.2 mm. thick at the temperature of liquid hydrogen is described. At the ordinary temperature potassium dichromate exhibits general absorption from 5500 Å. to the extreme ultra-violet, but at 20° Abs. it is pleochroic and the absorption band is split up into sharp lines. Thin plates of iodine which are opaque down to the temperature of liquid air transmit red light (>6700 Å.) at 20° Abs. and exhibit weak periodical bands. Azobenzene is pleochroic, transmitting orange light parallel to the *b* axis of the crystal and lemon-yellow at right angles to this. At -180° the colours change respectively to lemon-yellow and pale green. Spectroscopical examination of the former component shows general absorption at the ordinary temperature which breaks up at -196° into a series of narrow but still diffuse bands. At 20° Abs. a sharp absorption line spectrum appears in which a certain periodicity has been traced. Change of colour with lowering of temperature therefore depends on the narrowing of the absorption bands.

J. W. BAKER.

**Principal vibration quanta of alkali halide vapours.** K. SOMMERMEYER (Naturwiss., 1928, 16, 653—654).—Absorption experiments with alkali halide vapours yield continuous spectra only. Using an excitation method, certain bands can be observed. Their separation is less at the longer wave-lengths, whilst in the ultra-violet they become progressively feebler and finally disappear. They correspond with the vibration quantum of the normal state of the molecule, which would be strongly excited at the high temperature of the experiment (750—1100°). By measuring the greatest separation, which occurs in the farthest ultra-violet, the value of the quantum number can be obtained, and agrees well with that calculated by Born and Heisenberg. In the case of caesium iodide, higher quantum numbers of the normal state can be calculated, again with good agreement. Since, at least with small dispersion, only the structure corresponding with the principal quantum number appears, the indication is that all electron switches take place between states of equal excitation. This can be explained on the assumption that the combination is very weak. A fine structure of the bands is visible only with very high dispersion. From the position of the band of shortest wave-length the dissociation energy of the normal atom can be calculated, with certain reservations. The values so derived show fair agreement with those obtained by chemical methods.

A. J. MEE.

**Theory of the Raman effect.** M. BORN (Naturwiss., 1928, 16, 673).—Raman's discovery is not incompatible with quantum mechanics.

R. A. MORTON.

**Ultra-violet, visible, and infra-red reflectivities of snow, sand, and other substances.** E. O. HULBERT (J. Opt. Soc. Amer., 1928, 17, 23—25).—The diffuse reflectivities in the region 0.3—7 μ have been measured for snow, sand, crushed quartz,



plaster of Paris, white paper, white cotton cloth, sodium carbonate, and sodium chloride, using a small quartz-mercury lamp, a thermocouple, and absorbing screens for separating out various spectral regions. The ultra-violet reflectivity of snow is relatively high, being two to four times that of sand. This gives a physical basis for the current idea that ultra-violet glare is an important factor in snow-blindness.

L. L. BIRCUMSHAW.

**Temperature of the under-water spark as computed from distribution of intensity in OH absorption bands.** E. D. WILSON (*J. Opt. Soc. Amer.*, 1928, 17, 37—46).—Measurements of the wave-lengths of the OH bands absorbed in the under-water spark show that the bands at  $\lambda$  2811, 2875, 3064, and 3126 are developed nearly as completely as in emission. Measurement of intensity in branches of the bands at  $\lambda$  3064 gives a maximum at about  $m = 10.2$ , and from this the effective temperature of the under-water spark has been calculated. From Birge's formula this is found to be  $5115^\circ$  under the conditions of the experiment. Details are given of the experimental methods: the electrical circuits employed, the spectrographic and photometric procedure, and the measurement of the wave-lengths.

L. L. BIRCUMSHAW.

**Penetration of ultra-violet light into pure water and sea-water.** E. O. HULBERT (*J. Opt. Soc. Amer.*, 1928, 17, 15—25).—An apparatus consisting of a quartz spectrograph, a sodium hydride quartz photo-electric cell, and a quadrant electrometer is described. With this arrangement measurements have been made of the molecular absorption coefficient of sea-water and aqueous solutions of the principal salts in the sea. The coefficient  $A$  is defined by  $(\alpha - \alpha_0)/C$ , where  $\alpha$  is the absorption coefficient of the solution,  $\alpha_0$  that of the pure solvent (water), and  $c$  is the concentration in g.-mol. per litre of solution. Measurements were made in the region  $\lambda$  4000—2500, and the salts investigated were potassium chloride, sodium chloride, magnesium chloride, magnesium sulphate, and calcium sulphate. It was found that the transparency decreases rapidly with decreasing wave-length in the ultra-violet and becomes quite small below  $\lambda$  3000; that from  $\lambda$  3400 to 3000 calcium sulphate contributes about one half to the absorption of sea-water, water about one quarter, and the other salts the rest. From  $\lambda$  3000 to 2500 magnesium chloride, calcium sulphate, and water each contribute roughly one third, the other salts giving but little absorption. A close analogy is traced between the decrease of the transparency of the sea with decreasing wave-length in the ultra-violet and the spectral energy curve of sunlight. A possible function of the part played by the actinic effects of sunlight on the concentration of the sea and the air is suggested by these facts.

L. L. BIRCUMSHAW.

**Limits of ultra-violet transmission of certain inorganic compounds.** M. KIMURA and M. TAKEWAKI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, 9, 57—64).—The spectrum of the light transmitted by a 0.5 mm. layer of finely-powdered crystals has been photographed for a large number of inorganic compounds. Colourless compounds of alkali and

alkaline-earth metals are more transparent to ultra-violet light than the compounds of other metals. For halides, the limits of transparency are displaced towards the red in the order chlorides, bromides, iodides; e.g., cadmium chloride, bromide, and iodide cease to transmit at 240, 300, and  $385 \mu\mu$ , respectively. Colourless chlorides usually transmit well into the ultra-violet, as do some sulphates and phosphates. All nitrates absorb beyond  $320 \mu\mu$  owing to the selective absorption of the nitrate ion. The only oxides (among the large number tested) which transmitted ultra-violet light at all well were those of magnesium, calcium, and aluminium. All the sulphides studied absorbed strongly. Considering the chlorides, the ultra-violet limits of transparency are shifted towards the red as the at. wt. of the metal increases in the series lithium, sodium, potassium; magnesium, zinc, cadmium; tin, lead; but the reverse is true for the series calcium, strontium, barium. R. A. MORTON.

**Infra-red region of the spectrum. I. Prism spectrometer and apparatus. II. Calibration of prism spectrometer; general procedure; preparation of pure ammonia, phosphine, and arsine. III. Infra-red absorption spectra of ammonia, phosphine, and arsine. IV. Discussion of absorption bands of ammonia, phosphine, and arsine.** (SIR) R. ROBERTSON and J. J. FOX (*Proc. Roy. Soc.*, 1928, A, 120, 128—148, 149—160, 161—189, 189—210).—I. A very detailed account is given of the apparatus adopted for the investigation of the infra-red absorption by ammonia, phosphine, and arsine. Attention is directed to the necessity for keeping the source of energy constant, for calibrating the mechanism for reading wave-lengths, for shielding the thermopile from variations in air pressure, for keeping a close watch on the temperature of the prism, especially when made of rock-salt, on account of the high temperature coefficient of its refractive index, for accurate alinement of the observation tubes containing the gas, and for obtaining a galvanometer of great sensitiveness and freedom from external perturbations. The work was carried out as near  $18^\circ$  as possible. A current of 1 amp. and 110 volts from a battery of accumulators was supplied to a Nernst filament, backed by a concave mirror and enclosed in an asbestos housing. The radiation passed through a rock-salt lens of 21 cm. focus and 0.5 cm. aperture and thence through an observation tube, two being used (one empty, one containing gas) mounted on a rocking arrangement for throwing them alternately into the optical path. Two lengths of observation tube were used, according as strong or faint bands were being explored; the shorter tubes were of Pyrex glass, 50 mm. in diameter and 100 mm. long, and the longer tubes of soda glass, 50 mm. in diameter and 450 mm. long. After leaving the observation tube the beam was focussed on the collimator slit of the infra-red spectrometer, furnished with either a  $60^\circ$  rock-salt prism, a quartz or a fluorite prism, and having a Wadsworth mirror for securing minimum deviation. On emerging from the second slit of the spectrometer the radiation was received by a 20-junction bismuth-silver thermopile housed in an air-tight holder, whilst the current

generated here was carried by glass-encased leads to a Downing galvanometer of the Paschen type. A mercury lamp was used for calibration of the instrument as set up. Directions are given for correcting the observation tubes and for the transference of gas from the holders to the observation tubes.

II. [With E. S. HISCOCKS.]—Details are given for the calibration of the wave-length drum in terms of the angle of rotation of the prism table, for prisms of rock-salt, quartz, and fluorite. Paschen's values for the refractive indices were used, corrected to 18° (in the case of rock-salt and fluorite) by means of Liebreich's temperature coefficient determinations (Verh. Phys. Ges., 1911, 13, 1). The general procedure used in the setting up of the apparatus and the method of conducting an experiment are described, and details are given for the preparation of pure ammonia (from synthetic ammonium chloride and 50% potassium hydroxide solution), phosphine (from phosphonium iodide and 50% potassium hydroxide solution), and arsine (from zinc-arsenic alloy and 30% sulphuric acid).

III. A general description is given of the absorption bands found in the three gases, together with curves showing their occurrence in the region 1—17  $\mu$ , and evaluations of the maxima of the absorption bands. The quality of resolution was as follows: Bands were unresolved below 2.2  $\mu$  (quartz prism); bands were partly resolved from 2.2  $\mu$  (quartz), from 4  $\mu$  (fluorite), and from 5  $\mu$  (rock-salt); and bands were resolved to show fine structure from 3  $\mu$  (quartz), from 6  $\mu$  (fluorite), and from 8  $\mu$  (rock-salt). Unresolved bands show one peak, the centre near the top being taken as the position of the oscillation band; partly resolved bands show three peaks, the centre one being taken for calculation of the oscillation frequency; whilst for resolved bands, the positions of the maxima of rotation imposed on the oscillation band are recorded. All the readings have been converted into wave-numbers per cm. for purposes of calculation and comparison, and the figures are given to show percentage absorption/wave number. Graphs of the absorption bands found in the three gases are set out to show a general comparison. Whilst ammonia exhibits a more complicated spectrum, all three gases have in common a main sequence of harmonic bands (I, II, . . .); ammonia has a second sequence (C, D, . . .), not represented in phosphine or arsine, also a faint sequence (a, b, . . .) of which the farthest band measured is a member, and a band at 4.05  $\mu$  and a well-defined and resolved band at 10.55  $\mu$ ; phosphine and arsine have also a second sequence (A', B' . . ., and A'', B'' . . .) and a sequence ( $\alpha$ ,  $\beta$ , . . .) not represented in ammonia. The bands I—VI form a nearly harmonic sequence, and are all of the same type, characterised by an intense zero branch with less intense side branches. Fine structure has been found superimposed on this general contour in bands I and II of ammonia, and in band I of phosphine and arsine. The ammonia band at 10.55  $\mu$  has been resolved and has the unique feature of having two Q branches close to one another. Tables are given showing data for the oscillation bands of the three gases, the structure of bands I, II, and 10.55  $\mu$  of ammonia, the intermediate region between bands I and 10.55  $\mu$

of ammonia, the structure of bands I, II, and  $\alpha$  of phosphine, the structure of bands I and  $\alpha$  of arsine, the effect of pressure (varying from 1 to 1/16 or 1/32 atm.) on the maxima of the absorption bands, and the effect of pressure on the area under the absorption bands. The values for ammonia are in good agreement with those of Schierkolk from the visible to 14  $\mu$  (cf. A., 1925, ii, 180), and the data obtained by Spence for the ammonia band at 3  $\mu$  have also been confirmed (cf. *ibid.*, 350).

IV. The types of absorption bands in the near infra-red which are partly or completely resolved are described. It is found that there are nearly constant ratios between the vibration numbers of the members of the main sequence common to the three gases, and that the second sequence found in phosphine and arsine has a ratio similar to that in the main series. There are thus certain degrees of freedom common to these gases. Tables are given showing the harmonic relations of the oscillation bands in the three gases, and it is seen that, whilst the bands of the main sequences are approximately multiples of the fundamental, in none of the gases does Kratzer's relation hold (Z. Physik, 1920, 3, 289). In all cases the value for the fundamental is low when compared with the values for the other bands divided by their ordinal number. The structure of the rotation-oscillation bands is discussed. Consideration of the effect of pressure on the intensity of the bands shows that, whilst no generalisation can be made on the intensities of the central frequencies, in the resolved bands, Beer's law holds at the lower pressures for the bands of fine structure. This is shown well for the bands of the fine structure of ammonia band I and band 10.55  $\mu$ . The results obtained on evaluating the area under the contour of the same bands are in close agreement with those obtained from a consideration of the central frequencies alone. The moments of inertia of the molecules of the gases, calculated from the average spacing differences determined from the fine structure of bands I, II, and 10.55  $\mu$  (ammonia), I and  $\alpha$  (phosphine), and I and  $\alpha$  (arsine) are found to be  $2.78 \times 10^{-40}$ ,  $4.78 \times 10^{-40}$ , and  $5.53$  or  $6.51 \times 10^{-40}$  g. cm.<sup>2</sup>, respectively, for ammonia, phosphine, and arsine. The values are compared with those derived from the energy relation for three degrees of freedom. Evidence in favour of the tetrahedral model for the molecules of the gases is discussed. The existence of oscillation bands of various frequencies in the infra-red spectrum of ammonia shows that the ions are separating, and one of the modes of vibration may be considered to be the oscillation of nitrogen against the plane of the hydrogen atoms. In such a case, Hund's condition (Z. Physik, 1925, 31, 99) is fulfilled, and a tetrahedral structure is required for the model. The large temperature effect on the dielectric constant of gaseous ammonia, together with its high electric moment (cf. Watson, this vol., 107), is in favour of this view. The considerations leading to a tetrahedral structure for ammonia apply likewise to phosphine and arsine.

L. L. BIRCUMSHAW.

Short-wave infra-red absorption of artificial and natural sylvite. C. SCHAEFER and C. BORMUTH

(Z. Physik, 1928, 50, 363—365).—Artificial sylvite does not exhibit the infra-red absorption bands given by natural sylvite (cf. Coblenz, Bull. Bur. Standards, 1912, 7, 653). It is probable that the bands are due to traces of ammonium chloride.

W. E. DOWNEY.

**Band spectrum of water vapour. III.** D. JACK (Proc. Roy. Soc., 1928, A, 120, 222—233; cf. A., 1927, 808; this vol., 571).—The structure of the bands in the spectrum of water vapour has been investigated, using the new notation proposed by Mulliken (cf. this vol., 105). The connexion between the old and new notation is shown by means of a table. The water-vapour bands can be interpreted as arising from transitions between  ${}^2S$  and  ${}^2P$  levels. The  ${}^2P$  levels are subject to  $\sigma$ -type doubling (A, B), whilst the  ${}^2S$  levels are probably rotationally single. For the P and R branches the transitions are between 1A and 1B, or 2A and 2B states, whilst the Q branches show "crossing over," 1A to 1A, and 2A to 2A. The  $\sigma$ -type doubling and crossing over are capable of accounting for the failure of the combination principle,  $R(j-1)-Q(j)=Q(\gamma-1)-P(\gamma)$ , when applied to the main branches. The P, R, and Q satellites are considered; in some of the Q satellites the transitions violate the  $\sigma$ -selection rule in that they arise from transitions from A to B states whilst at the same time  $\Delta j_k = \sigma$ . The most remarkable feature shown by these bands is the presence of a singlet series for which the combination principle definitely indicates a transition of two units in  $\gamma_k$ . It is concluded that the only selection rule which holds rigidly is  $\Delta j = \pm 1, 0$ . The most probable transition of any momentum component is  $\pm 1$  or 0, but this rule cannot be taken as final.

L. L. BIRCHMESHAW.

**Quartz rod or sphere for condenser in spectroscopy.** H. NAGOAKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8 [Suppl.], 1—3).—The different methods of using quartz rods or spheres as condensing lenses in spectroscopy, especially for investigations in the ultra-violet region, and their respective advantages for this purpose are discussed.

J. W. SMITH.

**Absorption of light by iron pentacarbonyl.** J. DRECHSLER (Z. Elektrochem., 1928, 34, 320—323).—The absorption of visible light by iron pentacarbonyl in various solvents follows Beer's law at all concentrations between 99 and 0.5%, and is independent of the solvents employed (acetone, chloroform, carbon tetrachloride, benzene, toluene, *o*- and *m*-xylene). Qualitative experiments show, however, that the rate of decomposition of the carbonyl is influenced by the solvent. No connexion could be observed between the dielectric constant of the solvent and the rate of decomposition.

L. F. GILBERT.

**Band spectrum of mercury hydride.** E. HULTHÉN (Z. Physik, 1928, 50, 319—335; cf. A., 1925, ii, 470).—The band spectrum of mercury hydride has been studied in detail using an intense source of light and higher dispersion than in the previous work. New bands have been discovered and the  ${}^2P-{}^2S$  system has been completed. In the region 3100—2900 Å. some bands, degraded towards the red, were observed and classified in a  ${}^2S-{}^2S$  system. An isolated feeble band at 2700 Å. probably arises from

a more strongly excited  ${}^2S-{}^2S$  system. The theoretical bearings of the results are discussed. The energy of dissociation, calculated from the rotational terms, is found to be 0.369 volt.

W. E. DOWNEY.

**Light emitted by the recombination of halogens.** V. KONDRATĚEV and A. LEIPUNSKI (Z. Physik, 1928, 50, 366—371).—The light emitted by halogens heated at 1000—1100° has been spectroscopically examined. The spectrum coincides with the absorption spectrum of the halogen in question. The emission is explained as due to a reversed photodissociation according to the equation  $X+X' = X_2+h\nu$ .

W. E. DOWNEY.

**New class of spectra due to secondary radiation.** I. C. V. RAMAN and K. S. KRISHNAN (Indian J. Physics, 1928, 2, 399—419).—When light from a quartz-mercury lamp is diffused within a liquid and the scattered light spectroscopically analysed, a large number of new lines are observed in the scattered spectrum which are not present in the incident spectrum. These spectra have been photographed in the cases of benzene, toluene, pentane, ether, methyl alcohol, and water; each liquid shows a distinctive scattered spectrum, but certain general similarities are shown by liquids having chemically similar groups in their composition. In the case of benzene it has been shown that corresponding with each unmodified line in the spectrum there are seven modified lines observable, two being especially prominent. The frequency differences between the unmodified and modified lines are independent of the wave-length of the incident line; six of the modified lines have frequencies lower than the exciting line, the other having a higher frequency, the increase in wave number in this case being numerically equal to the decrease in the case of one of the other six lines. The shift in frequency of the modified lines is found to agree with certain characteristic infra-red frequencies of the molecule. Hence the observations are explained by supposing the incident quantum to be absorbed in part and scattered in part by the molecule, the former portion causing a change in energy level. The modified line of higher frequency is supposed to be due to the radiation inducing a return from a higher energy state to the normal state. The comparative feebleness of this line is explained thermodynamically.

J. W. SMITH.

**Wave-length shifts in scattered light.** A. E. RUARK (Nature, 1928, 122, 312—313).

**[Lamp] to obtain the maximum short-wave ultra-violet radiation.** N. IAROTZKY (Compt. rend., 1928, 187, 459—461).—A mercury-vapour lamp working at 80,000 volts is described which gives the ray 253  $\mu$ , and may be brought close to the subject without the use of filters to absorb thermal radiations.

J. GRANT.

**NH-Band and the dissociation energy of nitrogen.** E. GAVIOLA (Nature, 1928, 122, 313—314).—An explanation for the appearance of the band at 3360—3670 Å., with intensity proportional to the square of that of the exciting light, is sought. It is assumed that the atomic nitrogen is formed by

three-body collisions of  $N_2$  molecules with two excited mercury atoms, and it appears probable that the dissociation energy of nitrogen is less than, or about, 9.8 volts. A. A. ELDRIDGE.

Measurement of ultra-violet quanta by fluorescence photometry. W. T. ANDERSON, jun., and L. F. BIRD (Physical Rev., 1928, [ii], 32, 293—297).—Equally accurate results are obtained by the use of photometric and thermopile methods. A. A. ELDRIDGE.

Wave-length shifts in scattered light. R. W. WOOD (Nature, 1928, 122, 349).

Approximation method and application to some HCl bands. D. G. BOURGIN (Physical Rev., 1928, [ii], 32, 237—249).—Theoretical. A. A. ELDRIDGE.

Quantum mechanics of the rotational distortion of multiplets in molecular spectra. E. HILL and J. H. VAN VLECK (Physical Rev., 1928, [ii], 32, 250—272).—A study of the effect of molecular rotation on spin multiplets, and the development of an elementary theory of  $\sigma$ -type doubling. The authors consider Hund's limiting cases (*a*) and (*b*), the general intermediate case, the doublet case, and simple special cases of the doublet intensity formulæ. A. A. ELDRIDGE.

Influence of deformation on the interior photo-electric effect for rock-salt. M. N. PODASCHESKY (Naturwiss., 1928, 16, 653).—Plastic deformation of rock-salt crystals exerts a noticeable effect on the primary photo-electric current. This falls rapidly at first, then more slowly, finally reaching a constant value. The photo-electric sensitivity may even be reduced to zero by this treatment, but may be restored by repeated exposure to X-rays. A. J. MEE.

Dipole moment of symmetrical compounds and *cis-trans*-isomerism at "single" linkings. R. ENGELAND (Physikal. Z., 1928, 29, 626; cf. Weissberger, this vol., 689).—The question of *cis-trans*-isomerism and its connexion with valency discussed by Weissberger has already been decided by Schlesinger through his experiments with the copper salts of certain bis- $\alpha$ -imino-acids (cf. A., 1925, i, 1249). Final proof is furnished by the fact that  $\alpha$ -aminoacetic acid, which itself forms no optical antipodes, forms two different copper salts, one of which corresponds in colour and in water content with the optically active and the other with the racemic form of the higher homologues. The copper salt corresponding with the optically active acids can be prepared only from glycine which has been made by the hydrolysis of albumin. A. J. MEE.

Dispersion of conductivity. H. SACK (Physikal. Z., 1928, 29, 627—628).—A method is described for the determination of the change of conductivity of a solution with the frequency of the current traversing it (cf. Debye and Falkenhagen, this vol., 596). The method depends on the fact that in a tuned circuit consisting of a self-inductance and a capacity with parallel resistance (in this case a condenser with a conducting liquid), any change in the resistance will produce a change in the current strength at resonance

which can be measured. The results obtained are of the order of magnitude required by the theory. A. J. MEE.

Dielectric constant of air at radio frequencies. A. B. BRYAN and I. C. SANDERS (Physical Rev., 1928, [ii], 32, 302—310).—The value obtained for  $\epsilon-1$  at *N.T.P.* is 0.0005893. A. A. ELDRIDGE.

Applicability of Fresnel's law in deducing evidence in favour of surface structure from surface reflectivity. S. S. BHATNAGAR, D. L. SHRIVASTAVA, and N. C. MITRA (J. Indian Chem. Soc., 1928, 5, 329—342).—Measurements have been made of the intensity of the reflected beam of unpolarised light, incident at various angles on to surfaces of a number of liquids, in order to ascertain whether deviations from Fresnel's law exist on account of molecular orientation in the surface. No such deviation has, however, been observed, although some evidence has been obtained of differences between the optical properties of polar and non-polar liquids. H. F. GILLBE.

Quantum theory of scattering and dispersion. A. SMEKAL (Naturwiss., 1928, 16, 612—613).—When radiation is scattered by atoms, the energy of an electron in the atom can be changed by an amount corresponding with the quantum switch. There should thus be a frequency change, the scattered radiation consisting of one of the primary frequency and others above and below it. The effect should be obtained with visible light. Raman has succeeded in observing the effect using light from a mercury-vapour lamp and passing it through various liquids, e.g., benzene. In benzene, the frequency differences are constant with varying primary frequency, and correspond with the switch producing an observed infra-red radiation. This can be described in terms of the analogy between quanta and electrons. The change of an energy level of an electron in the scattering atom can take place through collisions of the first or second kind with light quanta of any primary frequency, just as with electrons of any original velocity. A. J. MEE.

Theory of the Ramsauer effect. J. HOLTSMARK (Naturwiss., 1928, 16, 614—615).—Ehrenfest and Rutgers sought to identify the Ramsauer effect with the disappearance of zero-order optical diffraction. On this view the scattering would vanish for electrons other than those corresponding with long wave-lengths. The application is doubtful, because inside the atom the electron wave-length becomes greatly changed owing to the high refractive index; however long the wave-length is outside, it will be short inside the atom. Thus the wave-length for disappearance of scattering will depend on the atomic field. The Ramsauer effect is treated as the analogue of Rayleigh's diffraction theorem. In place of Fourier coefficients there are coefficients of the expanded characteristic function, account being taken of the change of wave-length in the atomic field. Thus, contrary to Wentzel's view, there is no need to treat the problem in three dimensions. The calculation of scattering for argon on this theory is in good agreement with experimental values; with neon, the agreement is not so good. A. J. MEE.

**New phenomenon in the scattering of light in crystals.** H. KORNFELD (Naturwiss., 1928, 16, 653).—The change of wave-length occurring on scattering which was determined quantitatively for quartz by Landsberg and Mandelstam (this vol., 936) has been found to occur with calcite. The measured change of wave-length corresponds with the excitation of an infra-red oscillation of the wave-length  $9.1 \mu$ . In this region there lies a series of combination oscillations of  $\text{CO}_3$  ions.

A. J. MEE.

**Polychroism and the orientation of the ions in the crystals of the rare earths.** R. BRUNETTI (Physikal. Z., 1928, 29, 571—575).—The polychroism of the crystalline salts of certain rare-earth metals can be correlated with an axis connected with the structure of the ions in relation to the axes of symmetry of the crystal.

W. E. DOWNEY.

**Rotatory dispersion of certain isomeric butyl esters of *l*-mandelic acid.** C. E. WOOD, A. E. CHRISMAN, and S. D. NICHOLAS (J.C.S., 1928, 2180—2190).—The rotatory dispersions of the isomeric butyl esters of *l*-mandelic acid have been measured at a large number of temperatures between  $0^\circ$  and  $100^\circ$ . Mandelic acid was resolved by a modification of McKensie's method (*ibid.*, 1899, 75, 966) and from the morphine *l*-mandelate, m. p.  $223\text{--}224^\circ$  (McKensie, *loc. cit.*, gives  $202^\circ$ ), *l*-mandelic acid, m. p.  $133.5^\circ$ , was obtained. From this its *n*-butyl, m. p.  $38.5^\circ$  (corr.),  $d_4^{20}$  1.0443,  $[\text{M}]_D^{20} -186.99^\circ$  (cf. Smiles and Walker, A., 1909, ii, 846), *isobutyl*, m. p.  $35.5^\circ$  (corr.),  $d_4^{20}$  1.0536,  $[\alpha]_D^{20} -102.65^\circ$  (cf. Walden, A., 1896, ii, 135), *tert*-butyl, m. p.  $65^\circ$ ,  $d_4^{20}$  1.0665,  $[\alpha]_D^{20} -82.70^\circ$ , and *d*-*sec*-butyl, b. p.  $88^\circ/0.05 \text{ mm.}$ ,  $d_4^{15}$  1.0623,  $[\alpha]_D^{20} -77.50^\circ$ , esters were prepared. All the esters exhibit complex and normal rotatory dispersion. The *isobutyl* ester shows an increase and the *tert*-butyl a decrease of negative rotation compared with the normal ester. Pronounced decrease in rotation occurs, especially in the violet end of the spectrum, when two asymmetric centres of opposite sign are present in the molecule, as in *d*-*sec*-butyl *l*-mandelate, but the effect is not sufficiently marked to cause visual anomaly, since the mandelic acid radical dominates the rotatory power. For visual anomaly the two asymmetric centres must be of comparable magnitude, as in *d*-*sec*-butyl *d*-lactate. The dispersion ratios of the *n*-, *iso*-, and *tert*-butyl esters are sensibly constant, but the curve for the tertiary ester tends to diverge from those of the *n*- and *iso*-esters, the divergence becoming more marked at the violet end of the spectrum. Rise of temperature causes a decrease in rotation in each case, the change being more pronounced in the blue region. For the longer wave-lengths the temperature-rotation curves are nearly linear, but as the wave-length decreases the curvature increases uniformly. Comparison of the rotation data of the three esters affords no generalisation for the determination of the relative configuration. Acylation of both ethyl and methyl mandelates causes a displacement of the rotations, without change of order, further into the negative region. The rotational displacements of the esters of *l*-mandelic, *l*-lactic, *d*-tartaric, *d*-malic, *d*- $\alpha$ -hydroxybutyric, *l*-glyceric acids, and certain of

their acetyl and benzoyl derivatives are discussed as a guide to configuration, but no general rule could be formulated.

J. W. BAKER.

**Optical anisotropy of atoms and molecules.** I. R. RAO (Indian J. Physics, 1928, 2, 435—465).—The fact that the distances between the optical centres of atoms in molecules calculated from scattering data show large discrepancies from the values obtained by X-ray measurements is held to indicate that the assumption of the isotropy of atoms is untenable. The depolarisation of light scattered by rare gases leads to the same conclusion. The values of the anisotropy of several ions are calculated in the various compounds of which the scattering data are accurately known. The results indicate that of all similar ions the rare-gas atoms exhibit the least anisotropy and that heavier atoms show less anisotropy than lighter ones. The anisotropy of an ion increases, but the ionic deformability diminishes, with increasing opposite charge on the adjacent ion. The deformability of the heavier elements changes less with increasing adjacent charge than that of lighter ones. The theoretical basis of atomic anisotropy is also discussed.

J. W. SMITH.

**Optically active copper compounds.** W. WAHL (Comm. Phys.-Math., 1927, IV, No. 14, 5 pp.; Chem. Zentr., 1928, i, 1377).—Diethylenediaminediaquocopper sulphate must possess an octahedral arrangement of the co-ordinatively linked groups, as well as two ring planes. By means of barium *d*-tartrate the salt was obtained in two optical antipodes. *l*-Diethylenediaminediaquocopper iodide is considered to have  $[\text{M}]_D -190^\circ$ . Diethylenediaminediaquonickel sulphate was also resolved.

A. A. ELDRIDGE.

**Quantum mechanics of homopolar valency.** F. LONDON (Z. Physik, 1928, 50, 24—51).—Mathematical (cf. Heitler and London, A., 1927, 923; London, this vol., 344).

J. W. SMITH.

**Is the molecule of gaseous hydrogen chloride polar or non-polar?** F. I. G. RAWLINS (Z. Physik, 1928, 50, 440—442).—Polemical against Kondratév (this vol., 688). It is insisted that gaseous hydrogen chloride has a polar molecule.

W. E. DOWNEY.

**Problem of Brownian molecular motion.** (ERL.) F. STADIE (Ann. Physik, 1928, [iv], 86, 751—797).—Mathematical.

R. A. MORTON.

**X-Rays do not always give the true structure of crystals.** C. MAUGUIN (Compt. rend., 1928, 187, 303—304; cf. Friedel, this vol., 817).—An attempt is made to show that for biotite and the chlorites the X-ray method does not always give the true crystal structure, and a scheme is outlined for the approximate determination of the extent to which it is masked.

J. GRANT.

**X-Ray analysis of Heusler's alloy.** E. PERSSON (Naturwiss., 1928, 16, 613).—Heusler's alloy (a copper-manganese-aluminium alloy) consists of three phases. It is the second, or  $\beta$ -phase, which has been reinvestigated. The fundamental lattice is body-centred cubic, and the aluminium atoms are situated in a face-centred cubic lattice with double the para-

meter of the fundamental lattice. The elementary cell contains 16 atoms, 12 of which are copper and manganese, and the remaining 4 aluminium. The formula  $(\text{Cu}, \text{Mn})_3\text{Al}$ , which had previously been supposed to represent the constitution of this solid solution, is confirmed. The magnetic properties of this alloy are due to the presence of this  $\beta$ -phase. It is possible, however, for an alloy of copper, manganese, and aluminium to consist almost entirely of this  $\beta$ -phase and yet be non-magnetic. The concentration of manganese influences the magnetic properties; it must reach a definite value for the alloy to be magnetic. The X-ray observations also show the presence of a fourth phase, but it is improbable that this can account for the magnetic properties of the alloy.

A. J. MEE.

X-Ray examination of liquids by the rotating-crystal method. D. COSTER and J. A. PRINS (J. Phys. Radium, 1928, [vi], 9, 153—155).—Apparatus is described whereby an X-ray tube and spectrograph can be rotated with respect to a horizontal liquid surface. Mercury has been examined with the apparatus and three bands have been obtained.

W. E. DOWNEY.

Physical purity and powder röntgenograms. N. H. KOLKMEIJER (Z. physikal. Chem., 1928, 136, 45—48).—See this vol., 692.

X-Ray spectrography of alloys. H. WEISS (Bull. Soc. chim., 1928, [iv], 43, 697—711).—A lecture.

X-Ray analysis of silver-aluminium alloys. A. F. WESTGREN and A. J. BRADLEY (Phil. Mag., 1928, [vii], 6, 280—288).—The existence, at the ordinary temperature, of two intermediate phases in the Ag-Al system, both formed through transformation in the solid state, has been shown by X-ray analysis, thus confirming the previous result of Petrenko (A., 1905, ii, 635). The  $\text{Ag}_3\text{Al}$  phase is shown to be cubic, the edge of the unit cell, containing 20 atoms, measuring 6.920 Å. The other intermediate phase, stable over the range 27—40 at.-% aluminium, is a solid solution of close-packed hexagonal structure. The lattice dimensions change continuously from  $a_1=2.865$  Å,  $a_3=4.653$  Å, and  $a_3/a_1=1.625$  when saturated with silver to  $a_1=2.879$  Å,  $a_3=4.573$  Å, and  $a_3/a_1=1.588$  when saturated with aluminium.

A. E. MITCHELL.

X-Ray investigation of the changes in the alloy CuAu. W. GORSKY (Z. Physik, 1928, 50, 64—81).—An alloy consisting of equal atomic proportions of copper and gold was heated to various known temperatures, quenched, and examined by Debye's X-ray method. Below 385°, the stable form is a tetragonal lattice, but with no systematic distribution of copper and gold atoms. The axis ratio  $a/c$  changes from 1.07 at 380° to 1.08 at 300°, and  $\sqrt[3]{a^2c}=3.860$  Å. The transition from cubic into tetragonal forms and *vice versa* occurs through a process of recrystallisation. The gradual change in the axis ratio brought about by a sudden change in temperature occurs according to an exponential equation. The observed phenomena are explained by thermodynamic and statistical methods.

J. W. SMITH.

X-Ray spectroscopic measurements of the M-series of the elements uranium to gadolinium. E. LINDBERG (Z. Physik, 1928, 50, 82—96).—Using an accurate X-ray spectroscope of the Siegbahn type, new measurements have been made of the M-series lines of a number of elements between uranium (92) and gadolinium (66), a large number of new lines being observed. Several of the lines were traced systematically down the series of elements and constant intensity ratios found. Observations of the  $M_{\alpha, \alpha, \beta}$  doublet confirmed the results of van der Tuuk (A., 1927, 999).

J. W. SMITH.

Oven for X-ray investigations at high temperatures and preliminary results with pentaerythritol and quartz. W. M. COHN (Z. Physik, 1928, 50, 123—136).—A camera is described in which the fine structure of the X-ray spectrum of solid, non-conducting bodies may be determined, the preparation being brought to a known high temperature for long periods. Both in the cases of pentaerythritol and quartz the effect of rising temperature was to cause a general weakening of the intensity of the bands with equal times of exposure and a falling off of the higher interference bands. On the other hand, the broadening of the lines which was anticipated on theoretical grounds was observed only in the case of pentaerythritol.

J. W. SMITH.

Absolute intensity of X-rays. T. E. AURÉN (Medd. K. Vetens. Nobel Inst., 1927, 6, No. 13).—The absolute intensity of X-rays has been measured by the heat excited in metals on absorption of the rays. No difference in the energy measurements was found using plates of copper, silver, and lead. Up to 100 kilovolts, the intensity is exactly proportional to the current through the tube. The relationship between the total intensity of the energy radiated as X-rays and the voltage applied to the tube has been determined. The effect of an aluminium filter also was studied. The energy necessary to produce a pair of ions is not found to increase with decreasing wave-length.

W. E. DOWNEY.

Determination of the absorption coefficient of various metals and organic compounds in the short-wave X-ray region. H. STUMPEN (Z. Physik, 1928, 50, 215—227).—A new method has been devised for the measurement of X-ray absorption. The results obtained with the metals and organic compounds investigated confirm those of previous workers.

J. W. SMITH.

X-Ray diffraction and its bearing on molecular complexity in the liquid state. P. KRISHNAMURTI (Indian J. Physics, 1928, 2, 491—500).—The X-ray diffraction of 26 pure organic liquids has been investigated. In all cases where the surface-tension method indicates association the inner ring is very prominent. By substituting the spacing obtained by the X-ray method for the value of  $\sqrt[3]{m/d}$  in Ramsay and Shields' relationship, more probable values have been obtained for the degree of association and some anomalous values have been rectified. It is suggested that all liquids can be dealt with as solutions of double molecules in a solvent composed of single molecules, or of triple molecules in a solvent of

double molecules, and that the ideas derived from a study of aqueous solutions containing small and large molecules of solute at different concentrations can be applied equally well to this case in explaining the intensity and extent of the inner ring.

J. W. SMITH.

**X-Ray diffraction in aqueous solutions and liquid mixtures.** I. P. KRISHNAMURTI (Indian J. Physics, 1928, 2, 501—507).—The X-ray diffraction of ammonium nitrate and acetamide both in powder form and in their aqueous solutions at various concentrations has been investigated. The concentrated aqueous solutions tend to develop an inner ring, which is in favour of the existence of a regular arrangement of atoms as in the liquid or solid state. The general scattering which occurs in concentrated ammonium nitrate solutions but not in acetamide is attributed to a portion of the ions being distributed at random in the liquid. In both cases the two rings which appear in the solid state persist in the liquid state and in very concentrated solutions, both rings undergoing some contraction. As dilution increases the inner ring contracts and tends to disappear as a general halation, whilst the outer ring expands and merges with the water ring. Hence it is deduced that the outer ring is a superposition effect due to the water and solute taken in their proper proportions.

J. W. SMITH.

**X-Ray diffraction in liquids. Comparison of isomerides of *n*-heptane and of certain carbon chains.** G. W. STEWART (Physical Rev., 1928, [ii], 32, 153—161).—Diffraction ionisation curves for the  $K\alpha$  doublet of molybdenum were obtained for synthetic *n*-decane,  $\beta\beta\delta$ -trimethylpentane,  $\beta$ -methyl- $\Delta^2$ -hexene,  $\beta\beta\gamma$ -trimethylbutane,  $\gamma\gamma$ -,  $\beta\gamma$ -,  $\beta\beta$ -, and  $\beta\delta$ -dimethylpentane,  $\gamma$ -ethylpentane,  $\gamma$ -methylhexane, and  $\beta$ -methylhexane. The diameter of the normal paraffin chain throughout the range  $C_5$ — $C_{15}$  is 4.64 Å.; the length is given by  $L=1.24n+2.70$  Å., where  $n$  is the number of carbon atoms, it being assumed that the molecules are longitudinally parallel and in square array in the plane normal to their lengths. It is tentatively concluded that the attachment of two methyl groups to the same atom does not necessarily increase the diameter by the same amount, the effect depending on whether a third methyl branch is attached to an adjacent atom or to the next but one. Attachment of a methyl group to the penultimate carbon atom seems to produce two symmetrical branches of one methyl group each.

A. A. ELDRIDGE.

**Crystallographic identity of the two forms of mercuric oxide.** G. R. LEVI (Gazzetta, 1928, 58, 417—418; cf. A., 1924, ii, 860).—A reply to the criticisms of Kolkmeijer (this vol., 692).

F. G. TRYHORN.

**Dehydrated gibbsite.** J. DE LAPPARENT and E. STEMPEL (Compt. rend., 1928, 187, 305—306).—The changes in optical properties shown by crystalline gibbsite during dehydration at gradually rising temperatures (up to 1000°) indicate that the final product is also crystalline, the structure having changed from clinorhombic to orthorhombic at 600°.

J. GRANT.

**X-Ray observations with cellulose.** R. O. HERZOG and W. JANCKE (Naturwiss., 1928, 16, 618).—The Röntgen diagram of natural cellulose shows a blackening at a point corresponding with  $\sin \theta/2=0.0218\pm 0.0003$ . This also appears if mercerised ramie is used, but not so definitely. If it is due to the cellulose lattice, it corresponds with a lattice space of 35.3 Å. There is also a weak point which indicates a period perpendicular to the axis of 16 Å.

A. J. MEE.

**Crystal structures of the compounds  $RuS_2$ ,  $OsS_2$ ,  $MnTe_2$ , and  $AuSb_2$ .** I. OFTEDAL (Z. physikal. Chem., 1928, 139, 291—299).—Powder photographs show that the compounds  $RuS_2$ ,  $OsS_2$ ,  $MnTe_2$ , and  $AuSb_2$  exhibit the pyrites structure. Parameters of about 1/8 are found. The following lattice constants are given: pyrites (Kongsberg)  $a=5.414(\pm 0.003)$  Å.,  $MnTe_2$ ,  $a=6.943(\pm 0.002)$  Å.;  $AuSb_2$ ,  $a=6.636(\pm 0.010)$  Å.

R. A. MORTON.

**Crystal structure of tetraethylammonium iodide.** I. NITTA (Proc. Imp. Acad. Tokyo, 1928, 4, 292—296).—The structure of tetraethylammonium iodide has been examined by means of the Laue and ionisation methods. The lattice is found to be tetragonal body-centred, the unit cell consisting of two molecules. It is not possible to decide whether the structure is that of sodium chloride or that of caesium chloride.

W. E. DOWNEY.

**Slip-bands produced when crystals of aluminium are stretched.** K. YAMAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 289—317).—The plastic strain produced in pieces of aluminium when stretched has been found to be a simple shear on the slip plane and along the direction of slip, so far, at least, as general external form is concerned. The directions of the slip bands are in accordance with the predictions of Taylor (A., 1927, 1017), although some of the quantitative observations are not in agreement with those of the latter investigator.

J. W. SMITH.

**Anisotropy of the carbon atom.** (MRS.) K. LONSDALE (Phil. Mag., 1928, [vii], 6, 433—446).—From a consideration of the X-ray data for hexachloroethane and isomorphous compounds a structure is suggested for the carbon atom in which two of the valencies differ geometrically from the other two. This is in agreement with the Main Smith and Stoner configurations of the carbon atom. Evidence is adduced in favour of the non-tetrahedral carbon atom. A critical discussion of the structures of symmetrically substituted methane derivatives shows that the existence of the pyramidal carbon atom has not been established. The structure suggested agrees with crystallographic data and explains the non-symmetry of many simple carbon compounds.

S. K. TWEEDY.

**Oxides and hydroxides of cobalt.** G. NATTA and M. STRADA (Gazzetta, 1928, 58, 419—433).—Chemical and X-ray crystallographic analyses have been made of cobalt oxide and hydroxide preparations to determine which of those described in the literature may be accepted as definite compounds. Three oxides of cobalt with definite chemical and crystalline structures are recognised. Cobaltous oxide, with a

cubic face-centred lattice, has an elementary cell of edge 4.22 Å., containing four molecules of the sodium chloride type. The oxide  $\text{Co}_3\text{O}_4$  (cobaltous cobaltate) has a cubic structure with a lattice of the spinel type, with an elementary cell of edge 8.05 Å. containing eight molecules. Cobaltic oxide has probably an hexagonal or a rhombohedral structure with a cell of edge  $a=4.64$  Å.,  $c/a=1.24$ , containing two molecules. The calculated density is 5.34. Cobaltic hydroxide may be prepared satisfactorily by drying the hydrate at 250°. Above this temperature the oxide  $\text{Co}_3\text{O}_4$  is obtained. Products described previously as cobalt suboxide,  $\text{Co}_2\text{O}$ , are mixtures of the metal and cobaltous oxide. Of the hydroxides of cobalt recorded only cobaltous hydroxide has a definite composition and crystalline structure. The crystals are of rhombohedral form (type brucite) with an orthorhombic elementary cell ( $a=3.19$  Å.,  $c/a=1.46$ ) containing one molecule of cobaltous hydroxide. Cobaltic hydroxide could not be obtained in a definite crystalline form, but in X-ray photographs exhibits the lines of cobaltic oxide, which it forms on dehydration. Other oxides and hydroxides lower than  $\text{Co}_2\text{O}_3$  and  $\text{Co}(\text{OH})_3$  cannot be obtained as chemical individuals, and must be represented as mixtures of the above compounds. No oxide higher than  $\text{Co}_2\text{O}_3$  could be obtained in the dry state.

F. G. TRYHORN.

**Isomorphism, polymorphism, and monotropy. I. Compounds of the type  $\text{ABX}_3$ .** G. NATTA and L. PASSERINI (Gazzetta, 1928, 58, 472—484).—X-Ray crystallographic analyses by the powder, Laue, and rotating-crystal methods have been made of some complex halides of caesium and mercury and of caesium and cadmium. The cubic modifications of caesium trichloromercuriate and of caesium tribromomercuriate possess elementary cells of edges 5.44 and 5.77 Å., respectively, each containing one molecule;  $d_{\text{calc.}}$  4.53 and 4.97, respectively. These compounds are isomorphous and form a complete series of solid solutions. Caesium monochlorodibromomercuriate and caesium monobromodichloromercuriate do not exist as chemical individuals, but belong to the continuous series of solid solutions formed by the above two halogenomercuriates. They have the same lattice as these latter, but deformed. The dimensions of the cells of the mixed crystals follow closely Vegard's rule. Isomorphous with the preceding compounds are caesium tribromocadmiate and caesium trichlorocadmiate. The bromo-compound has an elementary cell of edge 5.33 Å. with a calculated density 5.38. Caesium triiodomercuriate and caesium triiodocadmiate are not isomorphous with the corresponding chloro- and bromo-derivatives and have a lower crystalline symmetry. The latter,  $\text{Cs}[\text{CdI}_3]$ , ( $d$  5.48, m. p. 193°) was prepared by the dehydration of the monohydrate. The relations which must exist among the atoms A, B, and X in the compounds  $\text{ABX}_3$  in order that certain types of structure may be possible have been determined. The values of  $t=(R_a+R_x)/\sqrt{2}(R_b+R_x)$ , where  $R_a$ ,  $R_b$ , and  $R_x$  are respectively the atomic radii of the ions A, B, and X, have been calculated for various series of compounds. For oxygen compounds,  $t$  is less than 0.8 for the rhombohedral struc-

ture (type corindon and ilmenite); between 0.8 and 1.0 for cubic crystals (type caesium chloromercuriate); between 1.0 and 1.2 for rhombohedral crystals of the calcite and sodium nitrate types, and between 1.20 and 1.30 for rhombic crystals of the aragonite type. Analogous relationships exist, within certain limits, among double halides of the type  $\text{ABX}_3$ . For the cubic modifications of compounds of the caesium chloromercuriate type the value of  $t$  is greater than 0.830. Compounds having values of  $t$  near 0.830 are dimorphous. When the value of  $t$  is less than 0.825 the compounds possess lower crystalline symmetry and belong to the rhombic or monoclinic systems. Iodo-derivatives alone form exceptions to these limitations; caesium tri-iodocadmiate with  $t=0.840$  is not isomorphous with the other halogenocadmiates of caesium, and, owing to the presence of the iodine ion, shows strong polarisation.

F. G. TRYHORN.

**Mechanical properties of brass crystals.** M. MASIMA and G. SACHS (Z. Physik, 1928, 50, 161—186).—It has been found that the electrical conductivity in brass crystals containing about 72% of copper is an isotropic property, whereas the elastic properties are strongly anisotropic. The directions of the slip-planes determined and the elasticity in different directions have been investigated. The shear along the slip plane at the elastic limit is constant and independent of the direction of the stress. The distortion produced by stretching beyond the elastic limit and breaking strain has also been investigated and the conditions required for the establishment of secondary slip-planes deduced.

J. W. SMITH.

**Method of crystal class determination.** A. HETTICH and A. SCHLEEDE (Z. Physik, 1928, 50, 249—265).—The piezo-electric methods of Giebe and Scheibe (*ibid.*, 1925, 33, 760) and of Meissner (A., 1927, 1014) have been applied to the determination of the structure of a large number of crystalline substances. The results indicate that the present classification of some of these crystal types requires modification.

J. W. SMITH.

**Structure of  $\text{Tl-}\alpha$  and  $\text{Tl-}\beta$ .** H. PERLITZ (Z. Physik, 1928, 50, 433—435).—The data of the resistance and volume changes of thallium at its conversion and m. p. are examined.  $\alpha$ -Thallium has a hexagonal structure with close packing and  $\beta$ -thallium a face-centred cubic structure.

W. E. DOWNEY.

**Space-filling forms in crystal lattices.** H. TERTSCH (Fortsch. Min. Kryst. Petr., 1927, 12, 89—90; Chem. Zentr., 1928, i, 1358).—The alkali halides exhibit two types, cubic and octahedral; sodium chloride belongs to the former, and caesium chloride to the latter, type, whilst rubidium chloride is partly intermediate. Metal ions do not vary from their type, as do negative ions. The change from cubic to octahedral type is considered to be associated with the number and distribution of the electronic orbits.

A. A. ELDRIDGE.

**Formula and crystal structure of tetrahedrite.** F. MACHATSCHKI (Norsk geol. Tidsskr., 1928, 10, No. 1, 10 pp.; Chem. Zentr., 1928, i, 1359).—Debye-Scherrer diagrams for tetrahedrite are very similar



to those for zinc blende; the bivalent metals are supposed to be present as admixed isomorphous sulphides, and the ratio  $R^I:R^{II}:S$  is 3:1:3. Silver fahl ore from Colquechaca, Bolivia, has  $a_0$  10.41 Å., and fahl ore from Felsőbanya has  $a_0$  10.29 Å. The unit cell contains 8 mols.  $R_3^I R^{II} S_3$  (56 atoms), whilst in a zinc sulphide cell 64 atoms are present. The following densities are computed:  $Cu_3SbS_3$  4.88,  $Cu_3AsS_3$  4.34,  $75Cu_3SbS_3 + 25Ag_3SbS_3$  5.28,  $75Cu_3AsS_3 + 25Ag_3AsS_3$  4.74. Tetrahedrite is hexakistetrahedral, space-group  $T_2^7$ ; distance Sb—S 2.45 Å., Cu—S 2.24 Å.; shortest distance Cu—Sb 3.25 Å., Cu—Cu 3.65 Å. A. A. ELDRIDGE.

**Crystal structure of solid mercury.** M. WOLF (Nature, 1928, 122, 314).—Debye-Scherrer analysis of the product of reduction of mercurous oxide by formic acid in gelatin supports McKeehan and Cioffi's result that solid mercury has a simple rhombohedral structure. A. A. ELDRIDGE.

**X-Ray studies on iron nitrides.** G. HÄGG (Nature, 1928, 122, 314).—Previous conclusions (this vol., 605) are modified; the nitrogen atoms have definite places in the lattice of the cubic  $\gamma$ -phase, for which the formula  $Fe_4N$  is given. A. A. ELDRIDGE.

**Crystalline structure of benzene.** E. G. COX (Nature, 1928, 122, 401).—The unit cell is simple orthorhombic,  $a$  7.44,  $b$  9.65,  $c$  6.81 Å. at  $-22^\circ$ , and contains four molecules; the space-group is  $Q_h^{15}$ . In the crystal the molecule has a centre, but no planes, of symmetry. A. A. ELDRIDGE.

**Iron-containing rings of smaller effective permeability.** U. RETZOW (Physikal. Z., 1928, 29, 534—538).—The order of magnitude of the effective maximal permeability for alloys, wires, and "mass cores" has been determined as follows: iron-nickel alloys (copper and manganese as minor constituents),  $\chi \times 10^4$ ; Elmen bronzes (nickel, cobalt, iron, manganese),  $\chi \times 10^3$ ; Heusler bronzes (copper, aluminium, manganese),  $\chi \times 10^1 - \chi \times 10^2$ ; ring wire cores of iron and steel wires,  $\chi \times 10^2$ ; "mass cores" of pressed powdered iron enclosed by an insulating material,  $\chi \times 10^{-1} - \chi \times 10^2$ ; iron and steel wires,  $\chi \times 10^1$ .

R. A. MORTON.

**Magnetic properties of cobalt.** (FRL.) M. SAMUEL (Ann. Physik, 1928, [iv], 86, 798—824).—The magnetic properties of two specimens of cobalt have been studied, but although both samples received the same heat treatment before the experiments, the results are not in agreement. The normal and ideal magnetisation curves, the reversible permeability, and the coercive force as a function of temperature differ for the two samples. No marked change in magnetic properties occurs on heating to  $1000^\circ$ . As in the cases of iron, steel, and nickel, the reversible susceptibility is clearly a function of the magnetisation, but the Gans law of magnetic corresponding states is not here valid. The coercive force is a definite function of the temperature, between  $-185^\circ$  and  $+400^\circ$ , but the function is not that observed by Gans for iron, steel, and nickel. R. A. MORTON.

**Magnetisation of single crystals of nickel.** S. KAYA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 639—663).—Oblate ellipsoids with equatorial planes

coinciding with the (100), (110), and (111) planes, respectively, were prepared from large single crystals of nickel, and their magnetic properties measured. Magnetisation curves in the direction of the principal axes showed the isotropic properties of the crystal up to an intensity of magnetisation of 205, but above this value magnetisation varies in different directions, the trigonal, digonal, and tetragonal axes being in decreasing order of magnetisability. This is the reverse of the order found for iron (cf. A., 1927, 298). The parallel and perpendicular components of magnetisation for a constant field vary periodically according to the space lattice in the three principal planes. C. J. SMITHELLS.

**Principal susceptibilities of manganese ammonium sulphate crystals at low temperatures.** L. C. JACKSON and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 346—349; cf. Jackson and Onnes, A., 1924, ii, 90).—The magnetic susceptibilities of small cylinders of manganese ammonium sulphate cut with their axes ( $a$ ) parallel to the axis of symmetry of the crystal, ( $b$ ) perpendicular to the 001 plane, and ( $c$ ) perpendicular to the 110 plane, have been separately determined at  $20.3^\circ$ ,  $18.9^\circ$ ,  $16.9^\circ$ , and  $15.0^\circ$  Abs. The curves obtained by plotting  $1/\chi'_m$  against  $T$  (where  $\chi'_m$  is the molecular susceptibility) are straight lines, all of which pass through the origin. Hence each of the principal susceptibilities of the crystal powder follows the simple Curie law  $\chi T = C$ , but with different values of  $C$  in each case. J. W. BAKER.

**Electric explosions.** H. NAGAOKA and T. FUTAGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 8, 269—288).—Photographs have been taken of the explosions resulting from the discharge of a large battery of condensers (capacity 1.7 microfarads) charged to 40 kilovolts through fine pieces of metallic wire. These indicate the projection of charged particles at right angles to the wire, the appearance of the explosion being considerably modified by the presence of a strong magnetic field. In the case of long and thick wires where the explosion is incomplete, a pole-effect is evident, the wire being more vaporised at the positive than at the negative pole. Cinematographic photographs have also been taken to show the progress of the explosion. Similar explosions carried out in oil, in an attempt to effect the transmutation of elements, yielded negative results. J. W. SMITH.

**Magnetic studies on salts, particularly those with complex ions.** L. A. WELO (Phil. Mag., 1928, [vii], 6, 481—509).—A descriptive paper in which magnetic data for 124 compounds are recorded. In connexion with salts having negative values of  $\theta$  [Curie's law:  $g$ -atomic susceptibility = const.  $\times (T - \theta)^{-1}$ ] it is suggested that organic groups are probably permanent electric dipoles and, following Debye, the elementary magnets in the molecule have permanent electric moments also; these dipoles provide the fields which resist magnetisation. On this view the negative values of  $\theta$  have a different origin from the positive values. Rosenbohm's conclusion that geometrical and co-ordination isomerides cannot be distinguished

by magnetic measurements is confirmed for chromium and cobalt compounds (A., 1920, ii, 160). The low moment in potassium ferricyanide is practically unaltered by substitution of other groups for the cyanogen radical. Evidence against paramagnetism in iron in the  $\text{Fe}(\text{CN})_6$  ion is recorded.

S. K. TWEEDY.

**Iron crystals. IV. Dependence of magnetisation on temperature.** E. DUSSLER (Z. Physik, 1928, 50, 195—214).—The dependence of the magnetisation of iron crystals on temperature has been investigated along both the diagonal and tetragonal axes between the temperature of liquid air and the Curie point. At all temperatures the  $B$ - $H$  curve is initially linear and inflects suddenly, slowly attaining saturation (cf. A., 1927, 924). The linear portion of this curve is independent of temperature, but the higher the temperature the smaller is the field at which saturation is attained and the lower the saturation magnetisation. The variation with temperature of the magnetisation at the point of inflexion and the saturation value both follow an exponential law.

J. W. SMITH.

**Magnetic susceptibility of ozonides. V. I.** VAIDYANATHAN (Indian J. Physics, 1928, 2, 421—433).—The magnetic susceptibilities of a few typical ozonides have been measured, a modified form of Curie balance being employed. All were found to be diamagnetic, but, owing to their superior stability, the most trustworthy measurements were those on phenanthrene and naphthalene diozonides. Assuming magnetic susceptibility to be an additive property, it is deduced from the data obtained that the susceptibility of ozone is about  $-25 \times 10^{-6}$  per g.-mol. The structure of the ozone molecule and the electron arrangements within it are discussed in relation with this result.

J. W. SMITH.

**Theory of forced double refraction (photo-elasticity).** K. F. HERZFELD (J. Opt. Soc. Amer., 1928, 17, 26—36).—Mathematical. The double refraction of crystals is discussed, and it is pointed out that it may be due to (a) the anisotropy of the ions taken separately, (b) the anisotropic arrangement of the ions in the lattice which results in an anisotropic force even if the ions are undisturbed, or (c) an anisotropic "Lorentz-Lorenz force" due to the anisotropic arrangement of the ions. Calculations are made to determine the magnitude of (c) in cubic crystals of rock-salt and sylvine under stress (forced double refraction, photo-elasticity), and it is concluded that the double refraction cannot be explained entirely by this means. It is also shown how the Lorentz-Lorenz force is built up in the unstrained crystal.

L. L. BIRCUMSHAW.

**Conductivity of powdered salts.** J. CICHOCI (Compt. rend., 1928, 187, 287—289).—Measurements of the conductivity of dry powdered barium chloride heated electrically in a copper tube by means of an axial copper wire support Peczalski's theory (A., 1927, 634, 710) that the increased conductivity of salts in the powdered state is due, not only to the conductivity of the solid particles, but also to that of the vapours of the salt and to dispersed metallic copper.

J. GRANT.

**Influence of the solvent on the mobility of electrolytic ions.** R. T. LATTEY (Phil. Mag., 1928, [vii], 6, 258—270).—It is shown that the mobility,  $l$ , of an ion in solution should be represented by the expression  $l = Fe/\eta\sigma \cdot \phi(3k_0D\sigma/2e^2)$ , where  $F$  is the Faraday charge,  $e$  ionic charge,  $\eta$  viscosity of solvent,  $\sigma$  ionic radius,  $(3k_0/2)$  thermal energy of the molecule at the temperature of the experiment,  $D$  dielectric constant of the solvent, and  $\phi$  an unspecified function. Examination of a large number of data shows  $l\eta = \alpha + \beta(0D)^2$ , where  $\alpha$  and  $\beta$  are constants characteristic of the ion, which from dimensional analysis is equivalent to  $FeA/\sigma_1 + 9Fk^2\sigma_2 B(0D)^2/4e^3$ , where  $A$  and  $B$  are constants and  $\sigma_1$  and  $\sigma_2$  are functions of the dimensions of the ion and in the case of elementary ions approximate to the radii.

A. E. MITCHELL.

**Superconductivity according to the Schrödinger wave-equations and the Fermi statistics.** E. KRETZSCHMANN (Ann. Physik, 1928, [iv], 86, 914—928).—In an earlier paper (*ibid.*, 1926, [iv], 80, 109—136) it was shown that on the basis of the Maxwell-Boltzmann statistics and classical mechanics the conditions for absence of electrical resistance were, in classical terms, no interpenetration of elementary charges, or, in quantum terms, no interchanges of bound and free electrons. It is now shown that the condition for superconductivity may be restated thus: only Coulomb forces shall operate between elementary charges, and the movement of free electrons must be determined solely by the Schrödinger equation, and the velocity and energy distribution by the Fermi statistics.

R. A. MORTON.

**Does grey tin become superconductive?** W. J. DE HAAS, G. J. SIZOO, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 350—352).—Measurements of the conductivity of grey tin pressed into the form of a bar at very low temperatures show that it does not become superconductive even at the lowest temperature used,  $1.8^\circ$  Abs. J. W. BAKER.

**Investigation of Tammann's theory of "resistance limits" for the gold-copper system.** M. LE BLANC, K. RICHTER, and E. SCHIEBOLD (Ann. Physik, 1928, [iv], 86, 929—1005).—Tammann's work on the limiting composition of gold-copper alloys such that when the gold content exceeds this limit the alloys are unattacked by various reagents has been repeated and his theory to account for the phenomenon has been criticised (cf. A., 1919, ii, 398, 406). Alloys of gold and copper were prepared of various compositions, and the action of nitric acid on them was investigated, the amount of copper dissolved being determined. The results do not agree with those of Tammann. The problem is also attacked by determining the crystal structure of the alloys by the X-ray method. The types of distribution of two atoms in a space lattice which Tammann has distinguished (cf. A., 1919, ii, 406) are discussed, and it is shown from the X-ray experiments that Tammann's "normal" distribution does not hold for alloys of copper content between 0.375 and 0.625 molar concentration, as Tammann supposed it would. Hence Tammann's theory to account for the "resistance limit" of the alloys is untenable. Indeed, it

is shown that there is no absolute "resistance limit" in the quantitative sense independent of temperature and of the solvent used. A new theory which will explain many of the phenomena is put forward and discussed.

A. J. MEE.

#### Electrometric titration curves of dibasic acids.

II.  $\beta$ -Substituted glutaric acids. R. GANE and C. K. INGOLD (J.C.S., 1928, 2267—2272).—The first and second dissociation constants of the following  $\beta$ -substituted glutaric acids have been measured by the potentiometric method (cf. this vol., 846) and the apparent distance ( $r$ ) between the two carboxyl groups has been calculated in accordance with the Bjerrum theory. The values of  $k_1$ ,  $k_2$ , and  $r$  (Ångström units) for the cases studied are, respectively, unsubstituted,  $4.60 \times 10^{-5}$ ,  $5.34 \times 10^{-6}$ , 9.22;  $\beta$ -methyl,  $5.77 \times 10^{-5}$ ,  $6.28 \times 10^{-7}$ , 2.27;  $\beta$ -*n*-propyl,  $4.97 \times 10^{-5}$ ,  $4.32 \times 10^{-7}$ , 2.12;  $\beta\beta$ -dimethyl,  $2.03 \times 10^{-4}$ ,  $5.51 \times 10^{-7}$ , 1.57;  $\beta\beta$ -diethyl,  $3.40 \times 10^{-4}$ ,  $7.85 \times 10^{-8}$ , 1.02;  $\beta\beta$ -di-*n*-propyl,  $2.03 \times 10^{-4}$ ,  $5.42 \times 10^{-8}$ , 1.01; cyclopentane-1 : 1-diacetic acid,  $1.68 \times 10^{-4}$ ,  $2.63 \times 10^{-7}$ , 1.40; cyclohexane-1 : 1-diacetic acid,  $3.36 \times 10^{-4}$ ,  $1.02 \times 10^{-7}$ , 1.04; cycloheptane-1 : 1-diacetic acid,  $2.78 \times 10^{-4}$ ,  $1.09 \times 10^{-7}$ , 1.10. The values are in general agreement with the predictions of the Thorpe-Ingold valency deflexion hypothesis, the anomalous position of the cycloheptane compound owing to its multiplanar strain-free configuration (cf. Baker and Ingold, J.C.S., 1923, 123, 122; Baker, A., 1925, i, 1277) again being evident. The much greater value for  $r$  in the unsubstituted acid suggests that whilst in this acid the carbon atoms form a straight (zigzag) chain, the presence of a  $\beta$ -substituent causes the molecule to assume a coiled configuration.

J. W. BAKER.

#### Electrical resistance of pure molten metals.

Y. MATSUYAMA (Kinzoku no Kenku, 1926, 3, 254—261).—The specific resistance of mercury, tin, antimony, cadmium, lead, bismuth, aluminium, and silver increases with rise of temperature, whilst that of zinc decreases slightly. The specific resistances of the molten metals at the m. p. are, respectively, 93.1, 48.1, 115.0, 32.2, 95.8, 126.7, 25.5, 17.3, 37.0.

CHEMICAL ABSTRACTS.

#### Theory of the electrical conductivity of metals.

P. LAPINSKY (Ukrain. physikal. Abhandl., 1926, 1, 70—74).—Thomson's and Borelius' formulæ can be deduced from the laws of thermodynamics if it is assumed that the condition of the conducting electrons as a thermodynamic system in the metal depends on the composition and on the temperature and other physical magnitudes. At low temperatures the relation between the electrical conductivity and the absolute temperature is expressed by:  $(\sigma + \alpha/T^2)(T - T_0) = (d\rho_e T_0)/k$ , where  $T_0$  is the original temperature,  $d$  the distance between two atoms,  $p$  the number of electrons passing per sec. from one atom to its neighbour,  $e$  the charge on the electron, and  $k$  and  $\alpha$  are constants.

CHEMICAL ABSTRACTS.

Physical properties of salicylaldehyde. T. S. CARSWELL and C. E. PFEIFER.—See this vol., 1009.

Influence of constitution on the stability of racemates. A. FINDLAY and A. N. CAMPBELL (J. J.C.S., 1928, 1768—1775).—The f.-p. and solubility

curves of active and racemic forms of tartaric acid, of its methyl ester, and of the methyl esters of diacetyl-, dipropionyl-, and dibenzoyl-tartaric acids and of the ethyl esters of diacetyl- and dibenzoyl-tartaric acids have been studied. Introduction of an acyl group into the methyl or ethyl ester of tartaric acid lowers the m. p. of the racemic form relatively to that of the active form, and reduces the range of stability of the racemic form. The acetyl group is much more effective in this respect than the propionyl or benzoyl group. The transition point of methyl diacetylacetate lies at about 23°. R. A. MORTON.

Heat capacity of hydrogen bromide from 15° Abs. to its b. p. and its heat of vaporisation. Entropy from spectroscopic data. W. F. GIAUQUE and R. WIEBE (J. Amer. Chem. Soc., 1928, 50, 2193—2202).—The heat capacities of solid and liquid hydrogen bromide are recorded; the results disagree somewhat with those of Eucken and Karwat. The heat of fusion is 575.1 g.-cal./mol.; m. p. 186.24°  $\pm 0.05$ ; b. p. 206.38°  $\pm 0.05$ ; heat of vaporisation, 4210  $\pm 4$  g.-cal./mol. The entropy at the b. p. is 44.9  $\pm 0.1$  g.-cal./1° per molecule, in agreement with the value calculated from the Sackur equation with the Tetrode constant enlarged by the entropy due to the rotational-vibrational energy, which is calculated from the band spectra (this vol., 228).

S. K. TWEEDY.

Volume change of manganese during solidification. Y. MATSUYAMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 731—733).—Manganese contracts 1.7% of its volume on solidification. C. W. GIBBY.

Heat of fusion and heat of the new transformation in tellurium. S. UMENO (Kinzoku no Kenku, 1926, 3, 498—501).—The latent heat of fusion of tellurium at 446° is 33.50 g.-cal., and that of a new transformation at 348° is 0.63 g.-cal.

CHEMICAL ABSTRACTS.

Precise determination of thermal capacities. Molybdenum. T. E. STERN (Physical Rev., 1928, [ii], 32, 298—301).—The specific heat of molybdenum, determined with a Bunsen ice calorimeter provided with a silvered vacuum jacket, is  $c_p = 0.05973 + 0.00001619t$  mean g.-cal./g. per 1° between 0° and 444.5°.

A. A. ELDRIDGE.

Simple relation between thermal conductivity, specific heat, and absolute temperature. C. C. BIDWELL (Physical Rev., 1928, [ii], 32, 311—314).—A relation of the form  $k/aC = K_1/T + K_2$ , where  $k$  is the thermal conductivity,  $aC$  the atomic heat, and  $T$  the temperature (absolute), is valid for zinc, sodium, lithium, copper, lead, aluminium, and mercury. The relation is considered in application to the theory of the double mechanism of heat conduction.

A. A. ELDRIDGE.

Gases with molecular attraction. K. SHIBA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 740—747).—Theoretical. The expression  $e^{-[3u/2e](n^2 + v^2 + w^2)}$ , in which  $\epsilon$  is the mean kinetic energy, is suggested as a correction to Maxwell's distribution law.

C. W. GIBBY.

Saturated vapour pressure and latent heat of vaporisation of liquids. M. LEVALT-JEZERSKI (J. Russ. Phys. Chem. Soc., 1928, 60, 743—763).—For

all liquids the relation between saturated vapour pressure and temperature may be expressed by the equation (i);  $p = p_0 \times 10^{\alpha \tau}$ , where  $p_0$  is the vapour pressure at the f. p. of the solution,  $\alpha$  is a constant, characteristic of the given liquid, and  $\tau = \delta/T$ , where  $\delta$  is the temperature above the m. p. and  $T$  is the absolute temperature. The value of  $\alpha$  can be calculated from the equation  $\alpha = (\log p_2 - \log p_1) / (\tau_2 - \tau_1)$ . Equation (i) may be substituted in the Clapeyron-Clausius equation,  $d \log_e p / dT = \lambda / RT^2$ , whence the equation  $\lambda = m \alpha RT_0^2$  is derived,  $m$  being the conversion factor to natural logarithms,  $\alpha$  the above constant, and  $T_0$  the f. p. of the given liquid. Values of  $\lambda$  calculated from this equation are in good agreement with experiment, except in those cases where the vapour contains associated molecules.

R. TRUSZKOWSKI.

**Vapour density and other properties of formic acid.** A. S. COOLIDGE (*J. Amer. Chem. Soc.*, 1928, 50, 2166—2178).—Pure formic acid,  $d^0$  1.2456,  $d^{20}$  1.2206, f. p. 8.26°, is prepared by vacuum sublimation of Kahlbaum's purest acid. The vapour pressures of aqueous solutions of the acid are recorded; that of the pure acid is 8.67 mm. for the solid and 11.16 mm. for the liquid at 0°. Decomposition of the pure acid may be prevented by keeping the latter frozen. The vapour densities of the pure acid are recorded between 10° and 156°, corrections being applied for wall adsorption. The results may be interpreted on the assumption that the vapour is an ideal mixture of two gases, containing single and double molecules, respectively, each deviating from the perfect gas laws in the same way as a unimolecular vapour of the same mol. wt. The heat of dissociation of the double molecules is approximately 14,125 g.-cal./mol.

S. K. TWEEDY.

**Critical isotherms and Wohl's equation of state.** R. WEGSCHEIDER (*Z. physikal. Chem.*, 1928, 135, 362—367).—Polemical against Wohl (this vol., 827). The conditions which a critical isotherm must fulfil are discussed in relation to the author's views (*A.*, 1922, ii, 192).

W. E. DOWNEY.

[Critical isotherms and Wohl's equation of state.] K. WOHL (*Z. physikal. Chem.*, 1928, 135, 368).—Polemical against Wegscheider (cf. preceding abstract).

W. E. DOWNEY.

**Method of determining the absolute zero of temperature.** J. R. POTTER (*Phil. Mag.*, 1928, [vii], 6, 318—320).—An electro-calorimetric modification of Kelvin's vapour-pressure thermometer is described. Electrical energy is used to cause a mixture of a liquid and its vapour to undergo an isothermal expansion from an initial to a final measured volume, the initial and final pressures at the unknown constant temperature being measured. The latent heat of vaporisation at constant temperature is thus found as a function of the pressure and the result employed in the integration of Clapeyron's equation  $dT/T = (v_2 - v_1) dp / Q$ .

A. E. MITCHELL.

**Physical properties of liquids as functions of the temperature.** G. ANTONOV (*J. Chim. phys.*, 1928, 25, 497—500).—The graphs expressing the variation with temperature of the latent heat, density, and mean of the densities in the liquid and vapour

states of pure benzene show slight discontinuities of a systematic character which are too high (0.5—2%) to be due to experimental errors or impurities, and may be explained by the author's hypothesis that the elementary constituents of matter at relatively low temperatures are highly complex molecular aggregates (*A.*, 1926, 786).

J. GRANT.

**Surface tension of liquid metals. III. Surface tension of mercury.** L. L. BIRUMSHAW (*Phil. Mag.*, 1928, [vii], 6, 510—525; cf. *A.*, 1927, 719).—The surface tension of mercury was measured by the method of maximum bubble pressure. Glass tubes gave slightly higher results than silica tubes; the latter gave consistent results only when the tips were roughened. With the exception of oxygen, the nature of the gas used for blowing the bubbles is practically without influence. Allowing the bubble to hang for various lengths of time resulted in a lower surface tension with one glass tip, but with another produced no effect. The time of formation of the bubbles had no influence between 35 and 150 sec., and the depth of immersion of the tip could be varied within wide limits without effect. The results of Stöckle (*Ann. Physik*, 1898, 66, 499) and of Popesco (*A.*, 1925, ii, 952) are discussed from the point of view of Bancroft's explanation ("Applied Colloid Chemistry," 1921, 134). It is deduced that the square of the time required for the surface tension to fall to the vacuum value is proportional to the density of the superincumbent gas, but this is not in agreement with Popesco's results.

S. K. TWEEDY.

**Coefficient of expansion of zirconium oxide.** W. M. COHN (*Ber. deut. keram. Ges.*, 1928, 9, 16—18; *Chem. Zentr.*, 1928, i, 1515).—The coefficient of expansion of rods of zirconium oxide (containing 1—3% of other oxides) ignited at 2100° is  $8.0 \times 10^{-6}$  at 40° or  $8.7 \times 10^{-6}$  at 200°; values for rods ignited at 1250° are 3.85 and 3.9, respectively.

A. A. ELDRIDGE.

**Free path of molecules and the coefficient of inner friction in fluids.** N. GERASIMOV (*Physikal. Z.*, 1928, 29, 575—584).—The internal friction of fluids is treated mathematically by means of the kinetic theory of gases.

W. E. DOWNEY.

**Viscosities of the rare gases.** A. NASINI and C. ROSSI (*Gazzetta*, 1928, 58, 433—442).—The viscosities of helium, krypton, and xenon have been redetermined by Rankine's method. The values obtained agree closely with Rankine's figures, except in the case of xenon. For this gas the new values are higher than the old:  $\eta_0$   $2122 \times 10^{-7}$ ,  $\eta_{16.5}$   $2250 \times 10^{-7}$ , and  $\eta_{99.4}$   $2871 \times 10^{-7}$ .

F. G. TRYHORN.

**Mixtures of ethyl and amyl alcohols and water.** B. LAMPE and W. KILP (*Z. Spiritusind.*, 1928, 51, 250).—The expansion and fall in temperature produced when amyl alcohol is mixed with aqueous ethyl alcohol are due to the affinity of the former for the ethyl alcohol. In the analysis of such mixtures by density determinations with an ordinary alcoholometer the correct proportion of water is obtained, for the amyl alcohol in the mixture produces the same effect as if it were ethyl alcohol.

J. GRANT.

**Physical properties of heterogeneous ternary mixtures.** P. MONDAIN-MONVAL (*Compt. rend.*,

1928, 187, 444—447).—Accurate determinations of the refractive indices of mixtures of ethyl and isoamyl alcohol and water have failed to confirm the anomalies recorded by Brun (this vol., 844) in the neighbourhood of the critical point (cf. Barbaudy, A., 1926, 671).

J. GRANT.

**Solutions. I. F.-p. diagrams and latent heats of evaporation of binary mixtures of volatile liquids.** W. F. WYATT (Trans. Faraday Soc., 24, 1928, 429—438).—On recalculation of Tyrer's results for the latent heats of evaporation of binary mixtures (J.C.S., 1911, 99, 1633) it was found that characteristically irregular curves were obtained when molal latent heats were plotted against the composition of the mixtures. To investigate the origin of these irregularities the f.-p. curves have been determined for the systems acetone-chloroform, ethyl alcohol-carbon tetrachloride, ethyl alcohol-benzene, and benzene-chloroform. A compound,  $\text{CHCl}_3 \cdot \text{C}_6\text{H}_5$  (m. p.  $-99.5^\circ$ ), was found in the first system. In the system ethyl alcohol-carbon tetrachloride there is a transition point on the liquidus at  $-47.6^\circ$ , corresponding with a mixture containing 44.6% of carbon tetrachloride. Simple eutectic curves were found for the other two systems. Analysis of the solids separating from these mixed liquids revealed the existence of extensive systems of mixed crystals, the transition point in the system ethyl alcohol-carbon tetrachloride being due to conjugate solid solutions. The probable nature of the forces acting among the molecules in these systems is discussed in the light of these results and with reference to other physical properties of the mixtures.

F. G. TRYHORN.

**Partition of light between two absorbing media.** J. PLOTNIKOV and K. WEBER (Z. Elektrochem., 1928, 34, 316—320).—The partition of the absorption of light between two media forming a homogeneous mixture is discussed.

L. F. GILBERT.

**Diffusion of hydrogen through nickel.** V. LOMBARD (J. Chim. phys., 1928, 25, 501—530; cf. A., 1923, ii, 570).—The number of c.c. of hydrogen (measured at  $0^\circ$  and 760 mm. of mercury) passing per hr. through a nickel plate 1 cm.<sup>2</sup> in area is proportional to the square root of the pressure, or of the partial pressure if the hydrogen is mixed with another gas (e.g., nitrogen) having a negligible power of diffusion. Between  $350^\circ$  and  $750^\circ$  the permeability ( $d$ ) is related to the temperature ( $t$ ) by the expression  $d = Ka^t$ , where  $K$  is a function of the pressure of the gas and of the thickness (for 0.16—2 mm.) and structure of the membrane, and  $a$  is a constant characteristic of the metal (cf. Deming and Hendricks, A., 1924, ii, 94). The permeability is inversely proportional to the thickness of the metal between  $408^\circ$  and  $555^\circ$  (cf. Johnson and Larose, A., 1924, ii, 750), and two membranes in contact behave as a single membrane having the thickness of the two combined. The values obtained were dependent on the structure of the metal, and even when membranes of the same origin were used variations of 15—20% were observable. The values are not affected by the presence of moisture or oxygen (of the order of 1%) in the hydrogen and are reproducible to within 6—7%,

the sources of error being considerable, but for the most part compensatory.

J. GRANT.

**Lead-antimony alloys.** W. BRONIEWSKI and L. SŁRVOVSKI (Rev. Mét., 1928, 25, 397—404).—Observations on the hardness, electrical conductivity, potential, thermo-electric power, coefficient of expansion, and microstructure of lead-antimony alloys after prolonged annealing have failed to disclose the existence of any definite compound of the two metals. The alloys form two series of limited solid solutions which form a eutectic with one another containing 13% Sb (m. p.  $250^\circ$ ). The saturated solid solution of lead in antimony contains about 11% Pb and that of antimony in lead about 0.5% Sb at  $0^\circ$  and about 2% Sb at  $250^\circ$ .

A. R. POWELL.

**Preparation and structure of palladium mono- and di-antimonide.** L. THOMASSEN (Z. physikal. Chem., 1928, 135, 383—392).—The alloys were prepared by heating the two metals enclosed in an evacuated quartz tube. The structures of the two alloys were examined by the powder method of Hull and Davey. The monoarsenide has a nickel arsenide structure with  $a = 4.070 \text{ \AA}$ ,  $c = 5.582 \text{ \AA}$ . The diarsenide has a pyrites structure with  $a = 6.439 \text{ \AA}$ .

W. E. DOWNEY.

**Eutectic crystals.** M. HAMAZUMI (Suiyō-Kwaishi, 1924, 4, 973—982).—The eutectic is the constituent inlaid within surrounding crystals in polygonal cells; both crystallise simultaneously and independently. The primary crystal affects the orientation of the eutectic.

CHEMICAL ABSTRACTS.

**Shrinkage of glass threads during heating.** I. SAWAI and O. MORISAWA (Z. anorg. Chem., 1928, 173, 361—372).—The behaviour of threads of lead borate glass when heated under varying loads has been determined. With small loads of the order of 50—500 g./mm.<sup>2</sup> the initial expansion is followed by a contraction beginning at  $180$ — $190^\circ$  and ending at  $395$ — $360^\circ$  according to the load. Then follows a small range during which no change in length takes place, and finally rapid expansion ensues, due to the great decrease in the viscosity as the softening point is approached. The shrinkage is shown to be due to release of the longitudinal strains in the thread produced in its formation by rapidly drawing it out from a molten mass of the glass. When the viscosity of the glass decreases sufficiently to make these strains greater than the sum of the load and the viscosity, shrinkage takes place. With loads of about 1 kg./mm.<sup>2</sup> shrinkage occurs, but the length of the thread remains constant between  $200^\circ$  and  $400^\circ$ . With higher loads the load is greater than the sum of the viscosity and the internal stresses, therefore no shrinkage takes place on heating.

A. R. POWELL.

**M. p. of mixtures of picric acid and mononitronaphthalene.** JOVINET (Mém. Poudres, 1928, 23, 36—42).—The m.-p. curve shows the existence of a 1 : 1 compound, m. p.  $71^\circ$ . The cooling curve for the mixture containing 70 parts of picric acid to 30 parts of mononitronaphthalene (the French shell-filling explosive M.M.N.) has been studied. To obtain homogeneous charges from the molten charge it must be agitated continuously until the temperature falls to  $71^\circ$  and then seeded at this point with cold powdered

explosive. If this is not done, picric acid will segregate on the walls of the container and the core will be poor in picric acid.

S. BINNING.

**Solubility of potassium ferricyanide in water between 0° and 100°.** J. A. N. FRIEND and W. N. SMIRLES (J.C.S., 1928, 2242—2245).—The density- and solubility-temperature curves for potassium ferricyanide do not show the break obtained from the less accurate results of earlier workers.

J. GRANT.

**Solubility of diphenyldiethylcarbamide in water, alcohol, and other organic solvents.** L. DESVERGNES (Ann. chim. analyt., 1928, [ii], 10, 226—228).—Diphenyldiethylcarbamide is practically insoluble in cold water and only very slightly soluble (0.03%) in boiling water. It is readily soluble in cold alcohol and very soluble in hot alcohol; in 77% alcohol the solution separates into two layers at 50°. A similar effect is obtained with a solution in 60% methyl alcohol at 50° and with an aqueous acetone solution at 40°. The solubilities of the compound in twelve organic solvents at 0°, 20°, and 50° are tabulated.

A. R. POWELL.

**Solubility of alkali soaps in hydrocarbons.** J. WEICHERZ (Naturwiss., 1928, 16, 654).—Contrary to the usual statements, it has been found that alkali soaps are readily soluble in hydrocarbons. The properties of the solution depend on the kind of soap used and on the structure of the hydrocarbon. The solutions are usually highly viscous or gelatinous, becoming more mobile at higher temperatures. The addition of small amounts of phenol, alcohol, or water often increases the solubility. The influence of this on the formation and properties of emulsions of the hydrocarbon-soap solution in water is discussed.

A. J. MEE.

**Determination of ionic partition coefficients.** E. ALLEMANN (Z. Elektrochem., 1928, 34, 373—387; cf. Baur and Allemann, A., 1927, 23).—A method is described for the measurement of single-phase boundary potentials by means of a cell of the type *N*-calomel electrode|conc. KCl|salt AB in water|salt AB in non-aqueous phase|connecting electrolyte|KCl in non-aqueous phase|*N*-KCl in water|*N*-calomel electrode. Fifty salts were investigated, the non-aqueous phase being amyl alcohol, butyl alcohol, or furfuraldehyde. The uni-univalent salts were measured in each of the three solvents, the salts with multivalent ions in butyl alcohol only. In the case of uni-univalent electrolytes, the boundary potentials between two liquid phases can be calculated from the specific ionic partition coefficients. A number of specific ionic partition coefficients for the partition between water saturated with butyl alcohol and butyl alcohol saturated with water are evaluated, and the values are found to be in fair agreement with those calculated from the law of mass action. A method is indicated for determining the influence of the concentration on boundary potentials, and the thermodynamic theory of phase boundary forces is discussed from the point of view of ionic activities.

L. L. BIRCUMSHAW.

**Adsorption of vapours.** A. FLEISCHER (Amer. J. Sci., 1928, [v], 16, 247—257).—Theoretical. A critical review of current theories of adsorption.

C. W. GIBBY.

**Charcoal and its adsorption.** T. OKAZAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 821—831).—No clear difference was found between samples of charcoal prepared from twenty different kinds of wood, when examined with reference to the adsorption of vapours of water, benzene, ethyl alcohol, and ammonia, and the decolorising of petroleum or aqueous methyl-violet. The activity is found to depend on the temperature of baking: charcoal baked at 300° adsorbs a greater amount of ethyl alcohol vapour than when baked at 500°.

C. W. GIBBY.

**Adsorption of arsenious oxide by ferric hydroxide.** A. BOUTARIC and (Mlle.) G. PERREAU (J. Pharm. Chim., 1928, [viii], 8, 211—221).—Adsorption of arsenious oxide by ferric hydroxide is almost instantaneous and reaches its limiting value in less than 1 hr. For the same volume of solution the quantity of arsenious oxide adsorbed per g. of ferric hydroxide increases with the initial concentration and for the same concentration the adsorption increases with the volume. The weight of arsenious oxide adsorbed increases with the weight of ferric hydroxide, but in a decreasing ratio. Similar studies with other hydroxides indicated the following order of decreasing adsorption activity: manganese, zinc, cadmium, chromium, iron, aluminium. Magnesium hydroxide exerted no appreciable adsorption.

E. H. SHARPLES.

**Adsorption of hydrogen, ethylene, acetylene, and ethane by stannous oxide.** J. N. PEARCE and (Miss) S. M. GOERGEN (J. Physical Chem., 1928, 32, 1423—1433).—The adsorption of hydrogen, ethylene, acetylene, and ethane by stannous oxide has been determined at 0°, 78.5°, and 100° and at pressures up to 75 cm. in an apparatus similar to that used by Pease (A., 1923, ii, 472). The stannous oxide, prepared by the addition of stannous chloride to sodium carbonate, was dehydrated in an atmosphere of carbon dioxide at the b. p. of aniline. The adsorption of hydrogen is small at all temperatures, but that of the hydrocarbons is relatively large and decreases rapidly with a rise in temperature. Except for the fact that at 0° ethane is the most readily adsorbed, adsorption decreases at all temperatures in the order acetylene, ethane, ethylene, and hydrogen. Acetylene polymerises slowly in contact with stannous oxide at 100°. Hydrogenation of ethylene occurs at 100° only when the proportion of hydrogen in the reacting mixture is large (75%). Stannous oxide is reduced by hydrogen at 183°.

L. S. THEOBALD.

**Adsorption of mixtures of easily-condensable gases.** S. KLOSKY and L. P. L. Woo (J. Physical Chem., 1928, 32, 1387—1395).—The adsorption isotherms of butane at 0° and 25°, and of methyl chloride at 25°, 35°, and 45° on titania gel have been determined by the dynamic method described by Klosky and Burggraaf (this vol., 580). They agree with the formulæ of Freundlich, Patrick, and Polányi. The adsorption of sulphur dioxide, alone and mixed with methyl chloride or butane, has also been measured. In this case, the ratio of the relative lowerings of adsorption of the two gases is approximately equal to the inverse ratio of the products of their mol. wt. and viscosities. This relation also applies to the data

of Richardson and Woodhouse (A., 1924, ii, 23) for the adsorption of mixtures of carbon dioxide and nitrous oxide by charcoal. L. S. THEOBALD.

**Selective adsorption from gaseous mixtures by a mercury surface formed in the mixture.** M. L. OLIPHANT (Phil. Mag., 1928, [vii], 6, 422—433).—Experiments in which mercury droplets are allowed to fall through columns of mixed gases show that an expanding mercury surface selectively adsorbs carbon dioxide from a mixture of this gas with an excess of hydrogen or of argon, and that the adsorbed gas, which is held with considerable force, forms a uni-molecular layer on the mercury surface. These results indicate that the "large-drop" method of measuring surface tension is more trustworthy than Harkins' "drop-weight" method, since only the former reveals an initial high surface tension in a gas. A rotating pump suitable for pumping mercury is described.

S. K. TWEEDY.

**Adsorption of vapours on an amalgamated platinum surface.** J. W. SMITH (J.C.S., 1928, 2045—2051).—In view of the criticisms of Frazer, Patrick, and Smith (A., 1927, 722), the experiments of Lenher (A., 1927, 198) on the adsorption of water vapour and benzene have been extended and confirmed at temperatures near saturation. The vapour pressure of the liquid was always too low, a constant difference of 1.3 mm. for water and 1.6 mm. for benzene being obtained at all temperatures.

J. GRANT.

**Electrical condition of hot surfaces during the adsorption of gases. II. A nickel surface at temperatures up to 850°.** G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1928, A, 120, 235—246; cf. A., 1927, 1135).—Using an apparatus and experimental procedure essentially the same as that previously described (*loc. cit.*), measurements have been made of the surface charge acquired by a nickel sheet when heated to 850° in a vacuum ( $p < 10^{-5}$  mm.), or in contact with hydrogen, oxygen, carbon monoxide, nitrogen, argon, electrolytic gas, steam, carbon dioxide, carbon monoxide "knall gas," and mixtures of nitrogen or argon with oxygen or hydrogen. The magnitude of the charge in a vacuum depends on the temperature of the metal and its previous thermal history. A complete oxidation and reduction is necessary to bring the surface into the "fully normalised" condition; after this treatment the charge due to a gas is characteristic of the latter and dependent on the temperature, but is independent of the gas pressure (between 1 and 760 mm.). The charge due to the various gases is readily removed by evacuation at 850°, except in the case of carbon monoxide, where the charge must be "burned off" with oxygen. The nickel sheet becomes covered with a dense film of oxide when heated in oxygen, but this oxidised surface acquires the same charge in a vacuum as the reduced oxide-free surface. The charge due to the reaction product of a mixture of combining gases is at all temperatures identical with that due to the original gaseous mixture. Argon or nitrogen diluted with 2.0% of oxygen or hydrogen gives the full charge due to either of the latter gases. These facts are discussed in conjunction with those established

previously. It is suggested that the charge on a hot metal surface in contact with a gas is due to activation of the adsorbed gas molecules, that the initial reduction and oxidation of a nickel sheet bring about a permanent rearrangement of the surface atoms of the metal into a more stable configuration, and that a gas can be held adsorbed on a hot metal surface in at least five different ways, ranging from a purely physical, electrically neutral adsorption to definite stable chemical compound formation, also electrically neutral. Observations on the electrical charging of hot surfaces do not afford any evidence of deep-seated occlusion.

L. L. BIRCUMSHAW.

**Hydrogen content of silver and copper alloys containing oxide.** GUICHARD, CLAUSMANN, and BILLON (Bull. Soc. chim., 1928, [iv], 43, 748—751).—See this vol., 602.

**Adsorption in solutions. XIV. Adsorption of homologous monobasic acids.** B. NEKRASSOV. **XV. Hydrolytic and molecular adsorption of the alkaline-earth halides on carbon.** M. TSCHEPPELEVETZKI (Z. physikal. Chem., 1928, 136, 18—33, 33—44).—XIV. The adsorption by various kinds of charcoal of the normal fatty acids from formic to stearic from solutions in water, methyl and ethyl alcohols, acetone, ethyl ether, light petroleum, chloroform, carbon tetrachloride, carbon disulphide, benzene, and toluene has been determined. The curves showing the relationship between the number of carbon atoms in the acid and the percentage adsorption exhibit in the case of solvents containing oxygen in the molecule a sharp minimum in the adsorption at about three carbon atoms, and thereafter a steady rise; for all solvents of this group the Traube adsorption law is valid from butyric acid onwards. The curves for the other solvents exhibit at most an ill-defined minimum, and the adsorption shows little agreement with the Traube rule. Water is anomalous, whilst light petroleum, probably since it is a mixture, conforms more to the first group than to the second. There is a qualitative relationship between the power of adsorption and the dielectric constant of solvents of the first group, but this does not hold for solvents of the second group. For the lower members of a homologous series wood charcoal has a greater adsorptive capacity than blood charcoal, but for the higher members the reverse is the case. The differences in behaviour of wood, sugar, and blood charcoals as regards adsorption are discussed with reference to the structure of the adsorbing surface.

**XV.** The adsorption by sugar and blood charcoal of the anions from *N*/60 solutions of magnesium, calcium, strontium, and barium chlorides, bromides, and iodides has been measured. The quantity adsorbed decreases in all cases in the order  $I^-$ ,  $Br^-$ ,  $Cl^-$ , the influence of the cation being relatively slight; beryllium salts exhibit comparatively high adsorption of the anions. The adsorption is not a primary effect, but is the result of an initial formation of insoluble carbonates. Molecular adsorption of certain salts is complicated by the secondary deposition on the adsorbent of insoluble basic salts and hydroxides.

H. F. GILLBE.

**So-called hygroscopic water of clays.** T. OKAZAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1928, 9, 15—49).—Isotherms showing the relation between vapour pressure and quantity of water absorbed by clays exhibit discontinuities. The results show that water combines with clay to form hydrates, the composition of which is indicated by the intersection points on the isotherms. The hydrates form solid solutions, the composition of which depends on temperature and humidity. Adsorption fails to account for the data. R. A. MORTON.

**Acidity of acidic earth and alkaline earth.** H. ISOBE and Y. YENDŌ (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 805—820).—The acidity of acid earth is due to the adsorption of acids or acid salts produced by weathering. C. W. GIBBY.

**Crystalline graphite and its capillary properties.** R. CORDEBAS (Chim. et Ind., 1928, 20, 223—230).—The capillary nature of the surface of crystalline graphite is discussed in relation to the uses of the latter in industry. The system graphite-water is an illustration of the author's explanation of the influence of surface energy on the physical properties of matter. J. GRANT.

**Variation of the capillary action of solutions with time.** H. M. TRIMBLE (J. Physical Chem., 1928, 32, 1211—1224; cf. Bigelow and Washburn, this vol., 472).—The variation of capillarity with time has been determined for mixtures of organic solvents at 25° by the capillary-rise method. Mixtures of ethyl ether with benzene, toluene, and acetone show an increase in capillary rise with time; with the mixtures ether-carbon disulphide, ether-nitrobenzene, and ether-amyl alcohol, the rise is more pronounced. Mixtures of carbon disulphide with benzene, chloroform, and carbon tetrachloride show a fall in the capillary rise with time, whilst pentane and acetone with carbon tetrachloride, and ether with chloroform, show a rise to a maximum followed by a fall. The systems benzene-toluene, and carbon tetrachloride-chloroform show no change, and the case in which a fall to a minimum is followed by an increase in capillarity has not been observed. The rate and magnitude of any change are greater the shorter and the smaller is the capillary tube used. Under constant conditions, the nature of the change can be predicted from a knowledge of the surface tension, volatility, and density of the components of the mixture. The conclusion of Washburn and Bigelow (*loc. cit.*) that preferential evaporation and diffusion account for the results is supported. In closed systems with no rubber connexions, changes in capillary rise with time are prevented, and the authors agree with Washburn and Bigelow (*loc. cit.*) that to obtain trustworthy data on the surface tensions of mixtures containing a volatile constituent, evaporation must be prevented. L. S. THEOBALD.

**Electrolytic behaviour of thin films. I. Hydrogen. II. Areas of catalytically active surfaces.** F. P. BOWDEN and E. K. RIDEAL (Proc. Roy. Soc., 1928, A, 120, 59—79, 80—89).—I. A quantitative investigation has been made of the changes of electrode potential at the surfaces of

metallic cathodes during the electrolytic deposition and removal of minute quantities of hydrogen. The potential of the test electrode was measured against a saturated calomel electrode, using an Einthoven string galvanometer. The cathodes employed were mercury, silver, amalgamated silver, platinum, and platinised surfaces, the electrolyte in most cases being  $N/5$ -sulphuric acid, carefully freed from oxygen by prolonged boiling under reduced pressure and cooling in a hydrogen atmosphere. The marked effect which even a small amount of oxygen has on the apparent rate of growth and decay of hydrogen overvoltage is emphasised. It is found that the electrode potential is a linear function of the surface concentration of the hydrogen, and not, as might be expected if the deposited hydrogen behaved as an amalgam electrode of finite bulk concentration, a logarithmic function. Moreover, the overvoltage depends only on the surface concentration of the added hydrogen, and is independent of the nature of the underlying metal. Apparent differences are due to differences in the real areas of the cathodes, and this gives a method of measuring the accessible areas of metallic surfaces. The amount of hydrogen deposited (measured by two methods) is very small, the deposition of sufficient hydrogen to form only  $1/3000$  of an atomic layer raising the potential of the cathode 100 millivolts. It is shown that the rate of decay,  $-d\Gamma/dt$ , of the active material is not proportional to  $\Gamma^2$  as usually assumed, but is an exponential function of the potential, viz.,  $-d\Gamma/dt = k_1 e^{-k_2 E}$ , where  $E$  is the electrode potential and  $\Gamma$  the true surface concentration of active hydrogen. The behaviour of the electrode potential and the magnitude of the quantities involved are compatible with the assumption that the potential of the electrode is due to the presence of electric doublets on its surface, the electric moment of these doublets being equal to that given by a proton and a negative hydrogen ion separated from each other by a distance equal to the diameter of a hydrogen atom.

II. The accessible areas of silver, platinum, carbon, and nickel cathode surfaces have been determined by measurement of the amount of deposited hydrogen required to raise the potential by a definite increment, and a comparison has been made of the catalytic activities of these surfaces by observation of the rate of hydrogen evolution. The effects of amalgamation and of treatment of the surfaces by alternate oxidation and reduction, annealing, etching with acid, electroplating, sand-papering, and rolling have been studied. The accessible area of bright platinum is about twice, whilst that of platinised platinum is about 2000 times its apparent area. If, however, the platinum is deposited on a mercury surface, the area is sensibly the same as that of mercury. The accessible area of a sand-papered metal is about ten times its apparent area, and in the case of nickel, activation by alternate oxidation and reduction causes an increase of nearly fivefold. Cold rolling reduces the accessible area. The specific catalytic activities of the various metals for the electro-deposition of hydrogen are found to differ very widely, but for any one metal the specific activity of the surfaces shows only small variations with chemical or thermal treatment. The effect of



alternate oxidation and reduction is chiefly to increase the accessible area by altering the grain size. Violent mechanical treatment, however, although it increases the surface to a much smaller extent, increases the proportion of surface atoms which are out of the crystal lattice and are catalytically the most active. The increase of activity gradually diminishes with ageing of the cathode.

L. L. BIRCUMSHAW.

**Benzyl ether as a cryoscopic solvent.** G. M. BENNETT and G. H. WILLIS (J.C.S., 1928, 2305—2307).—Benzyl ether purified by fractional freezing has m. p. 3·60°, b. p. 184°/2 mm., mean cryoscopic constant 62·7, and latent heat of fusion 24·4. For benzoic and acetic acids the apparent mol. wt. is less than when benzene is used as solvent, but the values are the same for benzyl alcohol. This is said to be due to the tendency for ethers to form complexes with hydroxylic substances.

J. GRANT.

**Cryoscopic determination of the molecular equilibria of resorcinol and pyrocatechol in aqueous solution.** F. BOURION and C. TUTTLE (J. Chim. phys., 1928, 25, 485—496; cf. this vol., 233).—At 0°, equilibria exist between simple and triple molecules in solutions of resorcinol (0·7–3*M*) and pyrocatechol (0·3–1·25*M*), but for concentrations less than 0·7*M* and 0·3*M*, respectively, no equilibria were detectable between simple and double molecules. At 100°, the ranges of concentration for single–double molecules are 0·375–1·25*M* and 0·25–1·0625*M*, and for single–triple molecules 1·375–2*M* and 1·125–1·875*M*, for resorcinol and pyrocatechol, respectively. The association of resorcinol decreases and that of pyrocatechol increases with rise in temperature, and the heats of association of 3 molecules to a triple molecule in aqueous solution at constant volume are +600 and –2400 g.-cal., respectively. J. GRANT.

**Dielectric constants of solutions of electrolytes.** H. HELLMANN and H. ZAHN (Ann. Physik, 1928, [iv], 86, 687—716).—A reply to Walden, Ulich, and Werner (this vol., 14). The experimental method used by the latter is regarded as subject to errors which are unimportant in the study of non-conducting liquids, but increase in significance as the conductivity increases. Theoretical and experimental evidence is adduced which tends to show that the recorded large decrease in dielectric constant in solutions of electrolytes is not real.

R. A. MORTON.

**Absorption spectra of solutions of cobalt chloride, cobalt bromide, and cobalt iodide in concentrated hydrochloric, hydrobromic, and hydriodic acids.** W. R. BRODE and R. A. MORTON (Proc. Roy. Soc., 1928, A, 120, 21—33).—By means of the apparatus previously described (cf. this vol., 458), a more detailed study has been made of the absorption spectrum of cobalt chloride in concentrated hydrochloric acid in the blue and green portions of the visible spectrum (400—600  $\mu\mu$ ). An extension of the analysis previously applied to the selective absorption between 600 and 720  $\mu\mu$  to the whole of the absorption spectrum under investigation indicates that the fine structure in the blue and green regions is a continuation of the vibrational system previously observed (*loc. cit.*). The absorption spectrum of

cobalt bromide in hydrobromic acid has also been determined throughout the visible portion of the spectrum, and that of cobalt iodide in hydriodic acid between 500 and 900  $\mu\mu$ , by a combination of visual and photographic methods. The absorption of the systems investigated is clearly influenced by the nature of the anion; the replacement of a lighter by a heavier halogen atom causes a shift of the absorption bands in the direction of lower frequencies, and increases the intensity of the low-frequency components as compared with the high-frequency components of the principal band. In the case of cobalt chloride, the resolution of the principal band into its components can be made only on the assumption of six constituents, and this probably holds also for the bromide and iodide. By this method of analysis, the principal band is composed in all cases of component bands, the frequencies of which are from 35 to 40 times the constant frequency difference between these components, this frequency difference being 12·28, 11·70, and 10·79 *f*, respectively, for the chloride, bromide, and iodide systems. L. L. BIRCUMSHAW.

**Refraction and dissociation of electrolytes.**

II. In methyl and ethyl alcohol. E. SCHREINER (Z. physikal. Chem., 1928, 135, 461—472; cf. this vol., 708).—The molecular refraction of hydrochloric acid and of lithium chloride in methyl and in ethyl alcohol has been measured. The refraction falls with increase of concentration, probably due to a deformation of the medium due to solvation of the cations. The refraction is greatest in water, less in methyl alcohol, and least in ethyl alcohol. The dissociation constants of the first and second kinds of hydrochloric acid in water are discussed.

W. E. DOWNEY.

**Chemical change of acids and salts in solution from the point of view of refractometric data.** A. HANTZSCH and F. DÜRIGEN (Z. physikal. Chem., 1928, 136, 1—17).—Measurements have been made of the densities and refractive indices of aqueous and alcoholic solutions of various acids and their alkali and alkaline-earth salts (cf. this vol., 834).

H. F. GILBE.

**Affinity between asymmetric ions. I and II.** S. W. BERGMAN (Arkiv Kemi, Min., Geol., 1928, 9, Nos. 34 and 42, 1—21, 1—11).—I. Conductivity measurements at 18·0±0·2° have been made with solutions of cinchonine *d*- and *l*-mandelates, cinchonine *d*- and *l*-tartrates, and quinine *d*- and *l*-camphorsulphonates. The values for  $\Lambda$  for each pair of diastereoisomeric salts were found to be approximately equal. Measurements of  $[\alpha]_{D}^{25}$  for cinchonine *d*-, *l*-, and *r*-mandelates show that the values  $[\alpha]_d - [\alpha]_l$  are about the same as  $[\alpha]_l - [\alpha]_r$  and  $[\alpha]_{D}^{25}$  the same as for ammonium *l*-mandelate. There is thus no difference in affinity between optically active acids and bases (cf. Marckwald and Chwolle, A., 1898, ii, 371). The difference in solubility of diastereoisomeric salts is explicable in terms of the energy content of the crystal lattice, and the Bjerrum dissociation theory affords a satisfactory explanation of the results.

II. A series of density determinations has been made with 8 pairs of crystalline and anhydrous

diastereoisomeric salts. The results show that in general the heavier salt has the smaller solubility.

H. BURTON.

**Affinity. III and IV.** H. VON EULER (Arkiv Kemi, Min., Geol., 1928, 9, Nos. 30 and 44, 1—6, 1—6).—Theoretical. The author cites examples of fission which may be explained in terms of the affinity between reactant groups and atomic groups of the substrate.

H. BURTON.

**Copper hydrosols of low electrical conductivity.** G. T. R. EVANS (Trans. Faraday Soc., 1928, 24, 409—412).—Very dark brown copper sols, of specific conductance less than 0.6 mho, may be prepared by striking an arc between a heavy rotating copper cathode and a light copper anode in a cooled vessel containing water of low conductivity. About 8—10 amp. at 80 volts are passed for 2 hrs. and the resulting sol is kept for a day so that the larger particles torn from the electrodes may settle.

F. G. TRYHORN.

**Protected silver hydrosols. VI. Sol formation by irradiation.** J. VOIGT (Kolloid-Z., 1928, 45, 319—322).—In order to reduce very dilute solutions of silver nitrate (0.106—0.0106%) and silver oxide (0.005%) by irradiation with a quartz—mercury lamp, the presence of reduction centres is necessary. Sols are not obtained, therefore, after the solutions have been passed through an ultra-filter. Pure gum arabic, before and after irradiation, cannot reduce dilute silver nitrate. Irradiation of a mixture of silver solution and gum arabic effects reduction, giving a precipitate with visible light and forming a silver sol with ultra-violet light. The submicrons of the gum arabic appear to act as reduction nuclei. Ultra-violet light has a peptising influence, for the precipitated silver can be dispersed to a yellow sol by shaking during irradiation.

E. S. HEDGES.

**Orange-coloured or orange-red colloidal gold solutions.** P. P. VON WEIMARN (Kolloid-Z., 1928, 45, 366—370).—Directions are given for the production of orange gold sols. Solutions of auric chloride and sodium citrate are mixed together in boiling distilled water and a small quantity of dilute potassium cyanide solution is subsequently added. The whole is then kept boiling for a period of many hours. Excess of potassium cyanide gives a quite colourless solution. The sols remain stable for some months; they generally become pure red in time. The change from orange-red to orange on addition of potassium cyanide is considered to be caused by the greater velocity of dissolution of the red colouring ultramicro-crystals of gold. Examples are also given of orange gold sols, the colour of which is due to suspension of a red sol in a yellow dispersion medium (often produced by the action of alkali on reducing substances such as sugar etc.), and it is pointed out that the colour of a sol is not a safe guide to its degree of dispersion.

E. S. HEDGES.

**Colloidal platinum. IV. Existence of hexahydroxyplatinic acid in colloidal platinum solutions.** S. W. PENNYCUICK (J.C.S., 1928, 2108—2117; cf. this vol., 476).—When the clear solution obtained after coagulation of a platinum sol by freezing is conductometrically titrated, curves are

obtained which are closely similar to those obtained with hexahydroxyplatinic acid,  $H_2Pt(OH)_6$ , the only known strong platinic acid. The acid, lower hydrates of which are probably also present, is probably produced by oxidation during the atomisation of the platinum, and forms part of the colloidal micelle. Its ionisation at the surface would account for the stability of the colloid, coagulation by bases being due to neutralisation. Initial preservation of the acid by means of a freezing mixture is essential for the preparation of a strong stable sol.

J. GRANT.

**Stability of colloidal ferrous phosphate prepared by means of gelatin or blood-serum.** M. MESSINI (Kolloid-Z., 1928, 45, 322—325).—Following the observation that intravenously injected ferrous sulphate is transformed in the animal body to colloidal ferrous phosphate, the stability of colloidal ferrous phosphate in presence of gelatin and of blood-serum has been studied. The material was prepared by mixing solutions of sodium phosphate and ferrous sulphate in presence of the colloid, and the time interval between mixing and the appearance of flocculation was noted. The protective action of gelatin is observable at a concentration of 2.5 g. per litre and reaches a maximum at 12.5 g. per litre, thereafter remaining constant. The smaller the concentration of ferrous phosphate the greater is its stability; the colloid remains stable for an indefinitely long period at a concentration of 0.006 g. per litre and in presence of 12.5 g. per litre of gelatin. Similar results were obtained with ox-blood serum as the protective colloid. The protective effect is observed at a concentration of 100 c.c. per litre and the colloid seems to be permanently stable when the concentration of ferrous phosphate is 0.006 g. per litre and that of serum 700 c.c. per litre.

E. S. HEDGES.

**Influence of concentration of a sol on its stability.** S. G. CHAUDHURY (J. Physical Chem., 1928, 32, 1231—1235).—Mainly polemical against Ghosh and Dhar (A., 1927, 305, 617). The possibility that a decrease in the charge of a sol with dilution will tend to sensitise it has been overlooked by previous workers. In explanation of the variation of the coagulating concentration for different electrolytes with dilution it is suggested that the diminution of the charge and of the total surface of sol particles with dilution tends to make the sol unstable if the potential at which the sol coagulates and the relative adsorption of all ions on the surface remain unchanged. The greater distances between the particles of a diluted sol favour stability.

L. S. THEOBALD.

**Particle size in precipitated zinc sulphide.** G. R. LEVI and C. G. FONTANA (Atti R. Accad. Lincei, 1928, [vi], 7, 502—508).—The particle size of zinc sulphide, obtained by passing excess of hydrogen sulphide into solutions of zinc salts, has been examined by an X-ray method. The solutions used were *N*-zinc sulphate with, respectively, *N*-sodium hydroxide, *N*-ammonia solution, *N*-acetic acid, and *N*-acetic acid with *N*-ammonium acetate. The precipitate was kept for 24 hrs. before examination; the following values were obtained for the particle size, respectively: 19.74, 18.60, 20.60, and 22.00 Å.

R. W. LUNT.

**Combining power of chromic oxide sol with acids and bases.** R. WINTGEN and H. WEISBECKER (*Z. physikal. Chem.*, 1928, 135, 182—198).—The fact that acids and bases have affinity for chromic oxide sol may be due to adsorption or salt formation. The experimental data agree within the limits of error with equations based on hydrolysis. The conception of chromic oxide sol as a colloidal solution of an amphoteric electrolyte is confirmed by the fact that the isoelectric point observed agrees with that calculated from the dissociation constants of acids and bases. The adsorption isotherm allows results to be obtained which are in tolerably good agreement with experimental values.

R. A. MORTON.

**Action of X-rays on colloidal ceric hydroxide.** J. A. V. FAIRBROTHER (*Phil. Mag.*, 1928, [vii], 6, 385—401; cf. *A.*, 1927, 935).—Irradiation by X-rays of ceric hydroxide sol is accompanied by a rise in viscosity, the rate of increase becoming rapidly larger with increasing doses of X-rays, until eventually the sol sets to a gel. The dose necessary to gel the sol decreases linearly with the time, suggesting that the ageing effect and the action of radiation are additive. The dose required to produce the maximum viscosity lowering in a diluted sol decreases as the stock solution ages; a dose sufficiently in excess of this gels the sol immediately. As the minimum viscosity is approached the percentage decrease in the size of the particles is proportional, in fact almost equal, to the fractional change in viscosity. Beyond the minimum point gelation occurs and the particles show a maximum increase to 1.6 times their normal size; this gelation takes several hours for completion in a dilute sol unless irradiation, which accelerates the process, is prolonged sufficiently. Theoretically, the viscosity (referred to that of water) should be a parabolic function of the dose applied; experiment does not bear this out, probably because the theory assumes the particles do not change in size.

S. K. TWEEDY.

**Dissolution of colloidal silver in hydrogen peroxide.** H. KOLLER-AEBY (*Kolloid-Z.*, 1928, 45, 371—374).—In the catalytic decomposition of hydrogen peroxide by colloidal silver, the catalyst does not remain unchanged, and the change undergone depends on the concentration of the sol. In general, the sol changes from a dark brown to a yellowish-brown, but at certain concentrations the colour vanishes completely and the solution fails to show a Tyndall cone. In this change there has been observed an intermediate stage in which the sol has a steel-blue colour. Various experiments with these sols are described. It is suggested that, in the reaction between colloidal silver and hydrogen peroxide, silver oxide or other oxidation products are formed.

E. S. HEDGES.

**Rôle of dielectric constants, polarisation, and dipole moment in colloid systems, especially in non-aqueous media.** III. The behaviour of organosols containing electrolytes. Wo. OSTWALD (*Kolloid-Z.*, 1928, 45, 331—345).—The orientation polarisation of a platinum alcohol sol prepared by Errera's electrical disintegration method is the same as that prepared by Svedberg's method, although

traces of water are not excluded in the former case. For both types of sol, substances which have not a flocculating effect have not only high dielectric constants, but also high dipole moments; conversely, liquids with very weak dipole moments (benzene, hexane, carbon tetrachloride) have the greatest coagulating effect, whilst toluene and ethyl ether (with slightly higher dipole moments) are more feeble coagulating agents. The chemically-prepared metal sulphide alcohol sols of Errera contain electrolytes and differ from the preceding examples. Although substances with small dielectric constant and low dipole moment are the best flocculants, substances with high dipole moments (*e.g.*, isoamyl alcohol) also can coagulate. Further, medium and not maximal concentrations of benzene, hexane, etc. produce the most effective coagulation. This result is unintelligible on the assumption that only the dielectric constant is concerned with the flocculating power. There is, however, a close agreement between the coagulation optimum and the maximum of the molecular polarisation calculated by Debye for alcohol in a dipole-free solvent. The stabilising adsorption layer of the sulphide alcohol sols consists not only of ions, but also of alcohol dipoles; it is considered as a diffuse double layer. In the process of flocculation, a desorption of ions to below the stabilising concentration must occur by the addition of another organic liquid and an adsorption minimum has been established, which agrees with the coagulation optimum. The relation between adsorbability and dipole content is discussed and also that between dipole content and solubility.

E. S. HEDGES.

**Structure viscosity of some sols of polymeric carbohydrates.** S. TSUDA (*Kolloid-Z.*, 1928, 45, 325—331).—A capillary viscosimeter having a horizontal capillary is described; it is especially suitable for the study of structure viscosity of colloids at different rates of flow. The Hagen-Poiseuille law is not valid for the viscosity of starch paste, but the three equations of Wo. Ostwald hold, and the properties of the constants of these equations have been studied with starch solutions of different concentrations. The relation between the relative viscosity and the concentration of the starch solution is expressed approximately by the Arrhenius formula, the constants of the formula being determined, not only by the substance, but also by the dimensions of the viscosimeter and by the pressure. At 50°, the viscosity of agar sol follows the Hagen-Poiseuille law, but at 30° it is in accordance with the de Waele-Ostwald law; when subsequently reheated at 50°, the sol still obeys the latter law for some time, but eventually reverts to its original condition.

E. S. HEDGES.

**Streaming potential and colloid stability.** II. H. R. KRUYT and P. C. VAN DER WILLIGEN (*Kolloid-Z.*, 1928, 45, 307—319).—Measurements of the streaming potential at a glass capillary have given the following results. The discharging effects of alkali metal ions are unequal, lithium having the least and caesium the greatest effect. Similarly, magnesium chloride has a greater discharging effect than barium chloride, the latter being nearly equal to hydro-

chloric acid. Tervalent cerium, lanthanum, aluminium, and hexamminocobaltic chlorides, and thorium tetrachloride, a quadri- and a sexa-valent cobalt salt, and a quadrivalent platinum salt were investigated. The discharging effect of the aluminium ion is observed when the concentration is one hundredth of that necessary with the other trivalent salts. The discharge is not connected with hydrolysis. Variation of the anion in a series of potassium salts does not influence the discharging effect, with the exception of the hydroxyl ion, which gives a strong increase in charge. Potassium hydroxide was found also to give a strong charge to capillaries of Jena glass and of quartz. The variation in the discharging effect of different ions of the same valency is ascribed to differences in the density of charge of the hydrated ions. The true *P.D.* between glass and pure water is considered to be indeterminable, since it is greatly affected by small changes in a large number of factors.

E. S. HEDGES.

**Liquid phase rule in the formation of oil emulsions.** R. KÖHLER (Kolloid-Z., 1928, 45, 345—348).—The amount of olive oil or pea-nut oil containing oleic acid which can be emulsified by dilute sodium carbonate or sodium hydroxide is dependent on the amount of oil present, when the alkali concentration and the total volume of aqueous solution remain constant. For small concentrations of alkali and with small amounts of free fatty acids in the oil, the amount emulsified is greatest for a medium amount of oil. The optimum amount of oil increases with increasing alkali concentration. The observations are in agreement with Wo. Ostwald's solid phase rule of adsorption peptisation. Reference is made to the technical bearing of these results. E. S. HEDGES.

**Model of the Pickering emulsion.** R. E. LIESEGANG (Kolloid-Z., 1928, 45, 370—371).—The objects are to show by visual demonstration (1) the partition of a substance in an emulsion and (2) that sodium chloride can act as a solid sheath to the particles. When chloroform is shaken with a dilute solution of methylene-blue, the drops afterwards run together and form a red layer at the bottom of the vessel; the aqueous top layer is blue. If sodium chloride has been dissolved in the methylene-blue solution, the whole of the colour goes into the chloroform layer. Chloroform remains unaltered when shaken with powdered sodium chloride, but when the mixture is covered with a layer of methylene-blue solution the drops of chloroform no longer run together after shaking, each blue drop being coated with a white sheath of undissolved sodium chloride. The diameter of the droplets may be 4 mm. and this is reduced to 1 mm. or less by increasing the amount of sodium chloride. With decrease in the size of droplets the volume of the paste-like mass increases, so that finally no separate aqueous phase is discernible.

E. S. HEDGES.

**Colloidal state of gelatin solutions and the effect of temperature changes.** M. FRANKEL (Kolloid-Z., 1928, 45, 355—366).—The colloidal character of gelatin solutions undergoes a complete change with gentle heating, the extent of the change depending on the duration of the treatment. This

phenomenon is termed dissociation. A study has been made of the lowering of viscosity, increase in dialysis, decrease in tendency to gelatinise, and the change in optical properties accompanying dissociation. Experiments on the effect of pepsin on gelatin solutions of different degrees of dissociation have shown that in all cases the same reaction products are formed and that the readiness to react is connected with the progress of dissociation. A constant temperature is necessary in order to obtain constant properties in a gelatin solution. The time required for production of a stable state depends on the temperature and is generally considerable (about 75 hrs.). The influence of temperature is most marked between 5° and 40°; outside these limits, constant properties are more quickly attained. The stable solutions are still affected by further changes of temperature; heating causes more dissociation, whilst cooling causes association. The changes are reversible, provided the alterations of temperature take place sufficiently slowly. Solutions of different degrees of association become closely similar when heated.

E. S. HEDGES.

**Absorption of water by gelatin. II. The nitrate system.** D. JORDAN-LLOYD and W. B. PLEASS (Biochem. J., 1928, 22, 1007—1018).—Sodium nitrate up to a concentration of 0.6*M* in the presence of nitric acid suppresses the swelling of gelatin due to acid. At greater concentrations its effect depends on the  $p_H$ . From  $p_H$  4.0 to 3.5 increasing salt concentration causes swelling; at  $p_H$  3.0 it causes coagulation of the gelatin; at 2*M* coagulation occurs at all  $p_H$  values less than 2.3, but dissolution at all values greater than 2.3. At  $p_H$  4.1 over a range of 0—0.7*M* nitrates have no effect on swelling; beyond this range they dissolve the gelatin. Up to a concentration of 0.1*M* sodium nitrate in the presence of sodium hydroxide suppresses the swelling of gelatin due to the alkali. At concentrations greater than this increasing concentration of nitrate is accompanied by an increase in swelling directly proportional to the concentration of the salt present. In solutions more concentrated than 0.1*M* the gelatin is dissolved at 18°. The swelling of gelatin due to nitric acid and sodium hydroxide increases as an exponential function of the temperature. At the isoelectric point ( $p_H$  5.0) sodium nitrate promotes water absorption, swelling being proportional to the logarithm of the concentration of the salt up to 0.1*M*. At greater concentrations swelling is directly proportional to the concentration of the nitrate. Over a  $p_H$  range from 5 to 10 and at concentrations of salt greater than 0.1*M* swelling in solutions of sodium nitrate is influenced only by the salt concentration and is independent of the  $p_H$ . At  $p_H$  5.0 a rise of temperature from 0° to 12° is accompanied by an increase in swelling which is the same in the absence of nitrate and at all concentrations of nitrate up to 1*M*. In the absence of salt, swelling is at a maximum at 12° and in dilute solutions of nitrate at about 15—18°; in more concentrated solutions there is no temperature of maximum swelling, the gelatin passing into solution as the temperature is raised. The temperature of dissolution is lower the greater is the concentration of

nitrate present. At  $p_H$  7.0 in the absence of salt or in dilute solutions of nitrates the effect of temperature on swelling is similar to its effect at  $p_H$  5. The temperature influences the position of minimum swelling at varying concentrations of nitrate, the salt concentration registered at this point diminishing with rising temperature. S. S. ZILVA.

**Influence of organic substances on the thixotropy of ferric oxide sol.** H. FREUNDLICH and K. SÖLLNER (Kolloid-Z., 1928, 45, 348—355).—The liquefying action of amino-acids on a thixotropic sol cannot be related to the diminution in hydrogen-ion concentration (which rather promotes setting), for addition of amino-acids (glycine, alanine) both to concentrated, thixotropic ferric oxide sols and to dilute, non-thixotropic sols lowers the hydrogen-ion concentration. The action is considered to be due to the tendency of amino-acids to form complex ferric salts, which are notably hydrophilic. The complexes bound to the colloid particle increase in water content and favour sol formation. Other substances (*e.g.*, sugar) which form complexes with ferric salts also influence the thixotropy in the same sense as do amino-acids. Contrary to results formerly obtained with small quantities of glycine, larger amounts have a peptising effect on ferric oxide sols and thus raise the coagulation value. The relation between time of setting,  $\theta$ , and electrolyte concentration,  $c$ , can be expressed for ferric oxide sols by the formula  $\theta = e^{-k \cdot c}$ , where  $k$  is a constant. E. S. HEDGES.

**Cataphoresis in copper oxide sols. Application of Debye and Hückel's theory of electrolytic conduction to colloid particles.** H. H. PAINE (Trans. Faraday Soc., 1928, 24, 412—429).—Measurements were made of the mobility of particles in copper oxide sols before and after addition of electrolytes. The highest mobility observed was  $52.8 \times 10^{-5}$  cm. per sec. per volt for a colloid solution of specific conductance  $0.46 \times 10^{-6}$  mho. Extrapolation indicated a mobility of about  $60 \times 10^{-5}$  unit for sols of zero conductance. The mobilities are reduced by the addition of electrolytes, the proportional decrement diminishing with increase in the amount of the electrolyte. The greater is the valency of the ion carrying a charge opposite in sign to that carried by the particles, the greater is its effect in reducing the mobility of the copper oxide particles. By the application of the theory of Debye and Hückel it follows that the addition of an electrolyte should cause a decrease in mobility from the value at zero electrolyte concentration which is directly proportional to the square root of the concentration of the electrolyte. This relationship is confirmed by results of measurements with copper oxide sols, and by reference to the data of Freundlich and Zeh for ferric oxide and arsenious sulphide sols. F. G. TRYHORN.

**Optical measurement of small degrees of dissociation of the vapours of metallic salts.** I. WYNEKEN (Z. physikal. Chem., 1928, 136, 146—158).—By comparison of the intensity of the mercury absorption line at 2536 Å. in mercuric chloride vapour with that of the same line in pure mercury vapour at known pressures, the degree of dissociation of the salt has been determined. At 180°,  $\alpha$  is  $2.2 \times 10^{-4}$ ,

and at 250°,  $6.5 \times 10^{-4}$ , in fair agreement with the values obtained theoretically by application of the Nernst heat theorem. H. F. GILLBE.

**Hydrolysis in solutions of potassium laurate as measured by extraction with benzene.** J. W. MCBAIN and M. EATON (J.C.S., 1928, 2166—2179; cf. this vol., 128).—A study has been made of solutions of potassium laurate with and without the addition of alkali or lauric acid. The hydrolysis of the soap solutions depends only on the simple fatty ions and its magnitude is determined by the extent of the conversion of the fatty acid into acid soap. Unaltered soap solutions contain only slight traces of the free fatty acid. The existence of a definite crystalline compound, potassium hydrogen laurate, reported by Oudemann (Jahresber., 1863, 331), has been confirmed.

F. J. WILKINS.

**Effect of salts on weak electrolytes. I. Dissociation of weak electrolytes in the presence of salts.** H. S. SIMMS (J. Physical Chem., 1928, 32, 1121—1141; cf. A., 1926, 681).—The influence of ionic strength on the activity coefficients of weak electrolytes as shown by the effect on the dissociation indices (the negative logarithm of the dissociation constant) has been investigated by means of titration data obtained from 0.01 *M*-solutions of various organic acids, bases, and ampholytes alone and in the presence of sodium chloride and of magnesium chloride. The value of the dissociation index ( $P_1$ ) is calculated and plotted against the square root of the ionic strength; the slopes of the resulting curves show the extent of the agreement between the activities found and those required by the Debye-Hückel equation. Singly-charged anions from uni- or bi-valent acids satisfy the Debye-Hückel equation in the presence of sodium chloride, magnesium chloride, or the salt of a weak acid. Multivalent anions in the presence of sodium chloride obey a form of this equation modified to include a correction for the distance between the charges. With magnesium chloride, the behaviour is anomalous, the effect being greater with oxalic, malonic, and citric acids than with succinic, azelaic, and sebamic acids. Sulphate ions produce an effect on uni- and bi-valent anions which is opposed to that of the magnesium ions. Cations from amines and amino-acids show a deviation from the Debye-Hückel relationship with both magnesium and sodium chlorides. The isoelectric points fall with an increase in ionic strength.

L. S. THEOBALD.

**Mean activity coefficient of the hydrogen ion, and of the hydrogen carbonate ion in potassium chloride and concentrated sodium chloride solutions. Dissociation constant of some indicators in these solutions.** E. GUNTEMBERG and E. SCHIÖDT (Z. physikal. Chem., 1928, 135, 393—443).—The mean activity coefficient of the hydrogen and hydrogen carbonate ion,  $\sqrt{f_H \cdot f_{HCO_3}}$ , and the apparent first dissociation constant of carbonic acid,  $K_c = c_H \cdot c_{HCO_3} / (c_{CO_2} + c_{H_2CO_3})$ , in potassium chloride solutions from 0.1 *N* to 3 *N*, and in sodium chloride solutions of 3 *N*, 4 *N*, and 5 *N*, have been measured. The value of  $K_c$  behaves as with other weak acids; it rises from  $3.2 \times 10^{-7}$  in pure water to more than

three times this value in *N*-potassium chloride solution, and then begins to fall; in saturated sodium chloride solution it is only 30% higher than in pure water. The difference between these values and those found by Szyszkowski (A., 1907, ii, 238) and Wilke (A., 1922, ii, 52) are discussed. The dissociation constants of methyl-orange, bromophenol-blue, and dimethyl-yellow were measured in the same solutions. It was found that the salts have a characteristic effect on the dissociation of those acids which yield a univalent cation and a mixed ion. The mean activity coefficient and the dissociation constant of benzoic acid in 3*N*-potassium chloride and in 3*N*-, 4*N*-, and 5*N*-sodium chloride were also measured. Benzoic acid has an unusually high activity coefficient in these solutions. The errors in colorimetric  $p_n$  determination due to the presence of salts are discussed. W. E. DOWNEY.

**Polyiodide equilibrium in aqueous and salt solutions.** J. S. CARTER (J.C.S., 1928, 2227—2230).—The values of  $K$  for the equilibrium  $I' + I_2 \rightleftharpoons I_3$  which may be derived from the solubility of iodine at 25° in solutions of sodium iodide in (a) water and (b) 1.7*M*-sodium sulphate solution are not constant, and indicate that the tendency to form higher polyiodides increases with increasing initial concentration of iodide. Both iodide and polyiodide are assumed to be completely ionised. The relation between active masses and actual concentrations is much closer than would be expected from considerations of the activities. Determinations of  $K$  from the distribution ratio, based on the assumption that neither the iodide nor the polyiodide affects its value, show that in dilute solutions the whole of the iodine is present as tri-iodide, but that more complex periodides exist in concentrated solutions. J. GRANT.

**Transition temperature of carbon tetrachloride as a fixed point in thermometry.** J. C. McCULLOUGH and H. E. PHIPPS (J. Amer. Chem. Soc., 1928, 50, 2213—2216).—A transition from cubic to monoclinic carbon tetrachloride is shown by the thermometric method to occur at  $-48.54 \pm 0.02^\circ$ , and this is suggested as a thermometric fixed point. S. K. TWEEDY.

**Influence of pressure on the high-low inversion of quartz. High-low inversion of quartz and the heat capacity of low quartz at 573°.** R. E. GIBSON (J. Physical Chem., 1928, 32, 1197—1205, 1206—1210).—I. The temperature of the high-low inversion of quartz under uniform hydrostatic pressures from 1 to 3000 megabars has been determined in an apparatus similar to that described by Smyth and Adams (A., 1923, ii, 490). The temperature of the high-low inversion rises according to the equation  $\Delta T = -0.3 + 2.1 \times 10^{-2}p + 8.6 \times 10^{-7}p^2$ , where  $p$  is the pressure in megabars. From the initial pressure coefficient and the "instantaneous volume change" at 575°, the latent heat of inversion calculated by means of the Clausius-Clapeyron equation is 3.1 g.-cal./g.

II. Heating and cooling curves for two cylinders of quartz confirm the observation of Bates and Phelps (A., 1927, 1018) that the high-low inversion of quartz

is a phase change which is generally accompanied by superheating and supercooling. At  $572.3^\circ \pm 0.2^\circ$ , it appears that low-quartz may be converted reversibly into high-quartz and only experimental difficulties prevent the two phases being obtained in equilibrium at this temperature. An hypothesis of forced inversion is unnecessary. Low-quartz before passing to the high variety superheats to such an extent that during the inversion the temperature never falls to the equilibrium value. The apparent heat capacity of the low form at 573° is calculated to be  $4 \pm 1$  g.-cal./g. per degree. Quartz at 570° is distinct from quartz at the ordinary temperature, and the inversion at 573° is comparable with any rapid enantiotropic change. L. S. THEOBALD.

**Dissociation of liquid crystals.** A. MŁODZIEJOWSKI (Z. physikal. Chem., 1928, 135, 129—146).—Liquid crystals having upper and lower dissociation temperatures have been obtained in which the only stable state of aggregation over a certain temperature range must be the liquid crystal state. Mixtures of cholesterol and cetyl alcohol form liquid crystals yielding two solid phases at the lower dissociation temperature and a liquid and a solid phase at the upper temperature. Liquid crystals formed from cholesterol-glycerol mixtures yield a solid and a liquid phase, and two liquid phases at the lower and upper dissociation temperatures, respectively. The possible diagrams corresponding with the above phenomena have been constructed on thermodynamic principles, and from the theoretical data the diagram corresponding with the cholesterol-glycerol system has been identified. The advantages of combining microthermal analysis with the thermodynamic deduction of diagrams in orienting work of the above type are discussed. R. A. MORTON.

**Decomposition pressure of sulphuric acid containing nitrogen compounds.** A. SANFOURCHE and L. RONDIER (Bull. Soc. chim., 1928, [iv], 43, 815—826).—A more detailed account of work already published (this vol., 943).

**Equilibrium diagram of the system antimony-arsenic.** Q. A. MANSURI (J.C.S., 1928, 2107—2108).—The thermal diagram shows that antimony and arsenic form a complete series of solid solutions but no chemical compound. The curve has a minimum at 605° (13% As). Micrographic analyses of the etched alloys show that all consist of a single constituent with some coring, fairly large six-sided crystals being observed in the alloy containing 80% As. J. GRANT.

**Equilibrium diagram of the copper-silicon system.** K. MATSUYAMA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 665—673).—The copper-silicon diagram has been re-determined and in essentials confirms that given by Rudolphi. The liquidus consists of four branches corresponding with the separation of the  $\alpha$ ,  $\beta$ , and  $\delta$  solid solutions and pure silicon. The  $\beta$  solid solution decomposes on cooling into  $\alpha$  and  $\gamma'$ , with a eutectoid at 795°. Two compounds,  $Cu_5Si$  and  $Cu_3Si$ , exist. The eutectic of silicon and  $Cu_3Si$  melts at 805° and contains 17% Si.

C. J. SMITHELLS.

**Equilibrium diagram of the aluminium-calcium system.** K. MATSUYAMA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 783—789).—The liquidus of the aluminium-calcium system consists of four branches corresponding with the separation of the  $\alpha$  solid solution,  $\text{CaAl}_3$ ,  $\text{CaAl}_2$ , and calcium, respectively. Aluminium dissolves 0.3% of calcium at the ordinary temperature and 0.6% at 616°. Alloys containing 0.6—33.03% Ca are eutectiferous, the eutectic containing 7.55% Ca and melting at 616°. Alloys containing 13.9—42.5% Ca undergo a peritectic reaction on cooling below 700°, forming  $\text{CaAl}_3$ . The liquidus has a maximum of 1079° at 42.5% Ca, corresponding with  $\text{CaAl}_2$ . Alloys containing more than 42.5% Ca are eutectiferous, the eutectic containing 73% Ca and melting at 545°.

C. J. SMITHELLS.

**Decomposition of alkaline-earth sulphates.**

IV. J. ZAWADZKI, I. KOWALCZEWSKI, and S. ZEROMSKI (Rocz. Chem., 1928, 8, 358—368).—Gypsum passes irreversibly and with considerable velocity into anhydrite at temperatures above 1000°. Measurements of the decomposition pressures of gypsum indicate that the influence of the irreversible subsidiary reaction increases with rise in temperature. The decomposition pressures of anhydrite between 1100° and 1220° are considerably lower than for gypsum, and are equal to those given by gypsum after long heating. The thermal decomposition of anhydrite is reversible, anhydrite being obtained by the action of sulphur trioxide on a mixture of 6 parts of calcium oxide with 1 part of sulphate. Anhydrite decomposes to form the basic sulphate,  $2\text{CaO}\cdot\text{SO}_3$ , the heat of reaction being  $-109.36$  g.-cal. The pressures of gas in equilibrium with basic sulphate at temperatures up to 1200° are lower than those found for anhydrite, and the same pressures have been attained by the partial saturation of calcium oxide with sulphur trioxide. R. TRUSZKOWSKI.

**Irreversible dehydration of some crystalline hydrated salts.** M. A. RAKUZIN (Bull. Soc. chim., 1928, [iv], 43, 744—747).—Studies of the dehydration and hydration of borax, Glauber's salt, and sodium carbonate have led to the conclusion that the phase rule may be applied only to those crystalline hydrated salts which undergo true thermal dissociation, although it cannot at present be said whether the dehydration reaction is one of dissociation or of decomposition. The spontaneous dehydration of sodium carbonate gives rise to a stable dihydrate and the anhydrite forms a monohydrate on re-hydration. J. GRANT.

**Transition points of compounds of organic solvents and salts.** H. OSAKA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 873—887).—The transition temperatures of compounds of inorganic salts with acetone have been determined cryoscopically, by observing the highest temperature reached when a crystal of the compound is added to a supercooled solution of the salt in acetone. C. W. GIBBY.

**System calcium oxide, silica, and water.** J. R. BAYLIS (J. Physical Chem., 1928, 32, 1236—1262; cf. Lerch and Bogue, this vol., 21).—The equilibria which are established between different amounts of calcium hydroxide in solution and the

hydrous oxides of silica have been investigated. A compound  $\text{CaO}\cdot\text{SiO}_2$  appears to be formed by the addition of calcium oxide to the washed silica gel obtained from sodium silicate and hydrochloric acid. This is followed by adsorption of further quantities of calcium oxide. The reversibility of the process is established, and it is shown that 30—45% of the calcium hydroxide united with the silica appears to be adsorbed by the compound initially formed. Surface equilibria due to adsorption may retard the rate of hydrolysis of some of the compounds in submerged concrete. Certain conclusions of Lerch and Bogue (*loc. cit.*) are criticised.

L. S. THEOBALD.

**System  $2\text{CaO}\cdot\text{SiO}_2$ — $\text{MgO}$ — $5\text{CaO}\cdot3\text{Al}_2\text{O}_3$ .** W. C. HANSEN (J. Amer. Chem. Soc., 1928, 50, 2155—2160).—The equilibrium diagram for the above system is given. There is no evidence that magnesium oxide forms a solid solution with, or replaces the lime in,  $5\text{CaO}\cdot3\text{Al}_2\text{O}_3$  or  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ .

S. K. TWEEDY.

**Ternary system strontium oxide-sucrose-water.** W. REINDERS and A. KLINKENBERG (Z. Elektrochem., 1928, 34, 406—407).—Polemical against Grube and Nussbaum (cf. this vol., 480).

L. L. BIRCUMSHAW.

**Mixed crystals, solutions, and fusions of the system  $(\text{K}\cdot\text{NH}_4)(\text{Cl}\cdot\text{NO}_3)$ .** E. JÄNECKE (Z. angew. Chem., 1928, 41, 916—924).—The fusion and solubility curves for the various possible binary and ternary systems are recorded. As all the salts except potassium chloride occur in several modifications, the diagrams are complicated. In the quaternary system, the stable solid pair at all temperatures is represented by the combination  $\text{NH}_4\text{Cl}+\text{KNO}_3$ . C. IRWIN.

**Composition of crystals obtained from solutions containing sodium sulphate and iodides.** III. (SIGMA.) E. FABRIS (Annali Chem. Appl., 1928, 18, 326—332; cf. A., 1927, 939).—The composition of crystals obtained from various solutions containing sodium sulphate and lithium iodide is investigated.

E. W. WIGNALL.

**Action of carbon monoxide on metallic chlorides.** L. BELLADEN and A. SOMMARIVA (Gazzetta, 1928, 58, 443—449).—If the action of carbon monoxide on metallic chlorides is determined by the equilibria  $\text{MCl}_2+\text{CO} \rightleftharpoons \text{M}+\text{COCl}_2$ ,  $\text{COCl}_2 \rightleftharpoons \text{CO}+\text{Cl}_2$ , and  $\text{MCl}_2 \rightleftharpoons \text{M}+\text{Cl}_2$ , the percentage of carbonyl chloride at equilibrium at 700° should be of the order of  $10^{-12}$ . Measurements were made of the quantity of carbonyl chloride produced when carbon monoxide was passed at various speeds over heated metallic chlorides, and the equilibrium quantity was obtained by extrapolating to zero velocity. With lead, silver, cupric, and nickel chlorides the percentages of carbonyl chloride formed at temperatures between 450° and 750° varied from 0.17 to 1.12. Since these values are much greater than those predicted for this reaction, it is suggested that a secondary reaction occurs,  $2\text{CO} \rightleftharpoons \text{C}+\text{CO}_2$ , followed by  $2\text{CO}_2 \rightleftharpoons 2\text{CO}+\text{O}_2$ , and  $2\text{MCl}_2+\text{O}_2 \rightleftharpoons 2\text{MO}+2\text{Cl}_2$ . Support is lent to this by the facts that barium hydroxide placed in the reaction tube is partly converted into carbonate, and that carbonyl chloride

(about 1.0%) is formed when pure carbon dioxide is passed over heated metallic chlorides.

F. G. TRYHORN.

**Thermodynamics based on statistics. I and II.** G. N. LEWIS and J. E. MAYER (Proc. Nat. Acad. Sci., 1928, **14**, 569—575, 575—580).—I. An attempt is made to derive the second law of thermodynamics in exact form from simple statistical principles, and also to obtain unambiguous definitions of correlated quantities such as temperature, pressure, and entropy. In defining the instantaneous state of a system it is unnecessary to consider in detail every mechanically significant property of each particle. The field of specification can be divided into a number of regions, and it is sufficient to describe the detailed state by specifying the number of molecules of each independent constituent comprised in each region. The possibility of finding a mode of partition into finite regions so that the individual detailed states are of the same order of probability is discussed, and the assumption made that not only is such a division possible for every system, but also that there is, for every system, a natural mode of partition into finite regions of this kind. It is not necessary to assume that the natural mode of division completely determines the sizes and shapes of the individual regions, but that it does determine completely the quantity  $\log \Omega$ , where  $\Omega$  represents the total number of recognisably different ways in which the particles can be distributed among the regions.

II. It is shown that the basic assumption laid down regarding the natural division of the field of specifications describing the states of individual particles into regions so as to give unique significance to  $\log \Omega$  includes within itself the second law of thermodynamics. The mode of partition for an ideal monatomic gas is considered. A. J. MEE.

**Thermodynamic equilibrium in the universe.** F. ZWICKY (Proc. Nat. Acad. Sci., 1928, **14**, 592—597).—The postulate of a thermodynamic equilibrium in the universe as ordinarily applied leads to conflicting results as regards the distribution of radiation in the universe and the equilibrium between matter and radiation. The basis of the problem must be extended if it is to agree with actual conditions, the postulate being applied to the whole chain of reactions: radiation = protons and electrons = higher nuclei = dust particles = gaseous nebulae = stars = swarms of stars (galactic systems). A consistent statistical treatment of the equilibrium of these different forms of matter in the universe on the basis of the postulate seems likely to give results in agreement with the facts. A. J. MEE.

**Thermodynamic integration factor for the derivation of the general form corresponding with the van der Waals-Clausius equation.** A. PRESS (Z. Physik, 1928, **49**, 306—310).—Mathematical. R. W. LUNT.

**Thermodynamic calculations [for hydrocarbons].** D. F. SMITH (Ind. Eng. Chem., 1928, **20**, 859—860).—Calculated free energy values for hydrocarbons are often based on unsatisfactory thermal data and are untrustworthy. Even when they are accurate, predictions relative to the products

of reactions which are based on free energy alone are fallacious, as the reaction velocity is an important additional factor. C. IRWIN.

**Free energy of formation of fused alkali hydroxides.** G. DEVOTO (Gazzetta, 1928, **58**, 450—457; cf. this vol., **135**, 955).—The polarisation curves for the fused hydroxides of lithium, sodium, and potassium have been derived by the method previously described. Owing to decomposition the values for lithium hydroxide are untrustworthy, but from the measurements with fused sodium hydroxide and potassium hydroxide the free energies of formation of these compounds have been determined for temperatures between 400° and 700°.

F. G. TRYHORN.

**Calculation of the fugacities of a solution.** G. VAN LERBERGHE (Bull. Acad. roy. Belg., 1928, [v], **14**, 349—371).—Mathematical. The formula for the fugacities of a solution previously deduced (Compt. rend., 1925, **181**, 851) may be derived by a simpler method. Analogous formulæ applicable to special cases of dissolution are derived by the asymptotic method of Donder (A., 1925, ii, 790) and the application of these to the systems carbon disulphide-methylal, ethyl iodide-ethyl acetate, water-sulphuric acid are considered. F. G. TRYHORN.

**Heat capacity and entropy of caesium alum from 18° to 300° Abs. Entropy of aluminium ion. Potential of the aluminium electrode from thermal data.** W. M. LATIMER and B. S. GREENSFELDER (J. Amer. Chem. Soc., 1928, **50**, 2202—2213).—The heat capacity of caesium alum measured between 18° and 300° Abs. gives the entropy at 298.1° Abs. as 163.85 g.-cal./1°. The f. p. of caesium and rubidium alum solutions were determined between 0.0017 and 0.0124*M*. The f.-p. depressions of the two salts are identical linear functions of the concentration. From these results the activity coefficients of the alums are computed. The heat of dissolution of caesium alum is  $+13,560 \pm 25$  g.-cal./mol. at 298.1° Abs., and from these results the entropy of the aluminium ion in hypothetical one-molal solution is  $-70.9$  g.-cal./1° per mol. at 298.1° Abs., giving  $+1.69 \pm 0.01$  volts as the potential of the aluminium electrode. S. K. TWEEDY.

**Heat of combustion of benzoic acid in international joules.** W. JAEGER and H. VON STEINWEHR (Z. physikal. Chem., 1928, **135**, 305—346).—The heat of combustion of benzoic acid has been redetermined using the same calorimeter as was used by Fischer and Wrede (*ibid.*, 1909, **69**, 218). The apparatus has been improved by the introduction of a stirring device underneath the bomb and an improved recorder for marking the commencement and end of the period of electrical heating used in standardising the calorimeter. The calculations involved in using a platinum thermometer to measure temperatures have been revised and an allowance has been made for the heat evolved by the iron wire used to start combustion. The applicability of Newton's law of cooling to the temperature rise of the calorimeter was tested and found valid. Benzoic acid of special purity from two sources was used. The mean result of seventeen experiments gave



26.437 kilojoules per g. at 19.3° as the heat of combustion of benzoic acid (cf. Fischer and Wrede, 26.449; Dickinson, 26.436). The mean of these three values, 26.441 kilojoules per g., together with the heat equivalent (1 g.-cal.=4.184<sub>2</sub> joules at 15°), gives 6319.3 g.-cal. per g. as the heat of combustion of benzoic acid. W. E. DOWNEY.

**Heat of dilution of solutions of low concentration.** S. M. NAUDÉ (Z. physikal. Chem., 1928, 135, 209).—Heats of dilution have been determined for the following: sucrose, chloral hydrate, glycine, carbamide, and mercuric cyanide; hydrochloric, nitric, sulphuric, salicylic, and benzoic acids; lithium and sodium chlorides and sodium nitrate. The results are in agreement with Nernst's theory (cf. this vol., 127, 368). R. A. MORTON.

**Heat of dilution of salts at low concentrations.** W. NERNST and W. ORTHMANN (Z. physikal. Chem., 1928, 135, 199—208).—See A., 1927, 733. R. A. MORTON.

**Strong electrolytes and the dependence of conductivity on *P.D.*** G. JOOS (Physikal. Z., 1928, 29, 570).—Polemical against Gyemant (this vol., 953). W. E. DOWNEY.

**Transport number of the cation in aqueous solutions of nickel salicylate.** F. E. JONES and C. R. BURY (J. Physical Chem., 1928, 32, 1272—1275; cf. A., 1927, 315).—Transport numbers determined at 25° throughout the range 0.02—0.2 mol./1000 g. water (maximum solubility at 25°) in aqueous solutions of nickel salicylate decrease from 0.612 to 0.573, and indicate that the salt ionises for the most part in a normal manner. The anomalous decrease in transport number with increasing concentration indicates the presence of small amounts of a complex acid ion. L. S. THEOBALD.

**Theoretical potential of alkaline-earth metals.** G. DEVOTO (Z. Elektrochem., 1928, 34, 326—327).—Polemical against Drossbach (this vol., 481). The results of Roth and Chall (*ibid.*, 593) are in close agreement with those of the author. L. F. GILBERT.

**Normal potential of the iodine-iodide electrode.** G. JONES and B. B. KAPLAN (J. Amer. Chem. Soc., 1928, 50, 2066—2076).—The change in activity of the iodide ion with dilution is computed from the *E.M.F.* of the concentration cells Ag, AgI | 0.1*N*-KI | *xN*-KI | AgI, Ag. Reproducible results were obtained only when *x* exceeds 0.02. The activity coefficients, *f*, at 25° are given by the formula (cf. Scatchard, A., 1925, ii, 397):  $\log f = 0.125c - 0.373\sqrt{c}$ . The *E.M.F.* of the cell Pt, I<sub>2</sub>(s) | 0.01*N*-KI | 0.1*N*-calomel electrode is -0.3374 volt at 25° and -0.3275 volt at 0°. The *E.M.F.* of the cells Pt | *xN*-KI + I<sub>2</sub>(unsat.) | *xN*-KI + I<sub>2</sub>(s) | Pt are recorded, where *x* = 0.01, 0.02, 0.05, and 0.1, the low concentration of the unsaturated solution being determined by means of the equilibrator (this vol., 863). From the results the normal potential of the saturated iodine-iodide electrode, with the iodide ion at unit activity, against the normal calomel electrode is calculated to be -0.2544 volt at 25° and -0.2522 volt at 0°. The value against the normal hydrogen electrode is -0.5362 volt at 25°. S. K. TWEEDY.

**Influence of movement of electrolyte on the steadiness of the potential of the oxygen electrode.** H. V. TARTAR and V. E. WELLMAN (J. Physical Chem., 1928, 32, 1171—1177).—A study of the influence of movement of the electrolyte on the potential of the oxygen electrode in acid, neutral, and alkaline solutions shows the potential to remain steady for a constant rate of flow of the electrolyte. Bright platinum electrodes gave values reproducible to within a few (3) millivolts with a carefully-controlled rate of flow, but heavily platinised electrodes show "drift" of potential and are affected to a greater extent by the rate of flow of the electrolyte. The apparatus used is described. The behaviour of the oxygen electrode is most easily interpreted by assuming the formation of a soluble substance, possibly hydrogen peroxide. L. S. THEOBALD.

**Electrokinetic potential between the solid and liquid states of a single substance.** F. FAIRBROTHER and F. WORMWELL (J.C.S., 1928, 1991—1997).—Observations on the contact potential between the solid and liquid forms of a substance have been made by a cataphoretic method in which the movement of the suspended solid in an electric field of 50—100 volts/cm. was measured. The solid is positively charged and the *P.D.* is in all cases less than that for glass in distilled water. The largest value is shown by ice in water, and no *P.D.* could be detected with benzene and other substances of low dielectric capacity. This apparent contradiction of Coehn's rule is discussed with reference to Errera's suggestion (this vol., 705) that the transition from liquid to solid involves an intermediate state in which the associated molecules have an electric moment greater than that of the ordinary molecules. J. GRANT.

**Reduction potential and oxidation.** L. RAPKINE (Compt. rend. Soc. Biol., 1927, 96, 1280—1282; Chem. Zentr., 1928, i, 706).—In certain cellular oxidations the mobilisation of hydrogen and simultaneous activation of molecular oxygen must be postulated. A. A. ELDRIDGE.

**Diffusion of a hydrogen potential or reduction potential through platinum and palladium.** R. KÖHLER (Z. physikal. Chem., 1928, 135, 369—382).—If a hydrogen potential is set up on the outer side of a platinum crucible of 0.05—0.10 mm. wall thickness, the effect slowly appears on the inner side of the crucible. The hydrogen potential may be set up by cathodic polarisation or by chromous chloride. For changes in the inner potential not exceeding 80 millivolts the time taken is such that the hydrogen must diffuse proportionately to the square of the thickness of the platinum. The diffusion through palladium obeys the law of diffusion. The diffusion effect of the reduction potential of twelve various reducing agents through thin palladium (0.02 mm.) has also been examined. It is found that the diffusion effect is greater the greater is the reduction potential of the substance used. The reduction potential depends, also, on the hydrogen absorption of the palladium. Continual use of a palladium plate enlarges the pores and thus gives different values for the rate of diffusion. Absorption and outgassing open up the metal structure. W. E. DOWNEY.

**Extrapolation of *E.M.F.* measurements to unit ionic activity.** D. I. HITCHCOCK (J. Amer. Chem. Soc., 1928, 50, 2076—2079).—The *E.M.F.* of a cell such as  $\text{Ag, AgCl}|\text{HCl}|\text{H}_2$ , the mean activity of the ions being  $\gamma$ , is given by (1)  $E = E_0 - 2k \log M - 2k \log \gamma$ , where  $M$  is the molality of the acid and  $k = 2.3RT/nF$ . According to the Debye-Hückel theory, (2)  $-\log \gamma = 0.5\sqrt{M} - BM$ . Combination of (1) and (2) gives  $E + 2k \log M - k\sqrt{M} = E' = E_0 - 2kBM$ , which is a linear relation between  $E'$  and  $M$  and may be used for extrapolation. The method, which, if a spline is used, is in agreement with the complete theoretical equation of Hückel up to  $0.1M$ , is applied to the above cell at  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$ , the respective values of  $E_0$  being  $0.2253$ ,  $0.2223$ , and  $0.2193$  volt. S. K. TWEEDY.

**Antimony-antimony trioxide electrode and its use as a measure of acidity.** E. J. ROBERTS and F. FENWICK (J. Amer. Chem. Soc., 1928, 50, 2125—2147).—Cubic antimony trioxide undergoes transition to the orthorhombic variety at  $570^\circ \pm 10^\circ$ , the free energy change of the transformation being  $+1800 \pm 200$  g.-cal./mol., and the free energy of formation of the cubic oxide  $-149,690$  g.-cal./mol. at  $25^\circ$ . Antimony trioxide formed by the hydrolysis of the trichloride consists chiefly of orthorhombic crystals. The potential of the antimony-antimony trioxide electrode attains its maximum accuracy when unstable solid phases (e.g., orthorhombic oxide) and dissolved oxygen are eliminated and when the equilibrium is approached from the alkaline side. Under these conditions, using cubic oxide, the potential is a linear function of the logarithm of the hydrogen-ion activity of the solution and has the value  $0.1445 \pm 0.002$  volt with respect to a hydrogen electrode in a solution of the same activity at  $25^\circ$ . Air need not be excluded if the electroaffinity,  $E_0$ , is fixed by means of two or more buffers in the desired range. The following concentrations must not be exceeded in the electrode: hydrochloric acid,  $0.16M$ ; phosphoric acid,  $0.15M$ ; sulphuric or nitric acid,  $1M$ ; sodium hydroxide,  $2M$ . The electrode, because it is permanent, constant, and requires only little attention, is considered to be superior to the hydrogen electrode. The  $p_{\text{H}}$  values at  $25^\circ$  of certain buffer solutions were measured against the hydrogen electrode. Data from two sources lead to a calculated value of  $-0.3341$  volt for the potential of the decinormal calomel electrode. S. K. TWEEDY.

***P.D.* measurements with a ferromagnetic compound of manganese and arsenic.** L. F. BATES (Phil. Mag., 1928, [vii], 6, 593—597; cf. this vol., 468).—The *P.D.* between a hot electrode of the above alloy in contact with manganous ions against a similar, cold electrode is investigated as a function of the temperature difference. Pronounced changes occur as the substance passes through its magnetic critical temperature. S. K. TWEEDY.

**Current density-potential measurements.** A. DADIEU (Z. Elektrochem., 1928, 34, 301—305).—Examples are given of the satisfactory determination of decomposition potentials in the electrolysis of solutions by commencing with high voltages and gradually diminishing them, where abnormal current-

voltage curves would result on raising the voltage from zero (cf. Monatsh., 1926, 47, 471).

L. F. GILBERT.

**Valency. X. Electrometric titration of Vernon's  $\alpha$ - and  $\beta$ -dimethyltellurium bases.** F. L. GILBERT and T. M. LOWRY (J.C.S., 1928, 1997—2010; cf. this vol., 349).—The molecular conductivity of the  $\alpha$ -base at  $25^\circ$  increases from 3 to 6 and that of the  $\beta$ -base from 31 to 36 for an increase in  $\nu$  from 32 to 512. In both cases saturation with carbon dioxide increases  $\mu$  to about 40 ( $\nu = 32$ ), but the normal value is restored when a current of pure air is passed through the solutions. Conductivity-titration curves show breaks corresponding with the compound  $[\text{TeMe}_2\text{OH}]\text{Cl}$ , but afford no indication of a more basic compound or of the normal salt. In addition, titrations of the  $\beta$ -base with a glass electrode show a second inflexion at about 50% neutrality corresponding with the basic salt,  $2\text{TeMe}_2\text{O, HCl}$ , which has not been obtained in the free state, although the formation of Vernon's oxy- and dioxy-iodides is not indicated. The f.-p. data taken during progressive neutralisation confirm the conclusion that the free bases are only slightly dissociated in the solution, the  $i$ -factor in both cases being about 1.1, whilst the hydroxy-halides are dissociated almost completely. Details are given of the products deposited from solution during neutralisation by hydriodic acid.

J. GRANT.

**Cells [with unattackable electrodes] contradicting the second principle of thermodynamics.** V. KAREN (Compt. rend., 1928, 187, 418—420; cf. this vol., 246).—The *E.M.F.* of a cell formed by a well-platinised platinum anode and an Acheson graphite cathode in air-free distilled water, or in a saturated solution of sodium hydroxide, depends on the temperature and varies in sense and magnitude according to the proportion of dissolved air. Since the electrodes are not likely to be attacked under these conditions, and since the heat of reaction calculated by the second law of thermodynamics from the *E.M.F.* of the cell is of an abnormal magnitude and varies abnormally with the temperature, such cells appear to contradict this law. J. GRANT.

**Periodic passivity of chromium and chromium alloys, and the influence of temperature on passivity potentials.** B. STRAUSS and J. HINNÜBER (Z. Elektrochem., 1928, 34, 407—415).—An apparatus is described for the continuous registration of the potential at an electrode, and by means of it the potentials in dilute sulphuric acid, dilute hydrochloric acid, and mixtures of both, of chromium-iron alloys and chromium-nickel-iron alloys of varying composition which could be rendered passive, have been measured over several days. It is found that periodic phenomena occur, not only with chromium, but also with the alloys (cf. Adler, A., 1912, ii, 891). A necessary condition for the active-passive change is the presence of two phases which act as local elements. In one case the second element is iron carbide, separated out from the austenite present, and in the other case it is iron oxide. Theories of passivity are discussed, and it is pointed out that the assumption of an oxygen film as the cause of passivity explains

the fact that the change from active to passive metal and *vice versa* takes place continuously and without transition potential; if, on the other hand, the oxide skin theory is accepted, a definite transition potential should occur. A mechanism is suggested for the periodic phenomenon, based on the action of local elements and on the occurrence of a concentration polarisation. Investigation of the influence of change of temperature on passivity potentials shows that, under certain conditions, the normal effect of fall of potential with rising temperature may be masked, and the potential may even rise. This phenomenon is explained from the point of view of the oxygen-film theory.

L. L. BIRCUMSHAW.

**Detonation-wave in gaseous mixtures and the pre-detonation period.** W. PAYMAN (Proc. Roy. Soc., 1928, A, 120, 90—109).—Intense compression- or "shock"-waves may be sent through a gaseous mixture by detonating or rapidly burning a solid or gaseous explosive in contact with the mixture. By means of an adaptation of Töpler's "Schlieren" method, photographic records have now been obtained of the shape and appearance of the hitherto invisible shock-wave and of its speed of propagation, and these have been used to supplement and extend the information obtained by other workers using direct methods of photography only. The method (for full details see Payman and Robinson, B., 1926, 421; Payman and Shepherd, B., 1927, 30) has been applied to a study of the pre-detonation period, and in particular of the mode of inception of detonation in a gaseous mixture. The effect of the position of the point of ignition (an electric spark) on the initial movement of the flame in a closed tube has been examined, and an explanation advanced for the observed retardation of the flame, which suggests that it occurs simultaneously with the break-up of the flame front into two separate portions moving in opposite directions. The character of the compression-waves has previously been postulated from their effects on the flame. It is now shown that they are not due to the spark, as has been hitherto supposed. They are much more marked than the spark-wave, and travel at a speed much greater than that of sound in the gaseous medium through which they are passing. They appear to have their origin in the gases behind the flame front, *i.e.*, in gases in which the process of combustion has begun some time previously, and are probably due to renewed chemical activity behind the flame front. Direct evidence in favour of the theory of renewed chemical activity has been obtained by Ellis and Wheeler (A., 1927, 317). Under the experimental conditions and with the mixtures used, the detonation-wave also always appears to have its origin behind the flame front. Experiments to ascertain under what conditions the detonation-wave might be set up in advance of the flame gave negative results. Investigations have also been made of the influence of the compression-waves on the movements of the flame when restrictions are present before detonation is set up, on their mode of propagation during the suppression of detonation when the flame passes from a narrow into a wider tube, and on the effect of ignition by a fuse or detonator on

the initial movement of the flame in electrolytic gas.

L. L. BIRCUMSHAW.

**Striated photographic records of explosion waves. II. Explanation of the striæ.** C. CAMPBELL and A. C. FINCH (J.C.S., 1928, 2094—2106; cf. A., 1927, 833).—Since striæ of gradually increasing periods are obtained when conical explosion tubes are used, they cannot be accounted for by vibrations in the photographic apparatus. Longitudinal or transverse vibrations in the walls of the explosion tube are also eliminated as a cause of the phenomenon, because the periods of the striæ are the same for rubber and glass tubes and also for glass tubes embedded in concrete. Photographs of the flame taken (a) through two windows at right angles and (b) with the explosion tube pointing towards the camera show that the flame traverses a helical path. Further, photographs of the flame taken through a horizontal slit in a vertical tube indicate that a luminous tail of flame persists for an appreciable time and that this tail is also rotating. It is suggested that the striæ may be most satisfactorily explained by assuming that the gaseous mixture is itself in a state of rotation.

F. J. WILKINS.

**Combination of hydrogen and oxygen by electric discharges.** R. D. RUSK (Physical Rev., 1928, [ii], 32, 287—292).—When a mixture of hydrogen and oxygen (2 : 1 vols.) is ignited by an electric spark or hot wire at about 3 cm. pressure, the usual explosion becomes a more quiet combustion with visible flame; below this pressure combination occurs only by collision. Logarithmic decrease in pressure was obtained in equivalent volumes in the Geissler discharge for constant current, whilst excess of oxygen increased and excess of hydrogen decreased the rate of combination. The number of water molecules formed per pair of ions at the lower pressures is much less than unity, but increases with increasing pressure, and approximates to unity at a pressure such that the time between molecular collisions is of the order of magnitude of the life of an excited hydrogen atom.

A. A. ELDRIDGE.

**Decomposition of nitrogen pentoxide. I. Unimolecular reaction and its arrest at low pressures.** G. SPRENGER (Z. physikal. Chem., 1928, 136, 49—76).—Nitrogen pentoxide reacts almost instantaneously with nitric oxide and with nitrogen trioxide. The complete decomposition equation  $2\text{N}_2\text{O}_5 = \text{O}_2 + 4\text{NO}_2 \rightleftharpoons 2\text{N}_2\text{O}_4$  is the result of a primary decomposition  $\text{N}_2\text{O}_5 = \text{N}_2\text{O}_3 + \text{O}_2$ , accompanied by the secondary reactions  $\text{N}_2\text{O}_3 + \text{N}_2\text{O}_5 = 4\text{NO}_2 \rightleftharpoons 2\text{N}_2\text{O}_4$  and  $\text{NO} + \text{N}_2\text{O}_5 = 3\text{NO}_2 \rightleftharpoons 1.5\text{N}_2\text{O}_4$ . At pressures between 0.01 mm. and 0.05 mm. the reaction no longer follows its normal course: on allowing the pentoxide to pass from a small vessel at about 15 mm. pressure to a larger one at about 0.01 mm. pressure, the ordinary reaction commences with about the normal velocity, but is then arrested. The results obtained are discussed relatively to those of Hirst and Rideal.

H. F. GILLBE.

**Kinetics of nitrous acid. IV. Kinetics of nitrous acid formation from nitric acid and nitric oxide.** E. ABEL, H. SCHMID, and S. BABAD (Z. physikal. Chem., 1928, 136, 135—145).—The

velocity of the total reaction  $\text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} \rightleftharpoons 3\text{HNO}_2$  is, if the back reaction be eliminated, independent of the partial pressure of nitric oxide, but proportional to the concentration of hydrogen and nitrate ions and of nitrous acid; the reaction is thus autocatalytic. The velocity diminishes as the ionic concentration increases. The retardation produced by sulphate ions is ascribed to the removal of hydrogen ions by the formation of  $\text{HSO}_4$  ions. The rate of formation of nitrous acid is given by  $k[\text{HNO}_2][\text{H}^+][\text{NO}_3^-]$ , where  $k$  has a value varying from 1.6 to 0.8 as the ionic concentration rises from zero to 1.1M, time being expressed in minutes. The mechanism of the reaction is given by  $\text{H}^+ + \text{NO}_3^- + \text{HNO}_2 \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O}$ , followed by  $\text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_2$ . H. F. GILLBE.

**Transition of butyl bromide.** G. DIENGER (Z. physikal. Chem., 1928, 136, 93—134).—The velocity of the reaction *isobutyl* bromide  $\rightleftharpoons$  *tert.*-butyl bromide has been determined at a number of temperatures between 178.5° and 240°. Michael's observation, viz., that having regard to the position of equilibrium the velocity of the reaction from right to left is much too small, is confirmed. In the temperature interval investigated there exists a range over which the reaction velocity is negligible, but is, however, attainable only from the *tert.*-butyl bromide side.

H. F. GILLBE.

**Hydrolysis of sucrose by acids: hydrogen-ion concentration and hydrolysing power.** H. COLIN and (MLLE.) A. CHAUDUN (Bull. Soc. chim., 1928, [iv], 43, 721—725; cf. A., 1927, 115, 835).—Variations in the rates of inversion of sucrose by acid do not correspond with variations in the sugar, acid, or hydrogen-ion concentrations, or with the addition of neutral salts. If, therefore, the *E.M.F.* of a concentration cell is strictly proportional to the hydrogen-ion concentration of the solution, the reaction cannot be considered as unimolecular and due to hydrogen ions alone.

J. GRANT.

**Hydrolysis of *o*-benzoisulphinide (saccharin) and of *o*-sulphonamidobenzoic acid.** K. TAUFEL, C. WAGNER, and W. PREISS (Z. Elektrochem., 1928, 34, 281—291; cf. A., 1926, 518).—The hydrolysis of *o*-benzoisulphinide and of the intermediate product *o*-sulphonamidobenzoic acid in the subsequent conversion into ammonium hydrogen *o*-sulphobenzoate has now been studied quantitatively in detail. Ionisation constants for the above substances and velocity coefficients for the reactions concerned have been obtained. The results confirm the previous view that the sweetness of food products containing "saccharin" or its sodium salt is only slightly affected by heating at 100°.

L. F. GILBERT.

**Kinetics of the decomposition of calcium carbonate hexahydrate.** B. TOPLEY and J. HUME (Proc. Roy. Soc., 1928, A, 120, 211—221).—A quantitative study has been made of the endothermic reaction  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O} = \text{CaCO}_3 + 6\text{H}_2\text{O}$  by means of dilatometric measurements. It has been previously found (A., 1927, 526) that the reaction is autocatalytic (the velocity passing through a maximum at about 50% decomposition) and that the autocatalysis is not eliminated by fine grinding of the crystals. The reaction rate is influenced by the inclusion in the

hydrate of small quantities of foreign substances, and is also extremely sensitive to temperature. The mechanism of the change is discussed from the point of view of an "interface reaction," in which the only molecules (ions or ionic groups) which react are those in a layer immediately adjacent to molecules in the space lattice of the resultant solid phase. This assumption is considered to be fundamental for the explanation of the apparent autocatalysis observed. *A priori*, several possibilities are considered, but the following hypothesis is the only one in accordance with the sigmoid form of the decomposition curve obtained experimentally: when the frequency of nucleus (calcite) formation on the surface of a particle, and the rate of propagation of the change from a point where a nucleus has formed, are relatively such that the majority of the particles have at least one nucleus before more than a very small fraction of the total reaction has taken place, then the total area of the interface for all the particles will increase as the reaction proceeds, and pass through a maximum. The observed reaction rate is proportional to the area of this interface. It is shown that the increase in the velocity of the reaction is due to a true temperature effect, and not to an increase in the effective surface due to break-up of the crystals at the higher temperature. On the basis of the above views, an expression is obtained which gives a curve for the decomposition velocity which falls off less rapidly than the experimental curve. Reasons are suggested for this. A consequence of the view that the reaction spreads from a limited number of nuclei is that the rate  $da/dt$  should increase as the particle radius diminishes. This is shown to be the case. The temperature coefficient has been measured from 0° to 15°, and the empirical Arrhenius constant  $A$  calculated from  $d \log k/dT = A/RT^2$ . For crystals of hexahydrate prepared from solutions containing  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $A$  was found to be 41,350, and from lime-sucrose solutions, it was 35,780. A kinetic mechanism is suggested which involves the vibration frequency of ions in the interface between the two solid phases, and the distribution of energy among the vibrating ions.

L. L. BIRCUMSHAW.

**Reaction between nitrogen pentoxide and ozone.** H. J. SCHUMACHER and G. SPRENGER (Z. physikal. Chem., 1928, 136, 77—92).—The reaction between nitrogen pentoxide and ozone is bimolecular, and is probably a result of a series of chain reactions. In agreement with the work of Warburg and Leithäuser, a new oxide of nitrogen, probably  $\text{NO}_3$ , is formed during the reaction.

H. F. GILLBE.

**Corrosion by acids and rusting of iron containing copper.** S. S. STEINBERG.—See B., 1928, 674.

**Principles of polymerisation.** J. SCHEIBER (Chem. Umschau, 1928, 35, 181—190).—Various examples of polymerisation (simple and complex) are considered in an endeavour to derive general principles of the mechanism. The presence of an unsaturated grouping is recognised as the activating factor in polymerisation, the degree of which depends on external conditions (temperature, catalysts, etc.) as well as on the state of aggregation. The effect on

polymerising power of substituent groups in the molecule is discussed and general rules for their action are derived.

E. LEWKOWITSCH.

**Acid and salt effects in catalysed reactions. XV. Catalytic activity of hydrochloric acid in the hydrolysis of ethyl acetate.** H. M. DAWSON and W. LOWSON (J.C.S., 1928, 2146—2154; cf. Harned and Pfanstiel, A., 1922, ii, 255).—The catalytic effects produced by hydrochloric acid in the hydrolysis of ethyl acetate have been examined over a range of acid concentration of 0.0002—0.2*M*. The initial velocity was in all cases proportional to the concentration of the acid. The catalytic activity of the hydrogen ion would thus appear to be determined by its concentration and not by its thermodynamic activity. This result indicates that the primary reaction is one which is not affected by the ionic environment. It is suggested, therefore, that hydrolysis is preceded by the interaction of hydrogen ions with electrically neutral ethyl acetate molecules.

F. J. WILKINS.

**Acid and salt effects in catalysed reactions. XVI. Catalytic effects in the iodination of mesityl oxide.** H. M. DAWSON and A. KEY (J.C.S., 1928, 2154—2165).—The reaction between mesityl oxide and iodine in dilute aqueous solution is similar to, but more rapid than, the reaction between acetone and iodine. It is catalysed by acids, and for a given concentration of hydrogen ions its velocity is proportional to the concentration of mesityl oxide and independent of the concentration of iodine. The rate of disappearance of iodine is therefore determined by the velocity of some preliminary transformation, probably keto-enol in character, of the mesityl oxide. The catalytic coefficients for  $H^+$ ,  $OH^-$ ,  $H_2O$ ,  $CH_3 \cdot CO_2H$ ,  $CH_3 \cdot CO_2^-$ ,  $H_2PO_4^-$ , and  $HPO_4^{2-}$  have been determined. The relative values of these coefficients for the mesityl oxide reaction differ very considerably from their relative values for the acetone reaction. The course of the autocatalysed reaction can be explained in terms of the joint catalytic action of the hydrogen ion and the water molecule.

Pure mesityl oxide has *m. p.* —41.5°.

F. J. WILKINS.

**Acidic and basic catalysis of acetylation reactions.** J. B. CONANT and G. M. BRAMMANN (J. Amer. Chem. Soc., 1928, 50, 2305—2311).—Measurements were made of the rate of acetylation of  $\beta$ -naphthol by acetic anhydride in glacial acetic acid solutions buffered to definite hydrogen-ion activities. The rate varied nearly a million-fold, and was dependent on the acidity or basicity of the medium. The maximum rate was at  $p_H^{(HOAc)} - 4.5$ , the minimum at about  $p_H^{(HOAc)} + 2.0$ ; over this range the rate was apparently proportional to hydrogen-ion activity. Between +2.0 and +5.0 the rate increased again, showing that the process was subject to both acid and basic catalysis.

R. K. CALLOW.

**Definition of "area" in the case of contact catalysts.** F. H. CONSTABLE (Nature, 1928, 122, 399—400).—The maximum area of a contact catalyst for physical chemical purposes is the area of the envelope of the unimolecular film of hydrogen atoms closely packed, all in contact with each other and

with the catalyst surface, which completely covers it. If the adsorbed molecules were large, the area of a very irregular surface measured by the number of adsorbed molecules would appear to decrease. Bowden and Rideal's method (this vol. 1088) would probably give smaller results than correspond with this definition.

A. A. ELDRIDGE.

**Decomposition of hydrogen peroxide on glass powder in the presence of salts.** (Miss) W. M. WRIGHT (Z. Elektrochem., 1928, 34, 298—300).—The rate of decomposition of aqueous hydrogen peroxide in the presence of glass powder is increased when various salts are added, by amounts greater than those due to the salts alone, thus confirming Elissafov's work with glass-wool (A., 1915, ii, 681). Mercurous chloride acts exceptionally, its addition retarding the rate of decomposition. The rate of decomposition in presence of glass powder and silver nitrate has been particularly carefully studied and is proportional to the amount of adsorbed silver. The adsorption, on glass powder, of silver ions follows the isotherm  $a = c^{1/n}$ .

L. F. GILBERT.

**Autocatalysis in the formation and decomposition of cupric oxide.** J. OKAYAMA (Z. Elektrochem., 1928, 34, 294—298).—The reduction of cupric oxide to copper by hydrogen, and the oxidation, by oxygen, of copper to cupric oxide are autocatalytic reactions, the first result confirming that of Pease and Taylor (A., 1922, ii, 148).

L. F. GILBERT.

**Thermal decomposition of ammonia on tungsten, molybdenum, and nickel.** I. C. H. KUNSMAN (J. Amer. Chem. Soc., 1928, 50, 2100—2113).—The thermal decomposition of ammonia on tungsten, molybdenum, and nickel filaments was investigated by observing the accompanying pressure increase. The reaction appears to be of zero order on the former two filaments (cf. Hinshelwood and Burk, A., 1925, ii, 691), but at sufficiently reduced pressure the reaction tends to become unimolecular. The reaction rate is lowered by the presence of nitrogen or hydrogen (contrary, in the case of molybdenum, to Burk's results; A., 1927, 426), but this retardation decreases and disappears at higher temperatures. Thoriated tungsten filaments showed no increase in activity over filaments of pure tungsten. At the lower temperatures (600—900°) the heat of activation *E* is approximately constant at 45,000 g.-cal. for the three metals; at the higher temperatures the decrease in *E* is greatest for nickel and least for tungsten. The relative catalytic activity of the metals seems to depend primarily on the catalyst surface, and therefore on the constant *A* in the formula  $k = Ae^{-E/RT}$ .

S. K. TWEEDY.

**Catalytic oxidation of ammonia. VII.** L. ANDRUSSOV.—See B., 1928, 669.

**Catalytic oxidation of ammonia.** F. RASCHIG.—See B., 1928, 669.

**Electrolytic preparation of cuprous oxide.** E. ABEL and O. REDLICH (Z. Elektrochem., 1928, 34, 323—326).—Details are given for the preparation of cuprous oxide, free from metallic copper and cupric

oxide, by the electrolysis, with copper electrodes, of slightly alkaline solutions of sodium chloride.

L. F. GILBERT.

[Controlled] electrolytic oxidation of organic substances. C. MARIE and G. LEJEUNE (Compt. rend., 1928, 187, 343—344).—The addition of anodic depolarising agents (oxidisable organic substances, e.g., alcohols) lowers the potential necessary for the electrolysis of pure solutions of acids and bases, the fall being characteristic for the substance added for a particular anode. In order to limit the oxidation of the alcohol and so obtain the aldehyde, a low anodic potential and a high alcohol concentration are used with intermittent current to enable reaction to take place between the alcohol and the unstable oxide formed on the platinum anode. If these conditions are not maintained the aldehyde is further oxidised to the acid.

J. GRANT.

Photochemical reactions promoted by intermittent monochromatic light. M. PADOA and N. VITA (Gazzetta, 1928, 58, 461—472; cf. A., 1927, 528).—Comparison has been made of the yields of the reaction  $2\text{FeI}_2 + \text{I}_2 = 2\text{FeI}_3$  when illuminated by continuous and intermittent light, respectively. In general the yield was increased by the use of intermittent light, but the augmentation depended both on the wave-length of the light and on the frequency of interruption of the illumination. The wave-lengths used were 670.8, 589.6, 587, 535, and 460.7  $\mu\mu$ , and the illumination could be interrupted up to a maximum of 560 times per second. With light of wave-length 460.7  $\mu\mu$  a maximum ratio of the yields in continuous and intermittent light of about 2.0 was obtained. This maximum occurred periodically as the frequency of interruption was increased, the maxima appearing irregularly at interruption frequencies of 32, 98, 138, 157, 202, 253, 270, 318, 357, 390, 450, and 513 per second. Similar results were obtained with green light, except that the yield ratio was lower (about 1.70) and the maxima (at frequencies 22, 259, and 532) were fewer in number. The yield with this light was unaltered except in the neighbourhood of these maxima. With yellow light the maximum yield ratio was 1.62 at an interruption frequency of 311. Except within the limits 20—40, 260—370 interruptions per second the yield was unaltered by intermittent illumination with this light. Intermittent red light gave a maximum yield ratio 1.37 with an interruption frequency 472. These results are discussed from a quantum point of view and it is suggested that the periodic maxima are due to the formation of active molecules which are the seats of adiabatic transformations, and that the life of these molecules is greater the greater is their energy level.

F. G. TRYHORN.

Influence of light on the colour of ferric chloride solutions. K. S. RITCHIE (J. Physical Chem., 1928, 32, 1269—1271).—Exposure to sunlight or other sources of intense light of hydrochloric acid solutions of ferric chloride results in an increase in intensity of the colour of the solution; on removal of the light the solutions slowly return to their initial condition. The fraction of incident light transmitted during a given exposure reaches a maximum near the

commencement of the yellow region of the spectrum and falls rapidly to the green. Increased light absorption also results from heating a solution of ferric chloride.

L. S. THEOBALD.

Photo-oxidation of organic compounds by dichromates. J. PLOTNIKOV [with G. DEUTSCH, B. KUNST, M. PAVLIČEK, D. VRANJICAN, D. BARBETTI, and N. MUIĆ] (Chem.-Ztg., 1928, 52, 669—671).—The action of sunlight on solutions of potassium dichromate containing various organic substances has been studied. No marked reaction is observed with ordinary charcoal, even after 3 months' irradiation, nor do salts of manganese, cobalt, copper, uranyl, or iron exert any catalytic influence. Colloidal carbon reacts vigorously, with the formation of a voluminous precipitate. Solutions containing hydrogen, methane, and coal gas become somewhat cloudy after irradiation, whilst ethylene and acetylene react rapidly. Methyl alcohol yields formaldehyde and a copious precipitate of chromic hydroxide; no formic acid is formed, although the reaction velocity increases after a certain time. Amyl alcohol yields an aldehyde and a brown precipitate of a chromium chromate, *n*-propyl alcohol yields propaldehyde and traces of propionic acid, whilst from *isopropyl* alcohol acetone, acetic acid, and formic acid are obtained. Acetone is oxidised to acetic and formic acids, with traces of the corresponding aldehydes. A solution of potassium dichromate in ethylene glycol rapidly becomes strongly alkaline and deep green in colour, glycollaldehyde and glyoxal being produced; under the same conditions glyceric acid and aldehyde and dihydroxyacetone are produced from glycerol solutions. Triphenylmethane is unaltered and benzene remains almost unchanged even in presence of ferric chloride, but toluene yields a variety of products. Phenol forms benzoquinone and a mixture of polyhydric phenols. *o*- and *m*-Xylenes yield tolualdehydes and acids, whilst from *p*-xylene some formic acid is produced. Quinol forms primarily benzoquinone, but phthalic acid also has been isolated from the reaction products. Resorcinol and pyrocatechol yield trihydric phenols, benzoquinone, and other similar compounds. A solution containing *o*-cresol decomposes with evolution of carbon dioxide and separates into two layers, of which the lower contains unchanged cresol, chromic hydroxide, and a tarry substance, and the upper benzoic and oxalic acids. Naphthalene and  $\alpha$ -naphthol are unchanged after 10 months' illumination. The behaviour of a number of aniline dyes is described: in several cases fluorescent solutions are obtained. Aniline is rapidly converted into aniline-black, and *p*-aminophenol into benzoquinone and ammonia. Results with  $\psi$ -cumene indicate that the possibility of terpene formation is dependent on a symmetrical molecular structure. Dihydroxy-antraquinone breaks down into benzoquinone and carbon dioxide. Mixtures of *isopulegol* and ammonium dichromate in various proportions yield on irradiation in aqueous or alcoholic solution only about 1% of *isopulegone*, whereas *isoeugenol* undergoes extensive oxidation. The oxidation of *n*-octyl alcohol, which is catalysed by uranyl nitrate, yields

only about 5% of aldehyde as a result of the absorption of the active radiation by a precipitate which forms on the walls of the vessel very soon after the commencement of the reaction. Similar conditions hold for the oxidation of *isosafrole*, but in presence of uranyl nitrate a yield of about 50% is obtained.

H. F. GILLBE.

**Oxidation of carbohydrates, fats, and nitrogenous products by air in presence of sunlight.** C. C. PALIT and N. R. DHAR (*J. Physical Chem.*, 1928, 32, 1263—1268; cf. *A.*, 1925, ii, 884).—The passage of air in presence of tropical sunlight through solutions of the following substances is accompanied by oxidation which increases with an increase in intensity of the light: galactose, arabinose, sucrose, dextrose, lævulose, lactose, maltose, starch, glycogen, carbamide, glycine,  $\alpha$ -alanine, hippuric acid, sodium urate, potassium stearate, palmitate, oleate, and oxalate. Zinc oxide is an effective photo-sensitiser in all these cases. Solutions of sodium nitrite and arsenite, and of arsenious acid, were not oxidised by this treatment. The efficacy of sunlight and other artificial lights in the treatment of disease is considered to be due to the increased metabolism which results from the activation of the cells of the body by absorption of the light.

L. S. THEOBALD.

**Action of light on diazo-derivatives.** A. SEYEWETZ and D. MOUNIER (*Bull. Soc. chim.*, 1928, [iv], 43, 827—838).—See this vol., 493.

**New photographic phenomenon.** F. WEIGERT (*Naturwiss.*, 1928, 16, 613—614).—When a silver chloride-gelatin plate is exposed to plane polarised light and is physically developed after fixing, the silver which separates is doubly refracting. The optic axis of the new anisotropic system is parallel to the electric vector of the polarised light. An experiment is described which shows that the anisotropic latent image is also latent to a sensitive polarimeter.

A. J. MEE.

**Optical sensitisation of silver iodide.** K. BAUKLOH.—See B., 1928, 655.

**Herschel effect by exposure to short wavelengths.** LÜPPO-CRAMER.—See B., 1928, 692.

**Sterry effect with silver chloride.** LÜPPO-CRAMER.—See B., 1928, 692.

**Condensable gas modifications formed under the influence of electrodeless discharges.** J. TAYLOR (*Nature*, 1928, 122, 347).—The condensable product obtained in a liquid-air trap when hydrogen is subjected to an electrodeless discharge is shown to give a spectrogram identical with that of water at low pressure; carbon dioxide bands were also in evidence. With oxygen a condensable product yielding a spectrogram similar to that obtained from a discharge in carbon dioxide is formed. The quantity of gas disappearing is proportional to the quantity of electricity that has traversed the walls of the containing vessel; the disappearance must be due to chemical interaction of the gaseous ions with the electrolytic products and ions of the glass. Thus, from the simplest point of view, for every two electronic charges transferred across the glass two atoms

of sodium are liberated and the  $\text{SiO}_3$  radical breaks down into  $\text{SiO}_2 + \text{O}$ , the latter atom then uniting with a hydrogen molecule. The glass is, however, a complex electrolytic solution containing carbon compounds and probably peroxides.

A. A. ELDRIDGE.

**Lithium sulphite and some derivatives.** J. A. N. FRIEND and D. W. POUNDER (*J.C.S.*, 1928, 2245—2248; cf. Röhrig, *A.*, 1888, 649).—Anhydrous *lithium sulphite*,  $\text{LiSO}_3$ , has been isolated and the existence of the monohydrate has been confirmed. No evidence of the dihydrate described by Röhrig has been obtained. Although all attempts to isolate lithium hydrogen sulphite were unsuccessful, its derivatives with acetone, acetaldehyde, and benzaldehyde were prepared.

F. J. WILKINS.

**Interaction of cuprous chloride and chromates of potassium in sodium chloride solution.** H. J. P. VENN and V. EDGE (*J.C.S.*, 1928, 2142—2146; cf. Rosenfeld, *A.*, 1879, 693).—When cuprous chloride, dissolved in a concentrated solution of sodium chloride, is mixed in the cold with a solution of potassium chromate or dichromate, precipitates are formed which vary in colour and composition according to the manner of mixing. The precipitates have been analysed, and equations involving basic copper salts have been proposed, according to which the formation of these basic salts is ascribed to secondary reactions. A new *basic copper chromate*,  $3\text{CuO} \cdot 2\text{CuCrO}_4 \cdot 4\text{H}_2\text{O}$ , has been identified.

F. J. WILKINS.

**Effect of alkalinity on basic cupric sulphates.** O. A. NELSON (*J. Physical Chem.*, 1928, 32, 1185—1190).—The products obtained by adding sodium hydroxide solution to copper sulphate at various values of  $p_{\text{H}}$  have been investigated. The ratio  $\text{Cu}/\text{SO}_3$  in the products varies from 3.40 to 20.73 over the range of  $p_{\text{H}}$  5.3—9.4 and a smooth curve results from plotting the values obtained. The existence of the many basic cupric sulphates previously reported is thus not supported; only one compound of the formula  $7\text{CuO} \cdot 2\text{SO}_3$  is indicated. The composition of the products obtained by laboratory methods depends on the method of preparation and on the ratio of the reacting substances. The case of copper sulphate is analogous to that of aluminium sulphate (Miller, *A.*, 1924, ii, 48).

L. S. THEOBALD.

**Basic magnesium carbonate.** T. NISHIMURA (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, 7, 838—872).—Normal magnesium carbonate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , loses carbon dioxide rapidly on exposure to air, but begins to absorb it again after some time. It is hydrolysed by water to  $\text{Mg}(\text{OH})_2 \cdot 0.82\text{CO}_2 \cdot n\text{H}_2\text{O}$ . If magnesium hydroxide is suspended in water and air passed through,  $\text{Mg}(\text{OH})_2 \cdot 0.74\text{CO}_2 \cdot m\text{H}_2\text{O}$  is produced. These two substances are stable when dry.

C. W. GIBBY.

**Calcium nitride.** P. DUTOIT and A. SCHNORF (*Compt. rend.*, 1928, 187, 300—302).—The nitridation of calcium is autocatalytic and is most rapid when the calcium is finely divided, e.g., is prepared by the complete decomposition of calcium hexammine (formed in a solution of calcium in liquid ammonia)

at a low temperature and pressure. Oxidising agents render the calcium passive, but reducing agents act in such cases as catalysts which suppress the passivity, whilst the alkali metals and moisture do not affect the reaction, the speed of which rises to a maximum at 450°, falls to zero at 600°, and increases again beyond the m. p. of calcium. Except at low temperatures, when there is a deficit of 2—3%, the amount of nitrogen fixed corresponds with the formula  $\text{Ca}_3\text{N}_2$ , and the pressure of nitrogen evolved on re-heating is highest if the original nitride is prepared at a low temperature, if the re-heating is rapid, and if the time between the two operations is short. The nitride may be black, bluish-black, reddish-brown, green, or yellow, according as it is prepared at 350°, 350—600°, 600—850°, 850—1100°, or above 1100°, respectively, and each type has a particular dissociation vapour pressure, the dissociation of the yellow variety alone being reversible. The black nitride is pyrophoric. These phenomena may be explained by the assumption that the unstable combination  $\text{CaN}$  is formed at low temperatures and then decomposes irreversibly. J. GRANT.

**Hydrated tricalcium aluminate.** A. TRAVERS and SEHNOUTKA (Compt. rend., 1928, 187, 381—382).—The salt,  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 21\text{H}_2\text{O}$ , is prepared in well-formed needles by the addition of 1000 c.c. of *M*/30-potassium aluminate hydrate ( $\text{KAlO}_2 \cdot 3\text{H}_2\text{O}$ ) solution to 1100 c.c. of a mixture of 1000 c.c. of *M*/47-calcium nitrate solution and 100 c.c. of saturated lime water. The  $p_{\text{H}}$  value must fall between 11.55 and 11.62 in order to avoid the formation of a microcrystalline variety of alumina, which, however, is distinguished from the aluminate by its insolubility in 0.1*N*-hydrochloric acid. J. GRANT.

**Electrolytic removal of iron from aluminium salts.** L. WASILEWSKI and S. MANTEL.—See B., 1928, 669.

**Aluminium arsenide.** G. NATTA and L. PASSE-RINI (Gazzetta, 1928, 58, 458—460).—Pure aluminium arsenide (*d* 3.60, m. p. 1200°) may be prepared by heating together the elements to about 800°. X-Ray analysis, by the powder method, of the microcrystalline product indicates crystals of the monometric type characteristic of blends, with a unit cell of edge 5.62 Å., containing four molecules of AlAs. The structure is non-ionic, and the density calculated from the crystallographic data is 3.81.

F. G. TRYHORN.

**Reactions in the evolution flask.** S. KITASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 832—837).—An investigation of the extent to which sulphur contained in iron is converted into hydrogen sulphide by hydrochloric acid. Free sulphur is attacked by hydrochloric acid only in presence of a large quantity of iron, when hydrogen sulphide is produced. Copper sulphide is attacked in the cold by 4—4.5*N*-acid, and by 0.3—0.35*N*-boiling acid, with evolution of hydrogen sulphide. Sulphates (copper, iron, manganese) are not attacked by concentrated hydrochloric acid. C. W. GIBBY.

**Molybdenum-blue, its properties and composition.** L. A. MUNRO.—See B., 1928, 640.

**Denigès' phospho-cœruleomolybdenum compound.** A. VERDA (Pharm. Acta Helv., 1928, 3, 4—9; Chem. Zentr., 1928, i, 1641).—Denigès' phospho-cœruleomolybdenum compound is not always obtained on reduction of molybdic acid in presence of phosphoric acid, but only when aluminium or tin is employed. The compound is soluble in ether.

A. A. ELDRIDGE.

**Uranyl sulphate.** A. COLANI (Bull. Soc. chim., 1928, [iv], 43, 754—762; cf. A., 1927, 830).—The solubility of uranyl sulphate in mixtures of water and sulphuric acid, and the equilibria produced between it and the alkali sulphates, have been studied at 25°, using the method of residues. This avoids errors due to supersaturation of the solutions with uranyl sulphate, and to the difficulty in removing the crystals of the solid phases in the pure state. The double sulphates,  $(\text{NH}_4)_2(\text{UO}_2)_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{K}_2(\text{UO}_2)_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ , and  $\text{Na}_4(\text{UO}_2)_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  are recognised for the first time, the solubility curve obtained for sodium sulphate differing in shape and in the nature of the solid phases from those for ammonium and potassium sulphates, although all the compounds obtained behaved like true double salts. A correspondence exists between the combination of uranyl sulphate with sulphuric acid and with the alkali sulphates indicating the existence of the compound  $\text{UO}_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ , stable at 100° (cf. Meyer and Kasper, A., 1926, 925). J. GRANT.

**Hydrofluorides of organic bases and a study of hydrofluoric acid.** J. F. T. BERLINER and R. M. HANN (J. Physical Chem., 1928, 32, 1142—1162).—The products obtained by the addition of an excess of hydrofluoric acid (48%) to each of 25 organic amines have been investigated. In most cases, they crystallise well and, excepting the cases of metanilic and sulphanilic acids and *o*-toluidine in which decomposition occurs, they sublime unchanged when heated. Characteristic m. p. were obtained for the hydrofluorides of *m*-nitroaniline 207—209°, *p*-nitroaniline 173—174°, anthranilic acid 217—218°, and ethylaniline 170—171°. Analysis indicated the derivatives to be of the type  $\text{Base}_4\text{HF}$ . They are soluble in and are hydrolysed by water to a certain extent. Titration with sodium hydroxide and indicators accounted for only 0.75 of the hydrofluoric acid, and electrometric titrations demonstrated that one of the four molecules of acid is distinct in the nature of its reactions and union to the base, whilst the remaining molecules are identical in this respect. An explanation is advanced and discussed in relation to the properties of hydrofluoric acid and its inorganic compounds. An electronic structure which explains the formation of compounds of the type  $\text{Base}_4\text{HF}$  is suggested, and previous work in this field is discussed. L. S. THEOBALD.

**Action of nitrogen on manganese.** G. VALENSI (Compt. rend., 1928, 187, 376—378).—The numerous formulae proposed for manganese nitride are explained by the fact that pyrophoric manganese, obtained from the amalgam by distillation, adsorbs pure nitrogen at 760 mm. pressure in quantities which are almost a linear function of the temperature. The dissociation isotherms of the product richest in nitrogen



are analogous to those for chromium (this vol., 956) and probably represent solutions of a nitride which always contains more nitrogen than that required by the formula  $Mn_3N_2$ . J. GRANT.

**Composition and properties of ferric sulphide.** F. FEIGL and E. BACKER (Z. anal. Chem., 1928, 74, 393—398; cf. A., 1927, 1042).—When the washed precipitate of empirical composition  $Fe_2S_3$ , formed by precipitation of a tartrate-containing solution of ferric salt with ammonium sulphide, reacts in neutral solution with mercuric and cadmium salts, it behaves as ferrous and ferric sulphide, respectively. This suggests that the substance is a mixture of the valency isomerides  $S:Fe:S:Fe:S$  and  $FeS,FeS_2$ . The dependence of the composition of the precipitated sulphide on the conditions of precipitation has been worked out by Krepelka and Podrouzek (A., 1925, ii, 703). These factors are also valid for the mercaptides of iron. Solutions of ferric salts give ferrous mercaptide with ethyl mercaptan. When, however, the concentration of ferric ion is depressed by addition of tartrate and such a solution is run slowly into an alcoholic solution of ethyl mercaptan, *ferric ethyl mercaptide* results. When a solution of ferric chloride is added to a solution of barium sulphide, or when freshly-precipitated ferric sulphide is treated with a solution of barium sulphide, a substance approximating to the composition  $BaFe_3S_4$  is obtained (cf. Malfatti, A., 1909, ii, 581). The compound reacts with mercuric salts as the original ferric sulphide. It is very unstable and is decomposed by mere washing with water. The compounds described by Malfatti are probably mixed sulphides rather than thioferrites. When moist ferric hydroxide is treated with ammonium sulphide the sulphide formed has the composition  $Fe_2S_3$ , whilst that obtained by precipitation from a solution of ferric salt containing tartrate has the initial composition  $Fe_2S_3 \cdot (NH_4)_2S$ .

J. S. CARTER.

**Iron carbonyl and carbonyl iron.** A. MITTASCH.—See B., 1928, 675.

**Nature of Prussian-blue.** D. DAVIDSON and L. A. WELO (J. Physical Chem., 1928, 32, 1191—1196).—The magnetic susceptibilities of soluble and insoluble Prussian-blue have been measured at  $-70^\circ$ ,  $2.1^\circ$ , and the ordinary temperature. The formulæ  $KFe[Fe(CN)_6]$  and  $Fe_4[Fe(CN)_6]_3$  for soluble and insoluble Prussian-blue, respectively, lead to values of the Curie constants 4.05 and 3.92, and of the magneton numbers 28.3 and 27.8, respectively, all of which are within the limits obtained for ferric ions by previous workers. Formulations as polynuclear compounds (cf. Reihlen and Zimmermann, A., 1927, 233) do not satisfy the magnetic data. Conductivity measurements on the closely-related ferric ferricyanide support this evidence against the existence of a complex polynuclear ion in the two forms of Prussian-blue. Magnetic data on hydroferrocyanic acid and the ferrocyanides of sodium, potassium, and calcium are also given.

L. S. THEOBALD.

**Sampling granular material.** B. BAULE and A. BENEDETTI-PICHLER (Z. anal. Chem., 1928, 74, 442—456).—Theoretical and mathematical. From

the theory of probability formulæ are derived from which the errors in sampling, the necessary degree of fineness, and the minimum weight of sample at any definite degree of fineness can be calculated at any stage of the process. A. R. POWELL.

**Method of evaluation of analyses.** I. O. LIESCHE.—See B., 1928, 657.

**Radiometric microanalysis.** V. R. EHRENBURG (Biochem. Z., 1928, 197, 467—475; cf. A., 1926, 328, 929; this vol., 383).—Since in most cases the precipitates obtained are neither further treated nor weighed, the reaction product may be added before precipitation in the solid form. Immediate and complete precipitation of the smallest amounts of the substance to be determined is thus obtained. The method involving the precipitation of lead as chromate, as described for nitrogen determination, can be used for the determination of many other elements. The delicacy of the method has been greatly increased and the time for analysis much shortened by the use of an electrometer fifty times as sensitive as that previously employed. Iron is determined by the procedure given for calcium, chromate precipitation being used. Potassium may be determined by the cobaltinitrite method, or the potassium permanganate, which is used for the radiometric analysis, may be decomposed with excess of oxalate and the excess of oxalate precipitated by lead or calcium. Sørensen's method for the titration of formaldehyde (cf. A., 1910, ii, 556) may be adapted for radiometric analysis. Carbon may be determined in the wet way and the process is also applicable to the determination of this element in elementary analysis. W. MCCARTNEY.

**Destruction of organic matter in toxicological examinations.** P. E. HEEDERIK (Pharm. Weekblad, 1928, 65, 861—879).—The methods proposed and in general use are described and discussed. Destruction is incomplete in the methods of Magnin and Stettbacher and of Fresenius and von Babo, but is complete in those of Kerbosch and of Wagenaar. A modified apparatus is suggested for the Kerbosch method; addition of potassium permanganate and use of increased quantities of sulphuric acid have no appreciable effect. In removing excess of nitric acid, an air-bath is recommended. S. I. LEVY.

**Volumetric micro-analysis and centrifugovolumetry.** R. F. LE GUYON (Ann. Chim., 1928, [x], 10, 50—112).—A more detailed account of work already published (A., 1925, ii, 1202; 1926, 927; 1927, 223, 372, 537; this vol., 36, 860).

H. BURTON.

**Analysis by sedimentation.** O. ARRHENIUS and H. RIEHM (Medd. K. Vetenskapsakad. Nobel-Inst., 1927, 6, No. 14).—Methods are described for the rapid analysis of small quantities of sulphate, calcium, magnesium, phosphate, and potassium ions by precipitation, centrifuging, and measurement of the volume of the precipitate. The smallest amount which can be determined in the case of phosphate is 0.1 mg., and in the case of sulphate 4 mg. For the determination of sulphate the solution must be between  $N/13$  and  $N/20$  and for calcium between

*N*/200 and *N*/450. For the other three ions, all concentrations can be used. W. E. DOWNEY.

Indicating equipment for industrial  $p_{\text{H}}$  measurements. H. C. PARKER.—See B., 1928, 627.

Use of the quinhydrone electrode in electro-metric titrations. II. A. J. RABINOVITSCH and V. A. KARGIN (Z. Elektrochem., 1928, 34, 311—316; cf. A., 1927, 221).—Discrepancies between  $p_{\text{H}}$  values as obtained from quinhydrone and hydrogen electrode measurements, respectively, are due to the effect of atmospheric carbon dioxide, as are the two maxima observed by MacInnes (this vol., 36) in the electrometric titration of acids, using the quinhydrone electrode. The agreement of  $p_{\text{H}}$  values obtained by Kolthoff and Bosch (A., 1927, 533) with the different electrodes in buffered solutions, in apparent contradiction to the authors' results, is ascribed to the fact that the solutions of Kolthoff and Bosch were more strongly buffered. L. F. GILBERT.

Determination of water in combustible materials by means of magnesium methyl iodide. A. TAUBMANN.—See B., 1928, 629.

Determination of water in bleaching powder, jelly, etc. T. SOMYA.—See B., 1928, 640.

Micro-analysis. L. BERMEJO Y VIDA (Chim. et Ind., 1928, 20, 221—222).—Determinations of the effects of time and temperature on Pregl's micro-Carius method show that the ease of the removal of halogen elements from an organic molecule is inversely proportional to their chemical activities, higher temperatures and longer times being required for aromatic halides and particularly for nuclear derivatives. Dihalogen derivatives are more readily resolved when the halogens are different than when they are the same, unless the halogens are attached to the same carbon atom, and poly-derivatives higher than tetrahalogen derivatives are removed with progressive facility. Removal is assisted by the presence of a nitro-group. Seasonal variations (in Madrid) in the weights of absorption tubes used for micro-combustions are avoided by the use of U-tubes with capillary ends. Sulphur compounds react more easily in the presence of a high proportion of lead chromate, and for cyanides, ferrocyanides, etc. traces of nickel or iron oxides should be added in addition. The volumetric method is preferable for the micro-determination of sulphur. J. GRANT.

Apparatus for micro-determination of dissolved oxygen [in water]. T. G. THOMPSON and A. C. MILLER.—See B., 1928, 656.

Determination of oxygen in water. F. LIEBERT and W. M. DEERNS.—See B., 1928, 656.

Micro-analytical determination of sulphur in organic compounds by titration. B. KUBOTA and S. HANAI (Bull. Chem. Soc. Japan, 1928, 3, 168—172).—The sulphur compound is volatilised from a platinum boat in a stream of hydrogen and the vapours are passed over heated, freshly-reduced nickel. The whole of the sulphur is retained as nickel sulphide. If the compound is not volatile, e.g., sulphonates, the material in the boat is covered with reduced nickel. The nickel is dissolved in acid

and the evolved hydrogen sulphide absorbed in an ammoniacal solution of cadmium chloride. Cadmium sulphide is determined iodometrically.

J. S. CARTER.

Detection of sulphide and thiosulphate. F. FEIGL (Z. anal. Chem., 1928, 74, 369—376).—No reaction occurs when solutions of iodine and sodium azide are mixed, but in presence of sulphide or thiosulphate vigorous evolution of nitrogen occurs. Although the reaction is represented stoichiometrically by the equation  $2\text{NaN}_3 + \text{I}_2 = 2\text{NaI} + 3\text{N}_2$ , it appears that a co-ordinative linking between iodine and sulphur is necessary before the reaction can proceed. Neither elementary sulphur nor, with the exception of thiocyanate, other sulphur compounds give this effect. The induced reaction is given by insoluble and naturally-occurring sulphides. Since arsenides, selenides, antimonides, or tellurides do not give the effect, the presence of sulphide in minerals etc. may be detected by adding the finely-powdered substance to a solution containing azide and iodine. When the substance becomes wetted, vigorous evolution of nitrogen occurs if sulphide is present. Reaction in presence of copper sulphide is rather slow. Minute quantities of thiosulphate or sulphide may be detected by this method, either by microscopical or direct observation. The presence of 1 part of sulphide in 1000 parts of sulphate may readily be detected using only 0.05 g. of material. The azide-iodine reaction is more sensitive than the lead acetate, nitroprusside, or methylene-blue method for the detection of hydrogen sulphide in natural waters. Thiosulphate may be detected at a dilution 1 in  $6 \times 10^6$ .

Using the above reaction it has been shown that the product obtained by fusing selenium with sulphur is a true sulphide and not a mechanical mixture.

J. S. CARTER.

Application of the catalytic effect of carbon disulphide to the iodometric determination of azides and to the detection of carbon disulphide. F. FEIGL and E. CHARGAFF (Z. anal. Chem., 1928, 74, 376—380).—The azide-iodine reaction (preceding abstract) occurs quantitatively and with great rapidity in presence of carbon disulphide, especially when alcohol or acetone is also present. The reaction scheme is apparently:  $2\text{NaN}_3 + 2\text{CS}_2 = 2\text{CS}(\text{NaS})\text{N}_3$ ;  $2\text{CS}(\text{NaS})\text{N}_3 + \text{I}_2 = 2\text{NaI} + \text{N}_3 \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{N}_3$ ;  $\text{N}_3 \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{N}_3 = 2\text{CS}_2 + 3\text{N}_2$ .

The presence of carbon disulphide may be detected by adding 1—2 c.c. of a solution 0.5*N* and 0.1*N* with respect to sodium azide and iodine, respectively, to 5 c.c. of the suspected solution. Immediate evolution of nitrogen occurs when the concentration of carbon disulphide is greater than 1 in  $5 \times 10^4$ . With smaller quantities the evolution is delayed. If the solution also contains sulphides a slight excess of 0.1*N*-iodine solution is first added. Minute quantities of carbon disulphide may be detected by adding starch and 1 drop of 0.01*N*-iodine solution followed by 2 c.c. of 0.5*N*-sodium azide solution, previously treated with 0.01*N*-iodine solution and starch until a blue colour just appeared. When carbon disulphide is present the blue colour disappears. A blank test should be carried out at the same time.

To determine azides a known excess of 0.1*N*-iodine solution is added to a solution of 0.5 c.c. of carbon disulphide in 6–8 c.c. of acetone. On adding the solution of azide, evolution of nitrogen occurs. After 5–10 min. 250 c.c. of water are added and the excess of iodine is titrated with 0.1*N*-arsenite solution. The back titration should be of the order 2–3 c.c. The method is applicable to the determination of insoluble azides which yield the corresponding iodide and soluble potassium azide with potassium iodide.

Addition of insufficient potassium iodide to silver azide gives a bright yellow additive compound,  $\text{AgI} \cdot \text{AgN}_3$ . J. S. CARTER.

**Colorimetric [micro-]determination of sulphuric acid.** J. YAMAZAKI (Bull. Chem. Soc. Japan, 1928, 3, 173–180).—Sulphate is precipitated from slightly acid solutions and in presence of acetone as benzidine sulphate. After filtration and washing with 90% acetone the benzidine sulphate is dissolved in a mixture of equal volumes of absolute alcohol and 0.1*N*-sodium hydroxide solution. A few drops of a solution of barium chloride are added and the whole is made acid. Excess of a 1% solution of furfuraldehyde is added to an aliquot and the yellow colour compared with that given by a standard solution. The method is suitable for the determination of inorganic and total sulphate in urine. Phosphates interfere and the presence of large amounts of chloride is not desirable. When the solutions concerned are colourless, sulphates can be determined rapidly by adding excess of benzidine hydrochloride and determining the concentration of benzidine in the supernatant liquid. The rapid method can be applied to urine after the latter has been decolorised by animal charcoal. J. S. CARTER.

**Iodometric determination of persulphate.** A. SCHWICKER (Z. anal. Chem., 1928, 74, 433–441).—In the direct iodometric determination of persulphate a large excess of potassium iodide is necessary to obtain complete reaction in a short time. This excess may be dispensed with and accurate results obtained in 10–15 min. if the persulphate solution is treated with 20% of its weight of ammonium chloride. The persulphate content of solutions free from ammonium salts may also be determined by boiling with sodium hydroxide and potassium iodide to convert part of the latter into iodate, acidifying with sulphuric acid, and titrating the liberated iodine. Alternatively, the neutral solution may be boiled with excess of sodium thiosulphate, with which persulphate reacts to form dithionate, and the excess of thiosulphate titrated with iodine. Persulphate oxidises ferrocyanide to ferricyanide in neutral solution and the latter may be determined iodometrically in acid solution; it also oxidises stannous chloride to stannic chloride in cold dilute hydrochloric acid and the excess of stannous chloride may be titrated with iodine.

A. R. POWELL.

**Determination of nitrites in cellulose nitrate.** KOEHLER and MARQUEYROL.—See B., 1928, 656.

**Detection of phosphate [in presence of arsenate] and molybdate.** F. FEIGL [with P. KRUMHOLZ] (Z. anal. Chem., 1928, 74, 386–392).—Phos-

phoric acid may be detected in presence of considerable amounts of arsenic acid by placing a drop of the suspected solution on a quantitative filter-paper (qualitative papers usually contain a small amount of phosphate) and adding one drop of a nitric acid–ammonium molybdate solution. A drop of a saturated solution of benzidine in acetic acid is now added and the moist paper held in ammonia vapour. A blue colour indicates the presence of phosphoric acid. The presence of phosphate in insoluble phosphates, minerals, or slags may be detected by treating about 10 mg. of substance on a filter-paper in the manner described. For the corresponding test-tube reaction 2 c.c. of solution are treated with three drops of the nitric acid–molybdate solution and three drops of the benzidine solution and 1% ammonia added until the turbidity persists. The limiting concentration of phosphoric acid detectable by this method is  $1 \text{ in } 3 \times 10^6$ .

Owing to complex formation many of the reactions of molybdic and oxalic acids are masked in presence of each other. The reaction between permanganate and oxalic acid, although not repressed, is considerably retarded in presence of molybdic acid. A solution of ammonium molybdate containing 5 mols. of tartaric acid per mol. of molybdic acid gives a precipitate with phosphoric acid, but not with arsenic acid. J. S. CARTER.

**Indophenol reaction in inorganic chemistry.** J. STIEPOVICH and A. SA (Rev. Cent. Estud. Farm. Bioquim., 1927, 16, 384–385; Chem. Zentr., 1928, i, 1556).—In the indophenol test for chlorine the production of hypochlorite is necessary, sodium or potassium hydroxide or carbonate, but not hydrogen carbonate, being added. Carbonate can be detected in a dilution of 1 in 5000. Tertiary phosphates yield indophenol-blue immediately in the cold; secondary phosphates react slowly in the cold but rapidly on warming, whilst primary phosphates do not react.

A. A. ELDRIDGE.

**Centigram elementary analysis. I. Determination of carbon and hydrogen, with automatic regulation of combustion. II. Nitrogen determination.** B. BOBRAŃSKI and E. SUCHARDA (Rocz. Chem., 1928, 8, 290–324).—A method is described for the micro-determination of carbon, hydrogen, and nitrogen, involving the use of only 2–3 centigrams of substance. The method for the determination of carbon and hydrogen is similar to that of Pregl, the combustion tube being filled with successive layers of silver gauze, copper oxide, and lead chromate precipitated on pumice, platinised asbestos, silver gauze, lead peroxide, and silver gauze. The temperature of the lead peroxide layer is maintained at 200°. The method for the determination of nitrogen is also based on that of Pregl, the volume of nitrogen evolved being read in a nitrometer graduated in 0.02 c.c., and 1.2% of the volume read being deducted as a correction for alkali solution adhering to the glass. R. TRUSZKOWSKI.

**Analysis of silicates by decomposition with alkali hydroxides in a nickel crucible.** C. J. VAN NIEUWENBURG and H. H. DINGEMANS.—See B., 1928, 671.

**Determination of sodium-ion concentration by means of a sodium amalgam electrode.** G. ETTISCH and K. JOACHIMSOHN (*Z. Elektrochem.*, 1928, 34, 404—406).—Details are given of an improved method for measuring sodium-ion concentrations by means of a sodium amalgam electrode. Special precautions are taken to prevent hydrogen evolution at the surface of the amalgam, and the formation of alkaline solution on account of the hydrolysis of the amalgam. Reproducible measurements are obtainable, using quite small quantities of solution and amalgam. L. L. BIRCUMSHAW.

**Specific reagents for silver and a new sensitive test for silver.** F. FEIGL (*Z. anal. Chem.*, 1928, 74, 380—386).—The silver salt of *p*-dimethylamino-benzylidenerhodanine,  $\text{AgC}_{12}\text{H}_{11}\text{N}_2\text{OS}_2$ , is precipitated from acid, neutral, or ammoniacal solutions of silver salts on addition of an acetone solution of the reagent as a flocculent, reddish-violet precipitate. When the concentration of silver is very small the precipitate is brown and contains the free base. Since the rhodanine base is readily soluble, and the silver salt absolutely insoluble, in carbon disulphide, carbon tetrachloride, etc., it is desirable when very small quantities of silver are concerned to shake the solution with one of these solvents after precipitation. A solution of 0.03 g. of base in 100 c.c. of acetone is recommended for the detection of small amounts of silver. The limiting concentrations of silver detectable by hydrochloric acid and the rhodanine base are 1 in  $10^5$  and 1 in  $5 \times 10^6$ , respectively, the latter reagent being sufficiently sensitive to detect the solubility of silver chloride in water. The above reaction may be used to detect the presence of traces of silver in minerals, metals, and salts. The presence of silver in coinage, platinum, etc. may be detected by making a scratch with the material on unglazed porcelain. The streak is treated with a drop of nitric acid and the porcelain warmed over a flame to remove excess of acid. The porcelain is now placed in an acetone solution of the rhodanine base to which a drop of dilute nitric acid has been added. If silver was present in the metal a reddish-violet zone occupies the position of the original streak. Mercury interferes, but may be removed by strongly heating the porcelain prior to treatment with nitric acid.

The reagent is prepared by boiling an equimolecular mixture of rhodanine (Nencki, *J.C.S.*, 1877, ii, 872; Holmberg, *A.*, 1906, i, 811) and *p*-dimethylamino-benzaldehyde in glacial acetic acid under reflux for 1 hr. The condensation product is precipitated with water and crystallised from boiling alcohol.

J. S. CARTER.

**Determination of salts in dilute solution by the opacity of fine suspensions produced in the solutions.** A. BOUTARIC and G. PERREAU (*Rev. gén. Colloid.*, 1928, 6, 113—117).—The opacity (measured by a Féry spectrophotometer) which is produced when a fine precipitate is formed in a solution of a salt by adding a suitable reagent may be prevented from changing appreciably with time by the addition of a solution of dextrin or of gum arabic. The concentration of the gum may vary between 0.4 and 20% without affecting the results. If the

temperature is maintained constant within  $0.1^\circ$  an accuracy of 0.5% may be attained in the determination of suitable salts. Silver and chlorine as silver chloride, phosphates as silver phosphate, and magnesium as magnesium hydroxide may be determined in this way. In determining barium or sulphates as barium sulphate, 15 min. should elapse before comparative readings of opacity are made. The method is not applicable to the determination of calcium as calcium oxalate, since the addition of gum arabic accelerates the formation of precipitates of this substance. F. G. TRYHORN.

**Micro-determination of calcium.** F. ROGOZINSKI (*Rocz. Chem.*, 1928, 8, 275—279).—Calcium is precipitated quantitatively as sulphate in presence of 4 vols. of alcohol, and is weighed as the hydrated sulphate, 0.27 mg. of calcium being determinable by this method. Chlorides and magnesium have a slight influence on the accuracy of this method only when present in very great excess.

R. TRUSZKOWSKI.

**Detection of magnesium in rocks by means of the diphenylcarbazide reaction.** F. FEIGL (*Z. anal. Chem.*, 1928, 74, 398—399).—X-Ray analysis supports the author's formulation of dolomite as the complex compound  $\text{Ca}[\text{Mg}(\text{CO}_3)_2]$  (*A.*, 1927, 1161).

J. S. CARTER.

**Sensitive colour reactions for magnesium.** H. D. BARNES (*J. S. Afr. Chem. Inst.*, 1928, 11, 67—68).—A neutral magnesium salt solution containing 0.5 mg. of metal/litre yields a definite orange colour when 10 c.c. of the solution are treated with 0.2 c.c. of a 0.1% solution of Clayton-yellow and 0.5 c.c. of 4*N*-sodium hydroxide solution. With more concentrated solutions of magnesium salts (5 mg./litre) a brick-red colour is obtained. Calcium in concentrations not exceeding 300 mg./litre does not interfere, but larger amounts produce opalescent solutions with the alkali. A. R. POWELL.

**Applications of the "zinc" test for cassiterite.** G. H. STANLEY.—See B., 1928, 614.

**Determination of copper in iron and steel.** E. ZINDEL.—See B., 1928, 643.

**Apparatus for the investigation of air, and its content of foreign vapours, especially of mercury vapour.** A. BUSS (*Chem. Fabr.*, 1928, 503—504).—A compact form of apparatus containing a small electrically-driven rotary air-pump which sucks the air to be tested through two condensation tubes, immersed in liquid air, and then into a measuring vessel, is described. Mercury vapour is totally condensed in the first U-tube when the velocity of flow does not exceed 1.5—2 litres/min. Using about 2 litres of liquid air the apparatus may be left to work without attention for about 2 hrs.

H. F. GILLBE.

**Potassium hydrogen sulphate fusions [in analysis of aluminous refractories].** W. R. KERR.—See B., 1928, 642.

**Colorimetric determination of iron by means of potassium thiocyanate.** L. S. VAN DER VLUGT (*Chem. Weekblad*, 1928, 25, 495—496).—0.1 mg. of iron present in 100 c.c. of solution may be detected,

even in presence of other salts, if the solution contains 2% of sulphuric acid and 10 c.c. of 20% thiocyanate solution be added. Oxidation to the ferric state is best effected by use of potassium persulphate in boiling acid solution.  
S. I. LEVY.

**Application of photo-electric spectrophotometry to micro-analysis.** H. VON HALBAN and E. ZIMPELMANN (*Z. Elektrochem.*, 1928, **34**, 387—393; cf. von Halban and Siedentopf, *A.*, 1922, ii, 332).—The photo-electric spectrophotometric method developed by von Halban and his collaborators has been applied to the determination of small quantities of ferric iron by means of thiocyanate and of titanium as titanium peroxide. Quantities of iron ranging from 1 to 0.001 mg. in 50 c.c. of solution can be determined by this means with an accuracy of 1%, whilst the smallest detectable quantity is 0.00002 mg. of iron in 50 c.c. of solution. The method could be applied to the determination of the iron in a drop of blood. The smallest detectable quantity of titanium in 50 c.c. of solution is 0.0001 mg., and 0.01 mg. can be determined with an accuracy of 1%. The possible sources of error in the practical application of the method are discussed.  
L. L. BIRCUMSHAW.

**Simultaneous potentiometric determination of iron, copper, and arsenic.** E. ZINTL and F. SCHLOFFER (*Z. angew. Chem.*, 1928, **41**, 956—960).—The difficulties of the methods of Kolthoff and Tomicek (*A.*, 1925, ii, 72) and of Buehrer and Schupp (*B.*, 1926, 282) in the simultaneous potentiometric determination of iron and copper are due to the presence of chloride ions. In sulphuric acid, using chromous sulphate as reducing agent, sharp endpoints are obtained for copper, iron, copper with iron, copper with iron and chromate, and copper with iron and arsenic. The results are unaffected by the presence of lead, nickel, cobalt, aluminium, chromic salts, or manganese.  
C. HOLLINS.

**Persulphate method for determining chromium plus vanadium in chrome vanadium tungsten steels.** H. H. WILLARD and P. YOUNG.—See *B.*, 1928, 643.

**Volumetric determination of vanadium in chrome vanadium tungsten steels.** H. H. WILLARD and P. YOUNG.—See *B.*, 1928, 643.

**Separation and determination of bismuth by means of cupferron.** A. PINKUS and J. DERNIES (*Bull. Soc. chim. Belg.*, 1928, **37**, 267—283).—Bismuth is precipitated completely from solutions of its salts containing free hydrochloric or nitric acid not exceeding a *N*-solution by the addition of a 5% solution of cupferron added drop by drop from a burette until at least 0.3 g. of cupferron has been added for every 0.1 g. of bismuth present. The yellowish-white, flocculent precipitate is collected, washed with a 0.1% solution of the precipitant, dried, and gently ignited to bismuth oxide for weighing. The method affords a rapid means of separating bismuth from cadmium, lead, zinc, arsenic, silver, and quinquevalent antimony. Cadmium and lead are precipitated quantitatively by cupferron from neutral solutions.  
A. R. POWELL.

**Spot of light-reading device for galvanometers.** T. T. SMITH (*J. Opt. Soc. Amer.*, 1928, **17**, 155—161).

**Spectrographs for the analysis of metals.** EWALD (*Chem. Fabr.*, 1928, 501—503).—A description of a number of commercial types.

H. F. GILLBE.

**Radon pump.** L. F. CURTISS (*J. Opt. Soc. Amer.*, 1928, **17**, 77—80).—The arrangement consists of two Töpler pumps in series and a number of accessories to provide for the purification of the radon and the manipulation of the mercury. The advantages of the design are that it eliminates all rubber tubing and all stopcocks through which the mercury may pass, and that it makes the use of liquid air very convenient and allows a more rapid manipulation than is possible with a pump depending solely on purification by chemical means.

L. L. BIRCUMSHAW.

**"Acid-alkalimeter"; a direct-reading  $p_{H}$  meter.** K. H. GOODE (*J. Opt. Soc. Amer.*, 1928, **17**, 59—71).—The objection to the use of a single thermionic valve in conjunction with a  $p_{H}$  meter is the necessity of employing a microammeter or millivoltmeter as an indicating device. An instrument of this type using three valves has been previously described (cf. *A.*, 1925, ii, 1196). Difficulties have been encountered in the use of this, however, and a new form is described. Two valves of the oxide-coated filament type are used and the indicating instrument is a special Weston three-terminal voltmeter-ammeter. Full details are given for the adjustment of the resistances and controls.

L. L. BIRCUMSHAW.

**McBain-Bakr balance for sorption of vapours by fibrous and film materials.** P. T. NEWSOME (*Ind. Eng. Chem.*, 1928, **20**, 827).—The material, such as cellulose or cellulose esters, is suspended in the apparatus maintained at constant temperature from the calibrated quartz spring and evacuated to constant weight at a pressure of <0.01 mm. By introducing successive small quantities of water from a capillary and observing the pressure and elongation of the spring, absorption curves at various temperatures may be obtained. Similar observations during the gradual removal of water vapour with a vacuum pump yield the corresponding desorption curves. A device is described for determining the absorption of vapours of liquids which attack stopcock grease.

F. R. ENNOS.

**Micro-apparatus for the determination of mol. wt. by the cryoscopic method.** K. IWAMOTO (*Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 719—722).—A Beckmann apparatus of reduced size is described with which the mol. wt. of small quantities of material (7—30 mg.) can be determined, using 1.5 c.c. of solvent.  
C. J. SMITHELLS.

**Simple method for measuring rotatory dispersion.** I. BENCOWITZ (*J. Physical Chem.*, 1928, **32**, 1163—1170).—The method described eliminates the use of a cadmium-quartz lamp, is accurate to within 0.02%, and permits a complete determination of rotatory dispersion for 10 wave-lengths to be made in 5 hrs. Monochromatic light is replaced by portions

of light from a continuous spectrum, and any wavelength of which the rotation in quartz is known can be employed.

L. S. THEOBALD.

**Apparatus for the determination of gas densities by the Bunsen effusion method.** H. KAHLE (Z. angew. Chem., 1928, 41, 876—880).—Errors due to irregularities in the aperture of the diffusion disc are eliminated by passing the gas, in an enclosed apparatus capable of rotation about its axis, alternately in opposite directions through the aperture.

F. G. TRYHORN.

**Laboratory aspirator.** E. N. BATES and G. P. BODNAR (U.S. Dep. Agric. Circ., 1927, 9, 1—12).—The device (U.S.P. 1,524,012) separates granular substances by means of a current of air passing through a thin stream of the substances.

CHEMICAL ABSTRACTS.

**Temperature measurement between 20° and 90° Abs.** F. HENNING (Naturwiss., 1928, 16, 617).—Onnes and Tuyn (Leiden Communications Suppl., 1926, 58) have prepared a table giving the resistance ratio  $w' = R_t/R_0$ , from degree to degree for a standard-

ised platinum resistance thermometer. This table can be used for any platinum resistance thermometer within the range of 20—90° Abs. by the aid of an empirical formula.

A. J. MEE.

**Automatic pipette.** O. ORTH (Chem. Fabr., 1928, 492).—The pipette has a glass tap at the bottom and is expanded to a bulb at the top. The graduation mark is on the constriction below the bulb and a capillary filling tube ends on a level therewith. The pipette is filled from a wash-bottle at a lower level and any surplus runs back. The filling and air release connexions are either fused in or taken through a rubber stopper.

C. IRWIN.

**Reproduction of scales by electric discharge to a photographic plate.** J. H. CHESTERS (Nature, 1928, 122, 349).

**Space model of the periodic system of the elements.** A. S. RAMONDT (Chem. Weekblad, 1928, 25, 496—498).—A method of constructing a model of a spiral representation is described, and the horizontal projection of a thread joining the positions of the elements is set out.

S. I. LEVY.

## Geochemistry.

**Medicinal muds of Crimean salt lakes.** A. F. SAGAJDACHNUI (Trans. State Inst. Appl. Chem. Moscow, 1927, No. 5, 25—52).—The composition of the waters of Moinak lakes is tabulated, and the formation and regeneration of the mud a low salt concentration, favouring bacterial life and gelation of colloids, is necessary; for its preservation it is necessary that the salt concentration of the water should increase, so as to suppress biochemical processes tending to form non-colloidal calcium carbonate.

CHEMICAL ABSTRACTS.

**Red soils of Cochin China.** V. AGAFONOV (Compt. rend., 1928, 187, 428—431).—These soils, which occur in layers 5—6 m. deep and consist of aggregates of amorphous grains (diameter 0.1 micron) principally of bauxite, stilpnosiderite, and hydrated aluminosilicates, are produced by the decomposition of basalts. This corresponds with the progressive disappearance of magnesia and the alkalis, the oxidation of ferrous oxide, and an increase in the water, alumina, and titania contents, transparent red bowlingite being formed as an intermediate product. Although they may contain 0.1% K and 0.43% N, their structure and low  $p_H$  value render them unsuitable for agriculture in rainy districts.

J. GRANT.

**Changes of certain clays into acidic ones through weathering.** T. OKAZAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 776—784).—It is suggested that the acidity of clays is due to the weakness of the combination of silica and alumina, and to the consequently easy decomposition of alkaline or neutral clays by weathering.

C. W. GIBBY.

**Lavas of the Sous-le-Vent islands of the Society Archipelago.** A. LACROIX (Compt. rend.,

1928, 187, 397—401).—The so-called granite of this region is in reality an olivine gabbro having the same composition as the porphyric basaltic olivine with which it is associated. Pegmatoids which are also found, are the result of a differentiation under special conditions of the same magma (cf. *ibid.*, 397), but are richer in alumina, alkalis, titania, and phosphorus, and poorer in magnesia than the related basalt. Other basalts are also found, with traces of free silica, the proportions of sodium and potassium being often the same; slatite is an exception.

J. GRANT.

**Zeolites as fossilising substances.** H. UDLUFT (Arkiv Kemi, Min., Geol., 1928, 9, No. 33, 15 pp.).—Fossilised wood from the basaltic tufa on the lower slopes of Mt. Elgon in British East Africa was found to contain crystals of natrolite, mesolite, and apophyllite, whilst calcite had apparently played a part in building up the structure and a certain amount of the original organic wood substance was still present. It is suggested that the wood was dehydrated above 150° in the tufa beds and then subjected to the action of hydrothermal epimagmatic solutions which deposited in succession natrolite, apophyllite, and calcite. The mineralisation appeared to have been affected by the original structure of the wood in that the mineral crystals were elongated in the direction of the circulation along the wood fibres and the wood cells seemed to be filled first.

A. R. POWELL.

**Some metamorphosed dolerites from Broken Hill.** W. R. BROWNE (J. Proc. Roy. Soc. New South Wales, 1927, 61, 383—400).—The petrographical characters of a series of basic rocks at Broken Hill are described and the probable chemical changes involved in their metamorphism are discussed.

C. W. GIBBY.

**Petrological notes on some New South Wales alkaline basic rocks.** W. R. BROWNE (J. Proc. Roy. Soc. New South Wales, 1927, 61, 371—382).—A description of six rocks found in New South Wales. C. W. GIBBY.

**The Great Bahama Bank. Marine carbonate sediments.** R. M. FIELD (Amer. J. Sci., 1928, [v], 16, 239—246).—Specimens of calcareous muds from the lagoons of the Great Bahama Bank have been collected and are being examined. C. W. GIBBY.

**Occurrence of tridymite and cristobalite in a granite xenolith.** A. A. WEYMOUTH (Amer. J. Sci., 1928, [v], 16, 237—238).—The following minerals have been identified in a disintegrated granite rock in Idaho: quartz, orthoclase, oligoclase, muscovite, biotite, chlorite, garnet, iron oxide, zircon, tridymite, and cristobalite. Its composition is compared with that of an artificially prepared silica brick. C. W. GIBBY.

**New platinum mineral in Rustenburg norites.** R. A. COOPER (J. Chem. Met. Min. Soc. S. Africa, 1928, 28, 281—283).—A new platinum sulpharsenide, discovered in Rustenburg norites, has the com-

position Pt 64.2, Pd 9.4, S 17.7, As 7.7%, corresponding with the formula  $Pt(S,As)_2$ . The greater part of the palladium is entirely independent of the platinum. C. W. GIBBY.

**Crystallophyllian rocks of Mayombe (French equatorial Africa).** V. BABET (Compt. rend., 1928, 187, 348—350).—These rocks, which are considered to belong to the superior zone characterised by albite and the hydroxyl minerals (chlorite, sericite, epidotite), fall into two classes: (1) Feldspathic (albite) gneiss type containing layers of sericite, and alkaline or calco-alkaline in character. Quartz when present is granoblastic and the free alumina content rises to about 5%, showing that in spite of the analogy to the granites in composition the rocks are derived from altered granites or arkoses. (2) Non-feldspathic mica schists and epidotites containing chlorite and albite crystals in quartz inclusions, with beds of primary calcite. With the exception of the epidotite they may contain up to 11% of free alumina. Analyses are given. J. GRANT.

**Minerals. III.** H. COLLINS (Chem. News, 1928, 137, 168—170).

## Organic Chemistry.

**Catalytic hydrogenation of different types of unsaturated compounds. III. Hydrogenation of conjugated systems.** S. V. LEBEDEV and A. O. YAKUBCHIK (J.C.S., 1928, 2190—2204).—The catalytic hydrogenation of diisopropenyl, b. p. 69°,  $d_4^{20}$  0.7262, divinyl, and piperylene, b. p. 41.5°,  $d_4^{20}$  0.6852, has been studied by the methods previously employed (this vol., 613). Hydrogenation in each case is of type II (*loc. cit.*), the curves consisting of three sections. Hydrogenation of diisopropenyl proceeds at a similar rate to that of isoprene. The first section of the curve is horizontal up to the critical point (69% hydrogenation); the rate of absorption then increases in the second portion corresponding with the hydrogenation of methylisopropylethylene, and finally decreases rapidly, this third stage corresponding with the hydrogenation of tetramethylethylene. In order to study the process of hydrogenation up to the critical point it was interrupted at 25% and 50% hydrogenation and the composition of the product determined by the methods previously employed. The proportion of the various products present at 25%, 50%, and 69% (critical point) hydrogenation are, respectively, diisopropenyl, 64, 28, 0%; diisopropyl, 14, 28, 38%; *as*-methylisopropylethylene, 16, 32, 45%; tetramethylethylene, 6, 16, 17%. The experimentally determined quantities of diisopropenyl, diisopropyl, and total hexylenes lie on almost straight lines, but the curve for the individual hexylenes shows breaks which are probably due to isomeric change produced by the action of sulphur dioxide, which is shown to isomerise *as*-methylisopropylethylene to tetramethylethylene. The hydrogenation of diisopropenyl in the presence of ethylene derivatives of different degrees of substitution has been studied and it is found that the

ethylene derivative is generally hydrogenated after the critical point (which retains its original position) in places determined by the degree of substitution. When camphene is added the beginning of the hydrogenation of this substance is distinctly separated from the end of the first section of the curve; the whole of the *as*-disubstituted ethylene is hydrogenated after the critical point and hence does not alter the amount of fully saturated molecules then present. The latter are therefore formed before the critical point and must arise from the simultaneous (or almost simultaneous) addition of 2 mols. of hydrogen to the conjugated system. The curve for divinyl is of similar type; the first section, relating to the conjugated system, ends at the critical point (76% hydrogenation, unchanged by admixture with substituted ethylene derivatives) when the composition of the product is divinyl, 0; butane, 52; *n*- $\Delta^{\alpha}$ -butylene, 34; *n*- $\Delta^{\beta}$ -butylene, 14%. The second portion of the curve pertains to  $\Delta^{\alpha}$ - and the third to  $\Delta^{\beta}$ -butylene. Similarly with piperylene, the first section ends at the critical point (74% hydrogenation) where the composition is piperylene, 0; propylethylene, 15; *s*-methylethylethylene, 39; pentane, 46%. The second portion, where more rapid absorption of a further 6.5% of hydrogen occurs, corresponds with propylethylene, and the third (19.5% hydrogen) with *s*-methylethylethylene. Hydrogenation of piperylene mixed with various ethylene derivatives was also studied, and of these camphene, methylheptenone, and tetramethylethylene form independent sections of the hydrogenation curve. J. W. BAKER.

**Allyl transposition and additive derivatives of erythrene hydrocarbons.** C. PRÉVOST (Ann. Chim., 1928, [x], 10, 113—146).—A more detailed

account of work already reviewed (A., 1926, 496; 1927, 131, 337, 748, 749, 851; this vol., 152, 613).

H. BURTON.

**Preparation of tetramethylethylene.** J. C. EARL (J. Proc. Roy. Soc. New South Wales, 1927, 61, 68—72).—A good yield of tetramethylethylene can be obtained by dehydrating dimethylethylcarbinol with oxalic acid to trimethylethylene, from the chlorohydrin of which dimethylisopropylcarbinol is obtained by the action of magnesium methyl iodide. This gives the hydrocarbon on dehydration with dilute sulphuric acid or concentrated oxalic acid.

C. W. GIBBY.

**Allene hydrocarbons.** M. BOUIS (Ann. Chim., 1928, [x], 9, 402—465).—Allenes,  $R\cdot CH:C:CH_2$ , where  $R$  is an alkyl group, are prepared from the appropriate substituted allyl alcohol,  $R\cdot CH(OH)\cdot CH_2\cdot CH_2$ , formed by the action of the appropriate Grignard reagent on acetaldehyde. The following compounds are described:  $\Delta$ - $\delta$ -methylpenten- $\gamma$ -ol, b. p. 125°/760 mm.,  $d^{20}$  0.8368,  $n_D^{20}$  1.4263;  $\Delta$ - $\epsilon$ -methylhexen- $\gamma$ -ol has b. p. 58°/15 mm., 146° (corr.)/760 mm.,  $d^{20}$  0.8288,  $n_D^{20}$  1.4285. These by the action of phosphorus tribromide with cooling in the presence of pyridine yield pure allyl bromides,  $R\cdot CH:CH\cdot CH_2Br$ , the isomeric change going to completion in each case (cf. Burton and Ingold, this vol., 634), and thus are obtained  $\Delta$ - $\beta$ - $\alpha$ -bromopentene, b. p. 123—124°, 35°/25 mm.,  $d^{20}$  1.2545,  $n_D^{20}$  1.4731;  $\Delta$ - $\beta$ - $\alpha$ -bromohexene, b. p. 42—44°/10 mm.,  $d^{18}$  1.2119,  $n_D^{18}$  1.4778;  $\Delta$ - $\beta$ - $\alpha$ -bromo- $\delta$ -methylpentene, b. p. 46°/18 mm.,  $d^{24}$  1.2208,  $n_D^{24}$  1.4723;  $\Delta$ - $\beta$ - $\alpha$ -bromohexene, b. p. 62—64°/10 mm.,  $d^{17}$  1.1682,  $n_D^{17}$  1.4760;  $\Delta$ - $\beta$ - $\alpha$ -bromo- $\epsilon$ -methylhexene, b. p. 60°/15 mm.,  $d^{21}$  1.1782,  $n_D^{21}$  1.4750. These by boiling with anhydrous sodium acetate in acetic acid yield the corresponding acetates and thus are obtained  $\Delta$ - $\beta$ -hexenyl, b. p. 171—173°,  $d^{18}$  0.8976,  $n_D^{18}$  1.4282,  $\Delta$ - $\beta$ - $\delta$ -methylpentenyl, b. p. 163°,  $d^{22}$  0.8990,  $n_D^{22}$  1.4260,  $\Delta$ - $\beta$ -heptenyl, b. p. 192—194° (corr.),  $d^{18}$  0.8915,  $n_D^{18}$  1.4314,  $\Delta$ - $\beta$ - $\epsilon$ -methylhexenyl, b. p. 182—184° (corr.),  $d^{20}$  0.8836,  $n_D^{20}$  1.4280, acetates;  $\Delta$ - $\beta$ -pentenyl acetate has  $d^{22}$  0.9019,  $n_D^{22}$  1.4219. Hydrolysis of these with aqueous methyl-alcoholic sodium hydroxide yields the corresponding carbinols,  $R\cdot CH:CH\cdot CH_2\cdot OH$ , and thus are obtained  $\Delta$ - $\beta$ -hexen- $\beta$ -ol, b. p. 158—160°,  $d^{16}$  0.8490,  $n_D^{16}$  1.4403 (naphthylurethane, m. p. 76°);  $\Delta$ - $\beta$ - $\delta$ -methylpenten- $\alpha$ -ol, b. p. 150°,  $d^{21}$  0.8348,  $n_D^{21}$  1.4357;  $\Delta$ - $\beta$ -hepten- $\alpha$ -ol, b. p. 177—179° (corr.),  $d^{20}$  0.8421,  $n_D^{20}$  1.4410;  $\Delta$ - $\beta$ - $\epsilon$ -methylhexen- $\alpha$ -ol, b. p. 169° (corr.),  $d^{20}$  0.8355,  $n_D^{20}$  1.4390. Addition of bromine at 0° to the allyl bromides (above) yields the tribromides,  $R\cdot CHBr\cdot CHBr\cdot CH_2Br$ , and thus are obtained  $\alpha\beta\gamma$ -tribromo- $\delta$ -methylpentane, b. p. 131—132°/18 mm., m. p. 35°,  $d^{25}$  1.9139,  $n_D^{25}$  1.5470;  $\alpha\beta\gamma$ -tribromo- $\epsilon$ -methylhexane, b. p. 134—135°/12 mm.,  $d^{21}$  1.8116,  $n_D^{21}$  1.5380;  $\alpha\beta\gamma$ -tribromopentane, b. p. 122—124°/18 mm.,  $d^{19}$  2.0741,  $n_D^{19}$  1.5589;  $\alpha\beta\gamma$ -tribromohexane, b. p. 127—129°/11 mm.,  $d^{18}$  1.9429,  $n_D^{18}$  1.5506;  $\alpha\beta\gamma$ -tribromoheptane, b. p. 142—143°/12 mm.,  $d^{17}$  1.8112,  $n_D^{17}$  1.5393. Fusion with 75—80% potassium hydroxide converts these into the allene dibromides,  $R\cdot CHBr\cdot CBr:CH_2$ , and thus are obtained  $\Delta$ - $\beta$ - $\gamma$ -dibromopentene, b. p. 75—76°/12 mm.,  $d^{19}$  1.7442,  $n_D^{19}$  1.5316;  $\Delta$ - $\beta$ - $\gamma$ -dibromohexene, b. p. 83—85°/9 mm.,  $d^{14}$

1.6381,  $n_D^{14}$  1.5248;  $\Delta$ - $\beta$ - $\gamma$ -dibromo- $\delta$ -methylpentene, b. p. 81°/124 mm.,  $d^{24}$  1.6035,  $n_D^{24}$  1.5180;  $\Delta$ - $\beta$ - $\gamma$ -dibromoheptene, b. p. 108—110°/12 mm.,  $d^{18}$  1.5595,  $n_D^{18}$  1.5200;  $\Delta$ - $\beta$ - $\gamma$ -dibromo- $\epsilon$ -methylhexene, b. p. 100—101°/12 mm.,  $d^{20}$  1.5493,  $n_D^{20}$  1.5155. The allenes,  $R\cdot CH:C:CH_2$ , are obtained (yield 50—60% calculated on the original allyl alcohol) by dropwise addition of these dibromides to zinc dust in boiling alcohol and thus are prepared ethyllallene ( $\Delta$ - $\alpha$ -pentadiene), b. p. 45°,  $d^{20}$  0.6890,  $n_D^{20}$  1.4100,  $n_D^{20}$  1.4149,  $n_D^{20}$  1.4209; propyllallene, b. p. 78°,  $d^{17}$  0.7198,  $n_D^{17}$  1.4246,  $n_D^{17}$  1.4298,  $n_D^{17}$  1.4353; isopropyllallene, b. p. 70°,  $d^{22}$  0.7061,  $n_D^{22}$  1.4201,  $n_D^{22}$  1.4232,  $n_D^{22}$  1.4308; butyllallene, b. p. 106° (corr.),  $d^{14}$  0.7374,  $n_D^{21}$  1.4321,  $n_D^{21}$  1.4360,  $n_D^{21}$  1.4427,  $n_D^{21}$  1.4493; isobutyllallene, b. p. 96° (corr.),  $d^{19}$  0.17225,  $n_D^{19}$  1.4251,  $n_D^{19}$  1.4282,  $n_D^{19}$  1.4353. These all show slight optical exaltation (about 0.5) which increases with the mol. wt. of the derivative and is greater with branched chains than with straight chains. Addition of 1 mol. of bromine in carbon tetrachloride solution to propyllallene occurs mainly at the  $\beta\gamma$  double linking, a little of the  $\alpha\beta$  product being formed as a by-product. Further addition of bromine yields, with the appropriate allene,  $\alpha\beta\beta\gamma$ -tetrabromopentane, b. p. 120°/3 mm.,  $d^{22}$  2.2939,  $n_D^{22}$  1.5916;  $\alpha\beta\beta\gamma$ -tetrabromohexane, b. p. 130°/3 mm.,  $d^{15}$  2.1873,  $n_D^{15}$  1.5850;  $\alpha\beta\beta\gamma$ -tetrabromoheptane, b. p. 140°/3 mm.,  $d^{20}$  2.0675,  $n_D^{20}$  1.5718. The action of a 35% acetic acid solution of hydrogen bromide on ethyllallene at 0° yields a mixture of products from which were isolated a mixture which probably contains  $\Delta$ - $\beta$ -bromopentene (since by treatment with alkali it yields an acetylene, forming a copper derivative) and  $\Delta$ - $\beta$ -bromopentene (yields propionic acid on oxidation) together with  $\beta\beta$ -dibromopentane, b. p. 62—63°/18 mm.,  $d^{16}$  1.6452,  $n_D^{16}$  1.5031. Hydration of the allenes with concentrated sulphuric acid at  $-10^\circ$  and subsequent treatment with water yields the corresponding methyl ketones,  $CH_2R\cdot CO\cdot CH_3$ , whilst by the action of sodamide the sodium derivative of the isomeric acetylene,  $CH_2R\cdot C:CNa$ , is obtained.

J. W. BAKER.

**Reaction between acetylene and sulphur at temperatures up to 650°.** J. B. PEEL and P. L. ROBINSON (J.C.S., 1928, 2068—2070).—In confirmation of the results of Meyer and Sandmeyer (A., 1884, 45) and contrary to those of Capelle (A., 1908, i, 201) and de Coninck (*ibid.*, 750) it is found that the liquid products obtained by the interaction of sulphur and acetylene consist of (a) carbon disulphide, (b) thiophen, and (c) thiophten. At most only 77% of the sulphur is found in the distillate, the remainder probably being converted into hydrogen sulphide. Ignition occurs at 275°, but the reaction is inconveniently slow below 300°. At 325°, 500°, and 650° the proportions of the three products formed are, respectively, (a) 77, 77, and 83%, (b) 9, 12, and 5%, (c) 6, 6, and 3%, the optimum temperature for the formation of thiophen,  $d^{20}$  1.0615,  $\gamma^{20}$  32.58, being 500°.

J. W. BAKER.

**Catalysts for the formation of alcohols from carbon monoxide and hydrogen.** I. Decomposition of methyl alcohol by catalysts composed of copper and zinc. P. K. FROLICH, M. R. FENSKE,



and D. QUIGGLE (Ind. Eng. Chem., 1928, 20, 694—698; cf. Lewis and Frolich, B., 1928, 359).—The catalytic decomposition of methyl alcohol at 360° and a total pressure of 1 atm. with mixtures of zinc and copper oxides in varying proportions has been studied. Maximum decomposition and formation of carbon monoxide occurred when zinc oxide was present in excess, although the addition of only 3 mol.-% of zinc oxide to copper oxide increases decomposition. The effect of adding a small amount of copper oxide to zinc oxide is not so marked. The decomposition of methyl alcohol is thought to proceed in two stages:  $\text{MeOH} \rightarrow \text{H}_2 + \text{H}\cdot\text{CHO} \rightarrow 0.5\text{H}\cdot\text{CO}_2\text{Me} + \text{CO} + \text{H}_2$ . The extent to which the reaction proceeds depends largely on the zinc : copper ratio of the catalyst. The addition of a small amount of copper to zinc oxide favours the formation of carbon monoxide, whereas the addition of a small amount of zinc oxide to copper favours the formation of methyl formate.

R. A. PRATT.

**Tests for methyl alcohol.** E. W. TODD (Proc. Nova Scotian Inst. Sci., 1927, 16, 147—151).—The tests for methyl alcohol in the presence of ethyl alcohol using morphine, or milk and resorcinol, as also the older U.S. Pharmacopœia test (oxidation by copper spiral and detection of formaldehyde by Schiff's reagent), are inferior to the 1926 U.S. Pharmacopœia test, viz., the oxidation by acid permanganate to formaldehyde, giving a violet colour with Schiff's reagent.

S. J. GREGG.

**Constitution of citronellol and rhodinol.** V. GRIGNARD and J. DÈUVRE (Compt. rend., 1928, 187, 270—273).—Ozonisation of citronellol in aqueous acetic acid solution shows that it consists of  $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -octen-0-ol and about 24% of  $\beta\zeta$ -dimethyl- $\Delta^{\beta}$ -octen-0-ol; the latter occurs in smaller amounts (18%) in samples previously submitted to acid treatment. By the action of acetic acid containing small amounts of water on citronellal, a glycol, b. p. 115—118°/3 mm., m. p. 65—66°, is obtained which is probably the intermediate compound concerned in the cyclisation of citronellal into isopulegol. It is pointed out that in this cyclisation it is immaterial whether the double linking is in the  $\alpha$ - or the  $\beta$ -position in citronellal, since isopulegol may arise by the dehydration of either of the isomeric intermediate compounds.

G. A. C. GOUGH.

**Citronellol and rhodinol.** V. GRIGNARD and J. DÈUVRE (Compt. rend., 1928, 187, 330—334).—Bourbon geraniol which, by Glichitch's method (A., 1923, ii, 661), contains 51.9% of free and 15.9% of combined alcohols gives on distillation a "geraniol-rhodinol" fraction, b. p. 116—122°/18 mm., containing 50% of "rhodinol" as determined by the warm formylation method, and giving on ozonisation 80% of acetone and 32% of formaldehyde and formic acid. Geraniol obtained by rectification of citronellol on ozonisation gives 51% of formaldehyde and formic acid and 92% of acetone, a result which supports the structure  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ . Glycollaldehyde is also formed, and formic acid and formaldehyde probably result from hydrolysis of its peroxide,  $\text{CH}_2\cdot\text{OH}\cdot\text{CH}\cdot\text{O}_2$ . Isomerides differing in the position of the double linking about the  $\xi$ -carbon

atom may also be present (cf. A., 1925, i, 772). *l*-Rhodinol, isolated by Barbier and Bouveault's benzoyl chloride method, and having b. p. 118—119.5°/18 mm.,  $d_4^{15}$  0.860,  $n_D^{15}$  1.4574,  $[\alpha]_D^{17}$  +1.87°, bromine value 103 (allophanate, m. p. 105—106°), gives on ozonisation yields of formaldehyde, formic acid, and acetone which indicate the presence of 45—45.7% of the  $\alpha$ -form and 52—53% of the  $\beta$ -isomeride. These figures are unchanged by a fresh treatment with benzoyl chloride. *l*-Rhodinol, prepared by Tiemann and Schmidt's method, had b. p. 117—118.5°/17 mm.,  $d_4^{15}$  1.0864,  $n_D^{15}$  1.4601, bromine value 102, and gave on ozonisation figures indicating the presence of 25% of the  $\alpha$ - and 71% of the  $\beta$ -form. *d*-Citronellol, b. p. 119—121°/20 mm.,  $d_4^{15}$  0.856,  $n_D^{17}$  1.4617,  $\alpha_D^{15}$  +2.33°, bromine value 109, obtained from Java citronella oil, gives results on ozonisation indicating the presence of 24% of  $\alpha$ - and 80% of  $\beta$ -form. When treated with benzoyl chloride at 150° for 8 hrs. and hydrolysed, this *d*-citronellol affords a product, b. p. 118—119°/18 mm.,  $d_4^{15}$  0.860,  $n_D^{15}$  1.4572,  $\alpha_D^{15}$  +2.30°, bromine value 96 (allophanate, m. p. 104.5—105.5°), containing 39% of  $\alpha$ - and 59% of  $\beta$ -isomeride. Treatment with dry hydrogen chloride for 2 hrs. at 150° yields a similar product,  $d_4^{15}$  0.863,  $n_D^{17}$  1.4577, containing 42% of  $\alpha$ - and 54% of  $\beta$ -isomeride. Both benzoyl chloride and hydrogen chloride thus produce isomerisation of the  $\beta$ - to the  $\alpha$ -form, and it is concluded that Barbier and Bouveault's "rhodinol" is not present as such in the natural essences. The latter contain "citronellol," a mixture of about 80% of the  $\Delta^{\beta}$ -octene (the "citronellie" form), and 20% of the  $\Delta^{\alpha}$ -octene ( $\alpha$ -form). Certain acid influences produce isomerisation until the mixture contains about 50% of the  $\alpha$ -form, and since this mixture forms the "rhodinol" of Barbier and Bouveault, it is proposed to term the  $\alpha$ -isomeride the "rhodinic" form.

R. BRIGHTMAN.

**Configuration of  $\beta\gamma$ -butylene glycol.** J. BÖESEKEN and (MLLE.) R. COHEN (Rec. trav. chim., 1928, 47, 839—848).—A sample of  $\beta\gamma$ -butylene glycol of biological origin (cf. Kluyver and others, A., 1926, 203), b. p. 177—180°,  $\alpha_D^{20}$  +2.42° ( $l=2$ ), gave on fractionation mainly the solid *meso*-glycol, m. p. 25°; the presence of a little racemic glycol was shown by resolution of the hydrogen sulphate or hydrogen 3-nitrophthalate with strychnine and brucine. Synthetic  $\beta\gamma$ -butylene glycol, prepared from  $\Delta^{\beta}$ -butylene by way of the dibromide and diacetate, or, better, by oxidation with peracetic acid to monoacetate followed by hydrolysis, was mainly the *dl*-compound and was resolved ( $[\alpha]_D -3.2^\circ$  and  $+5^\circ$ ) in the form of its hydrogen sulphate by means of brucine. The *meso*-glycol has little effect on the conductivity of boric acid, whilst the *dl*-glycol definitely lowers it, indicating a greater distance between the hydroxyl groups in the latter case. The formation of a *trans*-glycol by the action of peracetic acid shows that the stable butylene is a *cis*-compound.

C. HOLLINS.

**Ditertiary glycols and certain of their heterocyclic derivatives.** E. PACE (Atti R. Accad. Lincei, 1928, [vi], 7, 757—764).—Treatment of acetylacetone with a magnesium alkyl bromide

and decomposition of the resulting compound with water yield ditertiary glycols,  $\text{OH}\cdot\text{CMeR}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeR}\cdot\text{OH}$ , converted into tetrahydrofuran derivatives if left in a desiccator containing sulphuric acid or if heated in acetic acid solution at 120—150° in presence of sulphuric acid or zinc chloride, and into substituted tetrahydropyrroles if heated with a slight excess of concentrated alcoholic ammonia at 150° for about 2 hrs. The following compounds were obtained in this way:  $\beta\epsilon$ -*Dimethylhexane- $\beta\epsilon$ -diol*, m. p. 92—93°;  $\gamma\zeta$ -*dimethylheptane- $\gamma\zeta$ -diol*, b. p. 172—173°;  $\delta\eta$ -*dimethyloctane- $\delta\eta$ -diol*, b. p. 198—200°, which reacts readily with gaseous hydrogen bromide to give the corresponding dibromo-compound; 2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*, b. p. 119.5°, apparently identical with Pogorzelsky's diisocrotyl oxide (A., 1899, 785); 2 : 5-*dimethyl-2 : 5-diethyltetrahydrofuran*, b. p. 165°; 2 : 5-*dimethyl-2 : 5-dipropyltetrahydrofuran*, b. p. 186°; 2 : 2 : 5 : 5-*tetramethyltetrahydropyrrole*, b. p. 108° (cf. Pauly and Hültenschmidt, A., 1904, i, 88); 2 : 5-*dimethyl-2 : 5-diethyltetrahydropyrrole*, b. p. 125°, unstable in the air; 2 : 5-*dimethyl-2 : 5-dipropyltetrahydropyrrole*, b. p. 147—149°, unstable in the air.

T. H. POPE.

Reactions relating to carbohydrates and polysaccharides. XVI. Separation and identification of the isomeric ethylideneglycerols. H. S. HILL, A. C. HILL, and H. HIBBERT (J. Amer. Chem. Soc., 1928, 50, 2242—2249).—The separation of the two isomeric ethylideneglycerols from a mixture by fractional distillation was incomplete. The action of benzoyl chloride in dry pyridine on the mixture yielded a product which could be separated by crystallisation from light petroleum into  $\alpha\gamma$ -*ethylideneglyceryl  $\beta$ -benzoate*, m. p. 86°, and  $\alpha\beta$ -*ethylideneglyceryl  $\gamma$ -benzoate*, b. p. 144—145°/2 mm.,  $d_4^{17}$  1.1618,  $n_D^{17}$  1.5145. These were separated in the proportions of 1 : 1.8 and 1 : 4 from the products prepared by the action of acetylene and paracetaldehyde, respectively, on glycerol.  $\alpha\gamma$ -*Ethylideneglycerol*, b. p. 52°/2 mm.,  $d_4^{17}$  1.1477,  $n_D^{17}$  1.4532, and  $\alpha\beta$ -*ethylideneglycerol*, b. p. 68—70°/1 mm., were obtained by hydrolysis of the benzoates. The action of methyl iodide and silver oxide yielded  $\beta$ -*methyl  $\alpha\gamma$ -ethylideneglyceryl ether*, b. p. 80°/23 mm.,  $d_4^{17}$  1.0705,  $n_D^{17}$  1.4375, and  $\gamma$ -*methyl  $\alpha\beta$ -ethylideneglyceryl ether*, b. p. 58—61°/23 mm.,  $d_4^{17}$  1.0224,  $n_D^{17}$  1.4177, from which glyceryl  $\beta$ -methyl ether and  $\alpha$ -methyl ether, respectively, were obtained by hydrolysis.

R. K. CALLOW.

Colour reactions of mannitol. L. EKKERT (Pharm. Zentr., 1928, 28, 433).—Oxidation of mannitol with bromine water followed by the addition of a small quantity of phenacetin, resorcinol,  $\alpha$ -naphthol,  $\beta$ -naphthol, codeine, or morphine and then concentrated sulphuric acid or phosphoric acid or fuming hydrochloric acid led to characteristic colour reactions in each case.

I. VOGEL.

Nitric oxide and carbon monoxide compounds of so-called univalent iron and nickel. H. REIHLEN, A. VON FRIEDOLSHEIM, and W. OSWALD (Annalen, 1928, 465, 72—96).—A reply to Manchot (this vol., 35) and Hieber and Sonnekalb (*ibid.*, 511).

The following appears to be new. When ethyl mercaptan is treated with nitric oxide in presence of potassium hydroxide a 95% yield of ethyl sulphide is produced:  $2\text{EtSH} + 2\text{NO} = \text{Et}_2\text{S} + \text{N}_2\text{O} + \text{H}_2\text{O}$ . The reaction between nickel sulphate, nitric oxide, ethyl mercaptan, and potassium hydroxide gives 84% of almost pure ethyl hyponitritonickel sulphide,  $\text{NO}\cdot\text{Ni}\cdot\text{SEt}$ . When the reactants are modified, products of varying composition are obtained, but all of them contain a relatively large proportion of the hyponitrito-compound. A mixture of ferrous hydroxide and potassium ethyl sulphide is converted by carbon monoxide into the compound,  $\text{Fe}_2(\text{SEt})_2(\text{CO})_6$ , m. p. (high vacuum) 67° after softening.

H. BURTON.

Bromoformic esters. K. W. ROSENEMUND and H. DÖRING (Arch. Pharm., 1928, 266, 277—280).—Carbonyl bromide, prepared by Bartal's method (A., 1906, i, 731), interacts with ethyl alcohol in cold light petroleum to give a meagre yield of *ethyl bromoformate*, b. p. 116°. In a similar way, *n-propyl bromoformate*, b. p. 79—80°/108 mm., *isoamyl bromoformate*, b. p. 58°/14 mm., and *benzyl bromoformate*, b. p. 96°/15 mm., are obtained. These compounds are all violently lachrymatory, and are unstable, even when preserved in a sealed tube. Because of its instability, the ethyl ester cannot be used in the scission of alkaloids, like ethyl chloroformate. Carbonyl bromide interacts with 8-hydroxyquinoline as a brominating agent, the products being the 5-bromo- and 5 : 7-dibromo-derivatives.

W. A. SILVESTER.

Acidic and basic catalysts of acetylation reactions. J. B. CONANT and G. M. BRAMMANN.—See this vol., 1101.

Decomposition of acetyl peroxide and the mechanism of Kolbe's electro-synthesis. O. J. WALKER (J.C.S., 1928, 2040—2045; cf. Fairweather and Walker, A., 1927, 119; Fichter, A., 1926, 500).—The thermal decomposition of acetyl peroxide in the pure state or in solution gives rise to only small quantities of ethane, although comparatively large amounts of methane are formed. Methane is never found in the anode gases during the electrolysis of acetates. This evidence, together with the fact that peroxides have not been isolated by electrochemical means even at low temperatures, constitutes important evidence against the peroxide theory of the mechanism of Kolbe's reaction.

Acetyl peroxide in aqueous acetic acid solution is decomposed by ultra-violet light into carbon dioxide, ethane, and methane. The relative proportion of ethane is much higher than in the corresponding thermal decomposition.

F. J. WILKINS.

Resolution of racemic chlorobromoacetic acid. H. J. BACKER and H. W. MOOK (J.C.S., 1928, 2125—2130).—Chlorobromoacetic acid (Crompton and others, *ibid.*, 1920, 117, 691; 1921, 119, 1874), b. p. 103—104°/11 mm., m. p. 31.5° (lit. 25° and 38°),  $k_{25}$   $5.7 \times 10^{-2}$  (potassium hydrogen and normal potassium salts), is resolved by means of its *brucine* salt, *brucine l-chlorobromoacetate*, +2— $3\text{H}_2\text{O}$ , separating first. From this by treatment with excess of sodium hydroxide, extraction of the brucine with chloroform, and neutralisation the value  $[M]_D +6.3^\circ$  is found for

the sodium salt, the value for the undissociated acid being  $[M]_D -28^\circ$ . The rotations of the acid and its salts are determined for various wave-lengths. The active acid and its salts are stable in aqueous solution at the ordinary temperature, but not in the presence of strong bases and, contrary to the finding of Read and McMath (A., 1926, 1024), racemisation of the brucine salt in chloroform is more rapid than that of the neutral salts in aqueous solution. Hydroxyl ions rapidly catalyse the racemisation of the salts, the velocity coefficient of racemisation being determined with various concentrations of alkali. The catalytic action of the hydroxyl ion is increased by addition of neutral salts, especially with cations of higher valency.

J. W. BAKER.

**Conductometric titration of sodium salts of fatty acids of high mol. wt.** P. EK WALL (Kolloid-Z., 1928, 45, 291—306).—The conductometric titration of high-molecular, saturated fatty acids differs from that of sodium acetate in that the titration curve shows three breaks. This is due to the formation of acid soaps containing the sodium salt and free acid in the proportions 1:1 and 1:2. The breaks are less marked in the titration curve of sodium oleate, probably in consequence of the high colloid content of the original solution and also the greater solubility of the acid oleate. A rectilinear titration curve is obtained when the soap solution is at very great dilution. The conclusions reached from these experiments concerning the existence of acid soaps are in agreement with those deduced by other means.

E. S. HEDGES.

**isoOleic acids.** K. H. BAUER and J. MITSUOKI (Chem. Umschau, 1928, 35, 137—139).—The *isoleic* acids ( $C_{18}$ , with double linking elsewhere than  $\alpha:\kappa$ ) are solid at the ordinary temperature and give lead salts insoluble in alcohol; they may therefore be present in hardened fatty acids isolated by Twitchell's lead salt method. The acids from a hardened groundnut oil were ozonised in the form of their methyl esters and the fission products oxidised with hydrogen peroxide. From the products there were isolated: *n*-decane- $\alpha\kappa$ -dicarboxylic acid, m. p. 123—124°, azelaic acid, m. p. 106°, *n*-hexoic acid, b. p. 235—250°. These indicate the presence in the original hardened acid of  $\Delta^7$ -heptadecene- $\alpha$ -carboxylic acid, formed most probably by reduction of one double linking in linoleic acid.

C. HOLLINS.

**Esters of  $\alpha$ -linolenic acid hexabromide from Philippine lumbang oil.** M. L. A. VICENTE and A. P. WEST (Philippine J. Sci., 1928, 36, 73—77).—The following esters of  $\alpha$ -linolenic acid hexabromide (cf. A., 1927, 540) have been prepared: *n*-propyl, m. p. 144—146°; *isopropyl*, m. p. 141—143°; *isobutyl*, m. p. 136—138°, and *amyl*, m. p. 133—135°. The solubilities of these esters in numerous organic solvents are quoted.

H. BURTON.

**[Ethyl] hydrogen dicarboxylates.** E. FOURNEAU and S. SABETAY (Bull. Soc. chim., 1928, [iv], 43, 859—861).—When mixtures of dicarboxylic acids and their ethyl esters are heated below the decomposition temperature of the acid, ethyl hydrogen dicarboxylates are obtained. The reaction must be carried out in absence of moisture. Ethyl hydrogen

oxalate; succinate, b. p. 146—149°/17 mm.,  $d_{20}^{21}$  1.148,  $n_D^{20}$  1.4323; adipate, b. p. 169—170°/17 mm., m. p. 28—29°,  $d_{20}^{20}$  1.081,  $n_D^{20}$  1.4384; suberate, b. p. 186—188.5°/16 mm., m. p. 21—22°,  $d_{20}^{20}$  1.037,  $n_D^{20}$  1.4412, and sebacate, b. p. 202—203°/15 mm., m. p. 35°, have been prepared.

H. BURTON.

**Use of toluenesulphonic esters in place of halogen esters in malonic ester syntheses.** D. H. PEACOCK and P. THA (J.C.S., 1928, 2303—2305).—Esters of *p*-toluenesulphonic acid may be used in place of halogen esters in the preparation of substituted malonic esters from ethyl sodiomalonate, and ethyl methyl-, ethyl-, and phenoxyethyl-malonates have thus been prepared.  $\beta$ -Phenoxyethyl alcohol is converted by the action of *p*-toluenesulphonyl chloride and 20% sodium hydroxide solution into  $\beta$ -phenoxyethyl *p*-toluenesulphonate, m. p. 80°.

J. W. BAKER.

**Inversion of geometrical isomerides by an exothermic reaction. Conversion of maleic into fumaric acid.** P. NEOGI, S. NEOGI, and M. P. CHATTERJI (J. Indian Chem. Soc., 1928, 5, 279—283; cf. Skraup, A., 1891, 1320, 1338).—When an aqueous solution of maleic acid containing manganese dioxide in suspension is treated with sulphur dioxide for 5 min. a 50% conversion into fumaric acid takes place, and the temperature of the solution rises from 27° to 60°. At 15° there is only 10% conversion, but at 90° the transformation is again 50%. The interchange does not take place with either manganese or sulphur dioxide alone, or with both reagents in presence of alcohol or ether. Lead and barium peroxides with sulphur dioxide, or phosphoric oxide alone, do not cause any conversion, neither do the products of interaction of manganese and sulphur dioxides. The results support Skraup's vibration theory (*loc. cit.*).

H. BURTON.

**Rupture of the six-carbon chain of adipic acid. II.** J. VON BRAUN, F. JOSTES, and H. WAGNER (Ber., 1928, 61, [B], 1423—1431).—Revision of previous work (A., 1926, 1128) in the light of the criticisms of Fuson (this vol., 738) confirms the suggestion of the latter that ethyl  $\beta$ -diethylaminopropionate and not the  $\alpha$ -isomeride is produced by cleavage of ethyl  $\alpha\alpha'$ -dibromoadipate under the influence of diethylamine. The postulated intermediate formation of a cyclobutane derivative is accepted, but the structure of the amine molecule is regarded as the factor controlling fission or production of a diamino adipic ester.

Ethyl  $\alpha$ -diethylaminopropionate, b. p. 69—71°/13 mm., is prepared from ethyl  $\alpha$ -bromopropionate and a moderate excess of diethylamine (cf. Fuson, *loc. cit.*) and is converted by methyl iodide into the very hygroscopic *methiodide*, m. p. 69—70°. Reduction of the ester with sodium and alcohol gives  $\beta$ -diethylamino-*n*-propyl alcohol, b. p. 56—58°/13 mm. [*methiodide*, m. p. 263° (decomp.)].  $\gamma$ -Diethylamino-*n*-propyl alcohol *methiodide* has m. p. 188°. Methyl ethylamine, prepared from benzenesulphonmethylethylamide, b. p. 173°/13 mm., and ethyl  $\alpha\alpha'$ -dibromoadipate yield a mixture of ethyl  $\beta$ -methyl-ethylaminopropionate, b. p. 75—80°/13 mm. (non-crystalline *picrate* and *hydrochloride*), and ethyl  $\alpha\alpha'$ -di-

*methylethylamino adipate*, b. p. 160—165°/13 mm., which contains a little of the unsaturated ester,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NMeEt})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ . *Benzene-sulphonmethyl-n-propylamide*, b. p. 182—183°/13 mm., is hydrolysed by concentrated hydrochloric acid at 160° to methyl-n-propylamine, b. p. 61—62° (non-crystalline *picrate*; very hygroscopic *hydrochloride*, m. p. 150°; *phenylmethyl-n-propylcarbamide*, m. p. 95°). With ethyl  $\alpha'$ -dibromoadipate the base affords ethyl  $\beta$ -methyl-n-propylaminopropionate, b. p. 83—85°/13 mm. (very hygroscopic *hydrochloride*, m. p. 111—112°; *picrate*, m. p. 75—77°), and non-homogeneous ethyl dimethyl-n-propylamino adipate, b. p. 170—180°/13 mm. *Benzenesulphonisopropylamide*, b. p. 190°/13 mm., from isopropylamine and benzenesulphonyl chloride, is converted by methyl iodide and alkali hydroxide into *benzenesulphonmethylisopropylamide*, b. p. 175°/13 mm., from which *methylisopropylamine*, b. p. 50°,  $d_4^{19}$  0.7026, is derived; the *hydrochloride*, m. p. 77°, *acetyl derivative*, b. p. 69—70°/13 mm., and *benzoyl compound*, b. p. 144°/13 mm., of the base are described. *Phenylmethylisopropylcarbamide*, m. p. 131°, non-crystalline *methylisopropylcarbamide*, and *phenylmethylisopropylthiocarbamide*, m. p. 120°, have been prepared. With ethyl  $\alpha'$ -dibromoadipate, the base yields almost equal proportions of ethyl  $\beta$ -methylisopropylaminopropionate, b. p. 84—86°/13 mm. (*picrate*, m. p. 85—86°), and impure ethyl di- $\alpha'$ -methylisopropylamino adipate. 3-Methylhexahydropyridine, b. p. 125°, prepared by reduction of 3-methylpyridine with sodium and alcohol and purified through the *benzoyl derivative*, b. p. 185—186°/13 mm., m. p. 44—45°, converts ethyl  $\alpha'$ -dibromoadipate into a mixture of almost equal parts of ethyl  $\beta$ -3-methylpiperidylpropionate, b. p. 111—112°/13 mm. (*hydrochloride*, m. p. 167—169°; *picrate*, m. p. 98—99°), and ethyl di- $\alpha'$ -3-methylpiperidyl adipate, m. p. 61—63° (*hydrochloride*, m. p. 191°; *picrate*, m. p. 196°). 2-Methylpiperidine yields similarly ethyl  $\beta$ -2-methylpiperidylpropionate, b. p. 117—119°/14 mm. (*picrate*, m. p. 123°), and non-homogeneous ethyl di- $\alpha'$ -2-methylpiperidyl adipate. *trans*-Decahydroquinoline and ethyl  $\alpha'$ -dibromoadipate afford ethyl  $\beta$ -decahydroquinolylpropionate, b. p. 155—156°/13 mm. (*hydrochloride*, m. p. 165—167°; *picrate*, m. p. 102°), and ethyl di- $\alpha'$ -decahydroquinolyl adipate, m. p. 107—108°.

H. WREN.

**Synthesis of cyclic compounds. III. Reduction of some unsaturated cyano-esters by moist aluminium amalgam.** New synthesis of  $\beta\beta\beta\beta'$ -tetramethyladipic acid. Further evidence for the multiplanar configuration of the cycloheptane ring. I. VOGEL (J.C.S., 1928, 2010—2032).—A number of unsaturated cyano-esters of the type  $\text{CR}_1\text{R}_2\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , where  $\text{R}_1\text{R}_2$  is *gem*-dimethyl, or  $\text{CR}_1\text{R}_2$  is cyclopentylidene, cyclohexylidene, cycloheptylidene, or *trans*-decahydronaphthylidene, have been prepared. By reduction with moist aluminium amalgam in ether they yield a mixture of the saturated cyano-esters,  $\text{CHR}_1\text{R}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$  (I) (main product), and the bimolecular compounds,  $(\cdot\text{CR}_1\text{R}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et})_2$  (II), the relative yields of (I) and (II) in the cases enumerated above being 63 and 21, 79 and 13, 84 and 6, and 72 and 12%,

respectively. These results are in harmony with the alteration of the carbon tetrahedral angle postulated by the Thorpe-Ingold valency deflexion theory and confirm the earlier conclusions (Baker and Ingold, J.C.S., 1923, 123, 122; Dickens, Horton, and Thorpe, A., 1924, i, 1313; Baker, A., 1925, i, 1277) concerning the multiplanar configuration of the cycloheptane ring. The following new compounds are described and revised physical data given in the paper. Ethyl  $\alpha$ -cyano- $\beta\beta$ -dimethylacrylate, m. p. 33° (lit. 28°), which condenses with alcoholic potassium cyanide to give a 60% yield of *as*-dimethylsuccinic acid (ethyl ester, b. p. 100°/15 mm.,  $n_D^{25}$  1.4209,  $d_4^{25}$  0.9945); ethyl *r*-isopropylcyanoacetate, b. p. 99°/16 mm.,  $n_D$  1.4243,  $d_4^{20}$  0.9855,  $\gamma^{20}$  31.82; ethyl  $\alpha\delta$ -dicyano- $\beta\beta\gamma\gamma$ -tetramethylbutane- $\alpha\delta$ -dicarboxylate (*monoamide*, m. p. 95°), which by hydrolysis with concentrated hydrochloric acid for 12 hrs. yields  $\beta\beta\beta\beta'$ -tetramethyladipic acid. Ethyl *r*-cyclopentylcyanoacetate, b. p. 129°/13 mm.,  $n_D$  1.4536,  $d_4^{20}$  1.0246,  $\gamma^{20}$  34.77, by hydrolysis yields cyclopentylmalonic acid, m. p. 165°. Condensation of ethyl cyclopentylidene cyanoacetate with alcoholic potassium cyanide gives an 81% yield of 1-carboxycyclopentane-1-acetic acid, m. p. 160° (lit. 154.5—155.5°) [*anhydride*, b. p. 135—137°/13 mm., m. p. 32°; *anilic acid*, m. p. 169° (decomp.); ethyl ester, b. p. 129°/13 mm.,  $n_D^{20}$  1.4477,  $d_4^{20}$  1.0412]. Ethyl cyclohexylidene cyanoacetate has b. p. 151°/12 mm.,  $n_D$  1.4974,  $d_4^{20}$  1.0558,  $\gamma^{20}$  37.89; ethyl *r*-cyclohexylcyanoacetate, b. p. 145°/14 mm.,  $n_D$  1.4612,  $d_4^{20}$  1.0210,  $\gamma^{20}$  35.58; the ester,  $[\text{C}(>\text{C}_5\text{H}_{10})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$ , m. p. 87°; ethyl cycloheptylidene cyanoacetate, b. p. 160°/12 mm.,  $n_D^{18}$  1.5003,  $d_4^{18}$  1.0534,  $\gamma^{20}$  37.57, is obtained in 31% yield by the condensation of cycloheptanone with ethyl cyanoacetate in the presence of piperidine at 100°, and condenses with alcoholic potassium cyanide to yield 1-carboxycycloheptane-1-acetic acid, m. p. 159° [Dickens, Horton, and Thorpe, *loc. cit.*, give 153°; *anhydride*, m. p. 16°, b. p. 166°/13 mm.; *anilic acid*, m. p. 159° (decomp.)]: ethyl *r*-cycloheptylcyanoacetate, b. p. 149°/11 mm.,  $n_D$  1.4664,  $d_4^{20}$  1.0206,  $\gamma^{20}$  36.09, which hydrolyses to cycloheptylmalonic acid, m. p. 164.5° (decomp.): the ester  $[\text{C}(>\text{C}_6\text{H}_{12})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$ , m. p. 74°. Ethyl *trans*-decahydro- $\beta$ -naphthylidene cyanoacetate, b. p. 196°/14 mm.,  $n_D$  1.5108,  $d_4^{20}$  1.0519,  $\gamma^{20}$  37.51, is obtained in 61% yield by condensation of *trans*- $\beta$ -decalone, b. p. 106°/12 mm.,  $n_D$  1.4809,  $d_4^{20}$  0.9787,  $\gamma^{20}$  36.57, with ethyl cyanoacetate in the presence of piperidine; ethyl *r*-*trans*-decahydro- $\beta$ -naphthylcyanoacetate, b. p. 186°/12 mm.,  $n_D$  1.4802,  $d_4^{20}$  1.0301,  $\gamma^{20}$  36.33, hydrolyses to *decahydro- $\beta$ -naphthylmalonic acid*, m. p. 122° (decomp.); ethyl benzylidene malonate has b. p. 163°/14 mm.,  $n_D$  1.4872,  $d_4^{20}$  1.0759,  $\gamma^{20}$  35.59; cyclopentanone, b. p. 129.5°/761.5 mm.,  $n_D$  1.4383,  $d_4^{20}$  0.9486,  $\gamma^{20}$  33.85; cyclohexanone, b. p. 47°/15 mm.,  $n_D$  1.4521,  $d_4^{20}$  0.9457,  $\gamma^{20}$  34.51; cycloheptanone, b. p. 71°/19 mm.,  $n_D$  1.4635,  $d_4^{20}$  0.9496,  $\gamma^{20}$  35.37. The parachors of all the above compounds have been determined, the observed values for the ring constants in the five-, six-, and seven-membered rings being 10.2, 8.4, and 6.0, respectively, whilst that for the *trans*-decahydro- $\beta$ -naphthalene ring is 17.6, almost exactly twice the value obtained for the cyclohexane ring.

The volume of the methylene group ( $[P_1]/n$ ) in the *cycloheptane* ring is 39.7, a value which approximates closely to that of the methylene group in an open-chain hydrocarbon, and this gives further support to the view that the *cycloheptane* ring is multiplanar.

J. W. BAKER.

**Differentiation of tartaric, citric, and oxalic acids amongst themselves.** D. I. PERIETZEANU (Bul. Soc. chim. România, 1928, 10, 49).—A solution of copper acetate in presence of concentrated acetic acid gives with tartaric acid a precipitate of copper tartrate soluble in dilute hydrochloric acid and in 30% sodium hydroxide. Citric acid produces no precipitate, whilst the precipitate of copper oxide obtained with oxalic acid is insoluble in 30% sodium hydroxide solution, but soluble in excess of concentrated hydrochloric acid.

C. HOLLINS.

**Electrolytic reduction of dithiodiacetic acid.** E. LARSSON (Ber., 1928, 61, [B], 1439—1443).—Polarisation experiments indicate little hope of the successful reduction of dithiodiacetic acid to thiolacetic acid at a platinum cathode. On the other hand, thiolacetic acid is almost quantitatively produced when the dithio-acid dissolved in 2*N*-sulphuric acid is reduced at a lead cathode in a divided cell, the anode being a carbon rod immersed in dilute sulphuric acid. Reduction can be effected either with constant cathode potential or constant current density, but the current yields are usually higher if the former method is used unless a sufficiently small current density is employed.

H. WREN.

**Optically active  $\alpha$ -arsenocarboxylic acids.** H. J. BACKER and C. H. K. MULDER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 301—303).— $\alpha$ -Arsenocarboxylic acids are obtained in good yield by the action of potassium arsenite on the potassium salt of the appropriate  $\alpha$ -bromocarboxylic acid,  $\text{CHRBr}\cdot\text{CO}_2\text{K} + \text{K}_3\text{AsO}_3 = \text{CHR}(\text{AsO}_3\text{K}_2)\cdot\text{CO}_2\text{K} + \text{KBr}$ , and thus are prepared  $\alpha$ -arsenobutyric acid, m. p. 127° (diquinine salt, +5H<sub>2</sub>O), and  $\alpha$ -arsenovaleric acid, m. p. 114° (diquinine salt, +4H<sub>2</sub>O). These acids titrate as dibasic acids, and by fractional crystallisation of the diquinine salts from dilute alcohol the optically active acids are obtained. The rotatory dispersion of these acids and their barium salts has been investigated. Neutralisation of both acidic functions causes a reversal in the sign of the rotation. The following values are obtained: *d*- $\alpha$ -arsenopropionic acid,  $[M]_D +41.0^\circ$  (barium salt,  $-8.5^\circ$ ); *d*- $\alpha$ -arsenobutyric acid,  $[M]_D +25.7^\circ$  (barium salt,  $-10.5^\circ$ ); *d*- $\alpha$ -arsenovaleric acid,  $[M]_D +19.3^\circ$  (barium salt,  $-15.6^\circ$ ). The active barium salts are not racemised in aqueous solution at 100°, but the free acids readily racemise, especially in the presence of mineral acids, the racemisation being a unimolecular reaction.

J. W. BAKER.

**Photo-oxidation of organic compounds by dichromates.** J. PLOTNIKOV and others.—See this vol., 1102.

**Identification of hexamethylenetetramine and formaldehyde; rapid analytical differentiation of the compounds in a mixture.** M. V. IONESCU (Bull. Soc. chim., 1928, [iv], 43, 677—680).—Formaldehyde and dimethyldihydroresorcinol react in cold

solution with quantitative precipitation of methylene-bisdimethyldihydroresorcinol, m. p. 187°. The same product is formed from hexamethylenetetramine in boiling solution. Determination of the two substances in presence of one another is based on the observation that formaldehyde is quantitatively precipitated as the methylene derivative after 15 min. at the ordinary temperature, whereas hexamethylenetetramine does not react to an appreciable extent until the solution is boiled.

H. WREN.

**Stearaldehyde.** R. FEULGEN and M. BEHRENS (Z. physiol. Chem., 1928, 177, 221—230).—Reduction of acid chlorides to aldehydes by Rosenmund's method (A., 1918, i, 300) proceeds more rapidly if freshly-precipitated barium sulphate is used for the preparation of the palladium catalyst. Stearyl chloride furnishes a mixture of stearaldehyde (thiosemicarbazone, m. p. 111°) and a dimeride,  $(\text{C}_{18}\text{H}_{36}\text{O})_2$ , m. p. 55°, which is sparingly soluble in alcohol, does not react with Schiff's reagent, and does not reduce ammoniacal silver nitrate. When distilled from an oil-bath at 140—200°/1 mm., it gives stearaldehyde.

*Palmitaldehydethiosemicarbazone* has m. p. 109°.

H. BURTON.

**Heintz's aldol and its preparation.** F. ADAMANIS (Rocz. Chem., 1928, 8, 349—357).—Heintz's aldol is prepared by shaking acetone with sodium hydroxide for 30 hrs., and is converted by the action of magnesium methyl bromide into  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol, which on dehydration yields  $\beta\delta$ -dimethyl- $\Delta^8$ -penten-3-ol.

R. TRUSZKOWSKI.

**Alkali fission of pentoses.** F. FISCHLER and R. BOETTNER (Z. physiol. Chem., 1928, 177, 264—269).—When a 1% solution of xylose or arabinose is mixed with a solution containing 0.04*M*-sodium carbonate and 4—6% of sodium sulphite and then distilled carefully a neutral distillate is obtained which reduces ammoniacal silver nitrate and Fehling's solution in the cold, restores the colour to Schiff's reagent, and gives the iodoform reaction. The distillate contains methylglyoxal and glycollaldehyde (cf. A., 1926, 1170). Acetone, acetaldehyde, and formaldehyde are not formed. It is suggested that fission of the pentose molecule occurs, yielding glycollaldehyde and glyceraldehyde, which under the influence of alkali is transformed first into dihydroxyacetone and then into methylglyoxal.

**Oxidation of carbohydrates, fats, and nitrogenous products by air in presence of sunlight.** C. C. PALIT and N. R. DHAR.—See this vol., 1103.

**Mechanism of carbohydrate oxidation. IX. Action of copper acetate solutions on dextrose, lævulose, and galactose.** W. L. EVANS, W. D. NICHOLL, G. C. STROUSE, and C. E. WARING (J. Amer. Chem. Soc., 1928, 50, 2267—2285).—The oxidation of dextrose, lævulose, and galactose at 50° in aqueous solutions saturated with copper acetate was studied. The amounts of glucosone, formic, carbonic, glyoxylic, and oxalic acids formed were determined, and their relation to time and oxygen consumption (measured by the formation of cuprous oxide) was investigated. The presence of glycollic acid was shown by qualitative tests. The hydrogen-ion concentration was also

measured during the course of the reaction. Glucosone was formed from dextrose and levulose, and was apparently formed by oxidation of the enediol derived from the hexose by enolisation. No galactosone was found, probably owing to its being used up as rapidly as it formed. Formic acid is regarded as arising from the oxidation of hydroxymethylene resulting from decomposition of the enediol. In support of this hypothesis, it was found that hydroxypyruvic acid was oxidised by copper acetate to formic acid (2 mols.) and carbon dioxide (1 mol.). Moreover, glycinaldehyde was similarly oxidised to formic acid. Carbon dioxide began to appear in the sugar oxidation at about the same time that glucosone production reached a maximum. It was considered to be a decomposition product of an  $\alpha$ -ketogluconic acid formed by oxidation of the glucosone, and this was supported by the above experiments with hydroxypyruvic acid. Carbon dioxide was not produced from galactonic or gluconic acid, glyoxal, or glycollic acid, which were unaffected by copper acetate. The glyoxylic, oxalic, and glycollic acids were considered to be derived from the  $\Delta^{\beta}$ -diol formed from glucosone by enolisation and the fission of this into an active form of erythrose and a half-active form of glyoxal,  $>C(OH)\cdot CHO$ . The latter then yields the products found. The hydrogen-ion concentration increased in the course of the reaction. This would diminish the concentration of enediol and result in the decreased production of formic acid, which is actually found. The hexosone  $\Delta^{\beta}$ -diol does not appear to oxidise to a  $\beta\gamma$ -diketohexose. The view is expressed that aldehydes exist in two forms, those active towards oxidising agents and those not active. The former are derivatives of hydroxymethylene, *i.e.*, the hydrogen is bound to oxygen and the carbon is bivalent. In the inactive molecules the carbon is quadrivalent. An equilibrium exists between these two forms which may be shifted by a change in the hydrogen-ion concentration. The conversion of aldehydes into carbonates in alkaline solution is explained on this basis. R. K. CALLOW.

**System of the simple sugars and  $\alpha$ -substituted fatty acids.** K. FREUDENBERG (Naturwiss., 1928, 16, 581—587).—A discussion, in the light of modern work, of the systematic derivation of configuration and nomenclature. R. K. CALLOW.

**Reactions between sugars and amino-compounds. IV.** H. VON EULER, E. ERIKSSON, and E. BRUNIUS (Svensk Kem. Tidskr., 1928, 40, 163—171).—Dextrose and protein derivatives interact slowly with reduction of the amino-nitrogen, and the mixture will decolorise methylene-blue in approximately neutral solution. A similar reaction takes place when sodium zymophosphate or sodium hexosemonophosphate is substituted for the dextrose; in these cases a small amount of salt formation ensues as a secondary reaction. Dextrose and alkali hydroxide interact, forming sodium glucosoxide, slight decomposition also taking place. On account of the small extent of this decomposition, the resulting products cannot be certainly identified, but probably consist mainly of dihydroxyacetone and methylglyoxal. Experiments with *N*- and 2*N*-solutions of dextrose and glycine to which a dilute methylene-blue solution was

added showed that decolorisation took place when the  $p_H$  value of the solution was above 8, no action resulting below this. Incubation of the mixed solutions for varying periods before addition of the methylene-blue was found to shorten the time required for subsequent decolorisation; this could not be ascribed to action between the dextrose and the alkali used. If ammonia is used in place of sodium hydroxide no reduction takes place even after an incubation period of 24 hrs. Solutions of purified candioline-sodium (sodium zymophosphate) or sodium hexosemonophosphate and glycine reacted in a similar manner, decolorising methylene-blue. Dihydroxyacetone alone reduces methylene-blue, but as the time required for decolorisation increases greatly with diminishing concentrations of dihydroxyacetone, the action is possibly due to small amounts of impurities. Experiments with solutions of dihydroxyacetone to which a suspension of yeast had been added gave inconclusive results. Illumination of the above solutions by exposure to a quartz-mercury-vapour lamp showed that the system glycine-dextrose-methylene-blue was only slightly affected by light, the acceleration of the reaction being somewhat greater when the dextrose was replaced by sodium hexosemonophosphate. H. F. HARWOOD.

#### Mechanism of the formation of osazones.

B. GLASSMANN and (Mrs.) ROCHWARGER-WALBE (Ber., 1928, 61, [B], 1444—1451).—Small quantities of ammonia in the presence of aniline and phenylhydrazine can be determined accurately by destruction of the latter with boiling Fehling's solution, collection of the distillate in 0.1*N*-hydrochloric acid, and titration of the excess of the latter in the presence of methylorange. After titration, the aniline in the distillate is weighed as tribromoaniline and the ammonia is calculated from the difference. More rapid results are obtained by taking advantage of the quantitative adsorption of ammonia from a very dilute solution of ammonia, aniline, and phenylhydrazine by permutit, from which the two bases last named are readily washed away. The ammonia liberated from the permutit by treatment with alkali hydroxide is colorimetrically determined by Nessler's solution. It is thus shown that phenylhydrazine in acetic acid solution at 100° undergoes partial autoreduction to benzene, aniline, ammonia, and nitrogen. Determinations of total ammonia in the filtrates obtained in a series of osazone preparations give results agreeing with the calculated values and thus afford analytical confirmation of Fischer's formulation. When the decomposition of phenylhydrazine in acetic acid solution is taken into account, there is no reason to assume that the base has a direct oxidising action in the production of osazones in the sense of the equation  $NHPh\cdot NH_2 + H_2O = NH_2Ph + NH_3 + O$ . H. WREN.

**Action of titanium tetrachloride on derivatives of sugars. I. Preparation of  $\alpha$ -acetochlorosugars and transformation of  $\beta$ -methylglucoside into its  $\alpha$ -form.** E. PACSU (Ber., 1928, 61, [B], 1508—1513).—The action of tin tetrachloride on  $\beta$ -glucosides and  $\beta$ -acetylsugars is slow and accompanied by slight decomposition in its final stage (cf.

this vol., 275). Silicon tetrachloride has no appreciable action. Tetra-acetyl- $\beta$ -methylglucoside is rapidly isomerised by titanium tetrachloride in chloroform to the  $\alpha$ -variety without decomposition. The change appears to differ fundamentally from that effected by tin tetrachloride, since a coloured, additive compound immediately separates from the solution. This compound is immediately decomposed by water with production of colourless solutions. Completely acetylated mono- and di-saccharides are more drastically affected by titanium tetrachloride than by tin tetrachloride, since the 1-acetyl group suffers quantitative replacement by chlorine with the production of acetochlorosugars in excellent yield and in a high state of purity. The following transformations are recorded:  $\beta$ -penta-acetylglucose into  $\alpha$ -acetochloroglucose, m. p. 73°,  $[\alpha]_D^{20} +167.85^\circ$  in chloroform;  $\beta$ -penta-acetylmannose into  $\alpha$ -acetochloromannose, m. p. 83°,  $[\alpha]_D^{20} +90.58^\circ$  in chloroform;  $\beta$ -octa-acetylactose into hepta-acetyl- $\alpha$ -chlorolactose, m. p. 122°,  $[\alpha]_D^{20} +83.97^\circ$  in chloroform;  $\beta$ -octa-acetylgentiobiose into hepta-acetyl- $\alpha$ -chlorogentiobiose, m. p. 142—143°,  $[\alpha]_D^{20} +89.22^\circ$  in chloroform;  $\beta$ -penta-acetylsalicin into  $\beta$ -tetra-acetylchlorosalicin, m. p. 160°,  $[\alpha]_D^{20} +12.02^\circ$  in chloroform.

H. WREN.

[Octa-acetyl]tetrathiodiglucose. F. WREDE and O. HETTICHE (Z. physiol. Chem., 1928, 177, 298—300).—When tetra-acetylthioglucose (A., 1922, i, 525) is treated with excess of sulphur chloride in dry ether octa-acetylthioglucose, m. p. 208°,  $[\alpha]_D^{20} -307.6^\circ$  in chloroform, is obtained. On hydrolysis with cold methyl-alcoholic ammonia it gives sulphur and octa-acetyldithioglucose (A., 1920, i, 13). Similar products could not be obtained using sulphur dichloride and selenium monochloride.

H. BURTON.

Carbohydrates of the readily hydrolysable hemicellulose of the pine. E. HAGGLUND, F. W. KLINGSTEDT, T. ROSENQVIST, and H. URBAN (Z. physiol. Chem., 1928, 177, 248—263).—Pine wood is digested with a solution of sodium hydrogen sulphite in sulphurous acid and the hydrolysed extract (18% of the wood) obtained after neutralisation with calcium carbonate is acidified, treated with  $\alpha$ -naphthylamine sulphate to precipitate  $\alpha$ -ligninsulphonic acid (cf. Klason, this vol., 622), then with activated charcoal, and finally hydrolysed with dilute sulphuric acid. After evaporation and separation into fractions soluble and insoluble in 80% alcohol it is found that a small amount of lignin (0.3% of wood) remains in solution. Sugar determinations on both fractions gave the following results (figures express percentage of hydrolysed hemicellulose): xylose and possibly arabinose (17), mannose (42.7), galactose (4.2), galacturonic acid (3.2), levulose (4), and dextrose (28.9).

H. BURTON.

Pectin and hemicelluloses of the flax plant. S. T. HENDERSON (J.C.S., 1928, 2117—2125).—Extraction of unretted flax fibre with 0.5% ammonium oxalate solution at 80—90° for 7 hrs. and subsequent removal of the methoxyl groups from the product by alkaline hydrolysis yields a gelatinous pectin which has the composition of a galactosetetragalacturonic acid,  $(C_6H_{10}O_{5.1}4C_6H_8O_6 - H_2O)_n$  (containing 20.7% of -uronic carbon dioxide; cf. Nanji, Paton, and Ling,

J. Soc. Chem. Ind., 1925, 44, 253T, who found 17.6%). From this is obtained a copper salt,  $3(C_6H_7O_6)_2Cu, C_6H_8O_6, 4H_2O$ , derived from polygalacturonic acid without a combined hexose group. Hydrolysis of the pectin with 2% sulphuric acid (or, better, with 1% hydrochloric acid) gave yields up to 40% of an insoluble polygalacturonic acid  $(C_6H_8O_6)_n$  (probably a purer form of the  $\alpha$ -acid described by Ehrlich and Schubert, A., 1926, 547) together with a soluble acid (soluble barium salt) and a syrup containing galactose and arabinose, the latter arising either from adsorbed pentose or from partial decarboxylation of the galacturonic residues. Extraction of flax straw or fibre with water at 100—145° in a manner similar to that employed by Ehrlich leaves no pectin soluble in ammonium oxalate, the main product being calcium-magnesium salts (2% of the weight of the straw; 9.7% -uronic carbon dioxide), which yield free acids corresponding with the general hemicellulose formula  $C_6H_{10}O_5$ , but containing varying amounts of -uronic acid residues, and a solid hexopentosan (5%) which on hydrolysis yields arabinose, xylose, galactose, and a small amount of a fermentable hexose, and by oxidation with nitric acid (*d* 1.15) yields mucic acid. Hence flax fibre probably contains carboxylated hemicellulose of a non-pectic nature. Thus it is not trustworthy to determine pectin in flax by determining -uronic anhydride, *i.e.*, by the carbon dioxide evolved on boiling with hydrochloric acid (*d* 1.06).

J. W. BAKER.

Lignin. IV. Soluble pinewood lignin obtained by different methods. A. FRIEDRICH (Z. physiol. Chem., 1928, 176, 127—143; cf. A., 1927, 861).—In a series of soluble lignin preparations from pinewood by means of methyl alcohol and hydrochloric acid, the degree of methylation (14.5% OMe originally) depends, not only on the absence of water, but especially on the length of time the solvent is allowed to react; the maximum figure reached (20 hrs.) is 23.2% OMe (=2 methoxyl groups per mol.). This falls after treatment of the products with alkali hydroxide, one methoxyl group being lost, presumably from an ester group. Time of reaction being important, an ester or acetal linking between lignin and cellulose is excluded, since these would be alkylated very rapidly; the increase in methoxyl content therefore results from alkylation of already dissolved lignin.

A soluble lignin having the same methoxyl content as the original lignin is best obtained by treating wood-meal with a mixture of 1 vol. of glacial acetic acid and 3 vols. of concentrated hydrochloric acid at 100°, and precipitating the product by dilution of the filtered liquid, acetic acid being removed by dissolving in alcohol and reprecipitation with water; the product (10.5% OMe) is hydrolysed with alkali hydroxide to remove combined acetic acid (4 mols.), and then contains 14.4% OMe. This lignin reacts with 0.5 mol. of phenylhydrazine (thus confirming the double mol. wt. of lignin in its ketonic form), and takes up 2 methyl groups on methylation, one of which is removed by alkali hydroxide. It gives a tribenzoyl derivative, and with thionyl chloride a trichloro-compound. A soluble lignin with 14.5—15.5% OMe is also obtained by using acetone or chloroform and hydrogen chloride; chloroform does not react with

the lignin. Lignin precipitated from alcohol or chloroform by ether and benzene has the formula  $C_{33}H_{36}O_{12}$ ; the mother-liquors contain an ether-soluble substance of lignin-like composition, and a benzene-soluble substance richer in carbon and hydrogen; the residual wood contains a third lignin which is not solubilised by the acetic acid method. C. HOLLINS.

**Synthesis of glucosides and glucose esters of hydroxycarboxylic acids.** K. JOSEPHSON (Arkiv Kemi, Min., Geol., 1928, 9, No. 36, 1—11).—Acetobromoglucose and silver 2-hydroxy-*m*-toluate react in boiling xylene, yielding the *tetra-acetyl-d-glucose* ester of 2-hydroxy-*m*-toluic acid, m. p. 148°,  $[\alpha]_D -37.4^\circ$  in chloroform. Similar treatment of silver 4-hydroxy-*m*-toluate affords a mixture of the *tetra-acetyl-d-glucose* ester of 4-hydroxy-*m*-toluic acid, m. p. 147°,  $[\alpha]_D -33.7^\circ$  in chloroform, and 4- $\beta$ -*tetra-acetyl-d-glucosidoxy-m-toluic acid*, m. p. 161°. This last compound is hydrolysed by barium hydroxide solution to 4- $\beta$ -*d-glucosidoxy-m-toluic acid*, m. p. 148—149°,  $[\alpha]_D -48.4^\circ$  in water, which undergoes fission with emulsin. Acetobromoglucose and silver hydroxy-dimethoxybenzoate (Herzig and Wenzel, A., 1902, i, 463) give the *tetra-acetyl-d-glucose* ester, m. p. 161°,  $[\alpha]_D -15.4^\circ$  in chloroform. Sugar derivatives could not be obtained from quinic acid or isopropylidenequinide. H. BURTON.

**Digitalis glucosides. I. Digitoxigenin and isodigitoxigenin.** W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1928, 78, 573—581).—When kept for 1 hr. in solution in methyl-alcoholic potassium hydroxide digitoxigenin is converted into isodigitoxigenin, a neutral substance, m. p. 271°; this could not be hydrogenated. On warming with dilute sodium hydroxide and acidification with acetic acid there was obtained isodigitoxigeninic acid,  $C_{23}H_{36}O_5$ , m. p. 250° (identical with the dixigenic acid of Kiliani and Cloetta, A., 1899, i, 932; 1921, i, 39) [*methyl ester*, m. p. 128°; *methyl ester semicarbazone*, m. p. 156° efferv.]. The above ester, with chromic acid, gave isodigitoxigenic methyl ester,  $C_{24}H_{34}O_5$ , m. p. 190° (*semicarbazone*, m. p. 243°), which, on hydrolysis, neutralised two equivalents of alkali and, on re-acidification with mineral acid, gave isodigitoxigenic acid, m. p. 212—213°.

*iso*Digitoxigeninic acid gave, with hypobromite, a lactone acid, isodigitoxigenic acid,  $C_{23}H_{34}O_5$ , m. p. 229°. The results are therefore entirely similar to those previously obtained with isostrophanthidin, and indicate that in digitoxigenin also the lactone ring contains a  $\beta\gamma$ -unsaturated linking.

C. R. HARRINGTON.

**Production of bases from carbonyl compounds.** A. SKITA and F. KEIL [with A. VON GRAETZEL and E. BAESLER] (Ber., 1928, 61, [B], 1452—1459).—Catalytic reduction of Schiff's bases in acid solution can be effected satisfactorily only with the more stable members of the group, since with less stable compounds the rate of hydrolysis exceeds that of hydrogenation. In neutral solution or suspension the absorption of hydrogen is inadequate, but formation of secondary bases occurs readily after addition of ammonia or a primary amine. It is frequently more advantageous to start with a mixture of aldehyde and

amine instead of pre-formed Schiff's base. Aldehydes of high mol. wt. in presence of ammonia are reduced exclusively to secondary amines, whereas the simpler aldehydes afford tertiary amines. Ketones in presence of ammonia or primary amines give secondary bases.

*cycloHexyl- $\gamma\gamma$ -dimethyloctylideneamine*, b. p. 170—172°/18 mm., from citral and *cyclohexylamine* is converted by hydrogen in the presence of alcohol, acetic acid, and colloidal platinum into *cyclohexyl- $\gamma\gamma$ -dimethyloctylamine*, b. p. 151—153°/14 mm. (*hydrochloride*, m. p. 154—155°; *picrolonate*, m. p. 174—175°). In neutral solution, *isoamyl- $\gamma\gamma$ -dimethyloctylideneamine*, b. p. 150—154°/20 mm., affords *isoamyl- $\gamma\gamma$ -dimethyloctylamine*, b. p. 142—145°/17 mm. (*hydrochloride*, m. p. 168—169°; *picrolonate*, m. p. 142—145°/17 mm.). In aqueous suspension in the presence of ammonia, *ethyl- $\gamma\gamma$ -dimethyloctylideneamine*, b. p. 113—115°/12 mm., yields *ethyl- $\gamma\gamma$ -dimethyloctylamine*, b. p. 135—137°/13 mm. (*hydrochloride*, m. p. 102—103°; non-crystalline *nitroso-compound*; *picrolonate*, m. p. 196—197°). *Methyl- $\gamma\gamma$ -dimethyloctylideneamine*, b. p. 107—109°/13 mm., affords *methyl- $\gamma\gamma$ -dimethyloctylamine* in very modest yield.

Hydrogenation of citral in aqueous suspension in presence of colloidal platinum and ammonia gives *di- $\gamma\gamma$ -dimethyloctylamine*, b. p. 191—193°/15 mm. (*hydrochloride*, m. p. 141—142°), obtained also by reduction of citral oxime. Heptaldehyde, under similar conditions, yields diheptylamine, m. p. 30°, b. p. 270—272° (*hydrochloride*, m. p. 250°). Acetaldehyde and propaldehyde or the oximes afford triethylamine and tripropylamine, respectively.

Diisopropylamine, b. p. 84° (*hydrochloride*, m. p. 212—214°; *picrate*, m. p. 140°), is prepared from acetone, whilst methyl ethyl ketone affords methyl-ethylcarbinol and di-*sec*-butylamine, b. p. 230—233° (*hydrochloride*, m. p. 215—216°). Di- $\alpha$ -ethylpropylamine is prepared in about 20% yield from diethyl ketone. *cycloHexanone* yields a mixture of *cyclohexanol* and *dicyclohexylamine*, b. p. 128—130°/20 mm. (*hydrochloride*, m. p. about 340°). *Ethylsec-butylamine*, b. p. 96—98°, and *cyclohexylethylamine*, b. p. 161° (*hydrochloride*, m. p. 182—183°), are derived from ethylamine and methyl ethyl ketone or *cyclohexanone*, respectively. H. WREN.

**Reaction between  $\alpha$ -oxides and  $\alpha$ -monochlorohydrins and hydrazine.** A. K. PLISOV (Ukraine Chem. J., 1928, 3, [Sci.], 125—131).—Ethylene oxide on addition of excess of hydrazine hydrate yields a mixture of *as*-di- $\beta$ -hydroxyethylhydrazine and  $\beta$ -hydroxyethylhydrazine, b. p. 146—153°/25 mm. Trimethylethylene oxide similarly yields *as*-di- $\beta$ -hydroxy- $\alpha\beta$ -dimethylpropylhydrazine, b. p. 185—190°/44 mm. The use of the corresponding  $\alpha$ -monochlorohydrins leads to the production of the same products, indicating that the chloro-derivatives pass through the stage of oxide before combining with hydrazine.

R. TRUSZKOWSKI.

**General reaction of amino-acids. II.** H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, 78, 745—756).—The azlactones obtained by the action of acetic anhydride on leucine, phenylalanine, and aspartic acid yield, with acetic anhydride and pyridine, the same



acetamidoketones as do the amino-acids; it is possible, therefore, that such azlactones represent an intermediate stage in the reaction recently observed (this vol., 874). Methylaspartic acid gives no ketone, in accordance with the view previously expressed (*loc. cit.*) that the reaction cannot take place in the absence of replaceable hydrogen in the  $\alpha$ -position;  $\beta$ -amino-acids, on treatment with acetic anhydride and pyridine, undergo simple acetylation. Aspartic acid, when warmed with acetic anhydride and pyridine, gave a substance which, on hydrolysis with hydrochloric acid, yielded ammonium chloride and  $\beta$ -hydroxylævulinic acid and when heated with phenylhydrazine acetate gave carbon dioxide and diacetylbisphenylhydrazone, and is therefore regarded as  $\beta$ -acetamidolævulinic acid. Glutamic acid gave only 15–20% of the theoretical amount of carbon dioxide owing to formation of pyrrolidonecarboxylic acid; the remaining reaction product was  $\gamma$ -acetamido- $\delta$ -ketohezoic acid, since, on hydrolysis and treatment with ammonia, it gave 2 : 5-dimethylpyrazine-3 : 6-dipropionic acid, m. p. 211–213°. Serine gave a substance with the qualitative reactions of a ketone. Phenylserine gave no ketone, but was converted into the azlactone of  $\beta$ -acetamidocinnamic acid. Histidine gave methyl  $\alpha$ -acetamido- $\beta$ -iminazolethyl ketone, which on hydrolysis with hydrochloric acid yielded methyl  $\alpha$ -amino- $\beta$ -iminazolethyl ketone dihydrochloride, m. p. 205–206°. Tryptophan yielded methyl  $\alpha$ -acetamido- $\beta$ -indolylethyl ketone.

C. R. HARRINGTON.

#### Colour reaction of creatine and of carbamide.

E. PITTARELLI (Arch. Farm. sperim., 1928, 45, 173–176).—An alkaline solution of creatine when treated with sodium nitroprusside and a small quantity of a persulphate gives slowly a permanent red coloration, which can also be produced immediately if a trace of potassium ferrieyanide is added to the mixture. This reaction detects creatine at a dilution of 1 in 50,000; it is also given by carbamide, but in this case the limiting dilution is 1 in 500 only.

E. W. WIGNALL.

**Action of Grignard reagent on  $\alpha$ -aminodicarboxylic acids.** S. KANAO and S. INAGAWA (J. Pharm. Soc. Japan, 1928, No. 553, 238–252).—Ethyl aspartate gives with magnesium phenyl bromide tetraphenylaminobutanediol (Paal and Weidenkaff, A., 1907, i, 131). Tetra-alkylbutanediols undergo ring formation when heated with 33% sulphuric acid, yielding 2 : 2 : 5 : 5-tetra-alkyl-4-aminotetrahydrofurans. Thus,  $\gamma$ -amino- $\beta$ - $\epsilon$ -dimethylhexane- $\beta$ - $\epsilon$ -diol, m. p. 87–88°, b. p. 151–153°/19 mm.,  $[\alpha]_D^{20}$   $-17.7^\circ$  in absolute alcohol (*hydrochloride*, m. p. 89–89.5°; *N*-benzoyl derivative, m. p. 146–147°), obtained from ethyl *l*-aspartate and magnesium methyl iodide, is converted into 4-amino-2 : 2 : 5 : 5-tetramethyltetrahydrofuran, b. p. 66–67°/23 mm.,  $d_4^{20}$  0.9021,  $n_D^{20}$  1.4412,  $[\alpha]_D^{20}$   $-8.03^\circ$  in alcohol (*hydrochloride*, m. p. 262°; *N*-benzoyl derivative, m. p. 136°).  $\delta$ -Amino- $\gamma$ - $\zeta$ -diethyloctane- $\gamma$ - $\zeta$ -diol, b. p. 182–183°/19 mm., obtained from the same ester and magnesium ethyl bromide, is converted into 4-amino-2 : 2 : 5 : 5-tetraethyltetrahydrofuran, b. p. 113–113.5°/13 mm. (corr.),  $d_4^{20}$  0.9168,  $n_D^{20}$  1.4678,  $[\alpha]_D^{20}$   $-9.59^\circ$  (*hydrochloride*, m. p. 270–275°).  $\zeta$ -Amino- $\delta$ - $\eta$ -dipropyldodecane- $\delta$ - $\eta$ -diol, b. p.

173–174°/19 mm., and  $\zeta$ -amino- $\epsilon$ - $\theta$ -dibutyldecane- $\epsilon$ - $\theta$ -diol, b. p. 180–184°/19 mm., are described. Glutamic and  $\alpha$ -aminoadipic esters, on the contrary, give no tetra-alkyl or aryl derivatives with organo-magnesium halides; they take only two alkyl or aryl groups and close the ring, yielding  $\alpha$ -pyrrolidonyl or  $\alpha$ -piperidonyl derivatives. Thus, ethyl *d*-glutamate gives with magnesium methyl iodide  $\beta$ -2-pyrrolidonylpropan- $\beta$ -ol, b. p. 201–202°/15 mm., with magnesium ethyl bromide,  $\gamma$ -2-pyrrolidonylpentan- $\gamma$ -ol, m. p. 91–92°, b. p. 209–210°/11 mm.,  $[\alpha]_D^{20}$   $-7.1^\circ$  in water, which is reduced with sodium and methyl alcohol to  $\gamma$ -2-pyrrolidylpentan- $\gamma$ -ol, b. p. 214–218°/757 mm.,  $d_4^{20}$  0.9577,  $n_D^{20}$  1.4718 (*hydrochloride*, m. p. 160–161°,  $[\alpha]_D^{20}$   $-9.22^\circ$  in water; *picrate*, m. p. 147–148°), with magnesium butyl iodide  $\epsilon$ -2-pyrrolindonylnonan- $\epsilon$ -ol, m. p. 102–103°, with magnesium and bromobenzene  $\alpha$ -(2-pyrrolidonyl)diphenylcarbinol, m. p. 190–191°,  $[\alpha]_D^{20}$   $-86.38^\circ$  in chloroform (racemic compound, m. p. 182–183.2°), with magnesium benzyl chloride  $\alpha$ -(2-pyrrolidonyl)- $\alpha$ -benzyl- $\beta$ -phenylethan- $\alpha$ -ol, m. p. 202°. Ethyl  $\alpha$ -aminoadipate gives with magnesium phenyl bromide  $\alpha$ -(2-piperidonyl)diphenylcarbinol, m. p. 225–226°.

K. ISHIMURA.

#### Separation of histidine and arginine. IV.

**Preparation of histidine.** H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1928, 78, 627–635).—Crude dried hæmoglobin is hydrolysed with 8*N*-sulphuric acid; excess of the latter is removed as barium sulphate, the filtrate is concentrated and treated with silver oxide in excess and barium hydroxide to  $p_H$  7.4; the precipitate is decomposed with hydrogen sulphide and the filtrate treated with sulphuric acid to 5% and then with mercuric sulphate; the precipitate is collected and decomposed with hydrogen sulphide in presence of sulphuric acid, and the filtrate from the mercuric sulphide adjusted to  $p_H$  7.2 with barium hydroxide; the filtered solution is concentrated and treated with alcohol; a 4–5% yield of histidine, contaminated with traces of tyrosine, is obtained. The histidine is finally purified, with little loss, through the dihydrochloride, separated by treatment of the aqueous hydrochloric acid solution of the crude substance with saturated alcoholic hydrogen chloride.

C. R. HARRINGTON.

**Dibenzoylarginine.** K. FELIX and K. DIRR (Z. physiol. Chem., 1928, 176, 29–42).—Nitration of dibenzoylarginine affords *di*-*m*-nitrobenzoylarginine, decomp. indef. at about 225°, acid hydrolysis giving *m*-nitrobenzoic acid and arginine. Dibenzoylarginine heated with acetic anhydride yields dibenzoylacetyl-*m*-nitroarginine (not crystallised), converted by hot water into benzoylacetylcarbamide and 3-benzamido-2-piperidone, m. p. 186–187°. It is concluded, therefore, that dibenzoylarginine is  $\text{NH}_2\text{Bz}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ . *d*-Dibenzoylarginine has m. p. 235° (decomp.), the *hydrochloride* having the decomposition point, 218°, attributed by Gulewitsch (A., 1899, i, 834) to the parent substance. The *ethyl ester hydrochloride* has m. p. 148°, sintering at 140°, and  $[\alpha]_D^{20}$   $-8^\circ$ . *dl*-Dibenzoylarginine has m. p. 230° or (+1H<sub>2</sub>O) 176°. The *ethyl ester hydrochloride* has m. p. 143°, sintering at 135°. The significance of the acid-binding power of

dibenzoylarginine is discussed (cf. Felix and Müller, this vol., 535). Modifications are given for the preparation of arginine from gelatin by acid hydrolysis and separation as the flavianate. A. WORMALL.

**Synthesis of  $\gamma$ -dimethylaminocrotonic methylbetaine (crotonbetaine).** W. LINNEWER (Z. physiol. Chem., 1928, 176, 217—221; cf. this vol., 665).— $\gamma$ -Chlorocrotonic acid, prepared from epichlorohydrin, is heated with alcoholic trimethylamine and a trace of sodium iodide at 100° to give crotonbetaine identical with that isolated from ox-muscle. C. HOLLINS.

**Decomposition of polypeptides containing amino-acids not known to occur in nature.**

**VIII. Polypeptides containing  $\alpha\alpha'$ -diaminosuberic acid.** E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1928, 9, 336—361).—Suberic acid may be brominated at atmospheric pressure if care be taken to exclude moisture. By treating  $\alpha\alpha'$ -dibromosuberic acid with concentrated aqueous ammonia and ammonium carbonate in closed vessels at 85—95°, good yields are obtained of  $\alpha\alpha'$ -diaminosuberic acid. The *brucine* salt of the derived  $\alpha\alpha'$ -*di-formamidosuberic acid*, m. p. 209—210°, does not resolve optically. The following derivatives are described:  $\alpha\alpha'$ -*Bischloroacetamidosuberic acid*, m. p. 215—217°. *NN'*-*Bisglycyl- $\alpha\alpha'$ -diaminosuberic acid* (+2H<sub>2</sub>O), m. p. above 290°. *Bis- $\alpha\alpha'$ -bromopropionamidosuberic acid*, m. p. 207°. *NN'*-*Bis-(dl-alanyl- $\alpha\alpha'$ -diaminosuberic acid* (+1H<sub>2</sub>O), m. p. above 290°. *NN'*-*Bis-(dl- $\alpha$ -bromo- $\gamma$ -methylvaleroyl)- $\alpha\alpha'$ -diaminosuberic acid*, m. p. 208—209°. *NN'*-*Bis-(dl-leucyl- $\alpha\alpha'$ -diaminosuberic acid* (+3H<sub>2</sub>O), m. p. above 290°. *NN'*-*Bis-(dl- $\alpha$ -bromo- $\gamma$ -methylvaleroylglycyl)- $\alpha\alpha'$ -diaminosuberic acid*, m. p. 194—195°. *Bis-(dl-leucylglycyl)- $\alpha\alpha'$ -diaminosuberic acid*, m. p. 168—171°. *Bis-(chloroacetyl-dl-leucyl)- $\alpha\alpha'$ -diaminosuberic acid*, m. p. 170—175°, decomp. 188—190°. *Bis-(glycyl-dl-leucyl)- $\alpha\alpha'$ -diaminosuberic acid*, sinters at 165°, m. p. (strong frothing) 190—195°. *Bis-(chloroacetyl-dl-alanyl)- $\alpha\alpha'$ -diaminosuberic acid*, sinters 195—196°, m. p. 202—203°, decomp. 216—218°. *Bis-(glycyl-dl-alanyl)- $\alpha\alpha'$ -diaminosuberic acid*, m. p. 136—138°, decomp. 210°. Unless otherwise stated, these all decompose at the m. p. The pentapeptides are hygroscopic, give filterable precipitates with phosphotungstic acid, and give a good biuret reaction. They are not hydrolysed by yeast juice. When hydrolysed by heating in aqueous solution at 160—165°, bis-*dl*-leucylglycyl- $\alpha\alpha'$ -diaminosuberic acid gives glycyl-leucine anhydride, and in smaller quantities glycine and leucine. Bisglycyl-*dl*-leucyl- $\alpha\alpha'$ -diaminosuberic acid yields leucylglycine anhydride and leucine. Bisglycyl-*dl*-alanyl- $\alpha\alpha'$ -diaminosuberic acid gives alanylglycine anhydride (?) and glycine (?) or alanine (?). In no case were unaltered polypeptide,  $\alpha\alpha'$ -diaminosuberic acid, or its decomposition products detected. F. E. DAY.

**Reducing power of cysteine.** E. C. KENDALL and D. F. LOEWEN (Biochem. J., 1928, 22, 649—668; cf. Dixon and Tunnicliffe, A., 1927, 961).—Further experiments are recorded to show that cysteine cannot reduce indigo-carmin and that cystine cannot oxidise reduced indigo-carmin or reduced indigo in the absence of a third component

which functions as an activating agent and is produced through the action of oxygen or sodium disulphide on indigo-carmin. Iron cannot activate the  $\cdot$ SH or  $\cdot$ S $\cdot$ S $\cdot$  grouping, but it influences the velocity of reaction between oxygen and indigo-carmin. This results in an increased concentration of the activating agent. Agitation of the solution and other physical factors influence the formation of the activating agent. It is destroyed by heat. Iron neither accelerates nor prevents the action of sodium disulphide on indigo-carmin. The activating agent appears to be an unstable oxygen or sulphur additive product of indigo-carmin and its essential action involves the activation of the sulphur atom which permits the sulphhydryl and disulphide groupings to manifest their latent reducing or oxidising power. In the presence of a constant concentration of the activating agent the velocity of oxidation and reduction is determined by the ratio C $\cdot$ SH/C $\cdot$ S $\cdot$ S $\cdot$ C grouping. S. S. ZILVA.

**Hydrolysis of guanidine carbonate.** J. BELL (J.C.S., 1928, 2074—2077; cf. A., 1926, 825).—Guanidine carbonate is hydrolysed to carbamide in boiling aqueous solution. The carbamide undergoes further partial transformation to ammonium carbonate. The hydrolysis is dependent on the primary dissociation of the salt to guanidine and carbonic acid, the subsequent decomposition being due to the instability of guanidine in boiling aqueous solution.

F. J. WILKINS.

**Guanidine. II. Synthesis of creatinol** [*N*-methyl-*N*-( $\beta$ -hydroxyethyl)guanidine]. H. SCHOTTE, H. PRIEWE, and H. ROESCHEISEN (Z. physiol. Chem., 1928, 174, 119—176; cf. Schotte and Priewe, A., 1926, 717).—The best method of preparing amino-alcohols is that in which ethylene chlorohydrin is treated with liquid carbonyl chloride and the isolated  $\beta$ -chloroethyl chloroformate allowed to react with amines in benzene solution to give  $\beta$ -chloroethyl alkylcarbamates of the constitution CH<sub>2</sub>Cl $\cdot$ CH<sub>2</sub> $\cdot$ CO<sub>2</sub>NHR; on decomposition with excess of sodium hydroxide (3—4 mols.) the last named yield amino-alcohols, HO $\cdot$ CH<sub>2</sub> $\cdot$ CH<sub>2</sub> $\cdot$ NHR. The aminoethanols can be converted into the corresponding guanido-alcohol (*a*) by the Erlenmeyer synthesis, whereby the amine salt reacts with cyanamide, or (*b*) by the use of Rathke's method, in which the aminoethanol is treated with a salt of *S*-alkylisothiocarbamide. The mechanism of the latter reaction is discussed and the "addition" theories of Schenck (A., 1912, i, 424) and of Lecher and Graf (A., 1923, i, 761) are rejected in favour of a "decomposition" theory, which postulates the formation of cyanamide by decomposition of the alkylisothiocarbamide and a subsequent Erlenmeyer synthesis. *S*-Ethylisothiocarbamide hydrobromide and methyl- $\beta$ -hydroxyethylamine with small amounts of water yield creatinol hydrobromide. A large number of salts and derivatives of creatinol have been prepared and examined, but the free base has been isolated only as a colourless syrup. Creatinol is very stable towards acids and is not affected when kept for 15 hrs. at the ordinary temperature (or heated for 4 hrs.) with concentrated hydrochloric acid, but it is sensitive to the action of alkalis. 2*N*-

Sodium hydroxide at the ordinary temperature decomposes creatinol hydrobromide with the formation of ammonia; after several weeks the decomposition is complete and 2 mols. of creatinol yield 1 mol. of ammonia and 1 mol. of methylaminoethanol, together with some carbamide and a fourth substance (? hydantoin alcohol). *N*-Ethyl-*N*- $\beta$ -hydroxyethylguanidine and *N*-isoamyl-*N*- $\beta$ -hydroxyethylguanidine have also been synthesised by the Erlenmeyer method.

$\beta$ -Chloroethyl chloroformate treated with methylamine in benzene solution yields *\beta*-chloroethyl methylcarbamate, b. p. 110—112°/15 mm., which on treatment with sodium hydroxide yields methyl- $\beta$ -hydroxyethylamine; condensation of the last named with *S*-ethylisothiocarbamide hydrobromide yields creatinol hydrobromide, m. p. 101—103°. The following salts of creatinol are described: *picrate*, m. p. 166°; *hydrochloride*, m. p. 78° (after sintering); *picrolonate*, m. p. 236—237° corr. (sinters at 234°); double salts of the hydrochloride with mercuric chloride ( $C_4H_{12}ON_3Cl_6HgCl_2$ ), m. p. 220—221° (sinters at 216°), and cadmium chloride ( $C_4H_{12}ON_3Cl_2CdCl_2$ ), m. p. 190—191°; *chloroaurate*, m. p. 125—126° (sinters at 90°); *chloroplatinate*, decomp. at 185—186°. *Creatinol*, obtained as a colourless, strongly alkaline syrup by treatment of the hydrobromide with sodium ethoxide, gives a *carbonate*, decomp. at 171°. *Creatinol* hydrobromide treated with benzoyl chloride yields *tribenzoylcreatino*l, m. p. 98—99.5°, and with *p*-toluenesulphonyl chloride yields *di-p-toluenesulphonylanhydrocreatino*l, m. p. 174.5—175°. *Creatinol* is very stable towards acids, but when heated in a sealed tube at 160° for 16 hrs. with concentrated hydrochloric acid it yields ammonia, methylethylenediamine, *anhydrocreatino*l (iminotetrahydroglyoxaline) (isolated as the *picrate*, m. p. 194—195°), and a *substance*,  $C_3H_7O_2N$ , isolated as the *picrolonate*, m. p. 226°, and *picrate*, m. p. 101—102°. Treatment of creatinol with 48% hydrogen bromide solution for 6 hrs. at 200° yields ethylenediamine and methylethylenediamine.  $\beta$ -Hydroxyethylethylamine, b. p. 169—170° (*picrate*, m. p. 125—126°), on heating with cyanamide and ethyl alcohol in a sealed tube at 100° for 8 hrs., yields *NN-ethylguanidoethanol*, isolated as the *picrate*, m. p. 158°.  $\beta$ -Hydroxyethylisoamylamine, b. p. 203—204°/750 mm., 93—94°/10 mm., prepared from  $\beta$ -chloroethyl isoamylcarbamate, treated in the same way, yields *NN-isoamylguanidoethanol*, isolated as the *picrate*, m. p. 117—118°. The preparation of  $\beta$ -chloroethyl benzylcarbamate, b. p. 158°/0.8 mm. and 218—220°/15 mm., and of *benzyl- $\beta$ -hydroxyethylamine*, b. p. 105°/about 1 mm. and 148—149°/13 mm. (*picrate*, m. p. 134—135°), is also described. The reaction between aniline and *S*-ethylisothiocarbamide hydrobromide has been studied with varying amounts of the reactants and different conditions (temperature, time, and the solvent) and the yields of mono- and di-phenylguanidine are tabulated. Monophenylguanidine heated at 100° for 25 hrs. with aniline yields no diphenylguanidine, whilst only a small yield is obtained at 150°. Diethylcyanamide and aniline hydrochloride heated with ethyl alcohol for 20 hrs. in a sealed tube at 100° yield *N'*-phenyl-*NN*-diethyl-

*guanidine* (*picrate*, m. p. 120° corr.). Dimethylcyanamide and ammonium chloride in the presence of alcoholic ammonia yield dimethylguanidine, and diethylcyanamide yields diethylguanidine. The preparation of *NN*-dimethyl-*N'*-ethylguanidine, *s*-tetraethylguanidine,  $\omega\omega$ -diethylidguanide, and *s*-tetraethylidguanide (*picrate*, m. p. 147—148° corr.) is described. A. WORMALL.

**Rathke's guanidine synthesis and hydrolysis of guanidines.** H. LECHER (*Z. physiol. Chem.*, 1928, 176, 43—45).—A discussion of Rathke's method for synthesising guanidines from ammonia or amines and  $\psi$ -thiocarbamides or their salts (cf. preceding abstract), and on the rival views of Lecher and Schotte concerning the mechanism of hydrolysis of guanidines (cf. Lecher and Demmler, A., 1927, 755; Schotte, *Z. angew. Chem.*, 1926, 39, 677).

A. WORMALL.

**Malononitrile and malononitrile condensations.** I. R. SCHENCK and H. FINKEN [with P. MICHAELIS and H. PLEUGER] (*Annalen*, 1928, 462, 158—173).—Malononitrile condenses with ethyl oxalate in presence of (absolute) alcoholic potassium ethoxide to give the *potassium* derivative, m. p. 205°, of *ethyl  $\beta\beta$ -dicyano- $\alpha$ -hydroxyacrylate*, and with methyl oxalate etc. to give the *potassium* derivative of the corresponding methyl ester. The *sodium*, *silver* (m. p. 176°), and *diethylamine* salts of the ethyl ester and the *silver* salt of the methyl ester are described. When malononitrile is treated with a defect of ester etc., the *dipotassium* derivative of  $\alpha\delta\delta$ -tetra-cyano- $\beta\gamma$ -dihydroxybutadiene ( $\beta\gamma$ -dihydroxybutadiene- $\alpha\delta\delta$ -tetra-carboxylonitrile) results.

Similarly, malononitrile condenses with ethyl formate to give the *potassium* derivative, m. p. 268°, of *hydroxymethylenemalononitrile* (corresponding *silver* salt described), and with ethyl cyanoacetate to give the *potassium* derivative of *cyanohydroxymethylene-malononitrile*,  $(CN)_2C:C(CN)\cdot OK$ , whereas it does not condense with ethyl benzoate, and with ethyl carbonate gives a mixture of products. The last-named potassium derivative appears to contain an impurity of the constitution  $(CN)_2C:C(OEt)\cdot OK$ , or (less probably)  $CN:C(OEt):C(CN)\cdot OK$ .

The above silver derivative of methyl  $\beta\beta$ -dicyano- $\alpha$ -hydroxyacrylate is converted by methyl and ethyl iodides into *methyl  $\beta\beta$ -dicyano- $\alpha$ -methoxyacrylate* and *methyl  $\beta\beta$ -dicyano- $\alpha$ -ethoxyacrylate*, respectively. Similarly are obtained *ethyl  $\beta\beta$ -dicyano- $\alpha$ -methoxy-* and *ethyl  $\beta\beta$ -dicyano- $\alpha$ -ethoxy-acrylate*. All four esters decompose when distillation is attempted, and undergo hydrolysis in moist air to give either  $\beta\beta$ -dicyano- $\alpha$ -methoxy- or  $\beta\beta$ -dicyano- $\alpha$ -ethoxy-acrylic acid, decomposing when heated.

Careful addition of dilute alcoholic ammonia to an ethereal solution of ethyl  $\beta\beta$ -dicyano- $\alpha$ -ethoxyacrylate produces  $\beta\beta$ -dicyano- $\alpha$ -ethoxyacrylamide, m. p. 141° (corresponding *methoxy-amide*, m. p. 140°). Both amides are converted by concentrated aqueous ammonia into the *ammonium* salt,  $(CN)_2C:C(OH_4)\cdot CO\cdot NH_2$ .

When silver  $\beta\beta$ -dicyano- $\alpha$ -methoxyacrylate is decomposed with hydrogen sulphide in an anhydrous solvent, *methyl  $\beta\beta$ -dicyano- $\alpha$ -hydroxyacrylate* results

(*ammonium* salt, m. p. 209°; *phenylhydrazine* salt, m. p. 104°). The similarly formed *ethyl* ester gives an *ammonium* salt, m. p. 176°, and a *phenylhydrazine* salt, m. p. 100°.

E. E. TURNER.

**Malononitrile and malonitrile condensations.** II. R. SCHENK and H. FINKEN [with P. MICHAELIS, K. PAPE, and F. PLEUGER] (*Annalen*, 1928, 462, 267—283).—Malonitrile condenses with acetone in absolute alcoholic potassium methoxide solution to give *dicyanodimethylethylene*, m. p. 171.5° (decomp.), passing slowly into a *dimeride* (two possible formulæ proposed). Malonitrile and benzophenone similarly afford *dicyanodiphenylethylene*, m. p. 136°, fluorenone and the nitrile giving *dicyanomethylenefluorene*, m. p. 213°. Of the above new compounds only the first-named combines with bromine.

Prolonged heating of oxalic esters with malonitrile in presence of sodium ethoxide or diethylamine (see preceding abstract) gives rise to *trismalonitrile* I,  $(C_3H_2N_2)_3$ , m. p. about 290°, whilst when ammonia is passed into a suspension of malonitrile in benzene, *trismalonitrile* II, m. p. 218°, is formed. At 222°, the latter passes with vigour into *trismalonitrile* III, m. p. about 300° (charring). *Trismalonitriles* I and III are possibly identical. *Trismalonitrile* II is converted by boiling aniline into a *substance*,  $C_{12}H_6N_5$ , for which various formulæ are suggested. The possible constitutions of I and III are discussed.

The use of malonitrile as a cryoscopic solvent is suggested and some determinations are made. The depression constant is determined as 48.90 (Klostermann, *Diss.*, Münster, 1918, found 50.03). The nitrile is a strongly dissociating solvent, giving a normal mol. wt. for *p*-nitrophenol. Some mol. wt. determinations in succinonitrile are also described.

E. E. TURNER.

**Alkylation of hexacyanochromic acid [hydrochromicyanic acid].** F. HÖLZL and F. VIDITZ (*Monatsh.*, 1928, 49, 241—264; cf. Hartley, *J.C.S.*, 1914, 105, 521; Hölzl, *A.*, 1927, 864; this vol., 279).—The alkylation of hydrochromicyanic acid must be expected to yield products analogous to those from decomposition of the acid, on which they thus throw light; no derivatives of the undecomposed acid are obtained.

Potassium chromicyanide is treated with methyl sulphate in (or without) methyl alcohol for 3 hrs. at 40—50°, and the product is cooled and filtered. From the filtrate, potassium methyl sulphate is precipitated by ether; further addition of ether precipitates a red, tarry *substance* (I). The brown residue, the main product, is washed with water and dried at 105°, yielding a greyish-green product (II),  $Cr_2(CN)_4(OH)_2, 6H_2O, MeNC$ ; this on keeping over calcium chloride yields a product (III),  $Cr_2(CN)_3(OH)_3, 3H_2O, 2MeNC$ , which slowly absorbs water from the air to give (IIIA),  $Cr_2(CN)_3(OH)_3, 4H_2O, MeNC$ .

The action of methyl iodide on silver chromicyanide yields unsatisfactory products; that of dry hydrogen chloride on potassium chromicyanide in absolute ethyl alcohol yields  $[CrCl_3(EtOH)_3]$  (cf. Koppel, *A.*,

1902, ii, 83), and in acetonitrile a brown *substance* (V), containing acetonitrile:  $Cr_2(CN)_3(OH)_3, 7H_2O, MeCN$ . The action of methyl sulphate on an aqueous solution of potassium chromicyanide at 40—50° yields a red liquid, from which a silver *derivative* (Cr : Ag = 1 : 2) is obtained.

Schemes are given for the gradual evolution of these products: thus the hypothetical  $[(MeNC)_3Cr(CN)_3]$  (A) by loss of methylcarbonylamine from 2 mols. would yield the *substance*  $[(MeNC)_3Cr(CN)_3Cr(CN)_3]$  (B); a *product* which probably has this constitution (containing a triple bridge of co-ordinated cyanide ion) is obtained by the action of methyl sulphate on potassium chromicyanide in absolute alcohol. The *substance* (B) is then considered to be hydrolysed by water, yielding ultimately the *substance*  $[(H_2O)_3Cr(CN)_3Cr(OH)_3]$ , (VI), which can be prepared (+2H<sub>2</sub>O) by the action of methyl sulphate in absence of solvent, and treating the product with water, without removing adhering methyl sulphate; by adding silver nitrate the *substance*  $Ag_2[(H_2O)_3Cr(CN)_3Cr(OH)_3]$  is obtained. (This suggests that these *substances* may have amphoteric properties; and by the action of aqueous pyridine on (V) a *substance* is obtained, regarded as having the constitution  $(C_5H_5N)_2H_2\{(MeNC)(HO)_2[Cr(CN)_3Cr(OH)_3]_2\}, 11H_2O$ .

The above, and many other, bivalent compounds can be expressed by the general formula  $[n_3Zx_3Zx_3]$ , where Z is a central trivalent atom of sextuple co-ordination, x a univalent negative ion, and n a unitary co-ordinand, e.g., H<sub>2</sub>O, RNC. The limit of intramolecular decomposition of a bivalent compound from  $H_2[Zx_6]$  is  $H_3[x_3Zx_3Zx_3]$ .

From the decomposition schemes, the *substances* (II), (III), and (IIIA) are formulated:

$[(MeNC)(H_2O)_2Cr(CN)_3Cr(CN)(OH)_2], 4H_2O$ ,  
 $[(MeNC)_2(H_2O)Cr(CN)_3Cr(OH)_3], 2H_2O$ , and  
 $[(MeNC)(H_2O)_2Cr(CN)_3Cr(OH)_3], 2H_2O$ ; each of these has a triple bridge of co-ordinated cyanide ion.

As a side reaction, *substances* containing methosulphate ion are obtained; of these the *substance* (I) (see above) has the ratio Cr : MeSO<sub>4</sub>' = 1 : 2, and since it does not give a precipitate with silver nitrate except after long boiling, it is represented  $[(MeNC)_4Cr(CN)_2Cr(MeNC)_2](MeSO_4)'$ , in which there is a double co-ordinated CN bridge.

E. W. WIGNALL.

**Cyanogen compounds of the platinum metals.**

III. **Cyanogen compounds of osmium.** F. KRAUSS and G. SCHRADER (*J. pr. Chem.*, 1928, [ii], 119, 279—286).—The preparation of potassium osmium cyanide,  $K_4[Os(CN)_6], 3H_2O$  (Claus, *ibid.*, 1862, [i], 85, 160; Martius, *Annalen*, 1861, 117, 361), is repeated: the *substance* is obtained colourless. The corresponding *copper* and *nickel* salts, and their ammonia *compounds*,  $Cu_2[Os(CN)_6], 4NH_3$  and  $Ni_2[Os(CN)_6], 6NH_3$ , and *strychnine hydro-osmocyaniide* are prepared. A simple osmium cyanide could not be obtained (cf. Moraht and Wischin, *A.*, 1893, ii, 380) and the above compounds could not be oxidised to derivatives of trivalent osmium.

E. W. WIGNALL.

**Reaction between organo-magnesium halides and alkyl sulphonates.** H. GILMAN and L. L.

HECK (J. Amer. Chem. Soc., 1928, 50, 2223—2230).—The reaction between organo-magnesium halides and alkyl sulphonates, usually formulated as  $2\text{RSO}_3\text{Alk} + 2\text{R}'\text{MgX} \rightarrow 2\text{R}'\text{Alk} + (\text{RSO}_3)_2\text{Mg} + \text{MgX}_2$  (I), yields the product  $\text{R}'\text{Alk}$  in not more than 50% yield if the reagents are used in equimolecular proportions. Actually, an alkyl halide is formed as well, and each of these two products is formed in equivalent amount and in increased yield if the reagents are used in the proportions required by the equations now suggested, viz.,  $\text{RSO}_3\text{Alk} + \text{R}'\text{MgX} \rightarrow \text{R}'\text{Alk} + \text{RSO}_3\text{MgX}$  (II), and  $\text{RSO}_3\text{Alk} + \text{RSO}_3\text{MgX} \rightarrow \text{AlkX} + (\text{RSO}_3)_2\text{Mg}$  (III). Confirmation of this scheme is given by the separation of magnesium naphthalene-2-sulphonate and *n*-butyl iodide from the product of reaction of iodomagnesium naphthalene-2-sulphonate and *n*-butyl *p*-toluenesulphonate. The occasional formation of hydrocarbons is attributed to hydrolysis of unused  $\text{RMgX}$  in working up the reaction product. The alternative scheme of Rossander and Marvel (this vol., 732) is not favoured.

Reactions analogous to (III), with the formation of *n*-butyl halides, occurred between *n*-butyl *p*-toluenesulphonate and magnesium ethoxyiodide, magnesium phenoxyiodide, magnesium *p*-tolylsulphinyl bromide, magnesium iodide, and magnesium bromide. Ethyl sulphate and magnesium iodide or magnesium ethyl bromide yielded ethyl iodide and ethyl bromide, respectively. Ethyl *p*-toluenesulphonate and magnesium phenyl iodide yielded ethylbenzene and ethyl iodide. *n*-Butyl *p*-toluenesulphonate yielded *n*-butyl iodide with magnesium *n*-propyl iodide, *n*-amylbenzene and *n*-butyl chloride with magnesium benzyl chloride, phenyl *n*-butyl sulphide with magnesium *p*-thiophenyl iodide, and methyl-*n*-butylaniline, b. p. 225—230° (picrate, m. p. 93°) (cf. Fröhlich and Wedekind, A., 1907, i, 512; Komatsu, A., 1913, i, 39), with methylanilinomagnesium bromide. The *p*-toluenesulphonic ester of ethyl lactate and magnesium phenyl bromide (cf. Kenyon, Phillips, and Turley, A., 1925, i, 507) yielded only ethyl  $\alpha$ -bromopropionate, and none of the expected ethyl  $\alpha$ -phenylpropionate. Ethyl cyclohexylsulphonate and magnesium phenyl bromide yielded ethylbenzene, ethyl bromide, magnesium cyclohexylsulphonate (+6H<sub>2</sub>O), and a compound, m. p. 107°. The expected cyclohexylsulphone had m. p. 73°, and was prepared by oxidation of the sulphide, b. p. 145°/11 mm.,  $d_4^{20}$  1.0031,  $n_D^{25}$  1.5663. No reaction took place between phenyl *p*-toluenesulphonate and magnesium bromide.

R. K. CALLOW.

**Synthesis of tertiary aliphatic arsines using Grignard's reagent.** E. GRYSKIEWICZ-TROCHIMOWSKI (Rocz. Chem., 1928, 8, 250—253).—The following tertiary arsines were prepared by the action of Grignard's reagents on arsenious oxide: *tri-n-butylarsine*, b. p. 102—104°/8 mm.,  $d_4^{20}$  0.9931; *tri-n-amylarsine*, b. p. 146—149°/10 mm.,  $d_4^{20}$  0.9799; *tri-n-hexylarsine*, b. p. 165—169°/6—7 mm.,  $d_4^{25}$  0.9660; *tri-n-heptylarsine*, b. p. 197—199°/9 mm.,  $d_4^{17}$  0.9568; *tri-n-octylarsine*, b. p. 238—240°/9—10 mm.,  $d_4^{19}$  0.9357.

R. TRUSZKOWSKI.

**Relation between atomic grouping and specific affinity. VIII. Additive compounds of thallium**

**dienol salts and carbon disulphide.** F. FEIGL and E. BÄCKER (Monatsh., 1928, 49, 401—412).—The ability of the thallium salts of dienols to form coloured additive compounds with carbon disulphide appears to depend on the presence of the  $\text{CO}\cdot\text{CH}_2\cdot\text{CO}$  group. Substitution in the methylene group or replacement of carbonyl oxygen by the anil residue inhibits reaction. The compounds are resistant towards dilute acids and bases. When decomposed by sulphuric acid in the presence of potassium iodide and ether they yield thalious iodide, carbon disulphide, and the ketone, and hence are formulated  $\text{C} \ll \begin{matrix} \text{CR}^1\cdot\text{O}\cdot\text{Tl} \\ \text{CR}^2\cdot\text{O}\cdot\text{Tl} \end{matrix} \gg \text{CS}_2$ . They are usually prepared by

mixing a solution of the requisite thallium derivative with carbon disulphide. The following new compounds are described: *thallium acetylacetonate*,  $\text{C}_5\text{H}_7\text{O}_2\text{Tl}$ , and the corresponding additive compound,  $\text{C}_6\text{H}_6\text{O}_2\text{S}_2\text{Tl}_2$ , decomp. about 80°; *thallium  $\gamma$ -methylacetylacetonate*; *thallium salt of benzoylacetonate* and its additive compound; *thallium  $\gamma$ -methylbenzoylacetonate*; *thallium dibenzoylmethane* and its additive product, decomp. about 150°; additive compound,  $\text{C}_{17}\text{H}_{10}\text{O}_3\text{S}_2\text{Tl}_2$ , from ethyl acetoacetate, thallium carbonate, and carbon disulphide and the analogous product,  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{S}_2\text{Tl}_2$ , from ethyl benzoylacetonate; *thallium salts* and non-crystalline, additive compounds from ethyl acetylpyruvate, ethyl benzoylpyruvate, and ethyl oxalacetate. Thallium derivatives or additive compounds could not be obtained from  $\delta$ -ketopentan- $\beta$ -ol, benzoylacetonanil, ethyl malonate, ethyl diacetylsuccinate, diacetyl, or acetylacetonate.

R. A. PRATT.

***pp'*-Di-iododiphenylmethane.** A. M. NASTUKOFF and V. W. SCHELJAGIN (J. pr. Chem., 1928, [ii], 119, 303—305).—Iodobenzene condenses with formaldehyde in concentrated sulphuric acid, heated under reflux, to yield *pp'*-*di-iododiphenylmethane*, m. p. 92—93°, b. p. 238—241°/40 mm., identified by oxidation to *pp'*-*di-iodobenzophenone* (Hoffmann, A., 1891, 1236).

E. W. WIGNALL.

**Benzene model based on the electron theory and the substitution laws.** M. ULMANN (Z. angew. Chem., 1928, 41, 674—680).—A formula for benzene is proposed in which alternate carbon atoms assume complete electron octets, these CH groups thus having each a resultant charge of +3, at the expense of the remaining CH groups, which have a resultant charge of -3. The relation of this formula to the substitution laws is discussed.

A. DAVIDSON.

**Physical properties of *o*-dichlorobenzene.** T. S. CARSWELL (Ind. Eng. Chem., 1928, 20, 728).—By modifying Holleman's method of preparation from *o*-chloronitrobenzene (cf. A., 1905, i, 41) a product is obtained having b. p. 180.3° (corr.)/760 mm., crystallising point -16.7°,  $d_4^{15}$  1.3112,  $d_4^{20}$  1.3088,  $n_D^{25}$  1.5518.

R. A. PRATT.

**Hydrogenation of nitrobenzene by platinum-black.** G. VAVON and CRAJICINOVIC (Compt. rend., 1928, 187, 420—422).—Catalytic hydrogenation of nitrobenzene with platinum-black in presence of benzaldehyde yields phenyl-*N*-phenylnitron and

phenylbenzylhydroxylamine (cf. Cusmano, A., 1922, i, 143), and in presence of piperonal, *piperonyl-N-phenylnitron*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{NPh}\cdot\text{OH}$ , m. p. about  $135^\circ$ . This confirms the view that the reduction of nitrobenzene alone proceeds through the stage of phenylhydroxylamine (cf. Cusmano, A., 1917, i, 641; Nord, A., 1920, i, 21). E. W. WIGNALL.

Laws of aromatic substitution. IX. B. FLÜRSCHHEIM and E. L. HOLMES (J.C.S., 1928, 2230—2242).—In continuation of previous work (this vol., 876) the nitration of a further series of toluene derivatives of the type  $\text{PhCR}_3$  in which  $\text{R}_3$  is  $\text{H}_3\text{CN}$ ,  $\text{H}(\text{CO}_2\text{Et})\cdot\text{CN}$ ,  $\text{H}(\text{CN})_2$ ,  $(\text{CO}_2\text{Et})_2\cdot\text{CN}$ ,  $(\text{CO}_2\text{Et})(\text{CN})_2$ ,  $\text{HCl}(\text{CN})$ ,  $\text{H}(\text{OH})(\text{CN})$ , and  $\text{H}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2m)$ , has been studied, the proportion of *m*-nitro-compound produced being, respectively, 12.70 (cf. Baker and others, this vol., 403, found 14%), 37.20, 67.90, 69.55, 87.5, 50.05, 43.55, 87.05%. Benzonitrile gave 88.25% (cf. Baker, *loc. cit.*, 80.53%) and benzaldehyde gave 78.65%. It is supposed that benzylidene-*m*-nitroaniline (*hydrochloride*) nitrates as the free anhydro-base, since its solution in concentrated sulphuric acid is intensely yellow, and from the fact that addition of ammonium sulphate during nitration causes an inappreciable change in the proportion of *m*-isomeride formed. The results are discussed on the basis of the authors' theory of alternating affinity demand. *Ethyl phenylcyano-malonate*, b. p.  $140\text{--}141^\circ/1$  mm., is obtained by the action of sodium on a mixture of ethyl phenylacetate (? phenylcyanoacetate) and ethyl chloroformate. The action of ethyl chloroformate on the sodium derivative of phenylmalononitrile yields *ethyl phenyldicyanoacetate*, m. p.  $60^\circ$ , from which by nitration is obtained *ethyl m-nitrophenyldicyanoacetate*, m. p.  $133\text{--}134.5^\circ$  (crystallised from chloroform).

J. W. BAKER.

Nature of the alternating effect in carbon chains. XXVIII. Preparation and properties of benzyl fluoride. C. K. INGOLD and E. H. INGOLD (J.C.S., 1928, 2249—2262).—Distillation, in Jena glass vessels, of benzyltrimethylammonium, dibenzyl dimethylammonium, and tribenzylmethylammonium fluorides (prepared by neutralisation of the quaternary hydroxides with hydrofluoric acid) in a water-pump vacuum gives a 60% yield of *benzyl fluoride*, m. p.  $-35^\circ$  (corr.), b. p.  $40\text{--}40.5^\circ/14$  mm.,  $139.9^\circ/760$  mm. (corr.),  $d_{25}^{25}$  1.02278,  $n_D^{25}$  1.48919. When benzyl fluoride is stored in certain glass vessels an autocatalytic decomposition may set in with almost explosive violence, hydrogen fluoride being evolved and an opaque white vitreous mass of composition  $(\text{C}_7\text{H}_6)_x$  formed. The same product is obtained by the action of concentrated sulphuric acid or hydrofluoric acid in platinum vessels. The physical and chemical properties of benzyl fluoride are discussed from the point of view of the greater rigidity of the valency electrons and greater intensity of the external field in the case of combined fluorine than for the other halogens. Thus, in agreement with this, fluorine has the lowest refraction values and differs sharply from the other halogens in contributing practically nothing to dispersion. The ultra-violet absorption spectrum of benzyl fluoride,

plotted from experiments conducted in *N*/100- to *N*/1600-alcoholic solutions, shows that its maximum absorption ( $\epsilon$  508,  $\lambda$  2508) falls in place in the series *p*-xylene, benzene, benzyl fluoride, benzaldehyde, benzoic acid, as a somewhat feebly *m*-orienting member. In agreement with this, nitration with a mixture of nitrous acid-free absolute nitric acid, and acetic anhydride at  $5^\circ$  yields *o*- 28.1, *m*- 17.5, and *p*-nitrobenzyl fluoride, m. p.  $38.5^\circ$ , 52.5%, respectively. The ratios para/ $\frac{1}{2}$  ortho for benzyl fluoride and chloride are 3.89 and 3.28, respectively, showing that the direct effect (Ingold and Vass, this vol., 402) of fluorine in orientation is stronger than that of chlorine, the sequence for the halogens being  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ , the tautomeric effect (Ingold and Shaw, this vol., 164) being in the reverse order. In agreement with the former sequence, it is found that, under conditions in which benzyl chloride reacts completely, a large percentage of benzyl fluoride is recovered unchanged after treatment with boiling aqueous potassium carbonate solution, zinc dust and boiling alcohol, 33% alcoholic trimethylamine at  $44^\circ$  for 20 hrs., and boiling sodium ethoxide solution for 1 hr. Distillation of *o*-, *m*-, and *p*-nitrobenzyltrimethylammonium fluorides causes energetic decomposition with much charring, the only identifiable products being *o*-, *m*-, and *p*-nitrobenzaldehydes. J. W. BAKER.

Nature of the alternating effect in carbon chains. XXIX. Further experiments bearing on the problem of the *ortho*-*para* ratio in aromatic substitution. C. K. INGOLD and C. C. N. VASS (J.C.S., 1928, 2262—2267).—The nitration of *p*-fluorochlorobenzene (prepared by the Gattermann reaction from *p*-fluoroaniline) in the presence of increasing quantities of sulphuric and fuming sulphuric acids has been studied and the proportion of 2-nitro- (*o*-fluoronitro-) and 3-nitro- (*o*-chloronitro-) isomerides produced determined by thermal analysis. The ratio *o*-fluoronitro-/*o*-chloronitro- increases from 0.262 with 4.5 mols. of nitric acid in the absence of sulphuric acid to 0.429 with 1 mol. of nitric acid in the presence of 1.5 mols. of sulphuric acid and 2.8 mols. of free sulphur trioxide. This effect is explained by the greater affinity of the unshared chlorine electrons for a positive field (the sequence for the halogens being  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ ), the presence of the strong acid polarising the chlorine atom (incipient salt formation; cf. Baker, this vol., 870) to a greater extent than in the case of fluorine, and thus diminishing its *op*-orienting power. These considerations explain the result of Hove (A., 1927, 757), who obtained 40% of the *o*-fluoronitro-isomeride by nitration of *p*-fluorobromobenzene in the presence of a large excess of sulphuric acid. Swarts (A., 1916, i, 133) found 27.75% of the *o*-fluoronitro-isomeride by nitration of *p*-fluorochlorobenzene in the absence of sulphuric acid (cf. this paper, 20.8%), but it is shown that his thermal analysis data need revision, and, moreover, contrary to his observations, it is not possible to obtain quantitative decomposition of the *o*-fluoronitro-compound with sodium methoxide, and a simultaneous complete absence of any decomposition of the other isomeride.

J. W. BAKER.

**Rubrene.** Constitution of rubrene. C. MOUREU, C. DUFRAISSE, and L. ENDERLIN (Compt. rend., 1928, 187, 406—407).—Oxidation of rubrene by chromic acid yields *o*-dibenzoylbenzene; it is therefore suggested that the constitution of rubrene is  $C_6H_4 \left\langle \begin{smallmatrix} CPh \\ CPh \end{smallmatrix} \right\rangle C:C \left\langle \begin{smallmatrix} CPh \\ CPh \end{smallmatrix} \right\rangle C_6H_4$  (cf. Moureu, Dufraisse, and others, this vol., 53, 594, 628; Willemart, *ibid.*, 996).  
E. W. WIGNALL.

**Catalytic preparation of alkyylanilines.** I. B. C. ROY (J. Indian Chem. Soc., 1928, 5, 383—386).—When a mixture of aniline and ethyl alcohol is passed over an asbestos-thoria catalyst at 350—390°, the conversion into ethylanilines is 63.4—66.7%. With aniline and methyl alcohol at 410—430° the yield of dimethylaniline is 40—30%, with simultaneous production of 32.8—45% of methyl-aniline.  
H. BURTON.

**Odour and constitution among mustard oils [thiocarbimides].** IV. Effect of fluorine substitution. G. M. DYSON (Perf. Ess. Oil Rec., 1928, 19, 341—342; cf. this vol., 283, 514, 748).—The odours of 4-fluoro- and 4-fluoro-3-methyl-phenylthiocarbimides are intermediate between those of phenylthiocarbimide and its 4-chloro-derivative. The effect of the methyl group is to accentuate the true thiocarbimide odour. 3-Fluoro-, 3-fluoro-4- and -6-methyl-phenylthiocarbimides have been prepared and they possess a thiocarbimide odour. 3-Fluoro-4-nitrophenylthiocarbimide has no characteristic odour.  
H. BURTON.

**2:5:6-Trichloro-*m*-4-xylidine and its derivatives.** E. BUREŠ and J. BORGMANN (Časopis Českosloven. Lék., 1927, 7, 270—280; Chem. Zentr., 1928, i, 1171).—The action of chlorine in acetic acid on 4-acetamido-*m*-xylene, m. p. 123°, at the ordinary pressure and temperature, without a catalyst, yields 2:5:6-trichloro-4-acetamido-*m*-xylene, m. p. 208.5° (lit. 190—192°). 2:5:6-Trichloro-*m*-4-xylidine has m. p. 204° (sulphate); hydrochloride, m. p. 217°; benzoyl derivative, m. p. 174—175°; 2:5:6-trichloro-*m*-4-xylenol, m. p. 174° (lit. 169°), forms mercury and bismuth salts; the methoxy-compound has m. p. 53.5°. 2:5:6-Trichloro-*m*-xylene has m. p. 179.5°; 3:5:6-trichloro-2:4-dimethylbenzotrile, m. p. 218°; 3:5:6-trichloro-2:4-dimethylbenzoic acid, m. p. 191.5°; 2:4:5:6-tetrachloro-*m*-xylene, m. p. 219° (lit. 210°). A. A. ELDRIDGE.

**5-Bromo-*m*-4-xylidine.** E. BUREŠ and A. MANDEL-BORGMANNOVÁ (Časopis Českosloven. Lék., 1927, 7, 257—269; Chem. Zentr., 1928, i, 1170—1171).—Bromination of *m*-4-xylidine under pressure, at the ordinary temperature without a catalyst and in absence of sunlight, yields 5-bromo-*m*-4-xylidine, m. p. 49—50° (hydrochloride; sulphate, m. p. 183°; picrate, m. p. 122°; benzoyl derivative, m. p. 183°). 5-Bromo-3-methylbenzoic acid has m. p. 178°; 5-bromo-*m*-4-xylenol has b. p. 231°, m. p. 4°; it forms basic *mercuric*,  $C_6H_4BrMe_2(OH) \cdot HgOH$ , and *bismuth*,  $[C_6H_2BrMe_2O]_2 \cdot Bi(OH)_4 \cdot Bi_2O_3$ , compounds. 5-Bromo-4-methoxy-*m*-xylene has b. p. 140°; the *ethoxy*-compound has b. p. 142°, and the *acetoxy*-compound, b. p. 257—258°; 4:5-dibromo-*m*-xylene has

b. p. 257°; 6-bromo-2:4-dimethylbenzotrile, m. p. 218°; 6-bromo-2:4-dimethylbenzoic acid, m. p. 186° (*sodium* and *mercury* salts; *methyl*, m. p. 174°, *ethyl*, m. p. 176°, *propyl*, m. p. 178°, *isobutyl*, m. p. 182°, and *amyl*, m. p. 181°, esters). A. A. ELDRIDGE.

**5-Bromo-*m*-4-xylidine.** A. S. WHEELER and R. E. THOMAS (J. Amer. Chem. Soc., 1928, 50, 2286—2287).—5-Bromo-*m*-4-xylidine was prepared by a variation of the method of Noelting, Braun, and Thesmar (A., 1902, i, 588). The hydrochloride and benzoyl derivative, m. p. 186°, were prepared. Diazotisation in sulphuric acid and boiling yielded 5-bromo-*m*-4-xylenol (*methyl ether*, b. p. 232°,  $d_4^{25}$  1.362; *ethyl ether*, b. p. 246°,  $d_4^{25}$  1.290). By diazotisation of the amine and Gattermann and Sandmeyer reactions, 4-chloro-5-bromo-*m*-xylene, b. p. about 250°, and 5-bromo-4-cyano-*m*-xylene, m. p. 86—87°, were prepared. With  $\beta$ -naphthol and phenol the diazotised amine gave 5-bromo-*m*-xylene-4-azo- $\beta$ -naphthol, m. p. 136°, and -azophenol, m. p. 166°, respectively.  
R. K. CALLOW.

***p*-Cymene.** X. 2:5-Diamino-*p*-cymene and certain new [azo] dyes. A. S. WHEELER and R. W. BOST.—See B., 1928, 666.

**Molecular rearrangements accompanying deamination of aralkylamines.** (MLLE.) J. LÉVY and P. GALLAIS (Bull. Soc. chim., 1928, [iv], 43, 862—868).—When amines of the type  $CRAr_2 \cdot CH_2 \cdot NH_2$  ( $R=H, Me, \text{ or } Et$ ), prepared by reducing the corresponding aldoximes, are treated with nitrous acid, hydrocarbons of the form  $CRAr \cdot CHAR$  are obtained. Thus,  $\beta\beta$ -diphenylethylamine (*hydrochloride*, m. p. 237—238°; *acetyl* derivative, m. p. 88°; *benzoyl* derivative, m. p. 143—144°) affords stilbene.  $\beta\beta$ -Diphenyl-*n*-propylamine, b. p. 179—182°/22 mm.,  $d_4^{25}$  1.027 (*hydrochloride*, m. p. 261—263°; *acetyl* derivative, m. p. 106—107°; *benzoyl* derivative, m. p. 82—83°), gives  $\alpha$ -methylstilbene, and  $\beta\beta$ -diphenyl-*n*-butylamine, b. p. 125°/24 mm.,  $d_4^{25}$  1.20 (*hydrochloride*, m. p. 252°; *acetyl* derivative, m. p. 114°; *benzoyl* derivative, m. p. 144—145°), yields  $\alpha$ -ethylstilbene. H. BURTON.

**Comparison of mechanisms of deamination of aralkylamines and of dehydration of the corresponding alcohols.** (MLLE.) J. LÉVY, P. GALLAIS, and D. ABRAGAM (Bull. Soc. chim., 1928, [iv], 43, 868—881; cf. preceding abstract).—A study of the deamination by nitrous acid of amines of the type  $CHArAr' \cdot CHMe \cdot NH_2$  shows that unsaturated hydrocarbon formation is general but the type of product varies with  $Ar$  and  $Ar'$ . Thus when  $Ar=Ph$  and  $Ar'=p-MeO \cdot C_6H_4$ , migration of the phenyl group occurs, but when  $Ar=Ar'=Ph$  no migration takes place, hydrogen being lost by the methyl group. Dehydration of the corresponding alcohols by distillation with pumice moistened with concentrated sulphuric acid is not analogous. In the examples analogous to the above, migration of the anisyl group is effected, whilst in the diphenyl-substituted alcohol both migration of the phenyl group and loss of hydrogen from the methyl group occur. It is concluded that the alcohols are not necessarily intermediates in the deamination process, and also that

this change can take place either with or without molecular rearrangement.

$\beta$ -Amino- $\gamma\gamma$ -diphenylpropane (*hydrochloride*, m. p. 280—282°; *acetyl* derivative, m. p. 107—108°; *benzoyl* derivative, m. p. 203—204°) is converted by nitrous acid into  $\gamma\gamma$ -diphenyl- $\Delta^{\alpha}$ -propylene, b. p. 293°,  $n_D^{20}$  1.596, which is oxidised by chromic and acetic acids to benzophenone and by perbenzoic acid in chloroform solution to an *oxide*, b. p. 300°, 182—185°/16 mm.,  $n_D^{20}$  1.5745, differing from the oxide prepared from  $\alpha\alpha$ -diphenyl- $\Delta^{\alpha}$ -propylene (Lagrange, this vol., 270). When this oxide is heated with anhydrous zinc chloride, a *compound*,  $C_{15}H_{14}O$  (*semicarbazone*, m. p. 158°; *oxime*, m. p. 156°), is obtained. Dehydration of  $\alpha\alpha$ -diphenylisopropyl alcohol, b. p. 305—307°, m. p. 62° (*acetyl* derivative, m. p. 77—78°), gives a mixture of  $\gamma\gamma$ -diphenyl- $\Delta^{\alpha}$ -propylene and  $\alpha$ -methylstilbene. Distillation of  $\alpha$ -phenyl- $\alpha$ -anisyl-*n*-propyl alcohol affords  $\alpha$ -phenyl- $\alpha$ -anisyl- $\Delta^{\alpha}$ -propylene, b. p. 183°/16 mm., m. p. 53°, oxidised by perbenzoic acid to  $\alpha$ -phenyl- $\alpha$ -anisyl- $\beta$ -methylstyrene *oxide*. This is isomerised by treatment with hot 50% sulphuric acid or by distillation to  $\alpha$ -phenyl- $\alpha$ -anisylacetone, b. p. 225°/25 mm.,  $d_4^{20}$  1.159 [*oxime* (I), m. p. 189—190°; *semicarbazone*, m. p. 178—179°], which is unaffected by concentrated sulphuric acid at 0°, and after treatment with alcoholic potassium hydroxide and subsequent oxidation yields phenyl anisyl ketone. Reduction of (I) with sodium and alcohol gives  $\beta$ -amino- $\alpha$ -phenyl- $\alpha$ -anisylpropane, b. p. 207—208°/19 mm., m. p. 63—64° (*hydrochloride*, m. p. 215—216°; *benzoyl* derivative, m. p. 181—182°), deaminated to  $\beta$ -phenyl- $\alpha$ -anisyl- $\Delta^{\alpha}$ -propylene, m. p. 86—87°, prepared also by dehydration of  $\beta$ -phenyl- $\alpha$ -anisylisopropyl alcohol. Dehydration of  $\alpha$ -phenyl- $\alpha$ -anisylisopropyl alcohol gives  $\alpha$ -phenyl- $\beta$ -anisyl- $\Delta^{\alpha}$ -propylene, m. p. 103—104°, obtained also by dehydration of  $\alpha$ -phenyl- $\beta$ -anisyl-*n*-propyl alcohol, b. p. 210—215°/18 mm., in turn prepared from magnesium phenyl bromide and  $\alpha$ -anisylpropaldehyde.  $\alpha$ -Phenyl- $\alpha$ -anisylethane, prepared by reducing the corresponding ethylene with sodium and alcohol, has b. p. 180—182°/19 mm.,  $d$  1.06,  $n_D^{20}$  1.5735. H. BURTON.

*NN'*-Diphenyl-*o*-phenylenediamine. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 1988—1989).—The product of the action of *o*-aminodiphenylamine and iodobenzene (Wieland and Müller, A., 1913, i, 1386) is not *NN'*-diphenyl-*o*-phenylenediamine but *o*-aminotriphenylamine, identical with the compound prepared by Piccard and Brewster (A., 1922, i, 370). The former compound is most conveniently prepared by the method of Clemo, Perkin, and Robinson (A., 1924, i, 1337). J. W. BAKER.

*N*-Methyl derivatives of 2-phenylnaphthylene-1:3-diamine. C. S. GIBSON, W. S. KENTISH, and J. L. SIMONSEN (J.C.S., 1928, 2131—2142).—Re-examination of the isomeric *NN'*-dimethyl-2-phenylnaphthylene-1:3-diamines described by Lees and Thorpe (J.C.S., 1907, 91, 1296) has shown that these compounds are *cis-trans*-isomerides. The *cis*-configuration is ascribed to the  $\alpha$ -compound (I), which yields only monoacetyl and mono-*p*-toluenesulphonyl derivatives. In the *trans*- or  $\beta$ -compound (II), the hydrogen atoms of both secondary amino-

groups are highly reactive. Attempts to resolve the two bases into optically active forms were unsuccessful. Improved methods for the preparation of the bases, as well as indirect conversion of the  $\alpha$ - into the  $\beta$ -form, are described. *p*-Toluenesulphonyl chloride reacts with 2-phenylnaphthylene-1:3-diamine [acetylacetate, m. p. 175° (lit. 185°)] in pyridine solution, giving, as the main product,  $\alpha$ -*di-p*-toluenesulphonyl-2-phenylnaphthylene-1:3-diamine (III), dimorphic, m. p. 188—189° and 203—205° (stable). A second *disulphonamide* ( $\beta$ -*di-p*-toluenesulphonyl-2-phenylnaphthylene-1:3-diamine?), m. p. 173—175°, *tri-p*-toluenesulphonyl-2-phenylnaphthylene-1:3-diamine, m. p. 153—154°, and a *compound* (tetrasulphonyl derivative?), m. p. about 213°, are also obtained. Methylation of (III) yields *di-p*-toluenesulphonyl-*NN'*-dimethyl-2-phenylnaphthylene-1:3-diamine, m. p. 305°, giving, on hydrolysis, a quantitative yield of the  $\beta$ -base (II) (*diacetyl* derivative, m. p. 207—208°; *di-d*-methylenecamphor derivative, m. p. 277—279°). The  $\alpha$ -base (I) yields a *monoacetyl* derivative, m. p. 203°, *mono-p*-toluenesulphonyl derivative, m. p. 219—220°, and a *mono-d*-methylenecamphor derivative, m. p. 167—168°. The dinitrosoamine, m. p. 180—181°, prepared from either base (cf. Thorpe and Lees, *loc. cit.*), gives, on reduction with tin and hydrochloric acid, a quantitative yield of the  $\beta$ -compound (II), of which, accordingly, it is a derivative. Trimethyl-2-phenylnaphthylene-1:3-diamine, m. p. 104—105° (lit. 98—99°), gives an *acetyl* derivative, m. p. 178°.

M. CLARK.

Didiphenylmethane derivatives. J. TURSKI and J. DALINSKI (Rocz. Chem., 1928, 8, 281—289).—Benzidine condenses with formaldehyde to yield tetra-aminodidiphenylmethane (I), m. p. 159°, which



can be hexazotised but not octazotised. Azo dyes cannot be prepared from this base, but a number of reddish-brown triarylmethane dyes can be obtained from it by further condensation with various bases.

R. TRUSZKOWSKI.

Halogen derivatives of *o*- and *p*-azophenol. L. HUNTER and R. S. BARNES (J.C.S., 1928, 2051—2058).—The “dichloramine-*T*” method of halogenation (Orton and King, *ibid.*, 1911, 99, 1185), previously employed for chlorination and iodination (this vol., 629), is now extended to bromination. When the method is applied to the progressive halogenation of *o*- and *p*-azophenol (2:2'- and 4:4'-dihydroxyazobenzene), chlorine, bromine, and iodine can be introduced atom by atom up to the tetrasubstituted stage. The orientation of the halogen atoms in the azophenol molecule is determined by reduction to the corresponding aminophenol. *p*-Azophenol yields only the 3:3'- and not the 3:5-dihalogeno-derivative on dihalogenation. In the monosubstituted *o*-azophenols, the halogen atom occupies the 5-position to the exclusion of the 3-position; iodine oxidises and does not substitute *p*-azophenol, yielding the quinhydroneazine  $O:C_6H_4:N:N:C_6H_4:O, HO\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot OH$ , which



on further oxidation is converted into *p*-benzoquinone-azine,  $O:C_6H_4:N:N:C_6H_4:O$ . The following are described (A=4:4'-dihydroxyazobenzene; B=2:2'-dihydroxyazobenzene): 3-Chloro-A, m. p. 184° (diacetate, m. p. 160—161°; dibenzoate, m. p. 158—159°); 3:3'-dichloro-A, m. p. 195° (diacetate, m. p. 199°; dibenzoate, m. p. 226°); 3:5:3'-trichloro-A, m. p. 172° (diacetate, m. p. 207—208°; dibenzoate, m. p. 189°); 3:5:3':5'-tetrachloro-A (+6H<sub>2</sub>O), m. p. 225°, anhyd. m. p. 240° (diacetate, m. p. 240°; dibenzoate, m. p. 244°); 3-bromo-A, m. p. 153° (diacetate, m. p. 142°; dibenzoate, m. p. 165—166°); 3:3'-dibromo-A, m. p. 175° (diacetate, m. p. 161°; dibenzoate, m. p. 227°); 3:5:3'-tribromo-A, m. p. 184° (diacetate, m. p. 172°; dibenzoate, m. p. 216°); 3:5:3':5'-tetrabromo-A (diacetate, m. p. 240°; dibenzoate, m. p. 265°); 3:3'-dichloro-5:5'-dibromo-A, m. p. 262°; 5-chloro-B, m. p. 164° (diacetate, m. p. 117°; dibenzoate, m. p. 119°); 5:5'-dichloro-B, m. p. 267° (diacetate, m. p. 199°; dibenzoate, m. p. 243°); 3:5:5'-trichloro-B (diacetate, m. p. 189°; dibenzoate, m. p. 247°); 3:5:3':5'-tetrachloro-B, m. p. 246—247° (diacetate, m. p. 195°; dibenzoate, m. p. 186°); 5-bromo-B, m. p. 154° (diacetate, m. p. 142°; dibenzoate, m. p. 215°); 5:5'-dibromo-B, m. p. 249° (diacetate, m. p. 211°; dibenzoate, m. p. 202°); 3:5:3':5'-tetrabromo-B (diacetate, m. p. 210—211°; dibenzoate, m. p. 214°); 5-iodo-B, m. p. 149—150° (diacetate, m. p. 138°; dibenzoate, m. p. 159°); 5:5'-di-iodo-B, m. p. 153° (diacetate, m. p. 145°; dibenzoate, m. p. 147°); 3:5:3':5'-tetraiodo-B, m. p. 98—99° (dibenzoate, m. p. 241°); 4-chloro-2-acetamidophenyl acetate, m. p. 170°; 2:4-dichloro-6-aminophenol, m. p. 109° (decomp.) (hydrochloride); 4-iodo-6-aminophenol, m. p. 139° (hydrochloride); 2:4-di-iodo-6-aminophenol, m. p. 120° (hydrochloride). M. CLARK.

#### Preparation of some halogenoaminophenols.

I. Mixed tetrahalogen derivatives of *o*-azophenol. II. Halogen derivatives of *p*-hydroxyazobenzene. L. HUNTER and R. S. BARNES (J.C.S., 1928, 2058—2067).—I. The chloroamine method of halogenation has been applied to the progressive mixed halogenation of *o*-azophenol. Five of the six theoretically possible symmetrical 3:5:3':5'-tetrahalogeno-*o*-azophenols have been prepared and reduced to the corresponding 2:4-dihalogeno-*o*-aminophenols. The following are described (2:2'-dihydroxyazobenzene = A): 5:5'-Dichloro-3:3'-dibromo-A, m. p. 259° (decomp.) (diacetate, m. p. 203°; dibenzoate, m. p. 212°); 4-chloro-6-bromo-2-aminophenol, m. p. 89—90° (hydrochloride; diacetyl derivative, m. p. 130°; dibenzoyl derivative, m. p. 180.5°); 3:3'-dichloro-5:5'-dibromo-A, m. p. 263° (diacetate, m. p. 199°; dibenzoate, m. p. 201°); 6-chloro-4-bromo-2-aminophenol, m. p. 93° (hydrochloride; diacetyl derivative, m. p. 137°; dibenzoyl derivative, m. p. 182°); 5:5'-dichloro-3:3'-di-iodo-A, m. p. 272° (decomp.) (diacetate, m. p. 205°; dibenzoate, m. p. 254°); 4-chloro-6-iodo-2-aminophenol, charring at about 90° (hydrochloride; diacetyl derivative, m. p. 169°); 5:5'-dibromo-3:3'-di-iodo-A, m. p. 255° (decomp.) (diacetate, m. p. 186°; dibenzoate, m. p. 252°); 4-bromo-6-iodo-2-aminophenol, decomp. [hydrochloride; diacetyl derivative, m. p. 190° (decomp.); dibenzoyl derivative,

m. p. 185°]; 3:3'-dibromo-5:5'-di-iodo-A, m. p. 256° (diacetate, m. p. 217°; dibenzoate, m. p. 215°); 6-bromo-4-iodo-2-aminophenol, m. p. 90° (hydrochloride; diacetyl derivative, m. p. 196°; dibenzoyl derivative, m. p. 194—195°).

II. Since iodo-*p*-azophenols could not be prepared (preceding abstract), iodine-substituted *p*-aminophenols were obtained by reducing the iodo-derivatives of *p*-hydroxyazobenzene, which are readily accessible by the chloroamine method of halogenation. The iodo-aminophenols were separated from the aniline simultaneously formed by means of their differently soluble hydrochlorides. Direct halogenation of *p*-hydroxyazobenzene gave the 3:5-dihalogeno-compounds. The monohalogen derivatives were therefore synthesised by coupling diazotised aniline with the *o*-halogenophenols. The following are described (B=4-hydroxyazobenzene): 3-Bromo-B, m. p. 80° (hydrochloride, m. p. 159°; acetate, m. p. 98°; benzoate, m. p. 113°); 3-iodo-A, m. p. 77—78° [hydrochloride, m. p. 172° (decomp.); acetate, m. p. 103—104°; benzoate, m. p. 105°]; 3-chloro-5-bromo-A, m. p. 125.5° (acetate, m. p. 133.5°; benzoate, m. p. 118.5°); 2-chloro-6-bromo-4-aminophenol (diacetyl derivative, m. p. 168.5°; dibenzoyl derivative, m. p. 111—112°); 3-chloro-5-iodo-A, m. p. 110.5° (acetate, m. p. 124°; benzoate, m. p. 115°); 2-chloro-6-iodo-4-aminophenol, m. p. 169° (decomp.) (hydrochloride; diacetyl derivative, m. p. 155°; dibenzoyl derivative, m. p. 157°); 3-bromo-5-iodo-A, m. p. 128.5° (acetate, m. p. 127—128°; benzoate, m. p. 85°); 2-bromo-6-iodo-4-aminophenol, m. p. 185° (decomp.) (hydrochloride; diacetyl derivative, m. p. 186°; dibenzoyl derivative, m. p. 148°); 3:5-di-iodo-A, m. p. 128—129° (acetate, m. p. 162°; benzoate, m. p. 137—139°); 2:6-di-iodo-4-aminophenol, m. p. 173° (lit. 169—171°) (diacetyl derivative, m. p. 209°). M. CLARK.

Azo-derivatives of tyrosine. A. MOREL and P. SISLEY (Bull. Soc. chim., 1928, [iv], 43, 881—883; cf. A., 1927, 1212).—When tyrosine is treated with nitrous acid in the cold and in absence of light only part of the amino-nitrogen is lost (maximum 40%). When tyrosine is diazotised under the same conditions as fibroin (*loc. cit.*) and after 36 hrs. the mixture is treated with  $\beta$ -naphthol two colouring matters are obtained. These are 3- $\beta$ -naphtholazotyrosine,  $OH \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ , slightly soluble in alcohol, and  $\alpha$ -hydroxy- $\beta$ -3-( $\beta$ -naphtholazo)-4-hydroxyphenylpropionic acid, more readily soluble in alcohol. H. BURTON.

Diazo-compounds. A. ANGELI (Atti R. Accad. Lincei, 1928, [vi], 7, 699—705).—Largely polemical against Hantzsch. Consideration of the behaviour of diazo-compounds shows that their reactions may be explained satisfactorily without the help of stereoisomerism. T. H. POPE.

cycloHexyloxy-derivatives. L. PALFRAY and S. SABETAY (Bull. Soc. chim., 1928, [iv], 43, 900—903).—cycloHexyl chloromethyl ether (I) is converted by sodium methoxide in boiling toluene into cyclohexyl methoxymethyl ether, b. p. 61.5—62.5°/15 mm.,  $d^{20}_4$  0.9375,  $n^{20}_D$  1.4391, and by acetic anhydride and sodium acetate into cyclohexyl acetoxymethyl ether, b. p.

96.5—97°/13 mm.,  $d^{15}$  1.022,  $n_D^{15}$  1.4465. When (I) is heated with cuprous cyanide, *cyclohexyloxyacetone nitrile* (II), b. p. 102—103°/15 mm.,  $d^{18}$  0.9825,  $n_D^{18}$  1.4561, is formed: this is converted by methylalcoholic hydrogen chloride into *methyl cyclohexyloxyacetate*, b. p. 110°/16 mm.,  $d^{20}$  1.034,  $n_D^{20}$  1.4508. Treatment of (II) with magnesium methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride gives *cyclohexyloxyacetone*, b. p. 98—98.5°/17 mm.,  $d^{17}$  0.9686,  $n_D^{17}$  1.4522, *phenyl cyclohexyloxymethyl ketone*, b. p. 178°/14 mm.,  $d^{20}$  1.071,  $n_D^{20}$  1.5365 (*hydrazone*), m. p. 113°; *semicarbazone*, m. p. 123°, and *benzyl cyclohexyloxymethyl ketone*, b. p. 185—186°/14 mm.,  $d^{21}$  1.044,  $n_D^{21}$  1.520, respectively.

*cycloHexane-1:4-diol di(methoxymethyl) ether* has b. p. 121—122°/13 mm.,  $d^{17}$  1.038,  $n_D^{17}$  1.449.

H. BURTON.

**$\Delta^3$ -cycloHexenol.** S. SABETAY and L. PALFRAY (Bull. Soc. chim., 1928, [iv], 43, 906—909).—4-Chloro-cyclohexanol (*ethyl ether*, b. p. 84—85°/16 mm.,  $d^{20}$  1.028,  $n_D^{20}$  1.4622, from magnesium methyl iodide and the *chloromethyl ether*, b. p. 117.5°/15 mm.,  $n_D^{20}$  1.4942) is oxidised by chromic acid to 4-chlorocyclohexanone, which, when regenerated from its *semicarbazone*, m. p. 191°, has b. p. 95°/17 mm.,  $n_D^{20}$  1.4867. When 4-chlorocyclohexanol is heated with sodium in dry ether for 2 days,  $\Delta^3$ -cyclohexenol, b. p. 67—68°/14 mm.,  $d^{20}$  0.9425,  $n_D^{20}$  1.4627 (phenylcarbimide derivative, m. p. 82°), is obtained (cf. von Baeyer, A., 1894, i, 174).

H. BURTON.

**Extraction of phenols from alkaline solution with ether.** G. VAVON and N. ZAHARIA (Compt. rend., 1928, 187, 346—348).—All phenols are extracted by ether from their solutions in sodium hydroxide, to an extent depending on the hydrolysis of the phenoxide and the solubility of the free phenol in the phenoxide solution and in ether. The percentage extracted increases with the mol. wt. of the phenol and is considerably greater with *o*-substituted phenols than with the *m*- or *p*-isomerides. Ether extraction thus affords a means of distinguishing between *o*-phenols and the *m*- and *p*-isomerides and of partly separating a mixture of phenols. Excess of alkali decreases the extraction, but for substituted phenols it is advisable to replace ether by light petroleum or other solvent. Thus thymol dissolved in 1 mol. of sodium hydroxide is extracted to the extent indicated by the following solvents: ether 88%, benzene 38%, carbon tetrachloride 25%, light petroleum 22%. The following percentages of phenols are extracted by ether from a solution in 1 mol. of sodium hydroxide at 15°, using 0.01 mol. in 10 c.c. of solution, and extracting with 20 c.c. of ether: phenol 7.5, *o*-cresol 20.8, *m*-cresol 15.0, *p*-cresol 13.3, *o*-ethylphenol 44.7, *p*-ethylphenol 25.3, *m*-4-xylenol 43, *p*-xylenol 37.7, *o*-propylphenol 68.5, *p*-propylphenol 28.7, *o*-allylphenol 48, *p*-allylphenol 24.3, *o*-isopropylphenol 72.7, *p*-isopropylphenol 32.6, *o*-butylphenol 80.7, *p*-butylphenol 28.7, "*o*- $\psi$ -butylphenol" 97, "*p*- $\psi$ -butylphenol" 30.6, *o*-allyl-*o*-cresol 70.6, di-*o*-propylphenol 97.7, di-*o*-allylphenol 91.7, thymol 88, carvacrol 82.5, *o*-phenylphenol 52.5,  $\alpha$ -naphthol, 16.7,  $\beta$ -naphthol 23.

R. BRIGHTMAN.

**Constitution of dinitro-*m*-cresols.** S. M. SANE and S. S. JOSHI (J. Indian Chem. Soc., 1928, 5, 299—

301).—When 3-chloro-4:6-dinitrotoluene is fused with sodium acetate and acetamide (Borsche, A., 1918, i, 11), 4:6-dinitro-*m*-cresol, m. p. 74°, is obtained, the *p*-toluenesulphonate, m. p. 110—111°, of which, when treated with ammonia in boiling xylene, affords 4:6-dinitro-*m*-toluidine. Bromination of the dinitro-cresol gives 2-bromo-4:6-dinitro-*m*-cresol, m. p. 115—116°, which when treated with *p*-toluenesulphonyl chloride and diethylaniline yields 3-chloro-2-bromo-4:6-dinitrotoluene, m. p. 81—82° (Cohen and Smithells, J.C.S., 1914, 105, 1909). The compound described by Gibbs and Robertson (*ibid.*, 1889) as the bromo-derivative of 2:6-dinitro-*m*-cresol, m. p. 74°, is the 2-bromo-derivative of 4:6-dinitro-*m*-cresol.  
H. BURTON.

**Ethers of cyclohexanediols.** L. PALFRAY and S. SABETAY (Bull. Soc. chim., 1928, [iv], 43, 895—900).—Methylation of *cyclohexane-1:2-diol* with methyl iodide and dry silver oxide gives a mixture of the monomethyl, b. p. 74—76°/15 mm.,  $d^{18}$  1.001,  $n_D^{18}$  1.4572, and dimethyl ethers, b. p. 65—66°/15 mm.,  $d^{18}$  0.9652,  $n_D^{18}$  1.446. The action of hydrogen chloride on a mixture of the diol and 40% formaldehyde is to furnish *cyclohexane-1:2-diol di(chloromethyl) ether*, b. p. 136—137°/16 mm.,  $n_D^{21}$  1.488, which reacts with sodium in benzene solution, yielding a chlorine-free product, b. p. 62—65°/15 mm.,  $n_D^{18}$  1.4555 (cf. Sabetay and Sandulesco, this vol., 1140), together with solid derivatives. Methylation of *cyclohexane-1:3-diol* affords its monomethyl ether, b. p. 97—98°/15 mm., together with an iodine-containing product, b. p. 65—66°/15 mm. *cycloHexane-1:3-diol diethyl ether*, b. p. 85—86°/15 mm.,  $d^{18}$  0.9127,  $n_D^{18}$  1.440, is obtained by the action of magnesium methyl iodide on the corresponding *di(chloromethyl) ether*, b. p. 144—145°/14 mm.,  $n_D^{17}$  1.4922. Methylation of *cis-cyclohexane-1:4-diol* gives a mixture of the *cis*-monomethyl, b. p. 102—103°/15 mm.,  $d^{19}$  1.023,  $n_D^{19}$  1.4671, and *cis*-dimethyl ethers, b. p. 67.5—68°/14 mm.,  $d^{18}$  0.9526,  $n_D^{18}$  1.444. The corresponding *trans*-mono- and *di*-methyl ethers have b. p. 102.5—103°/15 mm.,  $d^{19}$  1.021,  $n_D^{19}$  1.4649, and b. p. 68—69°/15 mm.,  $n_D^{18}$  1.443, respectively. The question of possible isomerisation during etherification (cf. Palfray and Rothstein, this vol., 632) is reserved. *cycloHexane-1:4-diol diisobutyl ether*, b. p. 122—124°/13 mm.,  $d^{19}$  0.8833,  $n_D^{19}$  1.441, is prepared from magnesium isopropyl bromide and the corresponding *di(chloromethyl) ether*, b. p. 148—149°/14 mm., m. p. about 44°,  $n_D^{21}$  1.4936.

If the total amount of silver oxide is added at the beginning of the methylation experiment, a violent reaction results and by-products are formed. Methylene iodide was isolated from *cyclohexane-1:4-diol*, and a ketone, b. p. 84—87°/15 mm.,  $n_D^{18}$  1.471, probably *cyclohexanolone*, from the 1:2-diol. H. BURTON.

**Mixed ethers from alcohols used in perfumery.** P. SCHVING and S. SABETAY (Bull. Soc. chim., 1928, [iv], 43, 857—859).—Primary and secondary alcohols react with alkyl chloroformates in presence of chloroform and pyridine, yielding the corresponding *O*-carbethoxy-derivatives. Tertiary alcohols must be converted into the sodium derivative and then treated with the alkyl chloroformate in ether. *O*-Carbethoxy-derivatives of the following

alcohols are described:  $\beta$ -phenylethyl, b. p. 140—141°/17 mm.,  $d^{20}_4$  1.063,  $n^{20}_D$  1.4889; benzyl, b. p. 122—124°/20 mm.,  $d^{24}_4$  1.084,  $n^{24}_D$  1.4899; cinnamyl, b. p. 164—166°/16 mm.,  $n^{20}_D$  1.5214; anisyl, b. p. 166—167°/16 mm.,  $n^{20}_D$  1.501; geraniol, b. p. 145—148°/17 mm.,  $n^{20}_D$  1.453; citronellol, b. p. 141—142°/18 mm.,  $n^{20}_D$  1.442; linalool, b. p. 127—128°/16 mm.,  $n^{20}_D$  1.4508. Using allyl chloroformate, b. p. 110—111.5°/765 mm., from allyl alcohol and carbonyl chloride, *O*-carballyloxy-derivatives of the following alcohols have been prepared:  $\beta$ -phenylethyl, b. p. 152—152.5°/17 mm.,  $d^{20}_4$  1.06,  $n^{20}_D$  1.4936; cinnamyl, b. p. 176—178°/16 mm.; linalool, b. p. 139°/18 mm.,  $d^{22}_4$  0.9473,  $n^{22}_D$  1.459; geraniol, b. p. 157.5—158°/18 mm. The *O*-carbo-methoxy-derivatives of rhodinol, b. p. 137—138°/19 mm.,  $n^{20}_D$  1.451; cinnamyl alcohol, b. p. 158—161°/19 mm.,  $n^{20}_D$  1.5356, and  $\beta$ -phenylethyl alcohol, b. p. 133—134°/19 mm.,  $n^{20}_D$  1.494, are also described.  $\beta$ -Phenylethyl chloroformate, b. p. 120°/18 mm.,  $n^{20}_D$  1.511, reacts with rhodinol and cyclohexanol, yielding the corresponding mixed carbonates, b. p. 191°/2 mm.,  $n^{20}_D$  1.501, and b. p. 194°/19 mm.,  $n^{20}_D$  1.507, respectively.  $\beta$ -Phenylethyl carbonate has b. p. 190°/2 mm., m. p. 56°.

H. BURTON.

**Photo-oxidation of adrenaline.** T. VACEK (Compt. rend. Soc. Biol., 1927, 97, 1739—1741; Chem. Zentr., 1928, i, 1504).—Radiation of short wave-length increases the oxidisability of adrenaline. Pure adrenaline dissolved in hydrochloric acid is most stable; alkaline solutions decompose more rapidly.

A. A. ELDRIDGE.

**Reactivity of iodine in organic solvents.** I. F. FEIGL and E. CHARGAFF (Monatsh., 1928, 49, 417—428).—The action of iodine on the silver derivative of saccharin has been studied. Brown solutions of iodine in ether, alcohol, dioxan, cyclohexanol, and cyclohexene react with the silver derivative of saccharin to give silver iodide quantitatively. Of the violet solutions of iodine in chloroform, benzene, carbon disulphide, carbon tetrachloride, and light petroleum, the first two behave as if they belonged to the ether dioxan class, whilst the remainder react with the silver derivative of saccharin to form only small amounts of silver iodide. The velocity of silver iodide formation depends on the solvent used for the iodine. The authors consider that this is due to the state of combination of the iodine, and depends on the physical properties of the solvent, such as dielectric constant, only in so far as these are related to solvate formation. Hydrolysis of the product with acidified potassium iodide solution gives saccharin and iodine, the latter indicating formation of hypoiodous acid.

R. A. PRATT.

**Synthesis of certain iodo-alkoxy-acids and mechanism of reactions by which they are formed.** E. L. JACKSON and L. PASIUT (J. Amer. Chem. Soc., 1928, 50, 2249—2260).—The reaction of  $\beta$ -chloro- $\alpha$ -iodo- $\beta$ -phenylpropionic acid with water or alcohols to give  $\beta$ -hydroxy- or  $\beta$ -alkoxy-derivatives (cf. Erlenmeyer, A., 1896, i, 302) takes place in the absence of potassium hydroxide. The  $\alpha$ -iodo- $\beta$ -alkoxy-acids are also conveniently prepared by the reaction of iodine monochloride with cinnamic acid dissolved in the appropriate alcohol. Of the possible

mechanisms of the first reaction, the one involving the intermediate formation of the lactone is eliminated by the reaction of methyl  $\beta$ -chloro- $\alpha$ -iodo- $\beta$ -phenylpropionate with absolute methyl alcohol to give the  $\beta$ -methoxy-ester, whilst the reaction of the  $\alpha$ -iodo- $\alpha$ -methyl acid with methyl alcohol eliminates the possibility of intermediate formation of the  $\alpha$ -iodocinnamic acid. The remaining alternatives are direct replacement of chlorine by the alkoxy group and intermediate formation of cinnamic acid by elimination of iodine monochloride, the latter reacting with the alcohol to give the alkyl hypoiodite, which then adds on to the double linking of the cinnamic acid. This last hypothesis is favoured by several facts. Cinnamic acid is formed in the reaction, in small quantity with methyl alcohol, but in increasing quantity, concurrently with decreasing yield of the  $\beta$ -alkoxy-acid, with increase of mol. wt. of the reacting alcohol. The occurrence of the reaction in presence of excess of calcium carbonate makes unlikely the formation of the cinnamic acid by the action of hydrochloric or hydriodic acid. The decreased yield with higher alcohols is attributed to consumption of the iodine monochloride in side-reactions with the alcohol. This explanation of the mechanism is also consistent with the results of the preparations from iodine monochloride, cinnamic acid, and alcohol, in which the yield also falls with higher alcohols, but is improved by using excess of iodine monochloride, and brought down to the yield in the first method by gradual addition of the iodine monochloride. Further, the reaction of the alcohol and the  $\beta$ -chloro- $\alpha$ -iodo-acid is very slow in comparison with the reaction of iodine monochloride, cinnamic acid, and the alcohol.

$\alpha$ -Iodo- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid was also prepared by passing chlorine into a suspension of iodine and cinnamic acid in water, and the methoxy- and ethoxy-acids by passing chlorine into solutions in the appropriate alcohol. The  $\beta$ -chloro- $\alpha$ -iodo-acid was conveniently prepared in large quantity by addition of iodine monochloride to cinnamic acid in carbon tetrachloride solution. The following  $\alpha$ -iodo-alkoxy-acids are described: - $\beta$ -methoxy-, m. p. 168—169° (methyl ester, m. p. 68—69°); - $\beta$ -ethoxy-, m. p. 137—138°; - $\beta$ -*n*-propoxy-, m. p. 110—111°; - $\beta$ -isopropoxy-, m. p. 113—114°; - $\beta$ -*n*-butoxy-, m. p. 93—94°; - $\beta$ -isobutoxy-, m. p. 89—90°, and - $\beta$ -*tert*-butoxy- $\beta$ -phenylpropionic acid, m. p. 113—114°.  $\beta$ -Chloro- $\alpha$ -iodo- $\beta$ -phenyl- $\alpha$ -methylpropionic acid, m. p. 104—105° (decomp.), was prepared by addition of iodine monochloride to  $\alpha$ -methylcinnamic acid, and yielded, with methyl alcohol,  $\alpha$ -iodo- $\beta$ -methoxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid, m. p. 169—170°. The reaction of iodine monochloride and methyl alcohol with crotonic acid yielded iodomethoxybutyric acid, m. p. 83—84°. The structure assigned to the  $\alpha$ -iodo- $\beta$ -alkoxy-acids was confirmed by the formation of  $\beta$ -methoxy- $\beta$ -phenylpropionic acid by the action of zinc in methyl alcohol, and by the formation of acetophenone from  $\alpha$ -iodo- $\beta$ -isopropoxyphenylpropionic acid and of propiophenone from  $\alpha$ -iodo- $\alpha$ -methyl- $\beta$ -methoxyphenylpropionic acid by reaction with alcoholic potassium hydroxide followed by hydrolysis of the product by dilute sulphuric acid.

R. K. CALLOW.

**Betaines.** III. P. PFEIFFER [with H. BEHR, B. BREYER, O. CLARENZ, and H. KÜBLER] (Annalen, 1928, 465, 20—52).—Reduction of *cis*- $\alpha$ -*m*-nitrophenylcinnamic acid with ferrous hydroxide gives *cis*- $\alpha$ -*m*-aminophenylcinnamic acid, m. p. 189—191° [hydrochloride, m. p. 229—232° (decomp.); silver salt; benzoyl derivative + H<sub>2</sub>O, m. p. 184—185°], which when methylated with a large excess of methyl iodide and potassium hydroxide affords the *methiodide*, m. p. 158° (decomp.), of *cis*- $\alpha$ -*m*-dimethylaminophenylcinnamic acid. Treatment of this with moist silver oxide yields the corresponding *cis*-betaine,

$\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CPh} \cdot \text{COO} + \text{H}_2\text{O}$ , m. p. 186—188° [(decomp.); hydrochloride, m. p. 178° (decomp.); hydrobromide, decomp. 170°; nitrate, m. p. 144—146° (decomp.); perchlorate, m. p. 170° (decomp.); chloroplatinate + H<sub>2</sub>O, m. p. 168° (decomp.)]. The analogous *trans*-betaine + H<sub>2</sub>O, m. p. 112—114° [hydrochloride, m. p. 163° (decomp.); hydrobromide + H<sub>2</sub>O, m. p. 148—152° (decomp.); nitrate, m. p. 166—169° (decomp.); perchlorate, m. p. 173° (decomp.); chloroplatinate + 0.5H<sub>2</sub>O, m. p. 196°], is obtained similarly from the *methiodide*, m. p. 163—167° (decomp.), of *trans*- $\alpha$ -*m*-dimethylaminophenylcinnamic acid, prepared by methylation of *trans*- $\alpha$ -*m*-aminophenylcinnamic acid, m. p. 192° (benzoyl derivative, m. p. 255—256°; methyl ester, m. p. 117°; ethyl ester, m. p. 65°). The *hydriodides* of these betaines are identical with the above *methiodides*.

*p*-Dimethylaminobenzaldehyde when condensed with *p*-nitrophenylacetonitrile in presence of sodium ethoxide gives 4-nitro-4'-dimethylamino- $\alpha$ -cyanostilbene, m. p. 240—241° (*methiodide* + 2H<sub>2</sub>O), which is hydrolysed by warm concentrated sulphuric acid, forming two isomeric *p*-dimethylamino- $\alpha$ -*p*-nitrophenylcinnamamides, *A* and *B*, having m. p. 221—222° and 256°, respectively. Hydrolysis of *A* with methyl- and ethyl-alcoholic hydrogen chloride gives the *methyl* and *trans*-ethyl *p*-dimethylamino- $\alpha$ -*p*-nitrophenylcinnamate (I), m. p. 169—170° and 134—135°, respectively. Hydrolysis of *B* affords in addition to (I) a second (*cis*-)isomeride, m. p. 138—139°, oriented by the action of hot concentrated sulphuric acid, when indone ring-formation occurs. *p*-Dimethylamino- $\alpha$ -*p*-nitrophenylcinnamic acid has m. p. 249°. The *methiodide*, m. p. 160—161° (decomp.), of (I) is decomposed by silver oxide in hot aqueous solution, yielding the *betaine*,  $\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{COO}$ , m. p. 210—211° (perchlorate). Similar treatment of the *methiodide*, m. p. 201°, of *m*-dimethylaminocinnamic acid gives the corresponding *betaine* + H<sub>2</sub>O, m. p. 128°, m. p. (anhydrous) 206—207° (hydrobromide, m. p. 193—196°; perchlorate, m. p. 230—231°).

Reduction of 2-nitro-4'-dimethylamino-4-cyanostilbene [*methiodide* (II), m. p. 203°] with stannous chloride gives the corresponding 2-amino-derivative, m. p. 226° (*dihydrochloride*). The *methiodides* (III and IV) of *methyl* and *ethyl* 2-nitro-4'-dimethylamino-4-carboxylate (*methonitrate*) have m. p. 192° and 147°, respectively. When (II) and (III) are decomposed with silver oxide in hot aqueous solution the *betaine*,  $\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{COO}$ , + 3H<sub>2</sub>O, m. p. (anhydrous) 220—222° (hydrochloride + 2H<sub>2</sub>O),

is obtained, but the product from (II) has a low m. p.

Condensation of *p*-dimethylaminobenzaldehyde with *p*-cyanophenylacetonitrile in presence of a small amount of piperidine at 100—130° affords 4'-dimethylamino- $\alpha$  : 4-dicyanostilbene, m. p. 205°; hydrolysed by methyl-alcoholic hydrogen chloride to *methyl* 4'-dimethylamino- $\alpha$ -cyanostilbene-4-carboxylate, m. p. 178° [ethyl ester (V), m. p. 145°]. The *methiodide* of (V) is transformed in the usual way into the *betaine*,

$\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{COO} + 1.5\text{H}_2\text{O}$ , m. p. 205° (hydrochloride + 2H<sub>2</sub>O).

The successful isolation of *cis*- and *trans*-forms of betaines in the  $\alpha$ -phenylcinnamic acid series supports the authors' idea that the betaines are to be regarded as dipolar compounds, not as internal ring compounds (cf. A., 1922, i, 738). H. BURTON.

**Di(cyclohexylalkyl)acetic acids.** XIV. L. A. DAVIES and R. ADAMS (J. Amer. Chem. Soc., 1918, 50, 2297—2298; cf. Arvin and Adams, this vol., 1003).—Whilst the introduction of a cyclohexyl group at the end of certain straight-chained aliphatic acids produces compounds bactericidal toward *B. leprae*, the introduction of two such groups, producing compounds of the type  $\text{C}_6\text{H}_{11} \cdot [\text{CH}_2]_x \cdot \text{CH}(\text{CO}_2\text{H}) \cdot [\text{CH}_2]_y \cdot \text{C}_6\text{H}_{11}$ , did not enhance the activity. The following compounds were prepared by methods previously described (Hiers and Adams, A., 1926, 1136; Adams, Stanley, Ford, and Peterson, this vol., 62): diethyl esters of substituted malonic acids: cyclohexyl- $\beta$ -cyclohexylethyl-, b. p. 192°/4.5 mm.,  $d_4^{20}$  1.016,  $n_D^{20}$  1.4747; cyclohexylmethyl- $\beta$ -cyclohexylethyl-, b. p. 186—188°/3 mm.,  $d_4^{20}$  1.003,  $n_D^{20}$  1.4725; di-( $\beta$ -cyclohexylethyl)-, b. p. 200—202°/1.5 mm.,  $d_4^{20}$  0.9931,  $n_D^{20}$  1.4722;  $\beta$ -cyclohexylethyl- $\gamma$ -cyclohexylpropyl-, b. p. 210—211°/3.5 mm.,  $d_4^{20}$  0.9928,  $n_D^{20}$  1.4713; di-( $\gamma$ -cyclohexylpropyl)-, b. p. 216—218°/3 mm.,  $d_4^{20}$  0.9811,  $n_D^{20}$  1.4710;  $\beta$ -cyclohexylethyl- $\delta$ -cyclohexylbutyl-, b. p. 208—210°/2.5 mm.,  $d_4^{20}$  0.9817,  $n_D^{20}$  1.4710; and the following substituted acetic acids: cyclohexyl- $\beta$ -cyclohexylethyl-, b. p. 182—186°/4 mm.,  $d_4^{20}$  0.9915,  $n_D^{20}$  1.4852; cyclohexylmethyl- $\beta$ -cyclohexylethyl-, m. p. 50—51°, b. p. 207—208°/5 mm.; di-( $\beta$ -cyclohexylethyl)-, m. p. 73—76°, b. p. 210—213°/1.5 mm.;  $\beta$ -cyclohexylethyl- $\gamma$ -cyclohexylpropyl-, m. p. 46.5—47°, b. p. 213—214°/3 mm.; di-( $\gamma$ -cyclohexylpropyl)-, m. p. 42.5—45°, b. p. 216—218°/3 mm.;  $\beta$ -cyclohexylethyl- $\delta$ -cyclohexylbutyl-, b. p. 221—223°/4 mm.,  $d_4^{20}$  0.9647,  $n_D^{20}$  1.4831.

R. K. CALLOW.

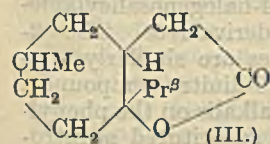
**Dicyclic hydroaromatic and cyclopentane lactones.** J. VON BRAUN and W. MÜNCH (Annalen, 1928, 465, 52—72).— $\Delta^1$ -cyclohexenylacetic acid (I), b. p. 140°/12 mm., can be distilled under reduced pressure without lactone formation, but lactonisation can be effected by treatment with sulphuric acid (cf. Wallach, A., 1907, i, 616). When cyclohexylideneacetic acid (II) is treated with sodium hydroxide solution an equilibrium mixture of 40% of (I) and 60% of (II) is obtained. Prolonged interaction of ethyl 1-hydroxycyclohexylacetate with an acetic acid solution of hydrogen bromide and subsequent treatment with zinc dust gives a halogen-containing oil (cf. Wallach, loc. cit.). When this is hydrolysed by

aqueous-alcoholic potassium hydroxide and then acidified with sulphuric acid, immediate extraction with ether affords a product completely soluble in sodium carbonate solution. If the acidified mixture is kept for some time there is obtained about 10%

of the lactone,  $C_6H_{10} \left\langle \begin{array}{c} CH_2 \\ O \end{array} \right\rangle CO$ , b. p. 129—130°/13 mm.,  $d_4^{25} 1.0913$ ,  $n_D^{25} 1.4784$ . An explanation of the formation of this lactone is advanced involving the elimination of hydrogen bromide from the intermediate bromo-ester, subsequent re-addition in a reverse direction, replacement of the bromine by hydroxyl, and final lactonisation. Oxidation of the lactone with 30% nitric acid gives a mixture of adipic and butane- $\alpha\beta$ -tricarboxylic acids (ethyl ester, b. p. 183—185°/20 mm.). Ethyl cyclohexylacetate has b. p. 100—101°/14 mm. Similar treatment of ethyl 1-hydroxycyclohexylisobutyrate gives, in addition to cyclohexylisobutyric acid, m. p. 62—63°, about 70% of the dicyclic lactone,  $C_6H_{10} \left\langle \begin{array}{c} CMe_2 \\ O \end{array} \right\rangle CO$ , m. p. 56°.

[With E. DEUSSER.]—Condensation of cyclopentenyl chloride with ethyl malonate in presence of sodium and toluene affords, in addition to ethyl cyclopentenylmalonate (cf. Noller and Adams, A., 1926, 1137), some ethyl dicyclopentenylmalonate, b. p. 192—193°/14 mm. Decarboxylation of the free acid yields dicyclopentenylacetic acid, b. p. 168—170°/11 mm. Lactonisation of  $\Delta^2$ -cyclopentenylacetic acid with sulphuric acid gives the compound  $C_5H_8 \left\langle \begin{array}{c} CH_2 \\ O \end{array} \right\rangle CO$ , b. p. 126—127°/14 mm.,  $d_4^{22} 1.113$ ,  $n_D^{22} 1.4778$ , oxidised by nitric acid to glutaric acid. Hydrogen bromide-zinc dust treatment of ethyl 1-hydroxy-2-methylcyclohexylacetate gives mainly the lactone, b. p. 136—137°/13 mm.,  $d_4^{23} 1.068$ ,  $n_D^{23} 1.4764$ , of 2-hydroxy-2-methylcyclohexylacetic acid, m. p. 107°. Reduction of this lactone with sodium and alcohol gives a 70% yield of  $\beta$ -2-hydroxy-2-methylcyclohexylethyl alcohol, b. p. 153—155°/13 mm., m. p. 75—76°, which is converted by 60% sulphuric acid at 100° into an internal oxide, b. p. 175—176°,  $d_4^{27} 0.9372$ ,  $n_D^{27} 1.4602$ , together with material of high b. p. Ethyl 2-methylcyclohexylacetate has b. p. 145—147°/13 mm.

Hydrolysis of ethyl mentheneacetate, b. p. 135—137°/10 mm.,  $d_4^{17} 0.9518$ ,  $n_D^{17} 1.4642$ ,  $[\alpha]_D^{17} +32.79^\circ$  (cf. Wallach, A., 1902, i, 799; *loc. cit.*), with aqueous-alcoholic potassium hydroxide and subsequent distillation of the acid obtained gives some lactone in addition to the corresponding acid. The hydrogen bromide-zinc dust treatment of ethyl mentholacetate affords 4% of menthylacetic acid, b. p. 164—166°/10 mm.,  $d_4^{21} 0.9761$ ,  $n_D^{21} 1.4698$ ,  $[\alpha]_D^{21} +18^\circ$ , together with a mixture of isomeric lactones (III), separable by prolonged cooling into A,

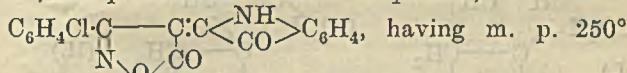


b. p. 156—159°/10 mm., m. p. 114—115°,  $[\alpha]_D^{15} -24.68^\circ$  in pyridine, and B, b. p. 156—159°/10 mm.,  $d_4^{17} 1.0153$ ,  $[\alpha]_D^{15} -30.6^\circ$  in pyridine. Reduction of A with sodium and alcohol gives a glycol,  $C_{12}H_{24}O_2$ , b. p. 144—146°/10 mm., m. p. 94°,  $[\alpha]_D^{23} +9.7^\circ$  in pyridine, whilst B furnishes an isomeric glycol, b. p. 163—166°/10 mm., m. p. 108°,  $[\alpha]_D^{23} +20^\circ$  in pyridine, together with a small amount of lower-melting sub-

stance. The glycol of m. p. 108° is converted by 60% sulphuric acid at 100° into a  $\gamma$ -oxide,  $C_{12}H_{22}O$ , b. p. 94—96°/9 mm.,  $d_4^{23} 0.9292$ ,  $n_D^{23} 1.470$ ,  $[\alpha]_D^{23} +23.4^\circ$ .

H. BURTON.

**Chlorobenzoylacetic esters and their derivatives.** A. WAHL and J. ROLLAND (Ann. Chim., 1928, [x], 10, 5—49).—Partly an account of work already abstracted (this vol., 289). The following is new. As by-products in the preparation of methyl *o*-, *m*-, and *p*-chlorobenzoylacetic esters (copper derivatives) there are formed *o*-, *m*-, and *p*-chlorobenzoyldehydracetic acids, m. p. 216°, 172°, and 242°, respectively. When the esters are treated with phenylhydrazine, 1-phenyl-3-*o*-, -*m*-, and -*p*-chlorophenyl-5-pyrazolones, m. p. 113—114°, 144°, and 140°, respectively, are produced. The corresponding 1-*p*-nitrophenyl derivatives have m. p. 203—204°, 189°, and 200—200.5°, respectively. The action of nitrous acid on the esters gives methyl oximino-*o*-, -*m*-, and -*p*-chlorobenzoylacetic esters, m. p. 90—91°, 113—114°, and 124—125°, respectively, whilst with hydroxylamine there are formed 3-*o*-chlorophenylisooxazolone, m. p. 138° (benzylidene, m. p. 152°; *p*-dimethylaminobenzylidene, m. p. 199°), and 3:4-dihydroxybenzylidene, m. p. 233—235° (decomp.), derivatives; 3-*m*-chlorophenylisooxazolone, m. p. 98° (benzylidene, m. p. 116°; *p*-dimethylaminobenzylidene, m. p. 192°), and 3:4-dihydroxybenzylidene, m. p. 190—192°, derivatives, and 3-*p*-chlorophenylisooxazolone, m. p. 152° (benzylidene, m. p. 154°; *p*-dimethylaminobenzylidene, m. p. 200°), and 3:4-dihydroxybenzylidene, m. p. 201—203°, derivatives). When these isooxazolones are treated with isatin chloride in presence of benzene and phosphorus pentachloride there are formed the *o*-, *m*-, and *p*-chloro-substituted compounds,



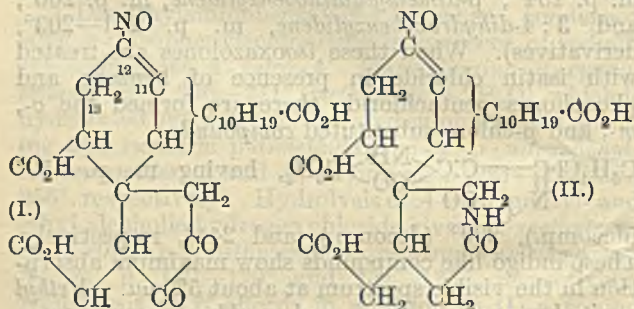
(decomp.), 239° (decomp.), and 244°, respectively. These indigo-like compounds show maximum absorption in the visible spectrum at about 520  $\mu$ . Methyl *p*-nitrobenzeneazo-*o*-, -*m*-, and -*p*-chlorobenzoylacetic esters, obtained from the original esters and *p*-nitrobenzene-diazonium chloride, have m. p. 104—105°, 174—175°, and 206—207°, respectively.

Determination of the amounts of enol form in the methyl chlorobenzoylacetic esters by the bromine titration method gives a value of approximately 25% for each isomeride, but it is shown that the percentage of enol in freshly-distilled *o*-ester (20.5) increases on keeping (25.5 after 1.5 hrs.). Hydrolysis of the esters with 20% sulphuric acid affords *o*-chloroacetophenone (*p*-nitrophenylhydrazone, m. p. 215°; semicarbazone, m. p. 159—160°), *m*-chloroacetophenone, b. p. 227—229°,  $d_4^{21} 1.213$  (*p*-nitrophenylhydrazone, m. p. 175—176°; oxime, m. p. 88°), and *p*-chloroacetophenone (*p*-nitrophenylhydrazone, m. p. 239°; semicarbazone, m. p. 200—201°), respectively. When these ketones are heated with aqueous sodium sulphite at 170° for 20 hrs. in an autoclave, the *m*-compound does not react, but with the *o*- and *p*-derivatives there are formed the sodium salts (+2H<sub>2</sub>O) of acetophenone-*o*- and -*p*-sulphonic acids [*p*-nitrophenylhydrazones, m. p. 212° (decomp.) and 215° (decomp.), respectively].

H. BURTON.

**Optical resolution of a spirocyclic compound of the allene type.** H. J. BACKER and H. B. J. SCHURINK (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 370—371).—*cyclo*Butanespirocyclobutane-1:1'-dicarboxylic acid, prepared in 80% yield by a modification of Fecht's method (A., 1907, i, 906), is resolved by crystallisation of its *dibrucine* salt, decomp. 135°, from water. The active ammonium salt has  $[\alpha]_D +0.13^\circ$ , from which the free acid,  $[M]_D +1.9^\circ$  (ether), is obtained. Röntgen analysis of dibenzylidenepentaerythritol (Read, J.C.S., 1912, 101, 2090) shows that the distribution of the carbon valencies of the spiran carbon atom is tetrahedral. It is obtained in both dextro- and lævo-rotatory crystals,  $\alpha_D \pm 2^\circ/\text{mm.}$ , the optical activity of which is due to the asymmetric distribution of the molecules, since no trace of optical activity can be detected in solution. J. W. BAKER.

**Bile acids.** XXI. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1928, 177, 280—294).—When the nitroso-compound (I) (this vol., 1007) is reduced with zinc dust and acetic acid, two substances,  $C_{24}H_{35}O_8N$ , possibly stereoisomerides, having m. p. 240—242° with frothing and 230—232°, respectively, are obtained. Hydrolysis of the former with hydrochloric acid gives hydroxylamine and bilianic acid, thus showing it to be bilianic acid oxime. Nitric acid converts it into (I). The nitroso-compound (II) (this vol., 764) is reduced similarly to bilianic acid



diisoxime, m. p. 258—260° (decomp.), the rearrangement product of bilianic acid dioxime. When this is hydrolysed with hydrochloric acid, hydroxylamine and the two stereoisomeric compounds,  $C_{24}H_{35}O_8N$ , m. p. 200—205° and 260°, respectively, previously described (*loc. cit.*) are obtained.

Attention is directed to a recent paper by Wieland and Vocke (this vol., 1007) showing that C<sub>11</sub> is quaternary. In this case the double linking between C<sub>11</sub> and C<sub>12</sub> should be placed between C<sub>12</sub> and C<sub>13</sub>.

H. BURTON.

**Benzoylisopropylidenequinide and benzoylquinide.** K. JOSEPHSON (Arkiv Kemi, Min., Geol., 1928, 9, No. 39, 1—5).—The isopropylidene ether of quinic acid lactone (cf. Fischer, A., 1921, i, 419) is converted by benzoyl chloride in presence of pyridine into *benzoylisopropylidenequinide* (I), m. p. 140°,  $[\alpha] +13.2^\circ$  in chloroform, which

is hydrolysed by warm aqueous-alcoholic sulphuric acid to *benzoylquinide*, m. p. 148°,  $[\alpha] -6.9^\circ$  in alcohol. H. BURTON.

**Naphthalene derivatives.** [Sulphonic acids of 6-hydroxy-2-naphthoic acid.] I. G. FARBENIND. A.-G.—See B., 1928, 597.

**Manufacture of hydroaromatic dicarboxylic acids.** J. D. RIEDEL A.-G.—See B., 1928, 665.

**Benzylideneaniline and benzylidene-*p*-toluidine as ammonoaldehyde-acetals.** H. H. STRAIN (J. Amer. Chem. Soc., 1928, 50, 2218—2223; cf. A., 1927, 767).—Franklin's view of Schiff's bases as aldehyde-acetals of an ammonia system of compounds is supported by the fact that they undergo an analogous series of reactions—ammonolysis, Cannizzaro reaction, benzoin condensation, nitridation, and polymerisation. Ammonolysis of benzylideneaniline and benzylidene-*p*-toluidine by keeping in liquid ammonia solution yielded aniline and *p*-toluidine, respectively, and amarine, the last being produced by condensation of the benzylideneimine first formed. The Cannizzaro reaction, carried out by treatment with potassium amide (2 mols.) in liquid ammonia, yielded, respectively, phenylbenzylbenzamide (*benzenesulphonyl* derivative, m. p. 148°) and *p*-tolylbenzylbenzamide, m. p. 127—127.5° (also obtained from benz-*p*-toluidide and benzamide by heating with phosphorus pentachloride), which are ammonoesters, together with aniline or *p*-toluidine. The mechanism of this reaction is discussed. The benzoin condensation, with potassium cyanide in liquid ammonia, yielded, respectively, *benzoinanilamide*, CHPh(NHPh)·CPh·NPh, m. p. 185—200°, and *benzoin-p-tolil-p-toluidide*, m. p. 122°. Nitridation, with iodine in liquid ammonia, gave a tarry product from benzylideneaniline, containing traces of phenylcarbylamine and benzonitrile. The action of potassium amide (less than 1 mol.) on benzylideneaniline and benzylidene-*p*-toluidine yielded, respectively, *polymerides*,  $C_{33}H_{29}N_3$ , m. p. 132—134° (*hydrochloride*), and  $C_{35}H_{33}N_3$ , m. p. 136—137°. An excess of potassium amide converted these into the corresponding benzamidines. R. K. CALLOW.

**Nitration of 4-halogeno-2-hydroxy- and 2-halogeno-4-hydroxy-benzaldehydes.** H. H. HODGSON and T. A. JENKINSON (J.C.S., 1928, 2272—2280).—Direct mononitration of the 4-halogenosalicylaldehydes gives exclusively the 5-nitro-derivatives, since bromination of these substances yields the identical compounds obtained by nitration of the 3-bromo-4-halogenosalicylaldehydes. The sodium salts of both nitro- and nitrobromo-derivatives are yellow, in accordance with their *p*-nitrophenolic structure. The sodium salts of the 5-bromo-4-halogeno-3-nitrosalicylaldehydes, prepared for comparison, are bright red, indicating an *o*-nitrophenolic structure. Dinitration of the 4-halogenosalicylaldehydes gives the 3:5-dinitro-derivatives. The 2-halogeno-4-hydroxybenzaldehydes are similarly converted into the 5-nitro- and 3:5-dinitro-compounds. The brown colours produced by alkalis on the phenylhydrazones of certain of these substituted *m*-nitrobenzaldehydes are in accord with the observations of Chattaway and Clemo (J.C.S., 1923, 123, 3043). The following are described (A=2-hydroxybenzaldehyde; B=4-hydroxybenzaldehyde): 4-chloro-5-nitro-A, m. p. 116° [*phenylhydrazone*, m. p. 188° (decomp.)];

*p*-nitrophenylhydrazone, m. p. 294° (decomp.); semicarbazone, decomp. above 300°; 4-chloro-3:5-dinitro-A, m. p. 153° [*phenylhydrazone*, m. p. 219°; *p*-nitrophenylhydrazone, m. p. 286° (decomp.)]; semicarbazone, m. p. 225° (decomp.); 2-chloro-5-nitro-B, m. p. 125° [*phenylhydrazone*, m. p. 166° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 266° (decomp.); semicarbazone, m. p. 266° (decomp.); 2-chloro-3:5-dinitro-B, m. p. 93° [*phenylhydrazone*, m. p. 210° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 267° (decomp.); semicarbazone, m. p. 192° (decomp.); 4-chloro-3-bromo-A, m. p. 124° [*phenylhydrazone*, m. p. 204°; *p*-nitrophenylhydrazone, m. p. 298° (decomp.)]; 3-chloro-2-bromo-B, m. p. 177° [*p*-nitrophenylhydrazone, m. p. 253° (decomp.)]; 3:4-dibromo-A, m. p. 129° [*p*-nitrophenylhydrazone, decomp. above 220°]; 2:3-dibromo-B, m. p. 192° [*p*-nitrophenylhydrazone, m. p. 254° (decomp.)]; 4-chloro-3-bromo-5-nitro-A, m. p. 137° [*phenylhydrazone*, m. p. 229° (decomp.)]; sodium salt; 4-chloro-5-bromo-A, m. p. 125° [*phenylhydrazone*, m. p. 200°; *p*-nitrophenylhydrazone, m. p. 280° (decomp.)]; 4-chloro-5-bromo-3-nitro-A, m. p. 116° [*sodium salt*; *phenylhydrazone*, m. p. 241° (decomp.)]; 2-chloro-3-bromo-5-nitro-B, m. p. 140° [*phenylhydrazone*, m. p. 205° (decomp.)]; 4-bromo-5-nitro-A, m. p. 128° [*phenylhydrazone*, m. p. 189°; *p*-nitrophenylhydrazone, m. p. 301° (decomp.)]; semicarbazone, decomp. above 210°; 4-bromo-3:5-dinitro-A, m. p. 143° [*phenylhydrazone*, m. p. 209° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 250° (decomp.); semicarbazone, m. p. 224° (decomp.); 2-bromo-5-nitro-B, m. p. 131° [*silver and copper salts*; *phenylhydrazone*, m. p. 181° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 265° (decomp.); semicarbazone, m. p. 267° (decomp.); 2-bromo-3:5-dinitro-B, m. p. 110° [*silver salt*; *phenylhydrazone*, m. p. 186° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 248° (decomp.); semicarbazone, m. p. 188° (decomp.); 2:3-dibromo-5-nitro-B, m. p. 155° [*phenylhydrazone*, m. p. 204° (decomp.)]; 3:4-dibromo-5-nitro-A, m. p. 114°; 4:5-dibromo-A, m. p. 132° [*silver salt*; *p*-nitrophenylhydrazone, m. p. 266° (decomp.)]; 4:5-dibromo-3-nitro-A, m. p. 118° [*silver salt*; *phenylhydrazone*, m. p. 236° (decomp.)]; 4-iodo-5-nitro-A, m. p. 118° [*silver salt*; *phenylhydrazone*, m. p. 177° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 297° (decomp.); semicarbazone, decomp. at 230—240°; 3-bromo-4-iodo-5-nitro-A, m. p. 145°; 4-iodo-3:5-dinitro-A, m. p. 160° [*silver salt*; *phenylhydrazone*, m. p. 229° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 257° (decomp.); semicarbazone, decomp.; 5-bromo-4-iodo-A, m. p. 117° [*sodium and silver salts*; *phenylhydrazone*, m. p. 151°; *p*-nitrophenylhydrazone, m. p. 266° (decomp.)]; 5-bromo-4-iodo-3-nitro-A, m. p. 153° [*silver salt*; *phenylhydrazone*, m. p. 245° (decomp.)]; 2-iodo-5-nitro-B, m. p. 162° [*silver salt*; *phenylhydrazone*, m. p. 204° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 273°; semicarbazone, m. p. 211° (decomp.); 2-iodo-3:5-dinitro-B, m. p. 162° [*silver and copper salts*; *phenylhydrazone*, m. p. 197° (decomp.)]; *p*-nitrophenylhydrazone, m. p. 240° (decomp.); semicarbazone, m. p. 205° (decomp.); 3-bromo-2-iodo-B, m. p. 204°.

M. CLARK.

Manufacture of unsaturated aldehydes. I. G. FARBENIND. A.-G.—See B., 1928, 634.

Synthesis of cyclic compounds. IV. Catalytic decomposition of suberic acid and preparation of suberone directly from mixtures of suberic and azelaic acids. I. VOGEL (J.C.S., 1928, 2032—2035).—A 40% yield of cycloheptanone is obtained by the dry distillation at 280—290° of an intimate mixture of suberic acid, an equal weight of iron filings, and 5% by weight of crystallised barium hydroxide, the product being colourless and free from the black, tarry impurities which are formed by the distillation of the calcium or thorium salts. The mixture of suberic and azelaic acids obtained by the oxidation of ricinoleic acid with nitric acid (Baker and Ingold, J.C.S., 1923, 123, 122) after crystallisation from benzene may similarly be converted directly into cycloheptanone (suberone) which is separated from a small quantity of a liquid of the same b. p. by means of its hydrogen sulphite compound.

J. W. BAKER.

Possibility of ring-chain valency tautomerism, and of a type of mobile-hydrogen tautomerism analogous to the Wagner-Meerwein rearrangement. V. Pinacolic electron displacement as an explanation of various intramolecular transformations. C. W. SHOPPEE (Proc. Leeds Phil. Soc., 1928, 1, 301—311).—The mechanism of various intramolecular changes is discussed, including the pinacol-pinacolin change, pinacolic deamination, the Wagner-Meerwein change, the benzil-benzilic acid transformation, and the conversion of  $\alpha$ -hydroxy- and  $\alpha$ -chloro-ketones into carboxylic acids, and an attempt is made to correlate them on the basis of tautomeric change (cf. this vol., 414). The mechanism advanced is termed "pinacolic electron displacement," and occurs when both an electron source and an electron sink are present in the molecule. A cationic or anionic reagent is necessary to achieve these conditions or to complete the reaction. Examples not accounted for or explained unsatisfactorily by previous theories are considered and shown to be explicable on this theory, which also predicts new types of intramolecular change. C. W. SHOPPEE.

Nierenstein reaction. M. NIERENSTEIN (Nature, 1928, 122, 313).—Polemical and explanatory (cf. Bradley and Robinson, this vol., 759).

A. A. ELDRIDGE.

Action of bromine on azomethine derivatives of fluorene. A. NOVELLI (Anal. Asoc. Quím. Argentina, 1927, 15, 423—429).—The addition of bromine to azomethine derivatives of fluorene (cf. this vol., 180) yielded products similar to those obtained from Schiff's bases (cf. Berg, A., 1925, i, 817), in which the bromine appeared to have added on at the  $>C:N$ -double linking. The bromine was sufficiently reactive to attack silver and gold in dry solvents, and the compounds were decomposed by water with the formation of the corresponding ketone and the hydrobromide of the brominated amine. 2:7-Dibromofluorenone-*p*-dimethylaminoanil dibromide and the corresponding *p*-diethyl compound, m. p. 210° (darkening at 180°), were prepared. Decomposition by water yielded 2:7-dibromofluorenone and a brominated amine (not isolated).

R. K. CALLOW.

**Configuration of *o*-substituted benzophenone oximes.** J. MEISENHEIMER, R. HANSEN, and A. WÄCHTEROWITZ (J. pr. Chem., 1928, [ii], 119, 315—367).—Further exceptions to the general rule that benzophenone oximes carrying one *o*-substituent exist only in the *syn*-form are recorded. By the Friedel-Crafts reaction with benzoyl chloride *m*-4-xylyl methyl ether yields 50—70% of 3-methoxy-4:6-dimethylbenzophenone, b. p. 199—200°/12—13 mm., 10% of the 3-hydroxy-compound, m. p. 140—141°, b. p. 202°/20 mm., and 10—30% of 2-hydroxy-3:5-dimethylbenzophenone, b. p. 202°/20 mm. The 3-methoxy-ketone gives two oximes; the  $\alpha$ -(*syn*-)oxime, m. p. 138—139°, b. p. 218°/10 mm. (*benzoate*, m. p. 135—136°), is converted by phosphorus pentachloride into 3-methoxy-4:6-dimethylbenzanilide, m. p. 141—142°, and thence by hydrolysis into the corresponding acid, m. p. 185—186°; Gunter's acid, m. p. 170.5° (A., 1884, 1347), is probably an isomeride. The  $\beta$ -(*anti*-)oxime, m. p. 119—120°, not obtainable from the  $\alpha$ -oxime, yields with phosphorus pentachloride benzoic 6-methoxy-*m*-4-xylylidide, m. p. 154—155°, isomeric with the 4-methoxy-*m*-5-xylylidide, m. p. 48—49° (*hydrochloride*, decomp. 70°), obtained synthetically from 5-nitro-*m*-4-xylyl methyl ether, b. p. 268—269°, and 5-methoxy-*m*-4-xylylidine. 3-Ethoxy-4:6-dimethylbenzophenone, b. p. 190—200°/10 mm. (crude), also gives two oximes; the  $\alpha$ -(*syn*-)oxime, m. p. 148—149°, is converted by phosphorus pentachloride into 3-ethoxy-4:6-dimethylbenzanilide, m. p. 156—157°; the  $\beta$ -(*anti*-)oxime melts at 133—134°. 3-Hydroxy-4:6-dimethylbenzophenone (cf. Linari, A., 1904, i, 64) yields a single (*anti*-)oxime, m. p. 182—183°, from which by the action of phosphorus pentachloride even at -20° only a phosphoric derivative, decomp. 90—100°, is obtainable, but is converted by Beckmann's reagent into benzoic 3-acetoxy-*m*-4-xylylidide, m. p. 127—128° (hydrolysed by alkali to the 3-hydroxy-*m*-4-xylylidide, m. p. 173—174°), and a little 3-hydroxy-4:6-dimethylbenzanilide, m. p. 211—212°, more easily obtainable by heating the oxime hydrochloride above its m. p. 2-Hydroxy-4:6-dimethylbenzophenone also gives only one oxime, m. p. 153—154°, the *syn*-configuration of which is shown by its conversion by phosphorus pentachloride into 2-phenyl-5:7-dimethylbenzoxazole, m. p. 99—100°, which yields benzoic 3-hydroxy-*m*-4-xylylidide, m. p. 187—188° (Auwers, Bundesmann, and Wieners, A., 1926, 608), on distillation.

4-*m*-Xylyl benzoate, m. p. 38—39°, b. p. 186—188°, when submitted to the Fries reaction (cf. Auwers and Jordan, A., 1925, i, 264), is recovered for the most part unchanged, small yields of 2:3:5- and 3:4:6-hydroxydimethylbenzophenones being obtained together with the 4:2:5-isomeride, m. p. 160—161° (cf. Bartolotti and Linari, A., 1903, i, 177), which is synthesised from *p*-xylyl methyl ether by way of 4-methoxy-2:5-dimethylbenzophenone, m. p. 60—61°, b. p. 202—204°/12—13 mm. By the use of fresh aluminium chloride, however, the normal 2:3:5-product is obtained almost exclusively.

The effect of *o*-halogen in determining *syn*-configuration in benzophenone oximes is not disturbed by the presence of an *o'*-methoxyl group, the orienting effect of various *o'*-methoxyl groups being in the

order: halogen or carboxyl, hydroxyl or methoxyl, amino, methyl. 2:4-Dichloro-2'-bromobenzophenone, m. p. 33—34°, b. p. 227—228°/20 mm., prepared from *m*-dichlorobenzene and *o*-bromobenzoyl chloride (b. p. 131°/19 mm.), gives no oxime, but under alkaline conditions yields 2-chloro-2'-bromo-4-hydroxybenzophenone, m. p. 158—160°, and 3-*op*-dichlorophenylindoxazen, m. p. 78°, b. p. 212—214°/12 mm., and probably traces of 6-chloro-3-*o*-bromophenylindoxazen. 2-Bromo-5-nitro-2'-hydroxy-5'-methylbenzophenone, m. p. 151—152°, prepared from *p*-tolyl methyl ether and 2-bromo-5-nitrobenzoyl chloride, is readily converted by alkali into 2-nitro-7-methylxanthone, m. p. 224°, from which by the action of methyl-alcoholic potassium hydroxide 5-nitro-2':2'-dihydroxy-5'-methylbenzophenone, m. p. 146—148°, is obtained; the xanthone yields no oxime. 2-Bromo-5-nitro-2'-hydroxy-5'-methylbenzophenone oxime, m. p. 218°, is converted by alkali into a compound, C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>, m. p. 148°, which may be either 5-nitro-3-(4-hydroxy-*m*-tolyl)indoxazen or the nitromethylxanthoxime, and by phosphorus pentachloride into a phosphoric derivative. 2-Bromo-2'-hydroxy-5'-methylbenzophenone, m. p. 78.5°, from *p*-tolyl methyl ether and *o*-bromobenzoyl chloride, is converted by hot alkali into 2-methylxanthone, m. p. 125.5° (lit. 105°); it also gives a single oxime, m. p. 144.5°, from which no Beckmann transformation products are obtainable. 2-Bromo-2'-methoxy-5'-methylbenzophenone, m. p. 50—51°, obtained by methylation of the hydroxy-ketone, yields a single oxime, m. p. 193°, the configuration of which (*syn* with reference to the bromophenyl group) is shown by its conversion by methyl-alcoholic potassium hydroxide into 3-(4-methoxy-*m*-tolyl)indoxazen, b. p. 170°/0.5 mm., and by phosphorus pentachloride into *o*-bromobenzoic 4-methoxy-*m*-toluidide, m. p. 130—131°.

C. HOLLINS.

**Application of the Hoesch reaction to nitrobenzonitriles.** M. YAMASHITA (Bull. Chem. Soc. Japan, 1928, 3, 180—182).—Resorcinol condenses with *p*-nitrobenzonitrile in presence of ethereal hydrogen chloride and zinc chloride (Hoesch, A., 1915, i, 820) to give 4-nitro-2':4'-dihydroxybenzophenone, m. p. 203° (cf. Korczyński and Novakovski, this vol., 523; *dimethyl ether*, m. p. 123—124°). Similarly, *m*-nitrobenzonitrile affords 3-nitro-2':4'-dihydroxybenzophenone, m. p. 228° (*dimethyl ether*, m. p. 116—117°). Phloroglucinol with *m*- and *p*-nitrobenzonitriles yields 3-nitro-, m. p. 194°, and 4-nitro-2':4':6'-trihydroxybenzophenone, m. p. 246—247°, respectively. *o*-Nitrobenzonitrile does not condense with resorcinol or phloroglucinol.

H. BURTON.

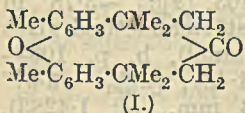
**Active component of paracoto bark. Synthesis of protocotin and methylprotocotin.** E. SPATH and H. BRETSCHNEIDER (Monatsh., 1928, 49, 429—437).—The nitrile of piperonylic acid is condensed with phloroglucinol in dry ether in presence of zinc chloride and gaseous hydrogen chloride and the resulting ketimine hydrolysed. The crude piperonylphloroglucinol is partly methylated with diazomethane and the products are separated by fractional distillation in a high vacuum. The protocotin obtained had, after purification, m. p.



140—141°, showing no depression when mixed with the natural product. Methylprotocotoin was recovered from the product insoluble in alkali. The transformation of natural protocotoin into 3:5-dimethoxy-3':4'-methylenedioxy-2-phenylcumarone, m. p. 117°, by the action of ethyl bromoacetate and sodium ethoxide, proves that the hydroxyl group of protocotoin is *ortho* to the carbonyl group. R. A. PRATT.

**Monoacetals of  $\alpha$ -bromodibenzoylmethane.** C. DUFRAISSE and A. GILLET (Bull. Soc. chim., 1928, [iv], 43, 883—888).—Phenyl  $\alpha$ -bromo- $\beta\beta$ -dialkoxy- $\beta$ -phenylethyl ketones,  $\text{CHBrBz}\cdot\text{CPh}(\text{OR})_2$ , are prepared by treating the dibromides of phenyl  $\beta$ -alkoxystyryl ketones with alcohols in presence of potassium acetate, and also by the addition of alcohols to phenyl  $\alpha$ -bromo- $\beta$ -alkoxystyryl ketones in presence of sodium alkoxides. Moisture must be excluded in the first method. Phenyl  $\alpha$ -bromo- $\beta\beta$ -dimethoxy- $\beta$ -phenylethyl ketone has m. p. 91—92°; the corresponding diethoxy- and dipropoxy-derivatives have m. p. 70° and 83—84°, respectively. These acetals are very readily hydrolysed by small amounts of acid, and the bromine is eliminated quantitatively by boiling alcoholic potassium hydroxide. When heated they lose the appropriate alcohol. Phenyl  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -ethoxy- $\beta$ -phenylethyl ketone, m. p. 89—90°, is obtained as the main product in each of the four methods used for its preparation, but a small amount of the second possible racemic modification appears to be formed at the same time. When this ketone is heated, methyl alcohol and phenyl  $\alpha$ -bromo- $\beta$ -ethoxystyryl ketone are produced. H. BURTON.

**New condensation of ketones with phenols.** "Phorone di-*m*-cresyl ether." J. B. NIEDERL (J. Amer. Chem. Soc., 1928, 50, 2230—2235).—Treatment of *m*-cresol and acetone or phorone with concentrated sulphuric acid yielded a condensation product, termed by the author "phorone di-*m*-cresyl ether" (I), m. p. 127°; b. p. 270°; [a better name would be *anhydrodi- $\beta$ -* (4-hydroxy-2-methylphenyl)- $\beta$ -methyl-*n*-propyl ketone]. The mechanism of formation appears to be the addition of sulphuric acid to



phorone, elimination of sulphuric acid between the product and *m*-cresol, and, finally, ether formation. The dibromo-derivative, m. p. 215°, was obtained by bromination in carbon tetrachloride, and the tetra-nitro-derivative, m. p. 243°, accompanied by  $\beta$ -(nitro-4-hydroxy-2-methylphenyl)isovaleric acid, m. p. 108° (disodium salt), by boiling with concentrated nitric acid. Chromic acid in glacial acetic acid oxidised the compound with the formation of dimethylmalonic acid and  $\beta$ -4-hydroxy-2-methylphenylisovaleric acid, m. p. 107° (dibromo-derivative, m. p. 140°).

R. K. CALLOW.

**Condensation products [ketones and naphthindanones] from aromatic hydrocarbons or derivatives thereof.** I. G. FARBENIND. A.-G.—See B., 1928, 665.

**Action of magnesium ethyl bromide on acenaphthenequinone.** N. MAXIM (Bull. Soc.

chim., 1928, [iv], 43, 769—778).—Magnesium ethyl bromide reacts readily with acenaphthenequinone, affording 9:10-diethylacenaphthene-9:10-glycol, m. p. 197°, which on dehydration with glacial acetic acid is converted into the orange-yellow 9:10-diethylideneacenaphthene, m. p. 140°, and not a  $\beta$ -pinacol in as in the dehydration of 9:10-diphenylacenaphthene-glycol (Beschke, A., 1909, i, 917). Oxidation of 9:10-diethylideneacenaphthene with chromic and acetic acids gives acenaphthenequinone and acetic acid.

R. BRIGHTMAN.

**Benzanthrone derivatives.** I. G. FARBENIND. A.-G.—See B., 1928, 598.

**Manufacture of benzantrones.** I. G. FARBENIND. A.-G.—See B., 1928, 666.

**Anthraquinone derivatives.** I. G. FARBENIND. A.-G.—See B., 1928, 598.

**Manufacture of 1-anthraquinonyl ketones.** I. G. FARBENIND. A.-G.—See B., 1928, 665.

**Nitro-compounds of arylaminoanthraquinones, their derivatives and substitution products.** I. G. FARBENIND. A.-G.—See B., 1928, 665.

**Manufacture of chloroperylenequinones.** F. BENZA.—See B., 1928, 666.

**Cornin : a glucoside from *Cornus florida*, L.** E. R. MILLER (J. Amer. Pharm. Soc., 1928, 17, 744—750).—Cornin was extracted from the root bark of *C. florida*, L., by cold percolation with water. The pure material,  $\text{C}_{19}\text{H}_{21}\text{O}_9\cdot\text{OMe}$ , has  $[\alpha]_{\text{D}}^{25}$  —180.6° to —181.4°, and m. p. 182—183° if heated rapidly. It is readily soluble in water, but sparingly soluble in the usual organic solvents. It hydrolysed by emulsion and is thus probably a  $\beta$ -glucoside of dextrose.

B. W. ANDERSON.

[Constitution of] sesamin. S. H. BERTRAM, J. P. K. VAN DER STEUR, and H. I. WATERMAN (Biochem. Z., 1928, 197, 1—7). Sesamin,  $\text{C}_{18}\text{H}_{16}\text{O}_5$ , m. p. 122.7°,  $[\alpha]_{\text{D}}^{25}$  +72.77°, was obtained in 0.11—0.27% yield from sesame oil and evidence is given that it is 2:2'-dipiperonyltetrahydrofuran. On distilling with zinc dust, sesamin gives a phenolic substance. Oxidation with chromic anhydride in acetic anhydride at 40° yielded a little piperonylic acid. Clowes and Tollens' method for the determination of methylenedioxy-groups was found untrustworthy for piperonyl derivatives, but indicated that two such groups were present. When boiled with 10% alcoholic hydrochloric acid, sesamin gave a compound, m. p. 122°,  $[\alpha]_{\text{D}}$  +121.5°; it is suggested that the ether of sec.-methylpiperonyl alcohol might be closely related to sesamin. The fact that the refraction of sesamin was considerably higher than that of this ether made it probable that sesamin contained a tetrahydrofuran ring. When boiled with acetyl chloride, sesamin gave an oily additive compound, which lost acetyl chloride on heating. L. C. BAKER.

**Kakishibu. IV. Constitution of shibuol. III.** S. KOMATSU and N. MATSUNAMI (Mem. Coll. Sci. Kyōto, 1928, 11, 205—210).—The tinctorial properties of shibuol, its azo-derivative, and its metallic salts have been compared with those of myricetin, quercetin, and catechin and their corresponding derivatives.

Shibuol closely resembles myricetin, but differs from catechin and quercetin, from which it is concluded that the number of free hydroxyl groups present in the phenolic portion of the shibuol molecule is probably the same as in myricetin. *Benzeneazoshibuol*,  $C_{26}H_{20}O_7N_4$ , is obtained in 85% yield as a reddish-brown powder by coupling shibuol with benzene-diazonium chloride; reduction with sodium hypsulphite yields a substance,  $C_{15}H_{14}O_7N$ . Shibuol, when treated with zinc dust in alkaline solution at 50°, yields phloroglucinol and gallic acid (cf. A., 1923, i, 1197), but is unaffected by zinc and acetic acid at 50°; with magnesium powder and acetic acid reduction occurs, giving a soluble, red substance similar to that obtained with flavones. Reduction of *tetramethylshibuol* (cf. following abstract) with hydriodic acid (*d* 1.18) at 130° gave a violet-brown substance insoluble in ether, but readily soluble in other organic solvents; an analysis is given but no formula is assigned.

C. W. SHOPPEE.

**Kakishibu. V. Methylation of shibuol.** S. KOMATSU, N. MATSUNAMI, and M. KURATA (Mem. Coll. Sci. Kyōtō, 1928, 11, 211—216).—Shibuol has been methylated using methyl sulphate under various conditions. The results (below) suggest that shibuol possesses four free hydroxyl groups: this agrees with the formation of tetra-acetyl-shibuol (A., 1925, i, 950). *Shibuol dimethyl ether* is obtained as a violet-brown powder when methylation occurs in sodium carbonate solution. *Shibuol trimethyl ether*, sinters at 220°, m. p. 260° (decomp.), is obtained as a yellowish-brown powder by methylation at 5° in alkali hydroxide solution; if the reaction temperature is raised, *shibuol tetramethyl ether* is also obtained as a brown powder sintering at 200°, m. p. 230—240°; which is insoluble in alkali. A specimen of shibuol tetramethyl ether prepared from the trimethyl ether (methyl iodide and silver oxide) had m. p. 208—210°. An *acetylshibuol trimethyl ether* was also obtained.

C. W. SHOPPEE.

**Toad poisons. I. Composition of Chinese drug "Senso." II. Poisonous constituents of secretion of Japanese toad (*Bufo bufo japonicus*).** M. KOTAKE (Annalen, 1928, 465, 1—11, 11—20, and Bull. Inst. Phys. Chem. Res. Tokyo, 1928, 7, 785—789, 790—804).—I. Extraction of powdered "Senso" with alcohol affords bufagin,  $C_{29}H_{38}O_7$ , m. p. 220—221° (cf. Shimizu, A., 1916, i, 698; Kodama, Act. Schol. Med. Univ. Imp. Kyōtō, 1920, 3, III, 299; 1921, 4, II, 213; 1922, 4, III, 355). Reduction of bufagin with hydrogen in presence of palladium-black and alcohol gives a mixture of  $\alpha$ -*tetrahydrobufagin* + 2H<sub>2</sub>O, m. p. 130—140°, m. p. (anhydrous) 225—230° (acetyl derivative, m. p. 238°), and  $\beta$ -*tetrahydrobufagin*, m. p. 208—210°. Acetylation of this last compound gives a mixture of the  $\alpha$ -acetyl derivative together with the  $\beta$ -acetyl derivative, m. p. 254—257°; the same mixture is produced when *diacetylbufagin*, m. p. 196—197°, is reduced catalytically. Oxidation of bufagin with chromic anhydride in acetic acid yields *bufagone*,  $C_{29}H_{36}O_7$ , m. p. 232—235° (oxime, m. p. 170—173°), which is not capable of being acetylated. Bufagin contains an acetyl group (hydrolysis with potassium hydroxide).

Bufalin chloride, m. p. 218—220° (cf. Kodama, *loc. cit.*), is obtained by the action of hydrogen chloride on the bufagin-free extract of "Senso." It is converted by acetic anhydride and sodium acetate into *acetyl-anhydrobufalin*,  $C_{29}H_{36}O_6$ , m. p. 221—225°, and oxidised by chromic and acetic acids to *bufalinone chloride*, m. p. 251—252°. When this is heated with acetic anhydride and sodium acetate *anhydrobufalinone*,  $C_{27}H_{32}O_5$ , m. p. 181—183°, is obtained.

II. Extraction of the skins of *Bufo bufo japonicus* with alcohol and subsequent removal of fat and cholesterol gives 0.7% of *gamabufotalin* (I),  $C_{27}H_{38}O_6$ , m. p. 261—263° with frothing (*diacetyl* derivative, m. p. 225°), which is hydrolysed by alcoholic potassium hydroxide to *gamabufotalinic acid*,  $C_{24}H_{36}O_6$ , m. p. 207—209° (decomp.), and formic acid. Reduction of (I) with hydrogen in presence of palladium-black gives *hydrogamabufotalin*,  $C_{24}H_{38}O_5$ , EtOH, m. p. 131—133°, together with an amorphous, acidic substance. The action of concentrated hydrochloric acid on (I) is to furnish *anhydrogamabufotalin*, m. p. 263° with frothing. Treatment of (I) with 95% formic acid gives after 20 hrs. at 12—15° a *diformyl* derivative, m. p. 156—157°, after 2 days at 27—30° a substance,  $C_{57}H_{72}O_{13}$ , m. p. 212—214°, and after 3 days an uncrystallisable product. These reaction products are converted by concentrated hydrochloric acid into *anhydrogamabufotalin*.

When the residue from the alcoholic extract of the toad skins after removal of fat, cholesterol, and *gamabufotalin* is treated with ethereal hydrogen chloride, *gamabufalin chloride*,  $C_{27}H_{38}O_5Cl$ , m. p. 217—219°, is obtained. This is converted by treatment with acetic anhydride and sodium acetate into *acetylanhydrogamabufalin*,  $C_{26}H_{40}O_6$ , m. p. 227—229°. *Acetylgamabufalin*, m. p. 256—258°, is obtained by acetylation of the above residue.

H. BURTON.

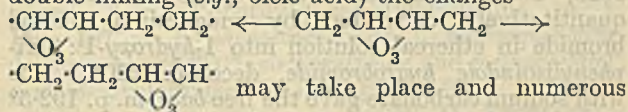
**Hydrogenation of acyclic terpenes.** S. SABETAY and J. BLEGER (Bull. Soc. chim., 1928, [iv], 43, 839—845).—Catalytic reduction of rhodinol, b. p. 113—115°/16 mm.,  $d_{20}^{25}$  0.8654,  $n_D^{25}$  1.463,  $[\alpha]_{D_{25}}^{25}$  -3.78° in 75% alcohol, by the Fokin-Willstätter method gives dihydrorhodinol ( $\gamma\gamma$ -dimethyloctanol), b. p. 109—109.5°/15 mm.,  $d_{20}^{25}$  0.830,  $n_D^{25}$  1.437,  $[\alpha]_{D_{25}}^{25}$  -3.67° (acetate, b. p. 115.5—116°/18 mm.,  $n_D^{25}$  1.4283), which has an odour resembling rose. When geraniol is completely hydrogenated the product appears to be identical with the alcohol obtained from  $\gamma\gamma$ -dimethyloctylamine and nitrous acid (Wallach, A., 1912, i, 569). Reduction of citronellal affords a dihydro-citronellal, b. p. 81.5—82°/13 mm.,  $d_4^{25}$  0.822,  $n_D^{25}$  1.4273,  $[\alpha]_{D_{25}}^{25}$  +10.8° (cf. von Braun, A., 1924, i, 3). The aldehyde grouping was not reduced in any experiment.

H. BURTON.

**Citronellal and rhodinol.** A. VERLEY (Bull. Soc. chim., 1928, [iv], 43, 845—854).—Pure citronellal, b. p. 82°/2 mm.,  $d_{20}^{20}$  0.8682,  $n_D^{20}$  1.4534,  $[\alpha]_D^{20}$  +9.19°, gives a homogeneous semicarbazone, m. p. 83.5°. From this and a study of the dispersion curve it is concluded that citronellal exists in one form only. When citronellal cyanohydrin is distilled in a vacuum, hydroxycitronellal, b. p. 116°/5 mm.,  $d_{15}^{15}$  0.931,  $n_D^{20}$  1.456,  $\alpha_D^{20}$  +8.3°, results. This compound is also obtained by treating citronellal-enolacetate with

dilute alkali. When hydroxycitronellal is heated in a vacuum with 0.05 part of kieselguhr there is obtained a mixture of  $\beta$ -isopulegol (pulegol) and rhodinal, together with a product,  $C_{10}H_{24}O$ . Rhodinal (semicarbazone, m. p. 75.5°) has b. p. 83°/2 mm.,  $d_{20}^{25}$  0.8709,  $[\alpha]_D^{25} +1^{\circ} 10'$ , when purified through its hydrogen sulphite compound and is also homogeneous. Oxidation of rhodinol with sodium dichromate gives resinous products together with rhodinal, which is transformed immediately into  $\beta$ -isopulegol, b. p. 90°/10 mm.,  $d_{20}^{25}$  0.9275, and finally oxidised to pulegone. The menthone-like odour of this ketone is probably the reason for the statement that rhodinol can be transformed into menthone (Barbier and Bouveault, A., 1896, i, 491). H. BURTON.

**Rearrangement of ozonides.** A. VERLEY (Bull. Soc. chim., 1928, [iv], 43, 854—857).—The ozonides of citronellal, citral, and geraniol undergo considerable transformation from the  $\alpha$ - to the  $\beta$ -form, probably during decomposition of the ozonides (cf. A., 1925, i, 406). The following rules are postulated to explain the author's work on the action of ozone on unsaturated compounds: (a) when the double linking is "privileged" (e.g., cinnamic acid) decomposition is normal; (b) in compounds containing an "indifferent" double linking (e.g., oleic acid) the changes



may take place and numerous by-products result; (c) if the ozonide is formed on a double linking bordering on a "privileged" position (e.g., citronellal), a partial transformation takes place. H. BURTON.

**Production of inactive menthol.** RHEINISCHE KAMPFER FABR.—See B., 1928, 691.

**Complete resolution of externally compensated acids and bases.** A. W. INGERSOLL (J. Amer. Chem. Soc., 1928, 50, 2264—2267; cf. A., 1925, i, 814).—In the method previously described (*loc. cit.*), after separation of the less soluble salt, e.g., *l*-B,*d*-A, from the mixture of *dl*-B and *d*-A, the residual mixture of bases *dl*-B and *d*-B was combined with the *dl*-form of the same acid and *d*-B,*l*-A, for instance, separated from the mixture of salts *dl*-B,*dl*-A, *d*-B,*d*-A, and *d*-B,*l*-A. Alternatively, the half-racemic salt *d*-B,*dl*-A may be formed, and be less soluble, and the application of this process to the separation of the second component of an externally compensated base, *iso*-diphenylhydroxyethylamine, has now been accomplished. *d*-Camphor-10-sulphonic acid yielded *d*-*iso*-diphenylhydroxyethylamine *d*-camphor-10-sulphonate (+H<sub>2</sub>O), m. p. 207—208° (anhydrous), from which the *d*-base was obtained (cf. Read and Steele, A., 1927, 557). The base recovered from the mother-liquors of the *d*-base-*d*-acid salt was treated with *dl*-camphor-sulphonic acid, and the *l*-base-*dl*-acid salt (+H<sub>2</sub>O), m. p. 206—207° (anhydrous), was separated, and yielded the pure *l*-base. The *l*-base-*d*-acid salt (+H<sub>2</sub>O), m. p. 205—206° (anhydrous), *d*-base-*dl*-acid salt (similar to the *l*-base-*dl*-acid salt), and *dl*-base-*dl*-acid salt (+H<sub>2</sub>O), m. p. 198—199° (anhydrous), were also prepared. R. K. CALLOW.

**"Furylangelic" acid.** A. S. CARTER (J. Amer. Chem. Soc., 1928, 50, 2290—2305).—"Furylangelic" acid, m. p. 95.5—97° (cf. Baeyer and Tönnies, A., 1877, ii, 746; Tönnies, A., 1879, 915), was prepared in 80% yield by heating furfuraldehyde with sodium butyrate and butyric anhydride. Ozonolysis yielded carbon dioxide, propionic acid, and possibly  $\alpha$ -keto-butyric acid, whilst oxidation by acid or alkaline permanganate yielded acetic and propionic acids. These facts support the assumption of the structure of  $\beta$ -2-furyl- $\alpha$ -ethylacrylic acid for "furylangelic" acid which would be expected from the known course of the Perkin reaction. Tönnies' preparation of azelaic acid from "furylangelic" acid (*loc. cit.*) is not in accord with this, and his work was repeated. Reduction of "furylangelic" acid by sodium amalgam yielded  $\alpha$ -furfurylbutyric acid, b. p. about 174°/46 mm., which, by the action of bromine water and silver oxide, yielded butyrofuronic acid ( $\Delta^3$ -hepten- $\gamma$ -one- $\alpha$ -dicarboxylic acid), m. p. 149—150° (Tönnies gives 140—142°). Reduction of butyrofuronic acid by red phosphorus and hydriodic acid yielded no product similar to that obtained by Tönnies, but  $\alpha$ -ethylpimelic acid, m. p. 41—43°, and a small amount of heptan- $\gamma$ -one- $\alpha$ -dicarboxylic acid, m. p. 83—84.5°, which appeared to be an intermediate product. The latter acid was prepared from "furylangelic" acid by the action of hydrogen chloride in alcohol and hydrolysis of the *ethyl* ester, b. p. 198—200°/25 mm., thus obtained. It was reduced by red phosphorus and hydriodic acid to ethylpimelic acid.

R. K. CALLOW.

**Styrylpyrylium salts. X. Anhydropyrylium bases and spiropyrans derived from dibenzyl ketone.** R. DICKINSON, I. M. HELBRON, and F. O'BRIEN (J.C.S., 1928, 2077—2082; cf. A., 1927, 834; also Dilthey and Wubken, this vol., 767).—Salicylaldehyde and dibenzyl ketone readily condensed in the presence of piperidine, giving 2-hydroxy- $\alpha$ -phenylstyryl benzyl ketone (I), m. p. 177° (semicarbazone, m. p. 196°; methyl ether, m. p. 140—141°), but in the presence of hydrogen chloride 2-benzylidene-3-phenyl- $\Delta^3$ -benzopyran (II), m. p. 115°, and (in small quantities) 3:3'-diphenyldibenzospiropyran,

$\begin{array}{c} \text{OH}:\text{CPh} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{C}_6\text{H}_4 \end{array}$  m. p. 197°, were obtained. The spiropyran was obtained directly as the sole product of the action of hydrogen chloride on mixtures of (a) salicylaldehyde (2 mols.), dibenzyl ketone (1 mol.); (b) salicylaldehyde (1 mol.), I (1 mol.); or (c) salicylaldehyde and II (cf. Decker and Fellenberg, A., 1909, i, 950; Ruhemann and Levy, J.C.S., 1913, 103, 551). Dibenzyl ketone and  $\beta$ -naphthol-1-aldehyde yielded, in the presence of piperidine, only 2-benzylidene-3-phenyl- $\Delta^3$ - $\beta$ -naphthopyran, but with hydrochloric acid both this substance and smaller quantities of 3:3'-diphenyldi- $\beta$ -naphthaspiropyran (*monohydrate*, m. p. 248°) were formed. The latter was prepared in better yield by the action of hydrogen chloride on a mixture of dibenzyl ketone (1 mol.) and naphthol-aldehyde (2 mols.). Observations of colour formation on heating in inert solvents and on styrylpyrylium salt formation with acids in the cases of 3'- and 3-methylbenzo- $\beta$ -naphthaspiropyran showed that, contrary to the expressed opinion of Dilthey and

Wübken (*loc. cit.*), the two processes were not analogous. R. J. W. LE FÈVRE.

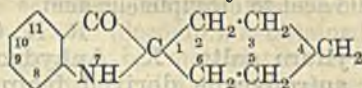
Ethylene ethers by cyclisation of chloromethyl ethers. S. SABETAY and G. SANDULESCO (Bull. Soc. chim., 1928, [iv], 43, 904—906).—When cyclohexane-1 : 2-diol di(chloromethyl) ether is treated with finely-divided sodium in presence of benzene there is obtained the dioxan,  $C_6H_{10} \begin{matrix} \diagup O \cdot CH_2 \\ \diagdown O \cdot CH_2 \end{matrix}$ , b. p. 65.5—66.5°/20 mm.,  $d^{20}_4$  1.035,  $n^{20}_D$  1.4585, together with undistillable products (cf. Palfray and Sabetay, this vol., 1130).

When piperonalsemicarbazone is heated with sodium ethoxide in an autoclave (cf. Wolff, A., 1912, i, 988) 3 : 4-methylenedioxytoluene, b. p. 80—81°/14 mm.,  $n^{20}_D$  1.533, is obtained. H. BURTON.

Manufacture of condensation products derived from thionaphthen-2 : 3-dicarboxylic acid. I. G. FARBENIND. A.-G.—See B., 1928, 635.

Manufacture of 2 : 3-phthaloylthionaphthen and derivatives thereof. I. G. FARBENIND. A.-G.—See B., 1928, 635.

Derivatives of  $\psi$ -indoxylspirocyclohexane. R. L. BETTS and S. G. P. PLANT (J.C.S., 1928, 2070—2074; cf. A., 1927, 765).—Alkali fusion of the appropriate alkylated 1-anilino-cyclohexane-1-carboxylic acids gave 10-methyl-, m. p. 164°, 8-methyl-, m. p. 197°, 4-methyl-, m. p. 189°, and 8 : 10-dimethyl- $\psi$ -indoxylspirocyclohexane, m. p. 190°. Acetylation (least easy with the 8-methyl and 8 : 10-dimethyl



compounds) gave the 7-acetyl derivative in each case (m. p. 144°, 226°, 102°, and 96°, respectively). By the action of dilute nitric acid the following nitro-compounds were obtained: (?8-nitro-10-methyl- $\psi$ -indoxylspirocyclohexane, m. p. 158°, (?10-nitro-8-methyl- $\psi$ -indoxylspirocyclohexane, m. p. 273—274°, (?10-nitro-4-methyl- $\psi$ -indoxylspirocyclohexane, m. p. 198°, (?10-nitro-4 : 7-dimethyl- $\psi$ -indoxylspirocyclohexane, m. p. 141°, and (?nitro-8 : 10-dimethyl- $\psi$ -indoxylspirocyclohexane, m. p. 183—184° (decomp.), all giving characteristic sparingly soluble sodium derivatives with aqueous sodium hydroxide.

The following compounds were prepared incidentally: 1-p-toluidino-1-cyanocyclohexane, m. p. 76°; 1-p-toluidinocyclohexane-1-carboxylamide, m. p. 156°; 1-p-toluidinocyclohexane-1-carboxylic acid, m. p. 172°; 1-o-toluidino-1-cyanocyclohexane, m. p. 72°; 1-o-toluidinocyclohexane-1-carboxylamide, m. p. 143°; 1-o-toluidinocyclohexane-1-carboxylic acid, m. p. 117°; 1-2' : 4'-dimethylanilino-1-cyanocyclohexane, m. p. 115—116°; 1-2' : 4'-dimethylanilino-cyclohexane-1-carboxylamide, m. p. 133°; 1-2' : 4'-dimethylanilino-cyclohexane-1-carboxylic acid, m. p. 125°; 1-anilino-1-cyano-4-methylcyclohexane, m. p. 107°; 1-anilino-4-methylcyclohexane-1-carboxylamide, m. p. 161°; 1-anilino-4-methylcyclohexane-1-carboxylic acid, m. p. 179°; 1-p-nitroanilino-1-cyanocyclohexane, m. p. 134°; 1-p-nitroanilino-cyclohexane-1-carboxylamide, m. p. 217°; 1-p-nitroanilino-cyclohexane-1-carboxylic acid, m. p. 201°; 1-p-aminoanilino-cyclohexane-1-carboxylic acid, m. p. 216—217°.

The anilino-cyclohexanecarboxylic acids described dissociated on distillation into the corresponding alkylated aniline and  $\Delta^1$ -cyclohexene-1-carboxylic acid (cf. A., 1925, i, 1271). R. J. W. LE FÈVRE.

Reduction of pyridine hydrochloride and pyridinium salts by means of hydrogen and platinum oxide platinum-black. XVIII. T. S. HAMILTON and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 2260—2263).—Hydrogen and platinum-black from platinum oxide (cf. Adams and Shriner, A., 1923, ii, 773; Adams, Voorhees, and Shriner, this vol., 600) may be used for the reduction of pyridine hydrochloride and pyridinium salts, although pyridine itself is a catalyst poison. Absolute alcohol is the best solvent. Traces of ferrous salts do not affect the reaction. The following compounds are reduced quantitatively to the corresponding hexahydro-derivatives: pyridine hydrochloride and phenyl-, *n*-butyl-, ethyl-, benzyl-, carbethoxymethyl-,  $\beta$ -hydroxyethyl-, and  $\gamma$ -hydroxypropyl-pyridinium chlorides. The pyridinium salts are more readily reduced than pyridine hydrochloride. R. K. CALLOW.

Action of magnesium phenyl bromide on methyl *o*-cyanobenzoate. 1 : 3-Diphenyldihydroisoidole. D. R. BOYD and D. E. LADHAMS (J.C.S., 1928, 2089—2093).—Methyl *o*-cyanobenzoate was quantitatively converted by magnesium phenyl bromide in ethereal solution into 1-hydroxy-1 : 3-diphenylisoidole hydrobromide, decomp. 220°; this with sodium carbonate gave the free base, m. p. 192.5° (decomp.), the reactions of which in solution are best explained by the equilibrium:  $COPh \cdot C_6H_4 \cdot CPh : NH = C_6H_4 - CPh : OH$ . Hydrolysis (dilute sulphuric

acid) easily gave *o*-dibenzoylbenzene; reduction (zinc dust and acetic acid) yielded only small quantities of (probably *trans*; racemic) 1 : 3-diphenyldihydroisoidole, m. p. 109° [hydrochloride, m. p. 270—280° (decomp.)]; nitroso-derivative, m. p. 175—175.5°; monobenzoyl derivative, m. p. 236°; *p*-toluenesulphonyl derivative, m. p. about 225° (decomp.), and much diphenylbenzofuran formed owing to reduction of *o*-dibenzoylbenzene produced by hydrolysis.

R. J. W. LE FÈVRE.

Manufacture of 4-alkylquinolines and derivatives thereof. SCHERING-KAHLBAUM A.-G.—See B., 1928, 730.

Quinoline derivatives. R. HUPE and A. SCHRÄMME [with A. WINDAUS] (Z. physiol. Chem., 1928, 177, 315—320).—Reduction of the oxime, m. p. 201°, of 2-quinolylacetaldehyde with hydrogen in presence of platinum-black and acetic acid gives  $\beta$ -2-quinolyethylamine, m. p. 174° (hydrochloride, m. p. 212°; picrate, m. p. 209° after sintering), but with sodium and alcohol as the reducing agent  $\beta$ -1 : 2 : 3 : 4-tetrahydroquinolyethylamine, b. p. 188°/16 mm. when purified through the dihydrochloride, m. p. 230°, is formed. Reduction of 4-nitropyrogallol trimethyl ether with stannous chloride yields the corresponding amino-derivative (I), b. p. 150°/2 mm. (hydrochloride, m. p. 200°; chloroacetyl derivative, m. p. 85°). When (I) undergoes the Skraup reaction 6 : 7 : 8-trimethoxyquinoline, m. p. 80° (picrate, m. p. 181°), results. 6 : 7 : 8-Trimethoxy-2-methylquinoline (picrate, m. p.

142°; oxalate, m. p. 148°) has m. p. 73° and condenses with chloral, giving  $\alpha\alpha$ -trichloro- $\gamma$ -6:7:8-trimethoxy-2-quinolylpropan- $\beta$ -ol, m. p. 114°. When a mixture of (I), pyruvic acid, benzaldehyde, and a small amount of alcohol is heated on the steam-bath 6:7:8-trimethoxy-2-phenylcinchoninic acid (trimethoxyatophan), m. p. 174—175°, is produced.

H. BURTON.

**Antiseptic compounds: further derivatives of anilquinoline.** C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1928, B, 103, 404—411).—In continuation of previous work (A., 1924, i, 990) a number of new anils have been prepared by condensing the appropriate nitroso-compound with a derivative of 2-methylquinoline, and the antiseptic action of these new anils has been investigated. The following new intermediate compounds are described: *methyl 2-methyl-6-quinolyl-carbamate* (m. p. 182—183°) from methyl chloroformate and 6-amino-2-methylquinoline; *ethyl 2-methyl-6-quinolylcarbamate* (m. p. 150.5°); *8-acetamido-2-methyl- $\beta$ -naphthoquinoline methochloride* derived from *8-acetamido-2-methyl- $\beta$ -naphthoquinoline*, m. p. 235—237°, which is prepared by the acetylation of *8-amino-2-methyl- $\beta$ -naphthoquinoline*, m. p. 169—170°, itself obtained by the reduction of the previously known 3-nitro-2-methyl- $\beta$ -naphthoquinoline, m. p. 166—167°; *6-phenylcarbamido-2-methylquinoline*, decomp. above 220° (*methosulphate* and *methoacetate*); *p-nitrosocyclohexylaniline*, m. p. 91—93°.

W. O. KERMACK.

**Metabolism of tryptophan. II. Synthesis of 6- and 8-methylkynurenic [4-hydroxyquinoline-2-carboxylic] acids.** W. ROBSON (Biochem. J., 1928, 22, 1157—1164).—*p*-Toluidine and ethyl acetoacetate were converted into 4-hydroxy-2:6-dimethylquinoline. This, with phosphorus oxychloride and pentachloride, gave *4-chloro-2:6-dimethylquinoline*, b. p. 119°/3.5 mm., m. p. 69—70°. On treatment with sodium methoxide this compound gave *4-methoxy-2:6-dimethylquinoline*, m. p. 106.5—107°, which with benzaldehyde gave *4-methoxy-2-styryl-6-methylquinoline*, m. p. 140—141° (*hydrochloride*, m. p. 204°). This compound, when oxidised in acetone solution with potassium permanganate, afforded *4-methoxy-6-methylquinoline-2-carboxylic acid*, m. p. 228°, converted by boiling hydrobromic acid into *4-hydroxy-6-methylquinoline-2-carboxylic acid* (*6-methylkynurenic acid*), m. p. 279° (decomp.) (*barium salt*).

The synthesis of 8-methylkynurenic acid followed similar lines: *o*-toluidine  $\rightarrow$  4-hydroxy-2:8-dimethylquinoline  $\rightarrow$  4-ethoxy-2:8-dimethylquinoline, m. p. 55° (by the action of ethyl *p*-toluenesulphonate on the preceding compound)  $\rightarrow$  4-ethoxy-2-styryl-8-methylquinoline, m. p. 115—116°,  $\rightarrow$  4-ethoxy-8-methylquinoline-2-carboxylic acid  $\rightarrow$  4-hydroxy-8-methylquinoline-2-carboxylic acid (*8-methylkynurenic acid*), m. p. 266° (*barium salt*). S. S. ZILVA.

**Preparation of quinoline derivatives.** I. G. FARBENIND. A.-G.—See B., 1928, 691.

**Manufacture of derivatives of substituted quinolinecarboxylic acids.** SOC. CHEM. IND. IN BASLE.—See B., 1928, 730.

**1-*o*-Chlorophenyl-3-methyl-5-pyrazolone and its derivatives.** Z. TOMASIK (Rocz. Chem., 1928, 8, 345—348).—*o*-Chlorophenylhydrazine condenses with ethyl acetoacetate to yield 1-*o*-chlorophenyl-3-methyl-5-pyrazolone, m. p. 199° (*4-benzylidene* derivative, m. p. 157°; *4-*o*-nitrobenzylidene* derivative, m. p. 160°), which when condensed with *o*-nitrobenzaldehyde yields *o*-nitrophenylbis-(1-*o*-chlorophenyl-3-methyl-5-pyrazolonyl)methane, m. p. 249°.

R. TRUSZKOWSKI.

**Replaceability of certain methylene groups and relation of constitution to stability of a C:C linking.** H. V. MOYER and F. B. DAINS (J. Amer. Chem. Soc., 1928, 50, 2293—2297).—The reaction which occurs between diphenylformamidine and the benzylidene derivative of methylisooxazolone, in which the benzylidene group is replaced by the anilinomethylene group, has now been found to take place in the case of aldehyde derivatives of certain heterocyclic compounds, particularly those in which the benzylidene group is readily removed by hydrolysis with dilute acids or heating with phenylhydrazine. Thus 4-benzylidene-3-phenylisooxazolone yielded 4-anilinomethylene-3-phenylisooxazolone when heated with diphenylformamidine, and the same reaction occurred with the piperonylidene, anisylidene, *m*-nitrobenzylidene, and cinnamylidene derivatives, but not with the furfurylidene derivative. The benzylidene and piperonylidene derivatives of 1-phenyl-3-methylpyrazolone yielded similarly the 4-anilinomethylene derivative. 1:3-Diphenylbenzylidenepyrazolone yielded the 4-anilinomethylene derivative, but 1:3-diphenylpyrazolone yielded both this and bisdiphenylpyrazolone. 3-Hydroxy-1-phenyl-4-benzylidenepyrazolone or the 4-anisylidene derivative yielded the 4-anilinomethylene derivative, m. p. 272—273°, also obtained from 3-hydroxy-1-phenylpyrazolone. 3-Phenyl- and 3-methyl-4-benzylidenepyrazolones did not react, and 3-methylpyrazolone reacted with difficulty to give the 4-anilinomethylene derivative, m. p. 204°. The benzylidene derivative of 3-phenylrhodanine, m. p. 192°, yielded the 5-anilinomethylene derivative, m. p. 247°, but the cinnamylidene derivative did not react. Benzylidene-*o*-tolylthiazolidone did not react. Benzylidene derivatives in which the methylene carbon was not part of the ring,  $\alpha$ -phenylcinnamionitrile, *m*-nitrobenzylideneacetylacetone, cinnamylideneacetylacetone, and acetylcoumarin, did not react. Phenyl styryl ketone yielded the *anil*, m. p. 168°, which was also prepared by heating the ketone with aniline and sodium acetate; the *p*-chloroanil, m. p. 167°, and *p*-tolil, m. p. 170°, were obtained in a similar way. R. K. CALLOW.

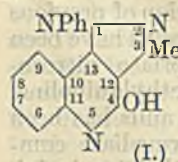
**Aromatic derivatives of substituted acetamidoacetones.** H. D. DAKIN and R. WEST (J. Biol. Chem., 1928, 78, 757—764; cf. this vol., 874).— $\alpha$ -Acetamido- $\alpha$ -phenylacetoxime has m. p. 152°;  $\alpha$ -amino- $\alpha$ -phenylacetone hydrochloride gave, with potassium cyanate, 4-phenyl-5-methylglyoxalone, m. p. 287—289°, and, with potassium thiocyanate, 2-thiol-4-phenyl-5-methylglyoxaline, m. p. 290—295°.  $\alpha$ -Amino- $\alpha$ -benzylacetone hydrochloride, m. p. 130°, gave 4-benzyl-5-methylglyoxalone, m. p. 270° (darkening at 250°)

and 2-thiol-4-benzyl-5-methylglyoxaline, m. p. 279—280°; with ammonia it gave 2:5-dibenzyl-3:6-dimethylpyrazine, m. p. 92—94°.  $\alpha$ -Acetamido- $\alpha$ -p-hydroxybenzylacetoxime has m. p. 189—190°;  $\alpha$ -amino- $\alpha$ -p-hydroxybenzylacetone hydrochloride gave 4-p-hydroxybenzyl-5-methylglyoxalone, m. p. 243—244°, and 2-thiol-4-p-hydroxybenzyl-5-methylglyoxaline, m. p. 273—275°. C. R. HARRINGTON.

**Glyoxaline-4:5-dicarboxylic acids.** C. A. YLLNER (Arkiv Kemi, Min., Geol., 1928, 9, No. 41, 1—20).—The following glyoxaline-4:5-dicarboxylic acids have been prepared by interaction of the requisite aldehyde, dinitrotartaric acid, and ammonia: glyoxaline-4:5-dicarboxylic acid (ammonium + H<sub>2</sub>O, lithium hydrogen + 3H<sub>2</sub>O, potassium hydrogen + H<sub>2</sub>O, m. p. 281°, potassium + 3H<sub>2</sub>O, sodium hydrogen + H<sub>2</sub>O, sodium + 2H<sub>2</sub>O, barium, and magnesium salts); 2-methylglyoxaline-4:5-dicarboxylic acid + H<sub>2</sub>O (potassium hydrogen, m. p. 271°, and sodium hydrogen + H<sub>2</sub>O, salts); 2-ethylglyoxaline-4:5-dicarboxylic acid + H<sub>2</sub>O (potassium hydrogen, m. p. 265°, and sodium hydrogen + 3H<sub>2</sub>O salts); 2-n-propylglyoxaline-4:5-dicarboxylic acid [potassium hydrogen + 1.5H<sub>2</sub>O, m. p. 263° (decomp.), and sodium hydrogen + 1.5H<sub>2</sub>O, m. p. above 300°, salts]; 2-isopropylglyoxaline-4:5-dicarboxylic acid + H<sub>2</sub>O (potassium hydrogen + 3H<sub>2</sub>O, m. p. 271°, and sodium hydrogen + 1.5H<sub>2</sub>O, m. p. above 300°, salts); 2-isobutyl-, and 2-n-hexyl-glyoxaline-4:5-dicarboxylic acids. The solubilities of the above acids in water at 12—18° increases with ascent of the homologous series, whilst the molecular conductivities of the sodium salts decrease slightly. Titration curves of 2-isopropylglyoxaline-4:5-dicarboxylic acid, sodium hydrogen glyoxaline-4:5-dicarboxylate, and sodium 2-methylglyoxaline-4:5-dicarboxylate, with 0.005N-, 0.005N-, and 0.1N-sodium hydroxide solutions, respectively, show the existence of a small third constant in addition to first and second dissociation constants. The conception that one carboxyl group in these acids is neutralised by nitrogen is thus regarded as erroneous. H. BURTON.

**Curtius rearrangement of carbamyl azides. Formation of benzpyrazolones and bimolecular carbonylhydrazines.** III. R. STOLLÉ [with M. MERKLE] (J. pr. Chem., 1928, [ii], 119, 275—278).—The products of decomposition of benzaldehyde-phenylhydrazone-N-carbonyl azide (I) and of the o-chlorobenzaldehyde analogue (II) (cf. Stollé, A., 1927, 1203) are not now regarded as benzpyrazolones, since the benzylidene residue cannot be removed. The product from (I) is now identified as 5-hydroxy-1:3-diphenyl-1:2:4-triazole (cf. Wheeler and Statropoulos, A., 1905, i, 721; Backer and Mulder, A., 1926, 182). The product from (II) is, however, regarded as 4-hydroxy-2-phenyl-5-o-chlorophenyl-1:2:3-triazole, since the action of alcoholic anhydrous ferric chloride on 2-phenyl-1-o-chlorobenzylidenesemicarbazide, C<sub>6</sub>H<sub>4</sub>Cl·CH:N·NPh·CO·NH<sub>2</sub>, m. p. 181° (obtained by treating o-chlorobenzaldehyde-phenylhydrazone-N-carboxyl chloride with aqueous ammonia), gives rise to 5-hydroxy-1-phenyl-3-o-chlorophenyl-1:2:4-triazole, m. p. 188°, different from the above-described substance. E. W. WIGNALL.

**Condensation of o-aminobenzaldehyde with 1-phenyl-3-methyl-5-pyrazolone and with 1-o-chlorophenyl-3-methyl-5-pyrazolone.** A. MUSIEROWSKI, S. NIEMENTOWSKI, and Z. TOMASIK (Rocz. Chem., 1928, 8, 325—344).—Fusion in equimolecular quantities at 140° of o-aminobenzaldehyde with 1-phenyl-3-methyl-5-pyrazolone produces the phenylhydrazone of 2-hydroxy-3-quinolyl methyl ketone, m. p. 236°, which when heated with benzaldehyde yields 2-hydroxy-3-quinolyl styryl ketone, m. p. 269°. Among the products of the original



condensation (carried out at 265°) is 4-hydroxy-1-phenyl-3-methylquinpyrazole (I), m. p. 273° (hydrochloride, m. p. 273°; methiodide, m. p. 273°), together with 2'-hydroxy-2:3'-diquinolyl, m. p. 313° [nitrate, m. p. 325°; sulphate, m. p. 299°; hydrochloride, m. p. 256° (decomp.); methiodide, m. p. 295°]. Fusion at 150° with 1-o-chlorophenyl-3-methyl-5-pyrazolone yields the o-chlorophenylhydrazone of 2:4-dihydroxy-3:4-dihydro-3-quinolyl methyl ketone, m. p. 184°, the o-chlorophenylhydrazone of 2-hydroxy-3-quinolyl methyl ketone, m. p. 280° (hydrochloride, m. p. 280°; O-acetyl derivative, m. p. 262°; N-acetyl derivative, m. p. 236°; monobromide, m. p. 230°; dibromide, m. p. 208°), and 4-hydroxy-1-o-chlorophenyl-3-methylquinpyrazole, m. p. 281°.

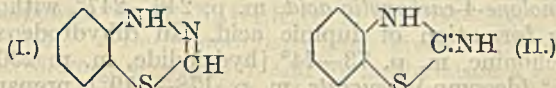
R. TRUSZKOWSKI.

**Action of hydrazides. II. Synthesis of bis-triazoles from thiocarbo- and carbo-hydrazides.** S. C. DE (J. Indian Chem. Soc., 1928, 5, 373—378).—2-Bromophenanthraquinone and thiocarbohydrazide hydrochloride react in presence of acetic acid, yielding bis-(2-bromophenanthraquinone)thiocarbohydrazone, m. p. 236°, whilst the monoxime of the diketone affords under similar conditions 2:2'-dibromo-10:10'-bis-10:9:11-phenanthratiazolyl thioketone (annexed formula), m. p. 145°. The following di-(substituted phenanthraquinone)thiocarbohydrazones are described: 2:7-dibromo-, m. p. 260°; 2-nitro-, m. p. 220°; 4-nitro-, m. p. 155°; 4:5-dibromo-, m. p. 270° after blackening at 260°; 4:5-dinitro-, m. p. 162°, and 2:7-dinitro-, m. p. above 300°. The corresponding carbohydrazones are prepared similarly and the following are described: diphenanthraquinone, m. p. 285°; di-2-bromo-, m. p. 275°; di-2-nitro-, m. p. 280°; di-4-nitro-, m. p. 240°; di-2:7-dibromo-, m. p. 295°; di-2:7-dinitro-, m. p. above 300°; di-2:5-dinitro-, m. p. 295°, and di-4:5-dibromo-phenanthraquinone, m. p. above 300°. From the requisite phenanthraquinone monoximes the following 10:10'-bis-10:9:11-phenanthratiazolyl thioketones were obtained: 2:7-dibromo-, m. p. 210°; 2-nitro-, m. p. 200°; 4:5-dibromo-, m. p. 235°; 4:5-dinitro-, m. p. 160°, and 2:7-dinitro-, blackens at 250° and does not melt at 295°. Substituted 10:10'-bis-10:9:11-phenanthratiazolyl ketones are obtained similarly and the following are described: 2-bromo-, m. p. 245°; 2-nitro-, m. p. 192°; 4-nitro-, m. p. 200°; 2:7-dibromo-, m. p. 210°; 2:7-dinitro-, m. p. 230°; 4:5-dinitro-, m. p. 160°, and 4:11(5?)-

dibromo-, m. p. 273°. 10:10'-Bisphenanthratiazolyl ketone has m. p. 272°. The colours of the sulphur derivatives are red, whilst the oxygen-containing compounds are mostly yellow. H. BURTON.

**Bromoporphyrin I and tetramethylhæmatoporphyrin iron salt.** (Addendum.) H. FISCHER and G. HUMMEL (Z. physiol. Chem., 1928, 177, 321; cf. this vol., 659).—Bromoporphyrin I and dibromodeuteroporphyrin ester are identical. H. BURTON.

**Silver and mercury salts of 1-aminobenzthiazole.** F. FEIGL and A. DEUTSCH (Monatsh., 1928, 49, 413—416).—The compound  $C_7H_6N_2S$  obtained by Fischer and Besthorn (A., 1882, 1094) by heating phenylthiosemicarbazide with hydrochloric acid and later by Hugershoff (A., 1903, i, 865) by the action of bromine on phenylthiocarbamide was regarded by Harries and Löwenstein (A., 1894, i, 305) as (I) and by Hugershoff as (II). In addition to the known



compound,  $C_7H_5N_2SAg$ , the compounds  $C_7H_4N_2S_2Ag_2$  and  $C_7H_4N_2SHg$ , corresponding with (II) but not with (I), have been obtained. The following compounds are also described:  $C_7H_6N_2S_2HgCl_2$ ;  $C_7H_5N_2S_2HgCl$ ; and  $C_7H_5N_2S_2Hg_2O(NO_3)$ . No metals other than silver and mercury form insoluble precipitates with the aminobenzthiazole, a fact which may be made use of for the detection and determination of these two metals.

The aminobenzthiazole, acting as a base, forms the periodide,  $C_7H_6N_2HI_2$ , its tautomerism thus being established. R. A. PRATT.

**Manufacture of carbazolequinones.** I. G. FARBENFND. A.-G.—See B., 1928, 635.

**Oxidation. I. Action of ferric chloride and hydrogen peroxide on thiosemicarbazones. Synthesis of thiodiazoles and triazoles.** S. C. DE and S. K. ROY-CHOUDHURY (J. Indian Chem. Soc., 1928, 5, 269—278).—When benzaldehyde thiosemicarbazone is oxidised with ferric chloride the sole product is 2-amino-5-phenyl-1:3:4-thiodiazole (cf. Young and Eyre, J.C.S., 1901, 79, 54), but if hydrogen peroxide is used the product is 5-phenyl-1:3:4-triazole, m. p. 177°, thus demonstrating that thiosemicarbazones can react in either the *syn*- or *anti*-modifications. With ferric chloride as the oxidising agent the following substituted 1:3:4-thiodiazoles have been prepared: 2-amino-5-styryl-, m. p. 260—261°, from cinnamaldehyde thiosemicarbazone; 2-anilino-5-o-hydroxyphenyl-, m. p. 190—191°, from salicylaldehyde 4-phenylthiosemicarbazone; 2-anilino-5-m-nitrophenyl-, m. p. 249—250° (acetyl derivative, m. p. 246°); 5(2?)-p-toluidino-2(5?)-phenyl-, m. p. 198—199° (acetyl derivative, m. p. 155°), from benzaldehyde 4-p-tolylthiosemicarbazone; 2-p-toluidino-5-p-nitrophenyl-, m. p. 197—198° (acetyl derivative, m. p. 243°); 2-p-toluidino-5-styryl-, m. p. 184°; 2-allylamino-5-phenyl-, m. p. 114—115° (acetyl derivative, m. p. 120°), from benzaldehyde 4-allylthiosemicarbazone; 2-allylamino-5-m-nitrophenyl-, m. p. 170—171°; 2-m-toluidino-5-p-nitrophenyl-, m. p. 257°;

2-m-toluidino-5-phenyl-, m. p. 176°; 2-o-toluidino-5-m-nitrophenyl-, m. p. 247°; 2-methylamino-5-m-nitrophenyl-, m. p. 201° (acetyl derivative, m. p. 225—226°; methyl derivative, m. p. 209°), from m-nitrobenzaldehyde 4-methylthiosemicarbazone; 2-methylamino-5-p-nitrophenyl-, m. p. 262° (acetyl derivative, m. p. 279°; methyl derivative, m. p. 203°); 2-m-xylyldino-5-o-nitrophenyl-, m. p. 229°; 2-m-xylyldino-5-m-nitrophenyl-, m. p. 205° (acetyl derivative, m. p. 197—198°); 2-β-naphthylamino-5-o-nitrophenyl-, m. p. 202°, and 2-ethylamino-5-phenyl-, m. p. 238—240°.

Oxidation of thiosemicarbazones with hydrogen peroxide gives either a disulphide derived by oxidation of a thioltriazole (cf. Young and Eyre, *loc. cit.*), or a sulphur-free triazole, probably formed through further oxidation of the disulphide. The following 1:3:4-triazole 2-disulphides are described: 5-o-nitrophenyl-1-m-xylyl-, m. p. 201—203°; 5-phenyl-1-allyl-, m. p. 90°; 5-phenyl-1-p-tolyl-, m. p. 155—156°; 5-phenyl-1-ethyl-, m. p. 88°; 1:5-diphenyl-, m. p. 232° (decomp.), and 5-m-nitrophenyl-1-allyl-, m. p. 173°. 5-m-Nitrophenyl-1-allyl-1:3:4-triazole has m. p. 194—195°.

Oxidation of acetone thiosemicarbazone with hydrogen peroxide gives 2:5-diisopropylidenehydrazino-1:3:4-thiodiazole, m. p. 260° (decomp.), hydrolysed by hot concentrated hydrochloric acid to hydrazine hydrochloride. Similarly, acetone 4-phenyl- and 4-p-tolyl-thiosemicarbazones yield the diisopropylidene derivatives of 2:5-diketo-3:4-diphenyl- and 2:5-diketo-3:4-di-p-tolyl-1:3:4-thiodiazole-dihydrazones, having m. p. 168° (decomp.) and 124°, respectively. H. BURTON.

**Synthetic homologues of dl-ephedrine.** J. F. HYDE, E. BROWNING, and R. ADAMS (J. Amer. Chem. Soc., 1928, 50, 2287—2292).—A series of compounds of the type OH·CHPh·CHR·NHR' was prepared by the method used by Eberhard (A., 1915, i, 834; cf. Fourneau and Kanao, A., 1924, i, 978) for the synthesis of dl-ephedrine (R and R' = Me), viz., the condensation of alkylamines with phenyl α-bromoalkyl ketones. The amino-ketone hydrochlorides COPh·CHR·NHMe, HCl were best purified by extraction from the excess of alkylamine hydrochloride by chloroform. In other cases the amine was removed from the basified mixture by distillation. The dl-amino-alcohol was obtained by reduction with hydrogen and platinum oxide-platinum-black. The following compounds are described: α-bromo-n-valerophenone, b. p. 150°/2.5 mm.,  $d_4^{20}$  1.3993,  $n_D^{20}$  1.5600; hydrochlorides of ω-methylaminoacetophenone, m. p. 219°, and α-methylaminopropiophenone, m. p. 176—177°; hydrochlorides of α-methylamino-n-butylphenone, m. p. 190—192°; α-methylamino-n-valerophenone, m. p. 183.5—184.5°; ω-n-butylaminoacetophenone, m. p. 214—215°; α-n-butylamino-n-butylphenone, m. p. 138—140°; hydrochlorides of substituted propiophenones: α-ethylamino-, m. p. 183°; α-propylamino-, m. p. 180°; α-isopropylamino-, m. p. 213—213.5° (base, b. p. 105—110°/3 mm.); α-n-butylamino-, m. p. 158—159° (base, b. p. 140—142°/8 mm.); α-dimethylamino-, m. p. 167—168°; the following hydrochlorides of α-phenyl-substituted alcohols: -β-methylaminoethyl, m. p. 105—106°

(base, m. p. 75—76°);  $\beta$ -methylaminopropyl, m. p. 189—190° (base, m. p. 76—77°);  $\beta$ -methylamino-*n*-butyl, m. p. 201—202° (base, m. p. 89—90°);  $\beta$ -methylamino-*n*-amyl, m. p. 224—225° (base, m. p. 76—77°);  $\beta$ -*n*-butylaminoethyl, m. p. 218—220° (base, m. p. 58—59°);  $\beta$ -*di-n*-butylamino-*n*-butyl, m. p. 114—116°;  $\beta$ -ethylaminoethyl, m. p. 190—191°;  $\beta$ -propylaminoethyl, m. p. 218°;  $\beta$ -isopropylaminoethyl, m. p. 193°;  $\beta$ -*n*-butylaminoethyl, m. p. 220—221°;  $\beta$ -*n*-amylaminoethyl, m. p. 219°;  $\beta$ -*diethylaminopropyl*, m. p. 205—206°.

The blood-sugar level on injection of both ketones and alcohols increased as the *N*-alkyl group was made larger, and decreased as the alkyl group on the  $\beta$ -carbon atom was increased in size. The dialkylamino-compounds produced no physiological action.  $\alpha$ -Phenyl- $\beta$ -methylaminoethyl alcohol alone gave a dependable increase in blood pressure.

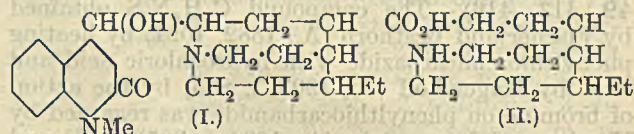
R. K. CALLOW.

**Alkaloids of lupins.** C. SCHOPF (Annalen, 1928, 465, 97—147). I. **Isomeric lupinic esters and lupinans.** [With O. THOMA.]—Lupinic acid,  $(C_8H_{15}N):CH \cdot CO_2H$ , gives two series of derivatives, (–) and (+)-*epi*-, according to the configuration of the terminal  $:CH \cdot CO_2H$  group; the  $C_8H_{15}N$  residue, which contains at least one asymmetric atom, remains the same in both series. Lupinic acid, obtained by chromic acid oxidation of lupinine,  $(C_8H_{15}N):CH \cdot CH_2 \cdot OH$  (Willstätter and Fournau, A., 1902, i, 557), is isolated as the *methyl ester*, b. p. 120—122°/10 mm.,  $[\alpha]_D^{20} -19.4^\circ$  to  $+5.8^\circ$  in different preparations. The (–)-*ester* gives a soluble, resinous *picrate*,  $[\alpha]_D^{20} -41.8^\circ$ , but the more (+)-preparations yield an insoluble *picrate*, m. p. 185°,  $[\alpha]_D^{20} +61.8^\circ$ , from which the pure (+)-*epi-ester*, b. p. 126°/11 mm.,  $[\alpha]_D^{20} +54.8^\circ$ , is obtained. Corresponding with the two methyl esters are the crystalline (–)-lupinic acid hydrochloride, m. p. 275°, of Willstätter and Fournau (*loc. cit.*), and a non-crystalline (+)-*epimeride*. The (–)-*ester* is converted by a little sodium methoxide into the (+)-*epi-ester*; it is not attacked by methylalcoholic ammonia at 100°, but at 140° undergoes isomerisation to the (+)-*epi-ester*, followed by racemisation to an inactive ( $\pm$ )-*epi-ester*, b. p. 128—130°/11 mm. (*picrate*, m. p. 208°), which is more readily obtained in a similar manner from the (+)-*epi-ester*. By the action of phosphorus pentachloride in benzoyl chloride suspension (–)-lupinic acid hydrochloride is converted into an *acid chloride* (not isolated), from which by treatment with methyl alcohol the (+)-*epi-methyl ester* is obtained. The acid chloride reacts with ammonia to give, in small yield, the (+)-*epi-amide*, m. p. 228°, subliming at 250° (bath temperature)/11 mm.,  $[\alpha]_D^{20} +41.3^\circ$ , together with the (+)-*epi-nitrile*, b. p. 120°/11 mm. (*hydrochloride*,  $[\alpha]_D^{20} +52.9^\circ$ ).

The only definite oxidation product obtainable from Willstätter and Fournau's anhydrolupinine,  $(C_8H_{15}N):C:CH_2$  (*picrate*, m. p. 94°), is the *glycol*, b. p. 165—167°/11 mm., but reduction with hydrogen and palladium yields two epimeric *lupinans*, b. p. 75—77°/11 mm. (*picrates*  $\alpha$ -, m. p. 187°;  $\beta$ -, m. p. 163°; cf. G.P. 396,508, A., 1925, i, 294), together with a trace of a lupinine, b. p. 110°/11 mm., which, since it gives a crystalline *picrate*, m. p. 163°,

is probably an isomerised or a racemised compound.

II. **Possible relations between lupinine and the cinchona alkaloids.** [With E. SCHMIDT.]—Attempts to correlate the  $(C_8H_{15}N):CH \cdot$  residue of lupinic acid with the quinuclidine residue of the hydrogenated cinchona alkaloids are unsuccessful. Dihydrocinchonine methiodide hydriodide (von Arlt, A., 1899, i, 962), m. p. 242—243°, is oxidised quantitatively by alkaline ferricyanide to a *quinolone* (I), m. p. 213—214° (hydrochloride, m. p. 301°), which is further oxidised by chromic acid to cincholoipone



(methyl ester, b. p. 122—124°/12 mm.) and 1-*methylquinolone-4-carboxylic acid*, m. p. 246—247°, without any formation of lupinic acid. In dihydrodeoxy-cinchonine, m. p. 73—74° [hydriodide, m. p. 230—231° (decomp.); *picrate*, m. p. 178—179°], prepared by reduction of deoxycinchonine or of cinchen, the secondary alcohol group is absent; it gives an amorphous *methiodide hydriodide (dipicrate)*, m. p. 170—171° which reacts with sodium hydroxide to form an unstable *oil* (probably a methylenedihydroquinoline), from which by oxidation with permanganate in acetone only 1-methyl-4-quinolone, m. p. 142—143° (*picrate*, m. p. 229°), is obtained, the quinuclidine residue being lost. An attempt to cyclise the  $\alpha$ -bromo-derivative of homocincholoipone (II) was unsuccessful, and no  $\beta$ -ethylquinuclidine could be obtained by decarboxylation of lupinic acid.

By the action of magnesium phenyl bromide on a methyl lupinate of  $[\alpha]_D^{20} -7.4^\circ$  there are obtained an oily *ketone*,  $(C_8H_{15}N):CH \cdot C(=O)Ph$ , b. p. 126—218°/1 mm. (*picrate*, m. p. 185°,  $[\alpha]_D^{20} +38.5^\circ$ ; *methiodide*, amorphous), and a *carbinol*,  $(C_8H_{15}N):CH \cdot CPh_2 \cdot OH$ , m. p. 170—171°,  $[\alpha]_D^{20} +79.2^\circ$  (*hydrobromide*, m. p. 205°), both belonging to the (+)-*epi-series*. The ketone shows no analogies with dihydrocinchonine; it gives no oxime, and is oxidised with great difficulty with production of benzoic and acetic acids but no cincholoipone. The carbinol is even more resistant to oxidation. A quinuclidine structure for lupinine is therefore improbable. It is suggested that lupinine  $(C_{10})$ , sparteine  $(C_{15})$ , lupanine  $(C_{15})$ , oxylupanine  $(C_{15})$ , sarothamnine  $(C_{15})$ , spathulatine  $(C_{15} + Me)$ , are built up from two, or three, isoprene molecules and ammonia [cf. galegine,  $CMe_2 \cdot CH \cdot CH_2 \cdot NH \cdot C(NH) \cdot NH_2$  (Barger and White, A., 1924, i, 272; Späth and others, A., 1924, i, 502; 1926, 81)].

III. **Sparteine.** [With W. BRAUN.]—The further oxidation of oxysparteine (Ahrens, A., 1905, i, 917; Willstätter and Marx, *ibid.*, 544) throws no light on the constitution of sparteine. The exhaustive methylation of sparteine is investigated. The only product of the prolonged action of cold hydrogen peroxide on oxysparteine, m. p. 87° (*picrate*, m. p. 183°), is the *N-oxide*, m. p. about 220° (decomp.) [*picrate*, m. p. 221° (decomp.)]. Hot peroxide gives acid products (W. Braun, Diss., München, 1928), which, however,



contain no lupinic acid. Sparteine  $\alpha$ -methiodide, m. p. 234°,  $[\alpha]_D^{18}$   $-48.5^\circ$ , is converted by Hofmann degradation under special conditions into  $\alpha$ -de-*N*-methylsparteine, b. p. 173.5—174°/10 mm.,  $[\alpha]_D^{21}$   $-47.6^\circ$  (cf. Moureu and Valeur, A., 1912, i, 210, 296), which is isolated as mercurichloride, m. p. 270—271°, together with two new bases,  $C_{16}H_{28}N_2$ , b. p. 160—161°/10 mm.,  $[\alpha]_D^{18}$   $-21.3^\circ$  [dihydriodide, m. p. 223—225° (decomp.),  $[\alpha]_D^{18}$   $-37.5^\circ$ ; mercurichloride, m. p. 182—185° (decomp.)], and  $C_{16}H_{30}ON_2$ , b. p. 183—189°/10 mm.,  $[\alpha]_D^{18}$   $+16.0^\circ$  [mercurichloride, m. p. 154—156° (decomp.)].  $\alpha$ -De-*N*-methylsparteine dihydriodide, m. p. 236—237°,  $[\alpha]_D^{18}$   $-37.6^\circ$ , is isomerised by water at 130—135° or by boiling alcohol, giving a compound (probably a quaternary salt),  $C_{16}H_{28}N_2 \cdot 3HI$ , m. p. 206—207°,  $[\alpha]_D^{18}$   $+19.5^\circ$ , which with alkali yields the dihydriodide, m. p. 182—184°,  $[\alpha]_D^{18}$   $+41.7^\circ$ ; no corresponding base is obtained, but the mother-liquors from the trihydriodide contain a compound,  $C_{16}H_{28}N_2 \cdot HI \cdot H_2O$ , m. p. 206—208°,  $[\alpha]_D^{18}$   $-13.3^\circ$ .  $\alpha$ -De-*N*-methylsparteine gives a dibromide (perchlorate, m. p. 267°), and by methylation a monomethiodide, m. p. 135° (+ $H_2O$ ) or 239° (anhyd.), and a dimethiodide, m. p. 266° (decomp.), together with a product, m. p. 75°. It is reduced by hydrogen and platinum oxide to a dihydro-derivative, m. p. 64° (dihydriodide, m. p. 267—268°), and is oxidised by permanganate to a glycol, m. p. 200°. C. HOLLINS.

**Histamine derivatives.** P. VAN DER MERWE (Z. physiol. Chem., 1928, 177, 301—314).—When  $\alpha\beta$ -tribenzamido- $\Delta^2$ -butylene is heated with acetic anhydride for 14 hrs. at 145° and a further 2 hrs. at 160°, excess of the anhydride removed by evaporation in a vacuum, and the residual oil heated with concentrated hydrochloric acid at 160°, there is obtained 2-methylhistamine [dipicrate, m. p. 237°, or (+ $2H_2O$ ) m. p. 208°; dihydrochloride, m. p. 217°]. Using propionic, benzoic, and phenylacetic anhydrides, 2-ethylhistamine (dipicrate, m. p. 219°; dihydrochloride, m. p. 209°); 2-phenylhistamine (dipicrate, m. p. 230°; dihydrochloride, decomp. gradually above 240°), and 2-benzylhistamine (dipicrate, m. p. 195°; dihydrochloride, decomp. 245°), respectively, are obtained. The following substituted histamines are described: *N*-acetyl-, m. p. 143°; *N*-isobutyl-, m. p. 123°; carbamido-, m. p. 148° (picrate, m. p. 150°; oxalate, m. p. 153°), from histamine hydrochloride and potassium cyanamide; phenylcarbamido-, m. p. 178°;  $\alpha$ -naphthylcarbamido-, m. p. 193°, and the corresponding guanidino-derivative [dipicrate, m. p. 245° (decomp.); dihydrochloride, m. p. 208° (decomp.)], from histamine and cyanamide or from histamine hydrochloride and silver cyanamide.

Anisylidenehistamine, m. p. 186° (dipicrate, m. p. 222°), is reduced by sodium and amyl alcohol to *N*-*p*-methoxybenzylhistamine (dipicrate, m. p. 213°). When the dihydrochloride of this base is treated with benzoyl chloride and sodium hydroxide the glyoxaline ring undergoes fission and  $\delta$ -*N*-*p*-methoxybenzyl- $\alpha\beta$ -tribenzamido- $\Delta^2$ -butylene, m. p. 205°, is obtained. Piperonylidenehistamine, m. p. 180° (dipicrate, m. p. 217°), is reduced to *N*-3:4-methylenedioxybenzylhistamine (dipicrate, m. p. 195°; dihydrochloride, decomp. 245°). When a mixture of histamine and  $\epsilon$ -chloroamylbenz-

amide is heated on the water-bath for 1.5 hrs. and an alcoholic solution of the reaction product treated with hydrogen chloride at 0° for 24 hrs. and the residue from this heated with concentrated hydrochloric acid at 160° *N*- $\epsilon$ -aminoamylhistamine (tetrapicrate, m. p. 215°; tripicrate, m. p. 169°) is produced.

H. BURTON.

Synthetical experiments on the aporphine alkaloids. IV. Synthesis of morphothebaine dimethyl ether. J. M. GULLAND and R. D. HAWORTH (J.C.S., 1928, 2083—2088).—2'-Nitro-3':4'-dimethoxyphenylaceto- $\beta$ -3-methoxyphenylethylamide, m. p. 107—108° (from 2-nitro-3:4-dimethoxyphenylacetyl chloride and 3-methoxy- $\beta$ -phenylethylamine), gave, on interaction with phosphorus pentachloride, 2'-nitro-6:3':4'-trimethoxy-1-benzyl-3:4-dihydroisoquinoline, m. p. 121—123° [hydrochloride, m. p. 217—218° (decomp.); sulphate, m. p. 237° (decomp.); methiodide, m. p. 220° (decomp.)]; the methiodide gave under conditions for alkaline fission only 2'-nitro-6:3':4'-trimethoxy-1-benzylidene-2-methyltetrahydroisoquinoline, m. p. 108—109°, and small quantities of 2'-nitro-6:3':4'-trimethoxy-1-benzoyl-3:4-dihydroisoquinoline, m. p. 164° (decomp.) (oxime), formed by atmospheric oxidation of the previous compound.

The above methiodide was reduced by zinc dust and hydrochloric acid to 2'-amino-6:3':4'-trimethoxy-1-benzyl-2-methyltetrahydroisoquinoline (dihydrochloride +  $1CHCl_3$ , has m. p. 155°, softening at 135°), which was converted by diazotisation and heating into dl-3:4:6-trimethoxyaporphine, an oil [hydrochloride, m. p. 227° (decomp.)]. Resolution of this base with *d*-tartaric acid gave a *d*-tartrate identical with *l*-morphothebaine dimethyl ether hydrogen *d*-tartrate, m. p. 208—209° (decomp.) (Klee, A., 1914, i, 1086, gives 205°). Similarly, the *l*-base, an oil,  $[\alpha]_D$   $-173.5^\circ$ , was identical with natural morphothebaine dimethyl ether,  $[\alpha]_D$   $-172.7^\circ$  (lit.  $-184.8^\circ$ ) (methiodides, both m. p. 195° with softening at 190°,  $[\alpha]_D$   $-87.1^\circ$ ,  $-88.2^\circ$ , respectively).

*d*-Morphothebaine dimethyl ether hydrogen *l*-tartrate, m. p. 208—209° (decomp.),  $[\alpha]_D$   $+75.5^\circ$ , gave the *d*-base,  $[\alpha]_D$   $+174.2^\circ$ . R. J. W. LE FEVRE.

**Colour reactions of atropine and some related compounds.** L. EKKERT (Pharm. Zentr., 1928, 69, 529—531).—The colorations obtained by addition of the commoner phenols in presence of sulphuric acid are described. S. I. LEVY.

**Determination of morphine.** L. DAVID (Ber. ungar. pharm. Ges., 1926, 2, 103—111; Chem. Zentr., 1928, i, 1560).—Debourdeaux' method, which is preferred, has a constant error of  $-1.5\%$ . Other methods give too low results. A. A. ELDRIDGE.

**Determination of morphine with barium hydroxide.** G. P. SCHOLTZ (Ber. ungar. pharm. Ges., 1927, 3, 435—437; Chem. Zentr., 1928, i, 1560).—In Debourdeaux' method calcium hydroxide is preferably replaced by barium hydroxide, the barium being removed with ammonium oxalate or sulphate.

A. A. ELDRIDGE.

**Sensitive modification of colour reaction for quinine.** H. W. VAN URK (Pharm. Weekblad, 1928, 65, 847—849).—The green colour is developed with

much more certainty, and is more stable, if the oxidation is carried out with sodium hypochlorite instead of with chlorine or bromine water. With this modification, the test will detect 1 part of quinine in 40,000 parts. S. I. LEVY.

**Thalleioquinine reaction of quinine salts.** G. MUKÓ (Ber. ungar. pharm. Ges., 1927, 3, 205—207; Chem. Zentr., 1928, i, 1559—1560).—The quinine salt (0.5—1 g.) is preferably boiled with 5*N*-hydrochloric acid (5 drops) and 3% hydrogen peroxide solution (3 drops) until a yellow coloration is obtained; the mixture is then diluted with water and 1 c.c. of 5*N*-ammonia solution is added, a green coloration appearing at the interface. A. A. ELDRIDGE.

**Isomerism of *p*-hydroxyphenylarsinic acid.** G. GILTA (Bull. Soc. chim. Belg., 1928, 37, 253—262; cf. this vol., 189).—The two isomeric forms of *p*-hydroxyphenylarsinic acid are described: (I), pinkish monoclinic crystals, *a*:*b*:*c*=0.4483:1:0.4936, obtained by diazotising *p*-arsanilic acid, and (II), yellowish monoclinic crystals, *a*:*b*:*c*=2.465:1:0.7968, obtained by fusion of phenol with arsenic acid. Spontaneous conversion of (II) into (I) proceeds slowly in aqueous solution, more quickly on boiling and seeding with a crystal of (I). The sodium and barium salts derived from (II), however, are more stable than the corresponding isomeric salts derived from (I). B. W. ANDERSON.

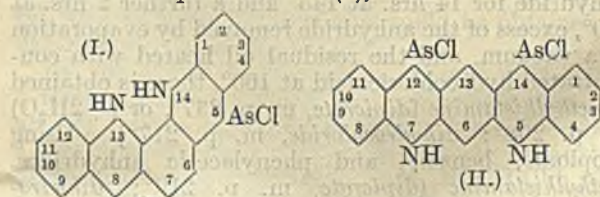
**Condensation of 4-chloro-3-nitrophenylarsinic acid with amines, in particular ethylenediamine and piperazine. Reduction of the nitro-derivatives to amines.** E. FOURNEAU and A. FUNKE (Bull. Soc. chim., 1928, [iv], 43, 889—895).—When 4-chloro-3-nitrophenylarsinic acid is heated with ethylenediamine at 135—140° in presence of anhydrous sodium acetate, 3-nitro-4-β-aminoethylaminophenylarsinic acid is obtained. When condensation is effected using an aqueous solution of the diamine the product is *NN'*-di-*o*-nitrophenylethylenediamine-4:4'-diarsinic acid, [AsO<sub>3</sub>H<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)·NH·CH<sub>2</sub>]<sub>2</sub>, reducible by ferrous hydroxide to the corresponding amino-acid. Reduction of 3-nitro-4-β-acetamidoethylaminophenylarsinic acid with ferrous hydroxide below 50° affords the corresponding 3-amino-acid, which has C/T=1/6. Piperazine reacts with 4-chloro-3-nitrophenylarsinic acid in presence of sodium hydroxide, yielding 3-nitro-4-piperazinophenylarsinic acid (acetyl derivative); when condensation is effected with piperazine hydrate at 110° in presence of sodium acetate the product is 1:4-di-*o*-nitrophenylpiperazine-*pp*-diarsinic acid, [AsO<sub>3</sub>H<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)·N·(CH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>. 3-Amino-4-acetyl-piperazino-, 3-nitro-4-*p*-carbethoxyphenylamino-, and 3-amino-4-*p*-carboxyphenylaminophenylarsinic acids are described. The majority of the above amino-acids have no trypanocidal action. H. BURTON.

**Arsenical quinoline derivatives.** S. BERLINGOZZI (Annali Chim. Appl., 1928, 18, 333—336; cf. A., 1927, 675; this vol., 434).—When coupled with various aminoquinolines, the diazo-derivative of arsenilic acid yields the following compounds: 3-amino-2-methylquinoline-4-azo-*p*-phenylarsinic acid, decomp. 150—152°; 3-amino-2-phenylquinoline-4-azo-*p*-phenylarsinic acid, decomp. about 100°; 3-amino-2-

*p*-methoxyphenylquinoline-4-azo-*p*-phenylarsinic acid, decomp. about 145°; 8-aminoquinoline-5-azo-*p*-phenylarsinic acid, not appreciably altered below 250°; 5-aminoquinoline-8-azo-*p*-phenylarsinic acid, not appreciably altered below 250°. T. H. POPE.

**Manufacture of organo-arsenic compounds.** R. W. E. STICKINGS, and MAY & BAKER.—See B., 1928, 691.

**10-Chloro-5:10-dihydrophenarsazine and its derivatives.** VI. Compounds containing two nitrogen and two arsenic atoms in six- and five-membered systems. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 2204—2215).—Condensation of benzidine with *o*-bromophenylarsinic acid gave 4:4-bis(diphenylamine-2-arsinic acid), readily converted into 2:2'-bis-(10-chloro-5:10-dihydrophenarsazine), also formed from *NN'*-diphenylbenzidine and arsenious chloride. Oxidation of the above chloro-compound gave 2:2'-bis(phenarsazinic acid) (disodium salt), from which was obtained 2:2'-bis-(10-bromo-5:10-dihydrophenarsazine). *NN'*-Di-*p*-tolylbenzidine similarly led to 2:2'-bis-(10-chloro-8-methyl-5:10-dihydrophenarsazine), 2:2'-bis-(8-methylphenarsazinic acid) (disodium salt), and 2:2'-bis-(10-bromo- and 10-iodo-8-methyl-5:10-dihydrophenarsazines). *o*-, *m*-, and *p*-Phenylenediamines and *o*-bromophenylarsinic acid gave 1:2-, 1:3-, and 1:4-phenylenediaminodi-*o*-phenylarsinic acid, respectively, the last two only being obtained pure. The 1:2-compound was reduced in presence of hydrochloric acid to 5:8-dichloro-13:14:5:8-tetrahydroisobenzarsazinephenarsazine (I), whilst the 1:3-com-



compound under similar conditions gave a yellow compound, either 12:14-dichloro-5:7:12:14- or 8:14-dichloro-5:13:8:14-tetrahydrobenzarsazinephenarsazine (II) or (III), which differed from the red condensation product from *NN'*-diphenyl-*m*-phenylenediamine (1 mol.) and arsenious chloride (2 mols.). Both apparently yielded the same diarsinic acid (5:7:12:14- or 5:13:8:14-benzarsazinicphenarsazinic acid; disodium salt) on oxidation and the same dibromo- and di-iodo-compounds on reduction in presence of the required halogen acid.

*NN'*-Diphenyl-*p*-phenylenediamine condensed with arsenious chloride, giving 7:14-dichloro-5:12:7:14- (or 13:14-dichloro-5:8:13:14-)tetrahydrobenzarsazinephenarsazine, converted by oxidation into 5:12:7:14- (or 5:8:13:14-)benzarsazinicphenarsazinic acid, m. p. above 320°, darkening at 290° (disodium salt), from which the analogous dichloro- and dibromo-compounds were obtained by reduction.

All italicised compounds had m. p. above 320°.

R. J. W. LE FÈVRE.

**Quadrivalency of selenium. I. 4-Carboxydiphenyl and *p*-carboxyphenyl methyl selenoxides.**

**II. Simple halogen derivatives and dihydroxide of 4-acetamidodiphenyl selenide.** W. R. GAYTHWAITE, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 2280—2287, 2287—2293).—I. *Phenyl p-tolyl selenide* (I), b. p. 175—178°/20 mm., obtained by the interaction of selenium with phenyl *p*-tolyl sulphone, m. p. 127—128° (lit. 124.5°), yields a *dibromide*, m. p. 149—150°. Oxidation of (I) with potassium permanganate or trituration of its dibromide with sodium hydroxide solution yields *phenyl p-tolyl selenoxide* (II), m. p. 131—133°. Oxidation of (I) with excess of potassium permanganate gives *4-carboxydiphenyl selenoxide* (III), m. p. 253—255° (decomp.) [*brucine* salt, m. p. 130° (decomp.); *strychnine* salt; *1-menthylamine* salt, m. p. 220—222° (decomp.); *d- $\alpha$ -phenylethylamine* salt, m. p. 194—195° (decomp.)], in addition to (II). Reduction of (III) with zinc dust and acetic acid gives *4-carboxydiphenyl selenide*, m. p. 182—184° (*dibromide*, m. p. 208—210°). 4 : 4'-*Dicarboxydiphenyl diselenide* (IV), m. p. 297°, is obtained by treatment of the diazole solution from *p*-aminobenzoic acid with potassium selenocyanate and subsequent treatment of the mixed precipitate of *p*-carboxyphenyl selenocyanate and (IV) thus obtained with boiling sodium hydroxide solution.

Reduction of (IV) with alkaline sodium hypsulphite, followed by treatment with methyl sulphate, gives *p-carboxyphenyl methyl selenide* (V), m. p. 174° (*dibromide*, m. p. 198—199°). Oxidation of (V) or treatment of the dibromide with sodium hydroxide solution gives *p-carboxyphenyl methyl selenoxide* (VI), m. p. 183—184° (*brucine* salt, m. p. 105—110°). Attempts to resolve compounds (II), (III), and (VI) were unsuccessful, and these substances could not be oxidised to selenones. It is concluded that the double linking between the oxygen and selenium atoms of a selenoxide may be symmetrical instead of unsymmetrical, as in the case of the corresponding double linking in sulphoxides.

II. Benzeneseleninic acid reacts with aniline, giving *4-aminodiphenyl selenide*, m. p. 93—94° (*hydrochloride*, m. p. 159°). *4-Acetamidodiphenyl selenide* (I), m. p. 169—170°, is converted by treatment with hydrogen peroxide into *4-acetamidodiphenyl selenide dihydroxide* (II), m. p. 147—148° (decomp.). When the dihydroxide is heated under reduced pressure, it loses water, giving *4-acetamidodiphenyl selenoxide* (III), m. p. 144—146°; when it is fused at the ordinary pressure, the selenoxide first formed is decomposed by further heating, giving *4-acetamidodiphenyl selenide* and oxygen. Addition of concentrated solutions of hydrochloric, hydrobromic, or hydriodic acid to a warm solution of (III) in glacial acetic acid gives, respectively, *4-acetamidodiphenyl selenide dichloride*, m. p. 131—132°, *dibromide*, m. p. 135—136°, and *di-iodide*, m. p. 144—145° (decomp.). The dibromide and di-iodide are alternatively prepared by the action of bromine and iodine, respectively, on an acetic acid solution of (I). Chlorine reacts with (I) under these conditions, giving a *compound*, m. p. 186—187°, containing chlorine, which is not displaced by the action of aqueous alkali. The dibromide is converted by heat into a *compound*, m. p. 167°, containing nuclear bromine (3 : 5-dibromo-4-acetamidodiphenyl

selenide?). The dichloride suffers a similar change, whereas the di-iodide evolves iodine, reverting to the selenide. Gradual dissociation of the di-iodide takes place at the ordinary temperature, as well as in ethereal solution. The dichloride and dibromide are converted by the action of water or dilute alkalis into the dihydroxide. Boiling water, however, is without action on the di-iodide, which with sodium hydroxide yields its parent selenide. *4-Aminodiphenyl selenoxide*, m. p. 188—189° (decomp.), obtained by treatment of (II) with sodium hydroxide solution, is unstable in the presence of acids. Its resolution was therefore impracticable.

M. CLARK.

**Quadrivalency of selenium. III. Instability of the compounds of quadrivalent selenium derived from phenyl methyl and phenyl ethyl selenides, and phenyl- and *p*-tolyl-selenoglycollic acids.** O. K. EDWARDS, W. R. GAYTHWAITE, J. KENYON, and H. PHILLIPS (J.C.S., 1928, 2293—2303).—*Phenyl methyl selenide dibromide*, m. p. 115—116° (decomp.), prepared by the addition of bromine to phenyl methyl selenide, decomposes quantitatively at 100° into methyl bromide and bromoselenobenzene. The dibromide is converted by trituration at 40° with potassium iodide solution into the corresponding *di-iodide*, m. p. 69—71°. Trituration in the cold yields *phenyl methyl selenide bromiodide*, m. p. 85° (decomp.), which is decomposed by heat into methyl iodide and bromoselenobenzene. *Phenyl ethyl selenide dibromide*, m. p. 84°, is decomposed by heat into ethyl bromide and bromoselenobenzene. *Phenyl methyl selenide dihydroxide*, a viscous oil, obtained by treatment of an aqueous solution of the dibromide with silver oxide and concentration of the filtrate in a vacuum, is decomposed by heat, yielding phenyl methyl selenide, diphenyl diselenide, and formaldehyde. *Phenyl ethyl selenide dihydroxide* is less stable and decomposes spontaneously, yielding mainly diphenyl diselenide. Phenylmethylselenetene bromide is decomposed at the m. p. into methyl bromide and phenylselenoglycollic acid, m. p. 36—37°, b. p. 197—198°/10 mm. (lit. m. p. 40°, b. p. 160°/750 mm.). *Phenylselenoglycollic acid dibromide*, m. p. 126°, is decomposed by heat into bromoselenobenzene and bromoacetic acid. *p-Tolylmethylselenine bromide*, obtained from *p*-tolyl methyl selenide and bromoacetic acid, is converted by heat into *p*-tolylselenoglycollic acid, and by treatment with a molecular proportion of bromine in cold carbon tetrachloride solution into *p*-tolylselenoglycollic acid dibromide, which is decomposed by heat into *p*-bromoselenotoluene and bromoacetic acid. Interaction of *p*-tolylselenoglycollic acid and excess of bromine yields *p-bromoselenotoluene dibromide*, m. p. 113—114° (decomp.), alternatively prepared by trituration of *p*-tolueneseleninic acid with concentrated aqueous hydrobromic acid or by reaction of bromine with di-*p*-tolyl diselenide. This substance is erroneously described by Morgan and Porritt (A., 1925, i, 1196) as *p*-tolylselenoglycollic acid tetrabromide. The sole product isolated from the interaction of phenyl ethyl selenide and bromoacetic acid was phenylselenoglycollic acid, owing presumably to the great instability of phenylethylselenetene bromide.

All the decomposition reactions described above support the contention that the withdrawal of aliphatic groups from their combination with quadrivalent selenium may be facilitated by their ability to provide a proton.

Diphenyl selenide dibromide, m. p. 154° (lit. 140°), is decomposed at the m. p. into bromodiphenyl selenide (?), m. p. 32—33°, and hydrobromic acid. Dibromodiphenyl selenide is obtained as a by-product (cf. Krafft and Lyons, A., 1894, i, 448). An improved method of preparation of diphenyl selenoxide, obtained by oxidation of diphenyl selenide with hydrogen peroxide, is described. M. CLARK.

Organo-antimony compounds. II. Constitution of *p*-aminophenylstibinic acid and its amine salts. S. C. NIYOGY (J. Indian Chem. Soc., 1928, 5, 285—291).—The following salts of *p*-aminophenylstibinic acid are described: dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, propylamine, isopropylamine, and allylamine. These salts dissolve in water to a red solution which becomes opaque after a few min., and are insoluble in all organic media except glycerol. Three mols. of the stibinic acid are combined with 1 mol. of base (cf. Schmidt, A., 1920, i, 900; 1922, i, 482).

H. BURTON.

Isolation of pure *l*-proline. B. W. TOWN (Biochem. J., 1928, 22, 1083—1086).—The hydrolysis products of gliadin are separated into three fractions by means of their copper salts, *i.e.*, copper salts soluble in water and in methyl alcohol, copper salts soluble in water but insoluble in methyl alcohol, and copper salts insoluble in both water and methyl alcohol. The proline is obtained from the first fraction, which also contains valine, hydroxyvaline, and phenylalanylproline, by dissolution in absolute alcohol and precipitation as the picrate, m. p. 148°. The proline thus obtained has a higher rotation ( $[\alpha]_D^{25} -86.7^\circ$ ) than those previously recorded. The phenylhydantoin, m. p. 143—144°, and *dl*-proline-phenylhydantoin, m. p. 118°, have also been prepared. There is also in the first fraction a product soluble in alcohol but giving no picrate and a product giving a picrate soluble in ether.

The second fraction contains glutamic acid as well as glycine, alanine, and serine, whilst phenylalanine, leucine, and aspartic acid are found in the third fraction. S. S. ZILVA.

Behaviour of polypeptides and their derivatives towards dilute alkali and acid. VII. *N*-Substituted polypeptides. E. ABDERHALDEN and P. MÖLLER (Z. physiol. Chem., 1928, 176, 207—216).—The fission of *N*-substituted *dl*-leucylglycines,  $X \cdot NH \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , where  $X = \beta$ -naphthoyl, phenylmethanesulphonyl, *p*-toluenesulphonyl, phenylacetyl,  $\beta$ -phenylpropionyl, phenylcarbamyl, and  $\alpha$ -naphthylcarbamyl, by alkali is followed by Van Slyke's method, the products being an acyl-leucine and glycine. The rate of hydrolysis is greatly accelerated by the introduction of carboxylic acyl groups, but arylsulphonyl derivatives show no appreciable acceleration. In the carbamyl compounds particularly the peptide linking seems to be loosened. The preparation of  $\beta$ -naphthoyl- (m. p. 193—194°),

phenylmethanesulphonyl- (m. p. 90°), *p*-toluenesulphonyl- (m. p. 120°), phenylacetyl- (m. p. 170°), and  $\beta$ -phenylpropionyl- (m. p. 187°) -*dl*-leucylglycines is described. C. HOLLINS.

Preparation of the unchanged modification of oxyhæmin and chlorohæmin. A. HAMSİK (Z. physiol. Chem., 1928, 176, 173—186; cf. A., 1925, i, 845, 1476).—Details of the method previously outlined (coagulation of defibrinated blood with acetone, removal of chlorides, extraction with acetone and oxalic acid, and precipitation with sodium acetate or dilute hydrochloric acid) are given. Success depends on the rapidity of separating the precipitate from the mother-liquor. C. HOLLINS.

Iron porphyratins. The reversible side-chain reaction of hæmatin and the behaviour of hæmin and hæmatins towards acids. Preparation of hæmateric acid from hæmin and organic acids. O. SCHUMM and E. MERTENS (Z. physiol. Chem., 1928, 177, 15—33; cf. A., 1927, 685, 798, 886; this vol., 80).—The four-stage reversible cycle of transformations of  $\alpha$ -hæmatin is confirmed and extended to  $\beta$ -hæmatin and hæmin. The conversion into hæmateric acid (phase III) proceeds either in boiling hydrochloric acid or, better, in glacial acetic acid containing a little sulphuric acid. The partial saturation of the unsaturated side-chain of hæmin by boiling with 1% methyl-alcoholic hydrogen chloride is confirmed by analysis; the product ("dimethoxyhæmin dimethyl ester") is the tetramethyl compound of the iron complex salt of Nencki's hæmatoporphyrin. The cycle may be shortened to two phases, the product of phase I being reconverted directly by boiling glacial acetic acid into the original hæmatin. "Dimethoxyhæmin dimethyl ester" and the iron salt of Nencki's hæmatoporphyrin, when boiled with hydrochloric acid, yield a hæmatin-like substance distinguished from hæmatin by its greater stability towards hydrazine-acetic acid. The same or a similar compound is obtained from hæmatin and from hæmin by prolonged boiling.

The action of organic acids on hæmin and hæmatins varies considerably. Glacial acetic acid produces no structural change; 10% oxalic acid gives two different porphyrins, together with hæmateric acid; 70% lactic acid gives mainly hæmateric acid; pyruvic acid very readily converts pure hæmin into porphyrins, whilst with hæmin dissolved in aniline no removal of iron is observed; 10% solutions of malonic, succinic, tartaric, and citric acids have no effect; 98% acetic acid and 100% formic acid yield hæmateric acid. Hæmatins prepared by different methods differ in their resistance towards the action of boiling hydrochloric acid or 25% sulphonic acid. C. HOLLINS.

Preparation of hæmin derivatives. I. O. SCHUMM (Z. physiol. Chem., 1928, 176, 122—126).—Hæmin is converted into mesohæmin by heating for a short time with a mixture of aniline and pyruvic acid, or with excess of aniline and acetic acid (reduced iron being added later), or with a mixture of hydrazine hydrate and aniline, *p*-toluidine, phenol, glycerol, glycol, amyl alcohol, olive oil, or liquid paraffin. With hydrazine hydrate alone heating under pressure

at 200° is necessary to bring about the change. By melting hæmin with resorcinol or pyrogallol some mesohæmin is first produced, and after 5–15 min. there is formed in good yield the iron complex salt of coproporphyrin, the two stages being easily followed spectroscopically; stronger heating finally gives copratin, and by removal of iron with hydrazine and acetic acid coproporphyrin and a yellow decomposition product are formed. Apparently no decarboxylation occurs. Nencki's hæmatoporphyrin behaves similarly. C. HOLLINS.

**Resorption of copper and ferrocyanide ions by coagulated proteins.** B. M. HENDRIX (J. Biol. Chem., 1928, 78, 653–660).—From very dilute acid solutions copper is taken up almost completely by a suspension of coagulated egg-albumin, the proportion taken up increasing as the neutral point is approached. Similarly, the ferrocyanide ion is taken up in increasing amounts as the  $p_H$  decreases to 3.7. The constancy of the results obtainable with different preparations of protein at the same  $p_H$  indicates that the phenomenon is one of chemical combination rather than adsorption. C. R. HARRINGTON.

**Instability of serine-phosphoric acid chains and the general reaction of tyrosins.** S. POSTERNAK and T. POSTERNAK (Compt. rend., 1928, 187, 313–316).—Treatment of ovotyrin (1 mol.) with boiling *N*-sodium hydroxide yields pyruvic acid (2 mols.) and ammonia (4.2 mols.). Lactotyrin behaves in a similar way and in both cases the phosphorus is completely mineralised by alkali at the ordinary temperature. It is suggested that the first stage of the reaction is the fission of phosphoric acid groupings with the resultant production of a polypeptide, containing aminoacrylic acid chains, which is then hydrolysed to ammonia and pyruvic acid. G. A. C. GOUGH.

**Action of carbon monoxide on the autoxidation of thiol compounds.** M. DIXON (Biochem. J., 1928, 22, 902–908).—Carbon monoxide has no effect on the rate of the autoxidation of cysteine or reduced glutathione induced by the addition of iron, copper salts, or freshly-dissolved hæmatin. The last compound breaks up into a mixture of simpler compounds after keeping for several days. This mixture although retaining the catalytic power of the original hæmatin

becomes susceptible to inhibition by carbon monoxide. S. S. ZILVA.

**Characterisation of small quantities of proteins by Van Slyke's method.** N. NARAYANA and M. SREENIVASAYA (Biochem. J., 1928, 22, 1135–1137).—A description of a micro-method requiring 0.1–0.15 g. of protein. S. S. ZILVA.

**Elementary organic analysis for carbon and hydrogen without the use of catalysts.** I. MAREK (Bull. Soc. chim., 1928, [iv], 43, 910–912).—See this vol., 82.

**Electrically-heated furnace for organic combustions.** M. PHILLIPS and R. HELLBACH (J. Assoc. Off. Agric. Chem., 1928, 11, 393–396).—Five electrically-heated units of suitable dimensions are mounted on a parallel bar stand for the purpose of preheating the stream of oxygen, and for heating the oxidised copper coil, the boat containing the substance, the wire-form copper oxide, and the lead peroxide. The first four units are wound with asbestos-covered nichrome wire on mica-covered copper tubes to ensure an even temperature throughout. To control the temperature of the lead peroxide, the last unit consists of two concentric tubes of brass, of which the outer is suitably wound with nichrome wire, the annular space containing *p*-cymene and connecting to a pyrex reflux condenser. F. R. ENNOS.

**Determination of reducing sugars.** N. SEMIGANOVSKY (Z. anal. Chem., 1928, 74, 400–402).—A modification of Bertrand's method (A., 1907, ii, 136). The precipitated cuprous oxide is dissolved in the minimum amount of a solution containing 150 g. of sodium chloride, 27 g. of hydrochloric acid (*d* 1.19), and 5 g. of manganous sulphate tetrahydrate per litre. Potassium permanganate solution is added until a pink colour persists for a few seconds. The resulting cupric salt is determined iodometrically. J. S. CARTER.

**Rapid determination of small quantities of phenol in glycerol solution.** G. DENIGES (Bull. Soc. Pharm. Bordeaux, 1927, 65, 118–120; Chem. Zentr., 1928, i, 1558).—The solution (1 c.c.) is heated with Millon's reagent (2 c.c.) and acetic acid (0.2 c.c.) on a boiling water-bath for 5 min., and the red coloration compared with that of controls. A. A. ELDRIDGE.

## Biochemistry.

**Blood-gases of the carp.** H. WASTL (Biochem. Z., 1928, 197, 363–380).—The oxygen content is 9.51 vol.-% and the carbon dioxide content is 44.86 vol.-% (mean values). The oxygen dissociation curve is much steeper and the carbon dioxide curves are much lower and flatter than the corresponding curves for warm-blooded animals.

The alkali reserve of the fish-blood is much smaller than that of warm-blooded animals. H. W. DUDLEY.

**Determination of carbon monoxide in blood.** W. M. M. PILAAR (Chem. Weekblad, 1928, 25, 509–513).—The various methods so far proposed are

criticised. That of Tervaert (A., 1925, i, 710) gives fairly accurate results, but is open to objection. A micro-method of carrying out this determination is described, by which the carbon monoxide content may be determined in 1 c.c. of blood with an accuracy within 1%. S. I. LEVY.

**Gasometric determination of hæmoglobin by the carbon monoxide capacity method.** D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1928, 78, 807–819).—Blood is shaken in an atmosphere of carbon monoxide at 25 mm. pressure; the gases are expelled, the carbon monoxide-hæmoglobin

is decomposed with acid ferricyanide, and the carbon monoxide determined gasometrically; the whole operation is conducted in the apparatus of Van Slyke and Neill (A., 1924, ii, 872). The method is applicable to 0.1—2.0 c.c. of blood.

C. R. HARINGTON.

**Gas and electrolyte equilibria in the blood.** X. Solubility of carbon dioxide at 38° in water, salt solution, blood-serum, and corpuscles. D. D. VAN SLYKE, J. SENDROY, jun., A. B. HASTINGS, and J. M. NEILL. XI. Solubility of hydrogen at 38° in blood-serum and corpuscles. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1928, 78, 765—799, 801—805).—X. For distilled water at 38° the solubility coefficient of carbon dioxide is 0.5452, for blood-serum 0.509, and for red blood-corpuscles 0.45, the last value being determined by extrapolation from observed values for aqueous solutions of the cells. The reduction of the solubility in serum is due to a combination of the depressant effects of the salts and proteins and the augmenting effect of the lipins. The effect of mixtures of salts on the solubility of carbon dioxide is the additive effect of the individual ions. Neither blood-serum nor solutions of blood-corpuscles showed any deviations from Henry's law.

XI. Coefficients of 0.01620, 0.01559, 0.01533, and 0.01454 were found for the solubility of hydrogen in water, 0.15*M*-sodium chloride, ox-blood-serum, and ox-blood-corpuscles, respectively, at 38°; consideration of the relative amounts of water present in the various cases indicates that the organic constituents of the blood dissolve appreciable amounts of hydrogen.

C. R. HARINGTON.

**Relation of copper to hæmoglobin content of rat blood.** J. S. MCHARGUE, D. J. HEALY, and E. S. HILL (J. Biol. Chem., 1928, 78, 637—641).—Dried blood-serum of cows contains 0.0044% of copper and dried calf liver 0.0125%. Increase in the hæmoglobin of the blood of rats on a milk diet was observed on administration of the ash of calf liver; no such effect was obtained after removal of copper from the ash (cf. Hart and others, this vol., 790).

C. R. HARINGTON.

**Reversible transformation of cathæmoglobin.** B. JIRGENSONS (Biochem. Z., 1928, 198, 206—208).—Cathæmoglobin changes reversibly at about 70° into hæmatin and globin. P. W. CLUTTERBUCK.

**Hæmochromogen, reduced hæmatin, and carb-oxyhæmatin.** C. DHÉRE (Compt. rend. Soc. Biol., 1927, 97, 1660—1663; Chem. Zentr., 1928, i, 1675).—An alcoholic (50—60%), slightly acid solution of reduced hæmatin, when sealed, acquires a red colour, and the absorption bands (564—528  $\mu\mu$ ) are equivalent to those of ordinary hæmochromogen. The pigment is named "acid carboxyhæmatin" or "acid carb-oxyhæmochromogen." A. A. ELDRIDGE.

**The spleen as the regulator of the amino-acid equilibrium of the blood.** I. Influence of splenectomy on the amino-acid content of the blood, red corpuscles, and plasma. II. Influence of denervation of the spleen on the amino-acid content of the blood, red corpuscles, and plasma. L. TUTKEVITSCH (Biochem. Z., 1928,

198, 47—59, 60—64).—I. Intravenous injection of amino-acids brings about within the first 10 min. a decrease of the amino-acid content of the corpuscles. Splenectomy in dogs and rabbits causes the disappearance of this phenomenon, and injection of amino-acids is then always accompanied by an increase in both corpuscles and plasma. The spleen is therefore responsible for the power of the erythrocytes to adsorb amino-acids and splenectomy causes the disappearance of this power, the amino-acids being displaced by some other nitrogenous substance of the plasma.

II. Differences in the amino-acid content of the blood of animals after splenectomy and after denervation of the spleen are indicated and discussed in correlation with the non-penetration of the spleen by carbon monoxide in Barcroft's experiments.

P. W. CLUTTERBUCK.

**Fractionation of serum-proteins by ammonium sulphate.** A. MUSCHEL (J. Biol. Chem., 1928, 78, 715—718).—Blood-serum is diluted and the total nitrogen determined in one portion; the globulin is removed from a second portion by half saturation with ammonium sulphate and the albumin+non-protein nitrogen determined in the mother-liquor after removal of ammonia by treatment with magnesium oxide and aëration. Finally, the non-protein nitrogen of the serum is determined in the usual manner.

C. R. HARINGTON.

**Relation of the viscosity of blood-serum to temperature and the hydration of the proteins.** L. DU NOUY (Ann. Inst. Pasteur, 1928, 42, 742—769).—The viscosity of the blood-serum of rabbits, determined from the moment exerted on a cylinder suspended in a larger, rotating cylinder containing the liquid, is least at 57°. Heating for 1 hr. at 55° does not increase the viscosity, but heating above 56° causes an irreversible increase. Under these conditions the viscosity may be increased threefold, and by an application of the principles of Einstein (Ann. Physik, 1911, [iv], 34, 591) to the results, the degree of hydration of the protein micelles may be calculated.

G. A. C. GOUGH.

**Refraction differences [of serum and plasma].** I—IV. F. HÖGLER and K. UEBERRACK (Z. ges. exp. Med., 1927, 58, 22—39, 40—50, 51—75, 76—80; Chem. Zentr., 1928, i, 1541—1542).—A study of the changes in the difference in refractivity between plasma or serum and the value calculated for the protein in various physiological and pathological conditions. There is no parallelism between refractivity and fibrinogen content. A. A. ELDRIDGE.

**Effect of sodium citrate, acetate, and lactate on ultrafiltrability of serum-calcium.** D. H. SHEL-LING and H. L. MASLOW (J. Biol. Chem., 1928, 78, 661—669).—Injection of 1 c.c. of a 30% solution of sodium citrate causes convulsions and death in normal rabbits; the blood of rabbits so treated contains a normal amount of calcium, but the latter can be filtered almost entirely through collodion membranes. No such effects were observed after injections of sodium acetate and lactate. Apparently, therefore, the citrate acts by the formation of a diffusible undissociated compound with the calcium.

C. R. HARINGTON.

**Modification of the Widmark micro-method for the determination of alcohol in blood.** A. GALAMINI and L. BRACALONI (Arch. Farm. sperim., 1928, 45, 97—112).—The apparatus of Widmark (cf. A., 1922, ii, 789) is modified in order to include a micro-pipette.

E. W. WIGNALL.

**Modified Salkovski reaction for the determination of cholesterol in blood-serum.** D. ABRAMSOHN (Biochem. Z., 1928, 198, 233—240).—Krastalevski's modification (A., 1924, ii, 127) of the Salkovski reaction is adapted for use at the ordinary temperature, when the yellowish-orange phase lasts 20—40 min., according to the amount of cholesterol present.

P. W. CLUTTERBUCK.

**Colorimetric determination of lævulose in blood by the diphenylamine method.** P. RADT (Biochem. Z., 1928, 198, 195—203).—A colorimetric method for determining small amounts of lævulose in aqueous solution and in blood is elaborated and the normal variation in the blood of a fasting animal is investigated.

P. W. CLUTTERBUCK.

**Action of glycine on blood-sugar.** G. PAASCH (Biochem. Z., 1928, 197, 460—466).—Glycine, intravenously or subcutaneously administered to dogs and rabbits, produces only slight increases in the amount of blood-sugar. If hyperglycæmia is caused this may not be due to the action of the amino-acid itself.

W. McCARTNEY.

**Distribution of bismuth in the blood.** S. LOMHOLT (Biochem. Z., 1928, 198, 98—102).—The predominating amount of bismuth, after absorption, is found attached to plasma-protein and may be precipitated in three fractions, the first with 37%, the second with 50% ammonium sulphate, and the third by boiling. A small amount is associated with the leucocytes, but the red cells contain either no bismuth or a very small amount. The ultrafiltrate of the plasma contains no detectable amount of bismuth nor do the lecithins of the plasma when precipitated with absolute alcohol at about 15°.

P. W. CLUTTERBUCK.

**Absorption and solubility coefficients of chloroform vapour in water, blood, serum or plasma, and milk.** M. NICLOUX and L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1927, 97, 1720—1724; Chem. Zentr., 1928, i, 1493).—Henry's law is followed for a chloroform vapour pressure of 10 mm. The solubility of chloroform vapour in water does not increase regularly with rise of temperature, the anomaly being comparable with the irregular solubility of liquid chloroform in water. For whole blood the solubility is greater than for serum or plasma, and for serum or plasma greater than for water. It is greater for pig's than for human or ox blood, which give almost identical values. For milk the coefficient is 3—4 times as great as for blood.

A. A. ELDRIDGE.

**Non-protein serum-colloids and their biological significance.** K. NIKAIKO (Biochem. Z., 1928, 198, 175—194).—A substance is present in the serum of rabbit, horse, and man which inhibits the agglutination of red cells by jack-bean extracts, the activity being greater when the agglutinin is purified and gradually added to the serum, than when serum

is added to the agglutinin. The inhibition is best obtained at  $p_H$  7. The active substance is salted out of serum by 60% saturation with ammonium sulphate. Edestin also has a slight agglutinating action and inhibits to some extent the jack-bean agglutination, but caseinogen neither agglutinates nor inhibits. The inhibitory substance is insoluble in ether, alcohol, acetone, and chloroform, and is not injured by these solvents. When serum is deproteinised with potassium dihydrogen phosphate, a highly active, protein-free inhibiting solution is obtained. Before deproteinisation, the substance is only slightly adsorbed by kaolin, but after deproteinisation it is completely adsorbed. It is only slightly adsorbed by cholesterol either before or after deproteinisation and is neither dialysable nor electro-dialysable, but in the latter case is carried down as precipitation proceeds. It is retained on the ultrafilter. Glycogen, colloidal copper and iron, and silicic acid do not inhibit jack-bean agglutination. The substance is resistant to putrefaction and fairly resistant to boiling with acids and alkalis. It does not appear to be present in normal human urine or saliva.

P. W. CLUTTERBUCK.

**Alleged acceleration of taurocholate hæmolysis by normal serum.** K. C. SEN and N. K. SEN (J. Indian Chem. Soc., 1928, 5, 261—268).—Sucrose appears to have an inhibitory effect on the hæmolysis, by sodium taurocholate, of human and sheep's erythrocytes, and normal serum inhibits hæmolysis in both normal saline and isotonic sucrose solutions. No acceleration of hæmolysis was observed (cf. Ponder, A., 1923, i, 975), except in experiments using small amounts of corpuscles. Serum inhibits the hæmolytic action of potassium oleate in isotonic sucrose solution. Inhibition is not due entirely to the sensitising action of serum on the membrane constituents (Sen and Basu, this vol., 663), but also to the large adsorption of serum on the surface of the stroma, where it displaces the adsorbed hæmolyte from the cell surface.

H. BURTON.

**Hæmolysis. II.** K. KLINKE (Biochem. Z., 1928, 197, 381—403).—The hæmolysin (amboceptor) is adsorbed on the erythrocytes and modifies the structure of the membranes in such a way that the actual lysis is enabled to take place. This consists in the adsorption of the modified constituents of the membranes on the serum-euglobulin.

H. W. DUDLEY.

**Permeability. I.** TRAUBE and F. DANNENBERG (Biochem. Z., 1928, 198, 209—224).—A critical examination of the existing theories of permeability is carried out and the "pore" theory as applying to gels is dismissed. Permeability, *e.g.*, of the vascular system, depends to a large extent on the material of the wall and on the substances in the body fluids which become concentrated on the wall in virtue of their surface activity.

P. W. CLUTTERBUCK.

**$p_H$  of fish muscle.** C. C. BENSON (J. Biol. Chem., 1928, 78, 583—590).—The resting muscle of haddock has an alkaline reaction, which, after death, becomes acid; if the fish be killed after struggling, however, the muscle is already acid at death and does not change much afterwards. Hake muscle remained alkaline long after death, whilst cod muscle remained

near the neutral point. The onset of *rigor mortis* cannot therefore be due to increasing hydrogen-ion concentration.

C. R. HARRINGTON.

**Vaccenic acid.** A fatty acid from beef, mutton, and butter fats. S. H. BERTRAM (Biochem. Z., 1928, 197, 433—441).—The acid, which occurs in quantities varying from about 0.01% (butter fat) to about 1.0% (beef fat) was shown to be a  $\Delta^{11:12}$ -*clardic acid*. The purest sample obtained, crystallised from cooled acetone, had m. p. 39°, solidif. pt. 35.5°, iodine value (Hübl) 86.5°,  $d^{20}$  0.85601.

W. MCCARTNEY.

[Normal and pathological] human fat. A. HEIDUSCHKA and C. HANDRITSCHK (Biochem. Z., 1928, 197, 404—409).—Small amounts of a higher unsaturated fatty acid, possibly arachidic acid, were found in one sample. Acids other than oleic, palmitic, and stearic acids were not encountered. The physical and chemical constants of normal and pathological fats were determined, but no appreciable distinctions could thus be made.

W. MCCARTNEY.

**Histological use of formaldehyde as preservative.** J. MILLOT and A. GIBERTON (Compt. rend. Soc. Biol., 1928, 97, 1674—1675; Chem. Zentr., 1928, i, 1443).—Formaldehyde does not inhibit changes in fat, which take place after 3 weeks, with disappearance of lipins and production of fatty acids. The rapidity of the change varies with the origin; fish liver changes most rapidly. The decomposition is attributed to a lipase which is active in the presence of formaldehyde, and is more rapid at 35—40° than at the ordinary temperature.

A. A. ELDRIDGE.

**Reversible crystallisation in tendons and its functional significance.** J. H. CLARK (Proc. Nat. Acad. Sci., 1928, 14, 526—532).—X-Ray pinhole diagrams have been investigated in the case of moist tendons and ligaments. The results show that collagen exists normally in skin and tendons as liquid crystals. The molecules are so arranged that X-ray reflexion takes place from planes with a spacing of approximately 6.2 Å. On stretching a living tendon some of the liquid crystals change to solid crystallites, arranged in fibre formation, the crystal units being one half the size of the molecules in the liquid crystal form. Depolymerisation thus occurs on stretching. The liquid crystals also change to the solid crystal form on dehydration. The formation of solid crystals in collagen probably increases its cohesion. Elastin also exists normally in the liquid crystal state, but does not form solid crystals on moderate stretching, although they may appear at the limit of extension. The X-ray diagram for elastin gives a different spacing from that for collagen.

A. J. MEE.

**Artefacts as a guide to the chemistry of the cell.** C. E. WALKER (Proc. Roy. Soc., 1928, B, 103, 397—403).—When methyl myristate, or methyl laurate, in which yellow phosphorus has been dissolved, is added in the form of an emulsion to certain colloidal mixtures and kept at a temperature of 30°, the microscopical appearances presented on fixation and treatment with osmic acid show that in about 2 hrs. a large proportion of the lipins is distributed

over the globules, whilst after about 24 hrs. most of the fatty acids of the lipins have become saturated or oxidised.

W. O. KERMAK.

**Copper content of milk.** G. N. QUAM and A. HELLWIG (J. Biol. Chem., 1928, 78, 681—684).—Cow's and sheep's milks contain 0.4—0.5 mg. per litre, goat's milk 0.2 mg. per litre, of copper. Pasteurised and condensed milks contain considerably greater amounts of copper which must have been introduced artificially.

C. R. HARRINGTON.

**Biochemical studies of iodine.** K. SCHARRER (Z. angew. Chem., 1928, 41, 980—982).—No ill effects followed the administration of iodine to milking goats even in doses of 60—180 mg. (as sodium iodide) per animal daily. Temporary increases in milk yields were observed, and at these periods the fat yield increased although the actual fat percentage declined. Very brief increases in the iodine content of milk occurred. Small doses of iodine (as iodide) tended to delay the decline of milk yield in the later stages of lactation. Following the use of iodised rations increases in the iodine content of the liver and kidneys, but in no other organs, were noted. The milk of cows feeding on the marsh lands of the North Sea coast had a higher iodine content than those of southern Germany.

Iodine in small amounts (as potassium iodide) accelerated the reproduction of yeasts without any notable increase in the total weight of yeast produced. Yeast appears in hold iodine to some form of loose combination. Toxicity of iodine compounds to yeast varied in the order iodide > iodate > periodate. The combined base exerts considerable effect on the toxicity of these compounds.

A. G. POLLARD.

**Determination of minute quantities of metals in biological material. I. Determination of lead in urine.** H. B. TAYLOR (J. Proc. Roy. Soc. New South Wales, 1927, 61, 315—336).—An accurate method for the determination of small quantities of lead in urine is described, based on the fact that it is completely adsorbed on calcium oxalate in solutions of  $pH$  4—5. The lead is then determined nephelometrically after addition of sodium hydrogen sulphite.

C. W. GIBBY.

**Rôle of biocatalysts in carbohydrate metabolism of carcinoma.** H. VON EULER and H. JOHANSSON (Svensk Kem. Tidskr., 1928, 40, 209—218).—Cancerous tissue (liver) has been tested for its content of the activator Z (cf. Euler and Swartz, A., 1925, i, 209) using extracts of the tissue, finely-divided tissue, or dry tissue, and when compared with normal tissue it is deficient in the Z factor. The results are somewhat complicated by the presence in the tissue of inhibiting factors. It has been found possible to effect considerable concentration of the Z factor from tumour tissues by means of a method dependent on precipitation by salts of the heavy metals. Extract from cancerous tissues increases the consumption of oxygen by yeast, but apparently not quite as markedly as does a similar extract of the corresponding normal tissue.

W. O. KERMAK.

**Cholesterol content of blood-serum after irradiation with X-rays.** E. HUBERT (Klin. Woch.,



1928, 7, 208—211; Chem. Zentr., 1928, i, 1677).—After irradiation of carcinomatous tissue a marked fall in serum-cholesterol is observed.

A. A. ELDRIDGE.

**Genesis of diabetic hyperglycæmia.** E. J. LESSER (Klin. Woch., 1928, 7, 25—26; Chem. Zentr., 1928, i, 1540—1541).—Polemical. The speed of glycogenolysis in the isolated frog's liver does not depend on the sugar content. Glycogenolysis is inhibited by products thereof in sufficiently high concentration. An extract of these products does not alone raise the sugar value in the liver cells, since ferment and substrate must be brought together.

A. A. ELDRIDGE.

**Insulin resistance in diabetes.** F. DEPISCH and R. HASENÖHRL (Z. ges. exp. Med., 1927, 58, 110—116; Chem. Zentr., 1928, i, 1540).—The serum of a patient (paraneuritic abscess) refractory towards insulin, when administered intravenously or subcutaneously to rabbits, diminished the action of insulin. The pus decomposed insulin after being heated for 2 hrs. at 80° or in presence of phenol.

A. A. ELDRIDGE.

**Employment of dihydroxyacetone ("oxantin") in diabetes.** M. GROSSMANN and S. POLLAK (Klin. Woch., 1928, 7, 211—213; Chem. Zentr., 1928, i, 1677).—The blood-sugar falls after a short rise; acidosis is favourably affected. A. A. ELDRIDGE.

**Primula idiosyncrasy.** B. BLOCH and P. KARRER (Vierteljahrsschr. naturforsch. Ges. Zurich, 1927, 72, Beibl. No. 13, 1—26; Chem. Zentr., 1928, i, 1535).—From the ethereal extract of the green leaves of *Primula obconica* was obtained a small yield of the toxic principle, *primin*,  $C_{14}H_{18}O_3$  or  $C_{14}H_{20}O_3$ , golden-yellow, m. p. 62—63°, volatile with steam; one oxygen atom is present as hydroxyl, and the others apparently as lactone groups. *Primin* immediately decolorises potassium permanganate in acetic acid, and reduces ammoniacal silver nitrate solution at the ordinary temperature; in cases of primula idiosyncrasy it causes eczematous dermatitis clinically identical with spontaneous primula dermatitis.

A. A. ELDRIDGE.

**Nitrogen balance and the urinary C:N coefficient in experimental scurvy, without complication by hunger.** N. JARUSOVA (Biochem. Z., 1928, 198, 128—137).—By maintaining an animal on a scorbutic diet which is sufficient to maintain its body-weight, the nitrogen balance passes during development of scurvy from positive to negative values. The change in nitrogen secretion is insignificant. Increased decomposition of protein therefore does not, but impairment of the utilisation of food-nitrogen does, occur. The absolute amount of urinary carbon, and therefore the urinary C:N ratio also, is increased. P. W. CLUTTERBUCK.

**Total chloride concentration and acidity of the gastric contents.** F. D. GORHAM, C. M. STROUD, and M. HUFFMANN (Arch. Int. Med., 1928, 42, 106—116).—The total chloride concentration and acidity of the contents of the stomach after fasting and after oral administration of water and phenolsulphonphthalein show wide variations under pathological conditions (increase in cases of pyloric stenosis and

duodenal ulcer), but approach the same value (in many instances similar to that of the normal blood-plasma) in normal subjects. The relation between the total acidity and the chloride concentration during fasting and of the gastric chyme after a test meal varies in normal subjects and even more under pathological conditions where the total acidity shows the greatest fluctuation (cf. Guy's Hosp. Rep., 1924, 74, 40). G. A. C. GOUGH.

**Alkalosis in patients with peptic ulcer.** W. E. GATEWOOD, O. H. GAEBLER, E. MUNTWYLER, and V. C. MYERS (Arch. Int. Med., 1928, 42, 79—105).—At a certain period a third of these cases showed uncompensated alkalosis, and alkalosis accompanied by high carbon dioxide content occurred in the remainder. Treatment with sodium hydrogen carbonate leads often to an increase in the alkalæmia and generally to a rise in the blood hydrogen carbonates and a fall in the chloride content of the plasma, whilst calcium carbonate or magnesium oxide seldom increases alkalæmia. G. A. C. GOUGH.

**Post mortem increase of lactic acid in the brain substance of animals.** M. E. MAYER (Arch. exp. Path. Pharm., 1928, 134, 218—224).—Dogs and calves subjected to various experimental procedures show an increase in the lactic acid in the brain after death as compared with the normal content, this increase being more marked in the grey substance than in the white. Similar results are also obtained with cats. W. O. KERMACK.

**Clinical calorimetry. XLII. Effect of dextrose and of dihydroxyacetone on metabolism.** W. S. McCLELLAN, A. BIASSOTTI, and R. R. HANNON (J. Biol. Chem., 1928, 78, 719—744).—Ingestion of dihydroxyacetone caused a rise in the respiratory quotient due to increased elimination of carbon dioxide. Heat production was increased to about the same extent as by dextrose. In normal individuals the blood-sugar fell; in diabetics it rose, but to a less extent than after dextrose. Acid phosphomolybdate-reducing substances (including dihydroxyacetone) were not increased in the blood of normal or diabetic individuals after ingestion of dihydroxyacetone or of dextrose; they were slightly increased in the urine in the former case. C. R. HARRINGTON.

**Mineral metabolism of the growing chick.** F. E. MUSSEHL, M. J. BLISH, and C. W. ACKERSON (Poultry Sci., 1927, 6, 239—242).—The addition of bone meal, calcium carbonate, or a mixture of these materials with sodium chloride, to a basal ration which was complete for vitamins, proteins, and mineral substances retarded the growth and increased the mortality of chickens. CHEMICAL ABSTRACTS.

**Phosphorus metabolism. II and III.** A. J. CHARIT (Arch. Sci. Biol., 1928, 28, 145—147, 148—154).—I. Blood leaving the spleen of dogs is richer in inorganic phosphorus than that entering, when the animal has performed muscular work, has been fed with substances containing phosphorus in organic combination, or is under the influence of insulin, the difference amounting in the first two cases to about 1 mg. %, on the average. This difference is apparently due to the elimination of phosphoric acid from organic

compounds containing phosphorus by an agent present in the spleen.

II. The subcutaneous injection of adrenaline into dogs and rabbits reduces the inorganic phosphorus content of the blood by 28—30%. No further diminution can be produced by administration of dextrose or insulin during adrenaline hypophosphæmia. The inorganic phosphorus of the blood would hence appear to consist of two types: one capable of combining with carbohydrates, and the other not entering into this reaction.

R. TRUSZKOWSKI.

**Metabolism of the bile. II. Changes in blood and bile following intravenous injection of bile or of its constituents.** C. H. GREENE and A. M. SNELL (*J. Biol. Chem.*, 1928, 78, 691—713).—Intravenous injection of bile acids or of bilirubin is followed by rapid elimination of the excess by excretion in the bile. The elimination is most rapid in the case of the bile acids which have a cholagogue action, and of which the excess is excreted by increase in the volume of bile; bilirubin, on the other hand, is eliminated more slowly and by means of increased concentration of the bile. Injections of whole bile give similar results except that the process is slower.

C. R. HARRINGTON.

**Metabolism of tryptophan. II. Synthesis of 6-methyl- and 8-methyl-kynurenic acids.** W. ROBSON.—See this vol., 1141.

**Metabolism of tryptophan. III. Mode of formation of kynurenic acid from tryptophan.** W. ROBSON (*Biochem. J.*, 1928, 22, 1165—1168).—*Bz*-3-Methyltryptophan or 8-methylkynurenic acid when injected into the rabbit is completely burnt. 6-Methylkynurenic acid, on the other hand, can be recovered from the urine of the animal almost quantitatively. In the formation of kynurenic acid from tryptophan, therefore, the pyrrole-nitrogen of the latter compound is eliminated and the side-chain with its amino-nitrogen forms the new pyridine ring.

S. S. ZILVA.

**Comparative nutrient value of the proteins of linseed meal and cotton-seed meal for different animals.** R. M. BETHKE, G. BOHSTEDT, H. L. SASSAMAN, D. C. KENNARD, and B. H. EDINGTON (*J. Agric. Res.*, 1928, 36, 855—871).—The effect of these meals varied considerably with the type of animal used in nutrition experiments, and in the case of chickens with age. Cotton-seed meal showed toxic effects with pigs. In digestibility and biological value the two meals were equally valuable as supplementary protein foods for rats and calves. For young chickens cotton-seed meal was slightly superior.

A. G. POLLARD.

**Fate of foreign fats in the organism.** L. SCHEFFER (*Arch. exp. Path. Pharm.*, 1928, 134, 66—73).—After the injection of "iodopin" (a fat containing iodine) into the jugular vein of a well-nourished dog very little or none is immediately deposited in the fatty tissue, but after 48 hrs. 98% and after 72 hrs. 70% is still found in the liver in an unaltered condition.

W. O. KERMAK.

**Fat metabolism after splenectomy.** S. LEITES (*Biochem. Z.*, 1928, 198, 157—162).—After splenectomy, hydrolysis of fat, probably in the liver,

is disturbed and partly transferred to the lungs, whilst decomposition of acetone substances is retarded, especially at the periphery. In splenectomised animals, feeding of fat leads to acetonæmia, which is not diminished by simultaneous administration of dextrose. The dextrose, however, does increase the hypercholesterolæmia accompanying fat feeding.

P. W. CLUTTERBUCK.

**Fat and lipin metabolism. VIII. Degradation of fat in the animal organism.** S. LEITES (*Biochem. Z.*, 1928, 197, 357—362).—After administration of oleic acid to dogs an increase in the amount of ketonic substances in the blood of the right heart and arteries is observed. Olive oil or olive oil and cholesterol, orally administered, cause an increase in the amount of these substances in the blood of the right heart and of the femoral vein, and the increase in that vein is accompanied by a decrease in the amount of neutral fat. Administration of fat also results in the formation of ketonic substances in the liver and lungs and peripherally. The retention of neutral fat in the lungs of normal dogs is not accompanied by any degradation of the fat with formation of ketonic substances; these are apparently formed in the lungs from free higher fatty acids. Dextrose exerts its antiketogenic effect in the liver and peripherally, but not in the lungs. Dextrose given with oleic acid produces considerably greater hypercholesterolæmia than does the administration of oleic acid alone. The decomposition of the ketonic substances occurs in the lungs and peripherally.

W. MCCARTNEY.

**Lipins and metabolism.** H. REITER and W. REISSMANN (*Klin. Woch.*, 1928, 7, 306—307; *Chem. Zentr.*, 1928, i, 1678).—In rats lack of lipins leads to increased degradation of protein; subsequent administration of lipin in the form of "Promonta" has a protein-sparing effect.

A. A. ELDRIDGE.

**Phosphatide content of organs after administration of large amounts of phosphatide.** B. REWALD (*Biochem. Z.*, 1928, 198, 103—111).—Administration of large amounts of phosphatide over prolonged periods does not appear to affect the health of the animal and 90% is absorbed. After administration for one month, considerable storage occurs, particularly in the brain, kidney, and liver. The phosphatide content of the blood is also increased.

P. W. CLUTTERBUCK.

**Dehydrogenation processes with choroid membranes of albino and pigmented animals.** A. CUCCHIA (*Arch. Farm. sperim.*, 1928, 45, 67—74).—Contrary to expectation on the oxidation theory of albinism and pigmentation, there is no distinct difference between the rates of reduction of *m*-dinitrobenzene by the choroid membranes of eyes of albino and of pigmented rabbits.

E. W. WIGNALL.

**Chemical factors which determine the deposition of colloids.** G. SPAGNOL (*Atti R. Accad. Lincei*, 1928, [vi], 7, 667—670).—In continuance of previous work, experiments have been made on the effect of chloroform, ethyl ether, and carbon tetrachloride (applied to the skin) on the deposition in the tissues of numerous colloids, both electropositive and electronegative, after their intravenous injection into

various animals. The deposition occurs in the locality to which the reagent has been applied. With chloroform, after an application for 5—15 sec., the deposition occurred in the skin and in the subcutaneous tissue; with longer application (1—2 min.) a certain amount of deposition occurred also in the underlying muscles. Negative results were obtained if the application of the chloroform preceded the injection of the colloid by an hour. The optimum conditions were represented by the application of the chloroform for 15—20 sec., when the infiltration of the colloid into the tissues was manifest after 5—10 min., and was complete after 1 hr. Injections of dilute aqueous solutions of amylen hydrate and of ethylurethane gave similar results. This infiltration is attributed to an enhanced permeability of the blood capillaries.

F. G. TRYHORN.

Strengths of action of alkaloids and their degree of hydrolysis in buffered solutions as a function of hydrogen-ion concentration of the medium. S. MAYEDA (Biochem. Z., 1928, 197, 410—417).—Mathematical and theoretical considerations led to the following conclusions which have been experimentally verified for the cinchona alkaloids. The degree of hydrolysis of a hydrolysable salt in a medium, the hydrogen-ion concentration of which is regulated, is a function of the  $p_H$ . For a salt from a strong acid and a weak base having a particular dissociation constant, the degree of hydrolysis can be calculated from an equation which is given. For the same dissociation constant the equation is identical with that for the dissociation curve of a weak base. The dependence of the biological action of the cinchona alkaloids on the  $p_H$  is to be traced solely to the base set free by hydrolytic dissociation; theoretically this should hold for other alkaloids also. The free quinine base alone is the bearer of the biological activity. Considered physico-chemically, the action of the alkaloids on the free living micro-organisms is a process of adsorption.

W. MCCARTNEY.

Pharmacological differentiation of the *Solanaceae* alkaloids. F. GARCIA (Arch. exp. Path. Pharm., 1928, 134, 149—154).—The narcotic action of ether vapour on mice is increased by the administration of atropine, hyoscyamine, or scopolamine to the animals. These three alkaloids show this effect in different degrees and this circumstance is combined with a chemical method for the purpose of differentiating and determining the three alkaloids.

W. O. KERMAK.

Toxicology of certain chlorine derivatives of methane and ethane. G. A. HALOFF (Arch. exp. Path. Pharm., 1928, 134, 168—172).—Chloroform and carbon tetrachloride produce fatty degeneration of the liver, whilst dichloromethane, ethylene dichloride, ethylidene chloride, and hexachloroethane have no such action.

W. O. KERMAK.

Transformation of benzene in the organism and a method for the determination of benzene. I. D. GADASKIN (Biochem. Z., 1928, 198, 149—156).—A colorimetric method is described for the determination of benzene, depending on its nitration, reduction of the nitro-compound, and subsequent treatment

with dimethyl-*p*-phenylenediamine. This test is sufficiently delicate to detect qualitatively sublethal amounts of benzene when present in blood. The toxic effect of benzene is the sum of its own toxicity and that of phenol arising by oxidation.

P. W. CLUTTERBUCK.

Solubility in stomach and duodenum of aluminium compounds found in baking powder residues. V. C. MYERS and J. A. KILLAN (J. Biol. Chem., 1928, 78, 591—594).—After administration to normal human subjects of 15—90 mg. of aluminium in the form of biscuits baked with aluminous baking powders, 2—20% of the aluminium was found in solution in the gastric contents and similar amounts in the duodenal contents.

C. R. HARRINGTON.

Influence of administration of aluminium on aluminium content of tissues and on growth and reproduction in rats. V. C. MYERS and J. W. MULL. Influence of aluminium on dogs. V. C. MYERS and D. B. MORRISON. Aluminium content of human autopsy tissue. V. C. MYERS and J. W. MULL (J. Biol. Chem., 1928, 78, 605—613, 615—624, 625—626).—Oral administration of 2 mg. of aluminium *per diem* had little or no effect on the aluminium content of the tissues or on the growth of rats. Intraperitoneal injection of aluminium was followed by an increase in the aluminium content of various tissues, particularly of the liver, of which the aluminium content rose to 8.22 mg.% as against the normal value of 0.14 mg.%. Similar results were obtained in dogs except that the aluminium content of the liver could be raised somewhat by oral administration of aluminium. The increased aluminium content of the tissues resulting from injection of aluminium was maintained for a considerable period after administration had ceased; excretion is therefore slow. Figures are given for the aluminium content of various human tissues determined at autopsy.

Determination of aluminium in animal tissues. V. C. MYERS, J. W. MULL, and D. B. MORRISON (J. Biol. Chem., 1928, 78, 595—604).—The tissue is incinerated with a mixture of sulphuric and perchloric acids; a trace of iron is added and then iron and aluminium are precipitated together by ammonia solution; the precipitate is re-dissolved and the iron alone removed with sodium hydroxide and acetic acid; the aluminium in the mother-liquor is determined colorimetrically by means of aurintricarboxylic acid. The method is applicable to the determination of 0.01—1.0 mg. per 100 g. of tissue with an error of  $\pm 10\%$ .

C. R. HARRINGTON.

Determination of arsenic in cadavers. R. FRIDL (Ber. ungar. pharm. Ges., 1926, 2, 84—87; Chem. Zentr., 1928, i, 1561).—The arsenic is separated as the element with Bettendorf's reagent, and weighed as such or as magnesium ammonium arsenate hexahydrate.

A. A. ELDRIDGE.

Detection of arsenic in ashes of cremated corpses. G. POPP (Z. angew. Chem., 1928, 41, 856—858).—Three experiments carried out on dogs to which arsenic had been administered showed that the arsenic detected in the calcined bones is about one sixth of the amount found in the bones before cremation, and less than one thousandth of the total

amount in the whole body before cremation. In each case, the liver was incompletely calcined, although the calcined bone ashes were white, and in one case, in which morphine was injected before death, the alkaloid was detected in the charred liver remains.

S. I. LEVY.

**Distribution of boric acid in human organs in six deaths due to boric acid poisoning.** W. D. McNALLY and C. A. RUST (J. Amer. Med. Assoc., 1928, 90, 382—383).

CHEMICAL ABSTRACTS.

**Distribution of gold in the organs of healthy and tuberculous rabbits following administration of gold preparations.** I. Non-tuberculous rabbits. B. BRAHN and G. WEILER (Biochem. Z., 1928, 197, 343—352).—A gold thiocarbamide compound ("lopion") containing 42% of gold, another organic compound ("preparation No. 2950"; 21.9% Au), and gold sodium thio-sulphate,  $(S_2O_3Au)Na_2 \cdot Na_2S_2O_3$  ("sanocrysin"; 37.35% Au), were the substances used, and the gold content of the kidneys, liver, lungs, spleen, heart, intestine, stomach, brain, bones, skin, and flesh was determined. The method adopted for the determination of the gold made it possible to determine accurately as little as 0.001 mg. In the experiments with "lopion" the chief amount of gold was found in the liver, whereas in those with the other two compounds by far the greatest amount was always found in the kidneys. The ratio of the amount of the element in the liver to that in the kidneys was about 3:1 when "lopion" was used, but when "preparation 2950" was used the ratio of the quantity of gold in the kidneys to that in the liver increased in proportion to the shortness of the time in which the animal died after injection. "Lopion" almost always caused high values for the gold content of the spleen, "sanocrysin" gave considerably lower figures, and with "preparation 2950" very low values were obtained. All three substances gave about the same, not very high, value for the content of the lungs. "Preparation 2950" gave lower amounts of gold in the heart than did the other two compounds. Almost throughout, the lowest values of all were for the brain. For the remaining organs very great variations were found. The toxicity of the three preparations used appeared to be proportional to the amount of gold which accumulated in the kidneys. Usually animals treated with "sanocrysin" lost weight considerably. The ratio of gold recovered from the organs to gold administered varied rather appreciably. The highest value found was 67.15%, "lopion" having been the compound used.

W. MCCARTNEY.

**Mobilisation of mercury from sparingly soluble depôts by halogen salts.** F. GARCIA (Arch. exp. Path. Pharm., 1928, 134, 142—148).—Rats to which a sparingly soluble mercury salt (calomel, mercuric oxide, di-iodide, or salicylate) had been administered in the form of a subcutaneous depôt showed symptoms of mercury poisoning after they were given sodium chloride, potassium bromide, or potassium iodide. The halogen salts apparently facilitate the dissolution and dissemination of the mercury salts, the activities being in the order  $Cl < Br < I$ .

W. O. KERMACK.

**Fatal thallium poisoning, and determination of thallium in cadavers as thallos iodide.** R. FRIDL (Ber. ungar. pharm. Ges., 1928, 4, 43—49; Chem. Zentr., 1928, i, 1561—1562).—The thallium was determined titrimetrically with 0.1N-potassium iodide solution. Of 2.5 g. of thallium acetate taken *per os*, there were found 3.3 mg. in 100 g. of liver, 1.6 mg. in 98 g. of kidney, 5.0 mg. in 100 g. of urine, the greater part having already been eliminated in the urine.

A. A. ELDRIDGE.

**Fatty degeneration of the liver.** A. GUBSER (Biochem. Z., 1928, 198, 65—80).—The fat appearing in the liver during phosphorus poisoning and during decrease of atmospheric pressure is distinguished by its high phosphatide content, whereas that caused by overheating and chloroform poisoning has a normal phosphatide content. In the liver rich in phosphatide, the total phosphorus content is not greater than normal, but the phosphatide forms a much greater part of the total phosphorus. The conversion of nuclein- into phosphatide-phosphorus is regarded as a step in the formation of this phosphatide.

P. W. CLUTTERBUCK.

**Absence of free aldehyde groups from enzyme solutions.** F. LEHR (Biochem. Z., 1928, 198, 204—205).—An attempt to detect the presence of free aldehyde groups in solutions of the following enzymes; 0.2% urease (jack bean), 0.5% taka-diastase, 1% pepsin and trypsin, freshly-prepared catalase, by means of the fuchsin-sulphurous acid method of Stepp, Feulgen, and Voit (A., 1927, 370) gave negative results.

P. W. CLUTTERBUCK.

**Specificity of intracellular dehydrogenases.** I. Dehydrogenase of cunner muscle. M. E. COLLETT (J. Biol. Chem., 1928, 78, 685—689).—The course of decolorisation of methylene-blue by a system consisting of washed muscle of the cunner together with one or more hydrogen donors in a vacuum was observed. Since decolorisation was no more rapid in presence of two donors than in presence of one, it is concluded that in the muscle of this fish there is only one dehydrogenase for which many substances may serve as hydrogen donors.

C. R. HARRINGTON.

**Potassium thiocyanate and diastatic action of saliva- and plant-diastases.** L. R. JOHNSON and A. WORMALL (Proc. Leeds Phil. Soc., 1928, 1, 318—324; cf. A., 1926, 1058).—Traces of potassium thiocyanate have a definite activating influence on the diastatic action of human saliva, which is significant at the concentration normally present. A similar effect is produced with malt diastase and with a diastatic preparation from potatoes. The effect is most pronounced when starch is used as substrate, but is still noticeable with dextrin or glycogen, or when sodium chloride is added to raise the concentration of this salt to the optimum value. The thiocyanate appears to accelerate only the first stages in the hydrolysis of starch and the rate of formation of reducing sugars is not markedly increased. The stimulating action of potassium thiocyanate on the germination of potatoes and barley is discussed in relation to the influence of the salt on diastatic action; preliminary experiments carried out with

barley indicate that potassium thiocyanate accelerates germination, although an excess retards or even destroys germinating power. C. W. SHOPPEE.

**Hydrolysis of starch by salts.** E. GLIMM and R. GRIMM (Biochem. Z., 1928, 197, 445—459).—Provided precautions are taken to maintain sterile conditions, starch is never hydrolysed by solutions of salts, of amino-acids, of peptones, or of mixtures of these substances. The results obtained by Hachn (cf. A., 1923, i, 443) and by Biedermann (cf. *ibid.*, 655) are thus explained, since these workers did not use sterile materials. From Witte's peptone were isolated two organisms which convert starch into dextrin. W. MCCARTNEY.

**Hydrolysis of sucrose by enzymes.** R. WEIDENHAGEN (Naturwiss., 1928, 16, 654—655).—The hydrolysis of disaccharides can be brought about by the action of simple glucosidases. For the hydrolysis of a disaccharide of the maltose type, only one glucosidase will be necessary, whilst the non-reducing sugars provide a possibility of the action of two. According to this theory the hydrolysis of sucrose can be brought about by the action of two different enzymes which are called  $\beta$ -*l*-fructosidase and  $\alpha$ -glucosidase. Some confirmation for the theory is to be found in the separation of maltase and invertase by Willstätter and Bamann, which may be regarded as a separation of  $\beta$ -*l*-fructosidase and  $\alpha$ -glucosidase. If "invertase-free maltase" is allowed to act on sucrose at the optimum  $p_H$  of 7.0 the hydrolysis taking place is of the order of a maltose hydrolysis, whilst at  $p_H$  4.6, which favours the fructosidase action, no hydrolysis can be proved. That no hydrolysis of raffinose occurs at  $p_H$  7.0 is also in complete agreement with the theory. A. J. MEE.

**Enzymic mutation and enzymic degradation of glycogen-lactic acid.** H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1927, 39, 287—295; Chem. Zentr., 1928, i, 1427).—The fission of aldehyde by liver juice takes place only in presence of co-enzyme; the reaction velocity diminishes considerably during the reaction. The effect is not shown with preparations obtained by precipitation with acetic acid; inhibiting substances are apparently thereby removed. In this isoelectric precipitation the purity of the enzyme is not greatly increased, but it is increased tenfold by fractional precipitation with ferric hydroxide. Liver juice showed no formation of lactic acid from glycogen or zymophosphate. With muscle juice lactic acid was formed, the reaction velocity being of the same order as that of the action of mutase. A. A. ELDRIDGE.

**Dry [enzyme] preparations from muscle.** H. VON EULER and S. PROFFE (Svensk Kem. Tidskr., 1927, 39, 295—297; Chem. Zentr., 1928, i, 1427).—The production of lactic acid and action of mutase by preparations from ox and rabbit muscle were studied. A. A. ELDRIDGE.

**Reactions of hexoses in the animal organism.** H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1928, 9, No. 38, 1—6).—The extract made by grinding washed rat liver with sand and water decolorises methylene-blue in absence and presence

of dextrose, lævulose, and rat's blood-serum. Mixtures of the serum with dextrose or lævulose do not cause decolorisation.

From experiments on the decolorisation of methylene-blue with yeast suspensions and sodium zymophosphate it is concluded that pure hexosediphosphate is not fermented in absence of co-enzyme, and is of no use as a hydrogen donor. H. BURTON.

**Properties of emulsin prepared 23 years ago.** M. BRIDEL and (Mlle.) M. DESMAREST (J. Pharm. Chim., 1928, [viii], 8, 201—205).—In a sample of emulsin prepared from almonds in 1905  $\beta$ -glucosidase and lactase were still active but had lost more than 50% of their activity. Invertase was only very feebly active (cf. B., 1928, 729).

E. H. SHARPLES.

**Stereochemical specificity of lipases.** P. RONA and R. ITELSOHN-SCHECHESTER (Biochem. Z., 1928, 197, 482—490; cf. A., 1927, 377).—Pig-liver lipase preferentially hydrolyses the *d*-component in *r*-ethyl mandelate. As regards rate of hydrolysis, *l*-ethyl mandelate is most rapidly attacked by this lipase, whereas the *d*- and *dl*-forms and a mixture of equal parts of the *d*- and *l*-forms are hydrolysed more slowly but at equal rates. The action of the enzyme does not begin immediately after mixture with the substrate. An induction period, the extent of which depends on the degree of purity of the substrate, is observed (cf. Willstätter and others, A., 1927, 793). The degree of purity of the ferment has no influence on its specificity and it is concluded that the specificity is a property of the pure enzyme. The extent of the period of induction appears to increase with increasing purity of the ferment. When methyl mandelate is used similar results are obtained. Pig-pancreas lipase affects ethyl mandelate in the same way as it affects the methyl ester. W. MCCARTNEY.

**Kidney phosphatase and its activation. II.** III. H. ERDTMAN (Z. physiol. Chem., 1928, 177, 211—220, 231—236).—II. Investigation has been made of the fission of glycerophosphate solution by kidney phosphatase activated by meat extract (cf. this vol., 671). It is shown that the activator is not an enzyme protector, and that an excess of phosphate retards the reaction (cf. Martland and Robison, A., 1927, 699). Fission of sodium zymophosphate is effected with the activated phosphatase, but not as readily as that of glycerophosphate.

It is shown that the activator contains magnesium sulphate, and a comparison of glycerophosphate fission using pure magnesium sulphate and the sulphate from the activator shows their identity.

III. Activation of kidney phosphatase is not effected by calcium, zinc, or beryllium sulphates. Active enzyme preparations can be obtained by precipitation with alcohol. After further adsorption on aluminium hydroxide at  $p_H$  5 and elution with Sørensen's secondary phosphate buffer an increased activity is manifested. The purest preparation obtained gives Millon's reaction, a negative Molisch's test, and an indistinct biuret reaction.

H. BURTON.

**Purification of nucleosidases.** H. VON EULER and E. BRUNIUS (Arkiv Kemi, Min., Geol., 1928, 9,

No. 40, 1—14).—The reaction between nucleosidase (prepared by extraction of pig or ox kidney with water) and adenosine, measured by determination of the ribose liberated, is unimolecular and 73% fission occurs at infinite time. Partial purification of the nucleosidase is effected by dialysis or better by isoelectric precipitation combined with dialysis. Kaolin is unsuitable as an adsorbent, and although aluminium hydroxide *B* at  $p_H$  6 effects 73% adsorption, subsequent elution yields only 10%. Alcohol and colloidal ferric hydroxide effect adsorption, but the enzyme is not recovered at  $p_H$  6 or 9. Precipitation with alcohol is unsuitable, but fractional precipitation with acetone gives some improvement, whilst a further purification is effected by isoelectric precipitation. H. BURTON.

**Pepsin.** I. H. PENAU and J. PLÉ (Bull. Soc. Chim. biol., 1928, 10, 779—783).—See this vol., 922.

**Effect of fluorides and iodides on the clotting of milk by pepsin.** W. M. CLIFFORD (Biochem. J., 1928, 22, 1128—1132).—The clotting of milk by pepsin is inhibited by the addition of sodium, potassium, and ammonium fluorides and lithium, sodium, potassium, and ammonium iodides. This inhibitory action depends on the concentration of the halide. The inhibition of coagulation occurs suddenly at a definite molarity of the halide added, a difference of 0.0036*M* changing the rate from 5—13 min. to absence of change for 4—6 hrs. The inhibitory action of fluorides is greater than that of iodides. The concentration of ammonium iodide has to be six times that of sodium or potassium iodide and ten times that of lithium iodide to produce a similar inhibitory effect. S. S. ZILVA.

**Action of fluoride on urease.** M. JACOBY (Biochem. Z., 1928, 198, 163—174).—Fluoride exerts its greatest action on urease when the enzyme is under optimal conditions of  $p_H$ , phosphate buffering, and cyanide activation, and the action cannot be replaced by that of oxalate or citrate. The action of fluoride is probably specifically on the urease, but no stoichiometric relationship exists between fluoride and enzyme. Urease adsorbed on cholesterol is elutable by water. By decreasing the concentration of the urease, adsorption by cholesterol at first decreases to a minimum and then increases. P. W. CLUTTERBUCK.

**Selective fermentation of dextrose and lævulose by brewer's yeast.** R. H. HOPKINS (Biochem. J., 1928, 22, 1145—1156).—Top and bottom types of brewer's yeast ferment dextrose faster than lævulose in mixtures of the two, both when the yeast is multiplying freely in the presence of various kinds of nutrients and when nutrients are absent. The relative specific rates of fermentation in such cases are dependent mainly on the species of yeast used and on the conditions of its nutrition. No lævulose could be detected in a solution of dextrose undergoing fermentation by living yeast. Zymin prepared from brewery yeast ferments dextrose faster than lævulose in a mixture of the two. A yeast trained by continual subculturing in a medium of lævulose and nutrients showed no change in its properties as regards selectivity. The temperature coefficients of

esterification of dextrose and lævulose by zymin under conditions of phosphate concentration yielding the optimum esterification of dextrose are approximately the same, *i.e.*,  $v_{25}/v_{15}=2.0$ . S. S. ZILVA.

**Fermentation of hexoses racemised by dilute alkalis.** A. FERNBACH, M. SCHOEN, and M. MORI (Ann. Inst. Pasteur, 1928, 42, 805—826).—The course of fermentation of solutions of dextrose or mannose, rendered optically inactive by treatment with sodium hydrogen carbonate (0.8%) at 40°, with different yeasts is followed by measurement of the alcohol produced, the iodine value, the reducing power, and the optical activity. In all cases the alcohol formed is about 90% of the theoretical and the reducing power and the iodine value fall to a low figure. With brewer's yeast the curve of rotatory power first becomes negative and then rises to a small positive value, whilst with another variety (Sauterne) it becomes strongly positive and finally falls to a similar value (possibly representing a small amount of an unfermentable sugar).

G. A. C. GOUGH.

**Enzymic production of hexosephosphates.** H. VON EULER, K. MYRBÄCK, and D. RUNEHJELM (Arkiv Kemi, Min., Geol., 1928, 9, No. 49, 1—6).—Fermentation of the sodium hexosemonophosphate of Robison gives carbon dioxide and hexosediphosphate, no inorganic phosphate being produced. Fermentation of dextrose with a very active yeast in presence of phosphates and subsequent purification of the hexosemonophosphate produced through the barium salt,  $[\alpha]_D +33^\circ$ , affords a new *hexosemonophosphoric acid* having  $[\alpha]_D +63^\circ$ . Fermentation of dextrose with dry yeast-*H* in presence of phosphates and some hexosediphosphoric acid gives, after removal of the diphosphate as the insoluble barium salt, a hexosemonophosphoric acid,  $[\alpha]_D +15^\circ$ , similar to Robison's. H. BURTON.

**Co-zymase.** XV. H. VON EULER and K. MYRBÄCK (Z. physiol. Chem., 1928, 177, 237—247).—When partly purified co-zymase (A., 1927, 993) is treated with picric acid solution an inactive *picrate*, m. p. 183°, is obtained. The base, m. p. 209° (slight decomp.), obtained from this is adenylnethylthiol-pentose,  $C_{11}H_{15}O_3N_5S$  (cf. Suzuki, Odake, and Mori, A., 1925, i, 338). The picric acid liquors when treated by methods previously described (*loc. cit.*) give preparations with an increased activity, which contain only small amounts of sulphur (0.3—0.5%), and about 14—15% N, 40% C, and 5.5% H. Hydrolysis with dilute acids produces adenine and a reducing nitrogen-free carbohydrate. The original co-zymase does not reduce alkaline copper solution. The carbohydrate contains pentose, since distillation with acid affords furfuraldehyde. It is concluded that the purest preparation yet obtained contains but a small proportion of co-zymase.

Co-zymase is very stable towards oxidising agents. A rapid air current at  $p_H$  4 and 7 at 25° for 24 hrs. has no effect. Acid permanganate has no action, but at  $p_H$  8 a slow decomposition occurs. Bromine water does not affect the co-enzyme during 15 min. even when the bromine is expelled at 50°.

H. BURTON.

**Co-zymase and enzymic carbohydrate metabolism.** H. VON EULER and K. MYRBÄCK (Arkiv Kemi, Min., Geol., 1928, 9, No. 37, 1—6).—Highly-purified co-zymase preparations are obtained from fresh yeast extracts by precipitating twice with lead (acetate?), then with silicotungstic acid, and finally with ammoniacal silver nitrate. Other methods of purification are also given. The pure preparations contain only a trace of phosphorus and do not exhibit protein or ninhydrin reactions. Molisch's test and the phloroglucinol reaction for pentoses are strongly positive. When heated with copper sulphate and hydrogen sulphite considerable inactivation of the co-zymase occurs.

H. BURTON.

**Purification of yeast co-zymase.** R. NILSSON (Arkiv Kemi, Min., Geol., 1928, 9, No. 31, 1—22).—Dialysis of co-zymase preparations affords a convenient method of purification. Precipitation of the co-enzyme with lead acetate and subsequent adsorption on lead hydroxide effects purification, but further treatment with lead acetate causes inactivation. Precipitation with colloidal iron hydroxide is not advantageous, although the co-zymase is remarkably free from ash and does not give a precipitate with lead acetate. Careful adsorption on lead hydroxide also effects purification. Adsorption on aluminium hydroxide at  $p_H$  10, subsequent elution with an acetate mixture at  $p_H$  5, and further adsorption on lead hydroxide at  $p_H$  10 gives an improved preparation. No adsorption on silicic acid was effected at  $p_H$  4.7 or 10.

H. BURTON.

**Co-zymase in respiring organs of plants.** H. VON EULER and E. NORDENFELDT (Arkiv Kemi, Min., Geol., 1928, 9, No. 35, 1—6).—An aqueous extract of green malt root-tips possesses a small co-zymase value. Malt embryo extract has a low co-zymase content and progressive germination causes a diminution of the enzyme. The oxygen consumption of fresh malt embryo is in large excess over the amount necessary to oxidise completely the sugar which is lost during the process.

H. BURTON.

**Biological oxido-reductions.** H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1928, 9, No. 29, 1—6).—The addition of dihydroxyacetone to a mixture of washed yeast and co-reductase causes a retardation in the time taken to decolorise methylene-blue both in absence and presence of dextrose. Insulin and a mixture of insulin and dextrose have no effect on the time factor (yeast-enzyme preparation only), but decolorisation is more rapid with added dextrose. Washed rabbit heart-muscle contains no donator, but it decolorises methylene-blue in presence of dihydroxyacetone, dextrose and dihydroxyacetone, and dextrose. Decolorisation is slowest in the last case. Zymophosphate has a powerful donator action causing decolorisation in presence of washed yeast in 10 min., whilst the yeast alone caused no reduction in 12 hrs. Methylene-blue is rapidly decolorised in presence of sodium succinate by washed yeast to which is added blood extract, thus demonstrating the presence of co-reductase in blood.

H. BURTON.

**Mutase.** H. VON EULER and E. GRABE (Arkiv Kemi, Min., Geol., 1928, 9, No. 50, 1—6).—A partial

transformation of furfuraldehyde is brought about by ordinary dried yeast or washed yeast to which has been added a boiled yeast extract or purified co-zymase (cf., A., 1927, 175, 484). Dismutation of formaldehyde occurs rapidly during the first hour and then ceases after 30% change, presumably owing to the inactivation of the enzyme by the aldehyde. The presence of a small amount of potassium cyanide does not affect the transformation of acetaldehyde, but 0.003*N*-cadmium and -zinc chlorides cause considerable retardation. A very slight retardation is caused by 0.1*N*-calcium and -potassium chlorides, and potassium iodide and fluoride.

Mutase is found to occur in fresh and dried wheat seedlings and extracts therefrom.

H. BURTON.

**State of combination of nucleic acid in yeast.** N. ISHIYAMA (Z. physiol. Chem., 1928, 177, 295—297).—When dried yeast is extracted with 10% copper chloride solution, the extract treated with sodium picrate solution, the precipitated picrates purified and finally converted into sulphate, 0.5% of a solid is obtained which when treated with a hydrochloric acid-pepsin solution is completely hydrolysed. It is concluded that there is no protamine-like substance in yeast and that yeast-nucleic acid is not in the same state of combination as the nucleic acids from fish sperm and the thymus gland.

H. BURTON.

**Enzymic nitrogen metabolism.** H. VON EULER (Arkiv Kemi, Min., Geol., 1928, 9, No. 47, 1—6).—*B. coli* effects a 15—20% conversion of alloxan into alloxanic acid, but has little action on barbituric acid and none on uric acid and uracil. Prolonged action of *B. prodigiosus* on Witte's peptone solution causes the disappearance of tryptophan (cf. A., 1926, 1177). Mandelonitrile is hydrolysed by expressed calf-liver juice in presence of calcium or sodium hydrogen carbonate to mandelic acid.

H. BURTON.

**Theory of the production of zymase by the living cell.** E. C. GREY (Proc. Roy. Soc., 1928, B, 103, 302—311).—Experiments are described demonstrating that the first anaërobic mode of decomposition of dextrose by *B. coli communis* (cf. following abstract) is exhibited by the bacterium after a period of aerobic activity. The enzymes responsible for the zymase type of fermentation are considered to be derived from the enzymes responsible for aerobic respiration.

W. O. KERMACK.

**Enzymes of *Bacillus coli communis*.** VI. Alternative modes by which *B. coli* may bring about anaërobic decomposition of dextrose. E. C. GREY (Proc. Roy. Soc., 1928, B, 103, 312—320).—*B. coli communis* decomposes dextrose anaërobically according to two mechanisms in the first of which carbon dioxide, alcohol, formic acid, and succinic acid are produced and in the second of which lactic acid is the characteristic product. Under disadvantageous conditions, e.g., as the result of age or in presence of chloroacetate, the second type of decomposition tends to persist longer than the first.

W. O. KERMACK.

**Behaviour of "β-lysin" with lipin solvents.** A. PETTERSSON (Z. Immunitätsforsch., 1928, 54, 292—302; Chem. Zentr., 1928, i, 1538).—The highly

thermo-resistant bactericidal component of serum ("β-lysin") does not lose its activity towards *Bacillus subtilis*, *B. putrificus*, or *B. coli* by treatment with ether, chloroform, or light petroleum, whilst the thermolabile serum-alexin is thereby destroyed. Acetone and serum afford a non-bactericidal precipitate.

A. A. ELDRIDGE.

**Spirochaeticidal properties of elemental vanadium. Asterogenesis around vanadium particles.** C. LEVADITI, P. LEPINE, and (MLLE.) R. SCHOEN (Compt. rend., 1928, 187, 434—436).—The anti-syphilitic properties of vanadium compounds are shared by the element itself, which, when injected as fine particles in suspension in oil, has a definite curative action on rabbits. Radiating masses are formed round the particles, resembling those formed by *Actinomyces*.

E. W. WIGNALL.

**Female sex hormone in yeast.** E. GLIMM and F. WADEHN (Biochem. Z., 1928, 197, 442—444).—The presence of the hormone in yeast has been confirmed. Brewer's yeast, probably because it grows in a medium rich in organic nitrogen, has a higher content of "feminin" than pressed yeast which is derived from a medium half of the nitrogen of which exists in the form of ammonium salts. When yeasts are preserved in the cold no change takes place in the content of hormone.

W. MCCARTNEY.

**Influence of adrenaline on formation of sugar.** E. GEIGER and E. SCHMIDT (Arch. exp. Path. Pharm., 1928, 134, 173—184).—Administration of adrenaline to fasting phloridzinised dogs does not increase the D/N ratio of the urine unless mobilisation of muscle glycogen occurs. The fat content of the liver is not decreased as a result of the administration of adrenaline. It therefore appears that adrenaline does not facilitate formation of dextrose from fat. The protein metabolism, which is raised as the result of phloridzin, and the excretion of acetone compounds in the urine, are both lowered during the process of glycogen mobilisation.

W. O. KERMAK.

**Cardaïssin, a new cardiac accelerator extracted from the suprarenal gland.** H. G. CAMERON (Endocrinol., 1926, 10, 577—601).—*Cardaïssin*, differing from adrenaline, was obtained by fractional precipitation of a de-fatted neutral acetone extract of ox adrenals.

CHEMICAL ABSTRACTS.

**Crystalline insulin. VI. An adsorption product?** V. DU VIGNEAUD, E. M. K. GEILING, and C. A. EDDY (J. Pharm. Exp. Ther., 1928, 33, 497—509).—Crystalline insulin (from beef pancreas) adsorbed from its solution in 0.01*N*-hydrochloric acid on charcoal and eluted with phenol exhibits no change in activity. When, in accordance with the method of Dingemans, the product is extracted with 0.06*N*-disodium hydrogen phosphate solution no differential solubility of the material could be detected, both the soluble fraction and the residue possessing the same activity, whilst the charcoal-phenol powder was reconverted into crystalline insulin identical in all respects with the original product. When crystalline insulin is heated with 0.1*N*-hydrochloric acid for 1 hr. at 100°, a precipitate, insoluble in hydrochloric acid and disodium hydrogen phosphate

solution, is obtained which, however, dissolves in dilute alkali and by acidification of this solution can be regenerated in its original acid-soluble form with only a slight loss of activity. The activity of solutions of insulin in disodium hydrogen phosphate decreases on keeping.

J. W. BAKER.

**Crystalline insulin. VII. Acetylation and behaviour of insulin towards alkali.** H. JENSEN and E. M. K. GEILING (J. Pharm. Exp. Ther., 1928, 33, 511—520).—Crystalline insulin (activity 45 units/mg.) treated with acetic anhydride for 15 hrs. at 0° yields acetylinsulin (4.5% Ac), which in 0.06*N*-disodium hydrogen phosphate solution has a very much smaller activity (8 units/mg.). The acetylinsulin is hydrolysed by 0.01*N*-sodium hydroxide at 0°, hydrolysis being almost complete in the first few minutes, the regenerated insulin having an activity of 25 units/mg., the whole of the activity being in the precipitate produced by adding excess of acetic acid to the alkaline solution. The lowered activity of the regenerated insulin is probably due to the loss of hydrogen sulphide, since even the dilute sodium hydroxide employed eliminates some hydrogen sulphide from acetylinsulin, whilst the original crystalline insulin is unaffected by the same concentration of alkali for 15 hrs. at 0°. The sulphur in acetylinsulin, therefore, appears to be much more labile than in insulin itself. Contrary to Freudenberg and Dirscherl (this vol., 675), it is found that acetylinsulin loses 30% of its activity by treatment with 0.03*N*-sodium hydroxide for 15 hrs. at 0°, and the much lower activity of the regenerated insulin of these authors is probably due to the greater amount of decomposition which occurs with the more concentrated alkali.

J. W. BAKER.

**Influence of diet on the physiological assay of insulin.** A. STASIAK (J. Lab. Clin. Med., 1926, 12, 256—258).—The actual range through which the blood-sugar is lowered by insulin is approximately the same in fed and starved rabbits.

CHEMICAL ABSTRACTS.

**Influence of a lipid pituitary hormone on the deamination process in organs.** R. AGNOLI (Arch. exp. Path. Pharm., 1928, 134, 74—87).—A definite quantity of glycine (3 g.) was administered intravenously to a dog and the concentration of the compound left in the circulating blood was determined at intervals by measuring the amino-acid content of the protein-free filtrate. The rate of disappearance of the glycine was not sensibly altered by the administration of extracts of the posterior lobe of ox pituitary nor by certain commercial preparations of pituitrin, but was slightly accelerated by an extract of the whole ox pituitary, whilst the lipid extract of the whole dried ox pituitary or of fresh pig pituitary had a marked accelerating action.

W. O. KERMAK.

**Influences of substances of the thyroid gland on fat metabolism.** I. ABELIN and P. KÜRSTEINER (Biochem. Z., 1928, 198, 19—46).—Considerable loss of fat is found in animals 24—72 hrs. after administration of thyroid substances (powdered gland, thyroidea, etc.), although during this time only a slight increase in combustion has taken place.



Striated muscle shows the greatest, and liver and lung a smaller loss. The chief characteristic of this action is the almost complete inhibition of the resynthesis of cellular from nutritive material. A glycogen-free liver stores much fat and can ordinarily form glycogen from suitable material. Administration of thyroid substances causes the liver not only to become free from glycogen but also poor in fat. This loss of fat disturbs the synthesis of glycogen, but injection of adrenaline causes a partial recovery of the power of the liver to form glycogen.

P. W. CLUTTERBUCK.

**Determination of vitamin-A.** H. C. SHERMAN and M. P. BURNIS (J. Biol. Chem., 1928, 78, 671—680).—The larger the weight of the test animal the less is its gain in weight with a given intake of vitamin-A; in testing for this vitamin male and female rats may be used equally well. It is considered best to adhere to an 8-week period for the test and to a weekly gain in weight of 3 g. as a standard; shortening of the period tends to give variable and higher results for the vitamin-A content of the material under test, whilst adoption of a higher standard rate of gain in weight decreases the delicacy of the test.

C. R. HARRINGTON.

**Fat-soluble growth factors.** H. VON EULER (Arkiv Kemi, Min., Geol., 1928, 9, No. 28, 1—6).—Rats fed on a vitamin-A-deficient diet supplemented by an irradiated 1% solution of cholesterol in ivory-nut oil show a normal blood-phosphorus content (A., 1925, i, 1515). Cholesteryl acetate and palmitate do not promote growth. Extracts of wheat seedlings and top yeast-*R* have a remarkably high antirachitic action. Betulin shows a doubtful antirachitic action.

H. BURTON.

**Irradiated vitamin-B and automatin action.** H. ZWAARDEMAKER (Proc. K. Akad. Wetensch. Amsterdam, 1928, 31, 258—260).—The beating of an eel's heart which has been arrested by washing out potassium salts is restored by the addition of vitamin-B, previously irradiated for 15 hrs., to the circulating fluid in a manner similar to that produced by the addition of automatin from another irradiated heart, the contractions continuing regularly for 13—16 hrs. The latent period before the contractions recommence depends only on the time required for washing out the potassium salts, whilst the frequency depends on the concentration of the stimulating substance. Addition of non-irradiated vitamin-B causes only spasmodic single beats which cease after a period of about 2 hrs.

J. W. BAKER.

**Nitrogenous metabolism during unbalanced nutrition. II. Nitrogenous metabolism in hens during avitaminosis-B.** B. A. LAVROV and S. N. MATZKO (Biochem. Z., 1928, 198, 138—148).—When hens are fed on polished rice, the early damage to the motor function of the crop leads to an avitaminosis complicated by starvation, and this method is therefore unsuitable for investigating the effect of avitaminosis on nitrogenous metabolism. When hens are fed on oats and starch and then transferred to rice, the body-weight at first remains steady and then slowly declines. The nitrogen balance is positive, but after 7 days becomes negative and the

uric acid excretion may increase 280%. It would appear therefore that in the initial stages of avitaminosis-B, a more intensive decomposition of nitrogenous body substances takes place, followed a week later by the usual symptoms.

P. W. CLUTTERBUCK.

**Content of vitamin-C in Japanese sand pear (*Pyrus serotina*, Rehder), kaki (*Diospros kaki*, L.), and Satsuma orange (*Citrus unshiu*).** Y. IWASAKI (J. Okitsu Hort. Soc., 1927, No. 22, 1—10).

CHEMICAL ABSTRACTS.

**Colour reactions of substances containing vitamin-D.** W. A. SEXTON (Biochem. J., 1928, 22, 1133—1134).—From the examination of a number of substances it is concluded that the colour tests of Shear and Kramer (Proc. Soc. Exp. Biol. Med., 1926, 23, 546) and Bezssonoff (A., 1925, i, 107) are not specific for vitamin-D.

S. S. ZILVA.

**Action of X-radiation on vitamin-D in activated ergosterol.** R. R. MORRISON, P. R. PEACOCK, and S. WRIGHT (Biochem. J., 1928, 22, 1138—1141).—A dose of 0.0002 mg. of ergosterol activated under the conditions described will partly protect against and cure experimental rickets. X-Rays when applied to a dry sample of activated ergosterol exposed to the air exert a destructive effect on vitamin-D.

S. S. ZILVA.

**Respiration of beans (*Phaseolus multiflorus*) grown on an iron-deficient medium.** H. VON EULER and S. STEFFENBURG (Arkiv Kemi, Min., Geol., 1928, 9, No. 48, 1—6).—Seeds of *Phaseolus multiflorus* were grown on artificial media and the oxygen consumption of normal and chlorotic leaves was compared. Although the chlorotic leaves contain more iron than the green leaves, the intensity of respiration per mg. of iron is higher for the latter. A similar relation holds per g. of dry leaf. It is suggested that the cytochromic iron will be found to be higher in the green leaves.

H. BURTON.

**Relations between pigment formation, leaf area, and dry weight of maize grown in sand cultures.** H. B. SPRAGUE (New Jersey Sta. Rep., 1925, 332—337).—The chlorophyll content was more closely related to the area than to the weight of the leaf, whilst the reverse held for carotin and xanthophyll.

CHEMICAL ABSTRACTS.

**Changes of fluorescent colours in ultra-violet light.** M. HAITINGER and V. REICH (Z. angew. Chem., 1928, 41, 982—983).—The slow decrease in intensity of the fluorescent colours of ethereal extracts of wines and plant juices in daylight is traced to the effect of ultra-violet rays. Exposure to a mercury-vapour lamp produces notable colour changes in 1 hr.

A. G. POLLARD.

**Cause of blueing in red roses.** G. S. CURREY (J. Proc. Roy. Soc. New South Wales, 1927, 61, 307—314).—The blueing of red roses is traced to insufficiency of tannin in the petals, and does not appear to depend on the nature of the anthocyanin pigment. There is a direct relationship between the quantities of tannin and of anthocyanin pigment present.

C. W. GIBBY.

**Cell-wall substances of plants; chemical changes taking place during lignification.** E. J. CANDLIN and S. B. SCHRYVER (Proc. Roy. Soc., 1928, B, 103, 365—376).—The action of dilute sodium hydroxide solution on pectic acid prepared from onion or citrus effects decarboxylation with the formation, amongst other products, of hemicellulose.

W. O. KERMACK.

**Composition and structure of the cell-wall of wood.** G. J. RITTER (Ind. Eng. Chem., 1928, 20, 941—945; cf. B., 1925, 985).—Examination of sections of the wood of the Western yellow pine, elm, and red alder shows that the lignin is distributed almost equally between the middle lamella and the cell-wall, that present in the former being more soluble in alcohol. Changes in the structure of the fibre on swelling have been examined microscopically. The optical phenomenon observed when the bordered pits are examined between crossed Nicols may be explained if it is assumed that the longitudinal chains of cellulose molecules in the cell-wall are continuous and are bent around either side of the circular pit orifice. When lignified and delignified fibres are treated with swelling agents (15% sodium hydroxide or concentrated acids) the walls thicken both outwardly and inwardly, the general angular cross-section of the former being unaltered, whilst that of the latter is changed to a circular form in which the circumference is limited by the outer layer of fibrils which are oriented at 90° to the axis of the fibre. Alternate swelling and shrinking of delignified fibres by treatment with alkali followed by neutralisation with acids separates the several layers of which the cell-wall is composed. These layers can, by more drastic alkali-acid treatment, or better by treatment with 68% phosphoric acid, be separated into fibrils, those in the outer layer extending at approximately 90°, and in the remaining layers at 0—30°, to the axis of the fibre.

J. W. BAKER.

**Acidity of root secretions.** E. G. MININA (Bull. inst. rech. biol. Univ. Perm, 1927, 5, 233—253).—Roots of bean, lupin, buckwheat, and cereals, in a soil of low buffering power, cause the soil solution to become more acid, then more alkaline, and finally more acid as the plant develops. Roots in distilled water excrete non-volatile organic acids.

CHEMICAL ABSTRACTS.

**Formation of starch in the needles of the pine.** M. A. BARGUES (Bull. Inst. Pin, 1928, 1—3; Chem. Zentr., 1928, i, 1537).—Starch is present in all cells of pine needles except those of the epidermis and the innermost tissue. Variations with season of the starch content are traced. Daily variations occur only in the peripheral green tissue. Branches which by being kept in the dark have lost much of their starch rapidly regain it when 5% dextrose solution is used as nutrient.

A. A. ELDRIDGE.

**Rôle of phosphorus in the intermediate carbohydrate metabolism of plants.** H. K. BARRENSCHEEN and W. ALBERS (Biochem. Z., 1928, 197, 261—277).—In plants during assimilation there is an increase in the amount of acid-soluble organic phosphorus due to the intermediate formation of carbohydrate-phosphoric esters. In germinating rye

and wheat grains the variations in the amounts of inorganic phosphorus, acid-soluble phosphorus, and acid-soluble organic phosphorus appear to depend on the time of year at which germination takes place, on the origin of the material used, and on other factors. The embryonic parts of the seeds exhibit the alterations in the way in which the phosphorus is combined most clearly and from those parts a substance which has the properties of a hexosemonophosphoric acid can be obtained. This acid, which forms an amorphous barium salt, probably  $(C_{12}H_{20}O_{10})_4 \cdot PO_3Ba_2 \cdot 2BaO$ , and a crystalline brucine salt, m. p. 168—169° (uncorr.), is believed to be an intermediate product in the synthesis or degradation of starch.

W. MCCARTNEY.

**Colorimetric determination of the phosphoric acid requirement of soils.** A. NEMEC (Biochem. Z., 1928, 198, 112—127).—The author's previous work (this vol., 95) on the influence of the soluble silicic acid content of soil on the absorption of phosphoric acid is extended using a variety of plants and soils. The phosphoric and silicic acid contents of the soils are tabulated and the phosphate requirement is thus determined indirectly.

P. W. CLUTTERBUCK.

**Current mineral nutrient content of the plant solution as an index of metabolic limiting conditions.** B. E. GILBERT, F. T. MCLEAN, and W. L. ADAMS (Plant Physiol., 1927, 2, 139—151).—In a study of the expressed plant solution from various tissues of spinach, beet, turnip, maize, cabbage, and carrot, three types of inhibited metabolism were noted, due to (1) a decreased supply of available manganese in a neutral soil, (2) limiting amounts of phosphate and nitrogen applied to the soil, and (3) unfavourable weather conditions.

CHEMICAL ABSTRACTS.

**Calcium and magnesium content of some plants of the Mediterranean area.** E. CANALS and (MLLE.) G. DAUCAN (Bull. Soc. chim., 1928, [iv], 43, 779—784).—Except in *Salicornia fruticosa* and *Suaeda fruticosa*, among the Phanerogams, the magnesium content is higher in the leaf than in the stem. Among herbaceous plants the xerophytes contain less magnesium than the hygrophiles. Plants grown on saline soils are low in magnesium, the non-halophile *Sedum altissimum* and *Opuntia ficus* being the richest. The variations in the magnesium content of leaves with age are less significant than those of calcium, except in the case of *S. altissimum*, the magnesium content of this plant being in October only about a third of its content in March. In woody shrubs and trees (halophiles and xerophytes), the calcium/magnesium ratio is higher in the stems than in the leaves, except in the case of *Phyllirea angustifolia*. In the hygrophile order the reverse is the case. The ratio may vary from year to year in the same plant examined at the same season and grown on the same soil. With the halophiles, e.g., *Salsola soda*, the ratio may be less than unity and in general it increases with the age of plant.

R. BRIGHTMAN.

**Distribution of calcium oxalate crystals in plant tissues; their probable rôle in plant metabolism.** G. P. MAJUMDAR (Indian Sci. Cong. Proc. Calcutta, 1925, 12, 187).—Excess of calcium is

supposed to be used in precipitating oxalic acid and soluble oxalates. It appears that calcium oxalate is re-introduced into the metabolic cycle, and that a limited supply of calcium may be sufficient for the life of plants. CHEMICAL ABSTRACTS.

**Nitrogen metabolism of *Pyrus malus*, L. III. Partition of nitrogen in the leaves and one and two year branch growth and non-bearing spurs throughout a year's cycle.** W. THOMAS (Plant Physiol., 1927, 2, 109—137).—The total water-soluble nitrogen, non-protein nitrogen, and amino-nitrogen are parallel with the total nitrogen in all tissues throughout the cycle, but the amide nitrogen and the residual nitrogen tend to vary inversely with the total and amino-nitrogen. Amino-nitrogen is probably connected with protein synthesis and residual nitrogen with protein degradation, but amino-acids show no catalytic effect in accelerating growth. Nitric nitrogen was found only as the buds opened. CHEMICAL ABSTRACTS.

**Cress grown on adrenaline.** J. H. THOMPSON (Nature, 1928, 122, 401).—Cress, when grown in adrenaline solution, appears to synthesise adrenaline or a similar compound from the products of oxidation of adrenaline. A. A. ELDRIDGE.

**Manganese content of plants affording officinal drugs.** O. WILLMANN (Ber. ungar. pharm. Ges., 1927, 3, 29—53; Chem. Zentr., 1928, i, 1533—1534).—The manganese content of a large number of drugs of the Hungarian Pharmacopœia (3rd ed.) has been determined. Aquatic plants contain more than others; young plants contain more than old, and the aerial more than the subterranean portions. The manganese is present chiefly in the cell plasma. A. A. ELDRIDGE.

**Nitrogenous constituents of the leaves of kuzu (*Pueraria hirsuta*, Matsum).** R. SASAKI (Bull. Agric. Chem. Soc. Japan, 1928, 4, 1—5).—After precipitation of the protein, adenine, asparagine, glutamic and butyric acids, and a base (chloroaurate, m. p. 117—118°) were isolated. CHEMICAL ABSTRACTS.

**Localisation of alkaloid in the seed of *Colchicum autumnale*, L.** P. LIPTÁK (Ber. ungar. pharm. Ges., 1927, 3, 346—351; Chem. Zentr., 1928, i, 1534—1535).—Colour reactions indicate that the alkaloid is contained in the endosperm and in the third layer of the seed coat. A. A. ELDRIDGE.

**Variation in composition of althæa root.** J. KABAY (Ber. ungar. pharm. Ges., 1928, 4, 19—23; Chem. Zentr., 1928, i, 1537).—Ash, sugar, starch, galactose, and mucilage determinations for the period April to October are recorded. A. A. ELDRIDGE.

**Mucilage of the rhizome of *Polygonatum officinale*, All.** B. GAAL (Ber. ungar. pharm. Ges., 1927, 3, 133—139; Chem. Zentr., 1928, i, 1534).—Arabinose, dextrose, and *d*-lævulose (81.7%) are present. When oxidised by Tollens' method the mucilage did not afford mucic acid. A. A. ELDRIDGE.

**Gum extracted from cotyledons of *Anagyris foetida*.** P. CONDORELLI and A. CHINDEMI (Anali Chim. Appl., 1928, 18, 313—317).—This gum contains

a paragalacto-araban,  $C_6H_{10}O_5, C_5H_8O_4, 8H_2O$ , on which potassium and calcium silicates and phosphates are adsorbed. It differs from the podalirin contained in the seeds (cf. Condorelli, A., 1926, 210) in being much less soluble in water, and in containing no ketonic sugars. E. W. WIGNALL.

**Formation of methyl alcohol in the autolysis of fresh tobacco leaves.** C. NEUBERG and B. OTTENSTEIN (Biochem. Z., 1928, 197, 491—501; cf. A., 1927, 385; this vol., 201).—Tobacco pectase is able to hydrolyse tobacco pectin. Under the conditions of experiment about 50% of the methyl alcohol present in the form of esters was eliminated in 2 hrs. by autolysis. Then the hydrolysis continued slowly until, after 5 weeks, the amount was 90%. Control experiments showed that the liberation of the alcohol was actually due to enzymic processes. Air-dried, unfermented tobacco leaf still contains considerable amounts of both firmly-combined and loosely-combined methyl alcohol, because rapid removal of water prevents hydrolysis of the pectin. The ribs contain more methoxyl than the remaining parts of the leaves, but since these contain more pectic methyl alcohol than the ribs, it follows that the ribs are richer in lignin. W. MCCARTNEY.

**Photocapillary reaction of plant phosphatides.** I. Influence of salts on the reaction. II. The photocapillary reaction in presence of iron. F. HERCÍK (Biochem. Z., 1928, 198, 81—87, 88—97).—I. The plant (pea) phosphatides dialysing into saline solutions show a characteristic positive or negative photocapillary reaction (the surface tension increases or decreases), cations promoting the reaction and anions being almost inactive. Most of the common ions are placed in series according to the extent of their activity.

II. The type of reaction obtained on dialysing plant (pea) phosphatides into ferric nitrate solutions varies with the concentration of the latter, higher concentrations giving a positive and lower concentrations a negative reaction. The largest reaction is obtained with 0.01*M*-ferric nitrate. P. W. CLUTTEBUCK.

**Diurnal variation of the gaseous constituents of river waters.** R. W. BUTCHER, F. T. K. PENTELow, and J. W. A. WOODLEY (Biochem. J., 1928, 22, 1035—1047).—This investigation (cf. A., 1927, 899; this vol., 87) is now extended to the autumn months. The maximum and minimum values of oxygen saturation from the months of September to November are lower than at any previous time in the river Lark. In the river Itchen there is a progressive lowering of the maximum value and a progressive increase in the minimum value in the oxygen saturation curves during the months of August to December. The ammoniacal nitrogen values in the river Lark for September to November vary roughly in inverse ratio to those of dissolved oxygen, whilst in the river Itchen, as in the spring and summer, no diurnal variation of ammoniacal nitrogen was observed. The  $p_H$  curves are again similar in structure and in general follow the oxygen curves, the range in the winter being less than that in the spring and summer. The temperature curves show the

expected diurnal similarity but over different ranges according to the month of the year and the prevailing weather conditions. S. S. ZILVA.

**Characterisation of strains of *Aspergillus niger* on the basis of their biochemical behaviour. I. Acid formation by different strains.** K. BERNHAUER (Biochem. Z., 1928, 197, 278—286); cf. A., 1926, 978).—Of the five strains used two, under all conditions, produced mainly gluconic acid with only inconsiderable amounts of citric acid. One strain was a relatively good producer of citric acid and the two remaining strains, which produced, under favourable conditions, approximately equal amounts of the two acids, could be regarded as intermediate types. W. McCARTNEY.

**Acid production by *Aspergillus niger*. IV. Importance of mycelium development.** K. BERNHAUER (Biochem. Z., 1928, 197, 287—308).—For the growth of moulds and for their capability for acid production the nature of combination and the quantity of the nitrogen used as a source are of the greatest importance. It is shown that, under the conditions of experiment chosen, the amounts of gluconic and citric acids formed vary according to the amount of nitrogen used and to the form in which it is combined in the medium. The various compounds which are used as sources of nitrogen seem to influence the formation of enzyme complexes or enzyme activators which stimulate production of citric acid. W. McCARTNEY.

**Citric acid production by fungi. I. Acid production from various carbon compounds. II. Production of citric acid from gluconic acid.** K. BERNHAUER (Biochem. Z., 1928, 197, 309—326, 327—342).—I. Only carbohydrates or closely-related compounds can be caused to yield citric acid by the action of *Aspergillus niger*, and important differences are observed in the amounts of the acid obtainable from different compounds. The yields also vary greatly according to the strain of the organism used. Although gluconic acid is also a product of the bacterial action in some cases and is one of the substances which yield citric acid, the former acid cannot be regarded as a necessary intermediate product in the formation of citric acid. The formation of citric acid is preceded by the breaking down of carbon chains so as to yield C<sub>3</sub> chains. The readiness or otherwise with which the various hexoses are attacked greatly affects the yields obtained. The yield of citric acid from the lævulose portion of the sucrose molecule is estimated to be much higher than that from lævulose itself and the significance of this fact is pointed out.

II. During the process of conversion of dextrose, first into gluconic acid, then into citric acid, there are formed, apparently, enzymes or enzyme activators which facilitate the transformation of gluconic acid into citric acid. Hence dextrose gives better yields of citric acid than does gluconic acid itself. An explanation of the chemistry of citric acid production and of similar processes is thus provided. It is also shown that a particular strain of an organism

may, for reasons unknown, lose its power to produce citric acid and that, in addition to citric acid, another acid (or acids) such as saccharic acid or glyceric acid, is formed. W. McCARTNEY.

**Loss of fermenting power and change in acid produced by *Aspergillus fumigatus*.** Fermentation giving gluconic acid in place of fumaric acid. C. WEHMER (Biochem. Z., 1928, 197, 418—432).—*A. fumigatus* gradually loses completely its power to produce fumaric acid and produces in its place chiefly gluconic acid. The possible reasons for this change in behaviour are discussed and it is concluded that one and the same species of organism may exist in more than one physiological form. Various tests for and methods of determining fumaric, citric, malic, and gluconic acids are discussed. W. McCARTNEY.

**Use of monochromatic indicators in the double-wedge colorimeter.** H. KROEPELIN (Biochem. Z., 1928, 198, 225—232).—A rule facilitating the determination of  $p_H$  by the double-wedge colorimeter is discussed and details are given for the use of nitrophenol dyes for this purpose. P. W. CLUTTERBUCK.

**Preparation of potassium "pyrogallate" solution for metabolic rate determinations.** F. F. SCHWENTKER (J. Lab. Clin. Med., 1926, 12, 287—288).—Hot potassium hydroxide solution,  $d$  1.517, is added to the pyrogallol and the mixture kept for a month. CHEMICAL ABSTRACTS.

**Micro-determination of glycogen.** A. SLOSSE (Compt. rend. Soc. Biol., 1927, 97, 1810—1812; Chem. Zentr., 1928, i, 1443).—0.5 g. of the finely-pulped organ is rapidly weighed in a centrifuge tube, 1 c.c. of hot 60% potassium hydroxide solution added, and the whole kept in a boiling water-bath for 3 hrs., after which 4 c.c. of water are added and the mixture is cooled. The glycogen is precipitated with 10 c.c. of 95% ethyl alcohol, and centrifuged after 12 hrs. After treatment with 60% alcohol it is again centrifuged, washed twice again with 95% alcohol, dissolved in 10 c.c. of water and 0.67 c.c. of hydrochloric acid ( $d$  1.175), kept in a boiling water-bath for 1 hr., neutralised with 0.45 c.c. of 60% sodium hydroxide solution, diluted to 15 c.c., and the dextrose determined in an aliquot portion by Hagedorn and Jensen's method. A. A. ELDRIDGE.

**Determination of iron [in organic substances].** G. DOMINICI (Folia Clinica, 1928, 3, 65—82).—A critical review of the methods for determining iron in blood, urine, etc. The most satisfactory method with regard to rapidity and accuracy of results is considered to be the colorimetric method using thiocyanate. O. J. WALKER.

**Determination of sodium in biology.** LAUDAT (Bull. Soc. Chim. biol., 1928, 10, 757—768).—Determinations in biological fluids by the pyroantimonate method (Kramer and Tisdall, A., 1922, i, 1087) and by the uranium method (Blanchetière, A., 1923, ii, 579) give similar results. The latter method is probably the most convenient if the recorded precautions are observed. G. A. C. GOUGH.

